

## 7. A BRIEF SUMMARY OF ELEMENTARY REACTIONS IN SOLUTION

### 7.1 Introduction

Elementary reactions also occur in the liquid phase. They can be reactions between two species dissolved in a solvent or reactions of solutes with the solvent. These reactions are quite different from gas phase reactions since the medium (solvent) is considerably denser and more viscous. The solvent may or may not participate in the stoichiometry of the reaction. In either event, since the concentration of the solvent is much greater than that of the solute reactants, the solvent concentration does not change due to reaction.

The effect of solvent on reaction rates can be negligible or considerable. These effects have been observed by comparing reactions rates in gas phase and in solution, and by comparison of rates in different solvents. Table 1 illustrates that solvents do not affect much the second order reaction rate of nitrogen pentoxide decomposition compared to its rate in the gas phase. In contrast, however, for reactions that typically do not occur in the gas phase (such as the reaction between triethylamine and ethyl iodide, the choice of solvent can change the rate by orders of magnitude as illustrated in Table 2. One notes that the pre-exponential factors for this reaction are consistently much lower than the typical values of  $10^{10}$ - $10^{11}$  (L/mol s) predicted by either collision or transition state theory. It appears that these low values are symptomatic of the steric complexity of reactants and are not affected much by the solvent.

**TABLE 1: Comparison of kinetic parameters for the decomposition of nitrogen pentoxide**

Medium	$k/10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25°C	$\log_{10} (A/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	$E_a/\text{kJ mol}^{-1}$
Gas phase <sup>a</sup>	3.38	13.6	103.3
Carbon tetrachloride <sup>b</sup>	4.09	13.8	106.7
Carbon tetrachloride <sup>c</sup>	4.69	13.6	101.3
Chloroform <sup>b</sup>	3.72	13.6	102.5
Chloroform <sup>c</sup>	5.54	13.7	102.9
Ethylene dichloride <sup>c</sup>	4.79	13.6	102.1
Ethylene dichloride <sup>c</sup>	6.56	14.2	104.2
Pentachloroethane <sup>c</sup>	4.30	14.0	104.6
Nitromethane <sup>c</sup>	3.13	13.5	102.5
Bromine <sup>c</sup>	4.27	13.3	100.4
Nitrogen tetroxide <sup>c</sup>	7.05	14.2	104.6
Nitric acid <sup>c</sup>	0.147	14.8	118.4
Propylene dichloride <sup>c</sup>	0.510	14.6	113.0

<sup>a</sup> F. Daniels and E.H. Johnston, *J. Am. Chem. Soc.*, **43**, 53 (1921).

<sup>b</sup> R.H. Lueck, *J. Am. Chem. Soc.*, **44**, 757 (1922).

<sup>c</sup> H. Eyring and F. Daniels, *J. Am. Chem. Soc.*, **52**, 1473 (1930).

Understanding and quantifying the role of solvent on chemical reactions has a large impact on designing environmentally benign processes. We strive to replace solvents, which if released can have undesirable effects on the environment with “benign” solvents which will also have a favorable effect on the values of the rates of the desired chemical reaction.

**TABLE 2: Comparison of kinetic parameters for the reaction between triethylamine and ethyl iodide in various solvents**

Medium	$k/10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at $100^\circ \text{C}$	$\log_{10} (A/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	$E_a/\text{kJ mol}^{-1}$
Hexane	0.5	4.0	66.9
Toluene	25.3	4.0	54.4
Benzene	39.8	3.3	47.7
Bromobenzene	166.0	4.6	52.3
Acetone	265.0	4.4	49.8
Benzonitrile	1125.0	5.0	49.8
Nitrobenzene	1383.0	4.9	48.5

## 7.2 Factors Determining Reaction Rates in Solution

Two main factors affect the rate of elementary reactions in solution: 1) The fact that solvent is denser and much more viscous than the gas phase leading to a less frequent encounter of the reacting molecules in the solvent than in the gas phase, thus lowering the occurrence of reaction events. 2) The fact that many molecules ionize in solution (especially in water) leading to reaction among ions and ions, and molecules, instead of reaction between neutral molecules. This has an effect on the Gibbs free energy of reaction and, hence, on the rate constant. We now in turn take a quick look at both of these phenomena.

We have already mentioned that solutions (including aqueous ones) are more dense and more viscous than gases. The rate of random movement of molecules is, hence, impeded which in turn is reflected in much lower diffusivities. The diffusivity multiplied by the concentration gradient (really activity gradient) of the transported species yields the flux of that species. While diffusion coefficients in gases are roughly 0.1 to 1 ( $\text{cm}^2/\text{s}$ ), solutes in water (and other solvents) have typical diffusivities of  $10^{-5}$  to  $10^{-6}$  ( $\text{cm}^2/\text{s}$ ). According to Einstein's equation the diffusion coefficient of solute  $i$  is given by

$$D_i = \frac{kT}{f_i} \quad (1)$$

$D_i$  ( $\text{cm}^2/\text{s}$ ) is the diffusivity,  $k = 1.381 \times 10^{-16}$  erg/K is the Boltzmann constant,  $T$  absolute temperature and  $f_i$  the friction coefficient for the solute molecule ( $f_i = |F_{r_i}|/v_i$  where  $F_{r_i}$  is the friction force on particle  $i$ ).

Assuming the molecule to be a solid sphere of radius  $r_i$  (cm), and solvent viscosity to be  $\eta$  ( $\text{gcm}^{-1} \text{s}^{-1}$ ), one gets the Stokes-Einstein formula for diffusivity

$$D_i = \frac{kT}{6\pi\eta r_i} \quad (1a)$$

While Stokes-Einstein formula is not always accurate, and better predictions of diffusivity are possible (see Sherwood, Prausnitz and Reed), it indicates the inverse proportionality of diffusivity on viscosity. As a matter of fact Walden's rule states  $\eta D \approx \text{const}$ .

The fact that the solutes are dilute in solution, and that their speed of random movement is considerably slower than in the gas phase, indicates that the diffusion process now can play a role in determining the rate

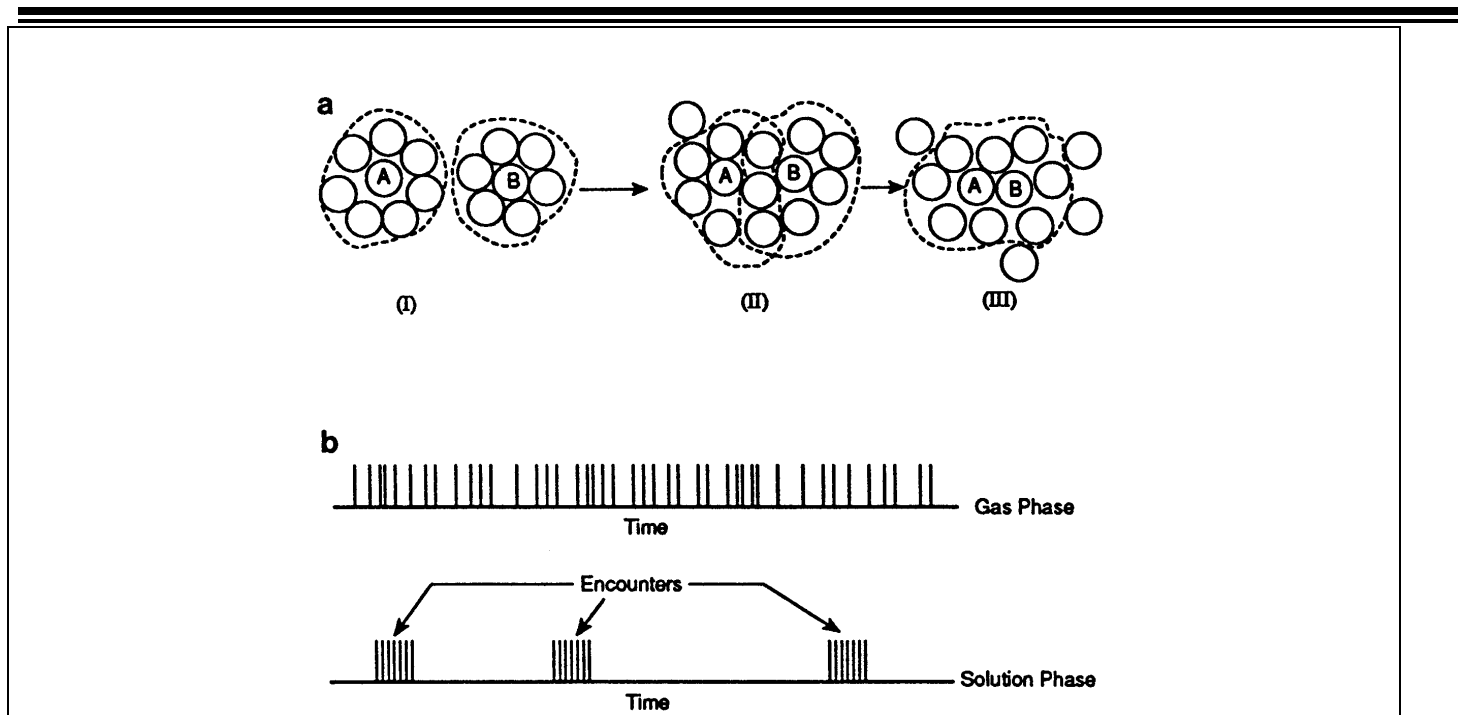
of reaction. In gas phase we can imagine the gas molecules colliding and interacting in our control volume, successful collisions leading to reaction. In dilute liquid solution, the solutes need to find each other by diffusion among an ocean of densely packed solvent molecules. This time that elapses between solute molecules collision can still be much smaller than the characteristic reaction time, in which case the situation is the same as in the gas phase. However, when the time between successive collisions is comparable or larger than the characteristic reaction time, then diffusion process must be considered as affecting the observed rate of reaction.

We can envision the process as consisting of three steps: i) diffusion of reactant species to each other, ii) actual chemical transformation via transition complex, iii) diffusion of products away from each other. For most processes the chemical transformation (step 2) is still the slowest in the sequence and determines (controls) the rate of reaction. This is evidenced by no effect on the rate of solvents of various viscosity, which change diffusivities by considerable factors, and by high activation energies observed, since "apparent activation energy" for a diffusion process is only about 20 kJ/mol. However, there are very rapid reactions that are controlled totally or partly by the diffusion process. Examples are ion combinations such as  $H^+ + OH^- \rightarrow H_2O$  and fluorescence quenching processes. For these processes clearly the existing theories must be extended.

### 7.3 Collision Theory

This theory has been extended successfully to the liquid state and was instrumental in identifying the "cage effect" or Franck-Rabinowitch effect. The effect is best explained with reference to Figure 1.

**FIGURE 1:** (a) Encounter of reactants A and B in solution: (I) reactants in separate cages; (II) cages of A and B overlap; and (III) A and B in same cage. (b) Frequency of collisions in gas phase and of encounters and collisions in solution (time scale not exact). (Redrawn from Adamson, A.W., *A Textbook of Physical Chemistry*, 2<sup>nd</sup> ed., Academic Press, New York, 1979).



In gas phase collisions between a pair of molecules occur relatively evenly distributed in time. In the liquid

phase they are clustered together, i.e sets of rapid collisions are separated by considerable time intervals without collisions. Such a set of successive frequent collisions is referred to as an encounter. The overall collision frequency is similar in gas and liquid but the distribution of collisions is clearly different. The reason for the "encounter" is that in the liquid state the surrounding solvent molecules form a "cage" which holds the colliding solute molecules together and causes a finite set of rapid collisions before they can separate. The tendency of collisions to occur in sets will not affect ordinary reactions which have a finite activation energy and, hence, allow only a small fraction of collisions to succeed and lead to reaction. However, for reactions with no activation energy this makes a difference in pre-exponential factors since reaction occurs at first collision and subsequent ones do not contribute to the rate. Hence, the pre-exponential factor is now related to the reciprocal of the average time elapsing between successive 'encounters'. This "cage" effect has important consequences on the photochemical reactions in solution since a pair of free radicals produced by light may recombine before they can separate from each other if initiation occurred just prior to or during an encounter. This is primary recombination to be distinguished from secondary recombination caused by normal free radical termination after they had a chance to separate.

#### 7.4 Transition State Theory

Partition functions are difficult to formulate and calculate in the liquid phase but the thermodynamic formulation of Conventional Transition State Theory (CTST) is as applicable to the liquid phase as it is to the gas.

This leads to the prediction of the rate constant for the reaction  $A + B \rightarrow Z$

$$k = k_g \frac{\gamma_A \gamma_B}{\gamma_Z} \quad (2)$$

where  $k_g$  is the rate constant for the gas phase reaction predicted by transition state theory in an ideal gas,  $\gamma_A, \gamma_B, \gamma_Z$  are activity coefficients of the reactant and the activated complex in the liquid solvent, respectively.

Since by transition state theory

$$k_g \propto K^* = e^{-\frac{\Delta G^*}{RT}}$$

by changing the standard state from pure component at 1 atm pressure to infinite dilution at 1 atm we can rewrite eq (2) as

$$k = k_o \frac{\gamma_A^d \gamma_B^d}{\gamma_Z^d} \quad (3)$$

where  $k_o$  is the rate constant in an ideal solution and activity coefficient now relate to infinite dilution.

The internal solvent pressure effect can now be rationalized as theory leads to the following expression

$$RT \ln k = RT \ln k_o + V_A \Delta_A + V_B \Delta_B - V_Z \Delta_Z \quad (4)$$

where  $\Delta_i = (P_{in,sol}^{1/2} - P_{in,i}^{1/2})^2$ . Here  $V_i$  is the molar volume of reactant or activated complex,  $\Delta_i$  is the

difference in internal solvent pressure and species pressure where  $P_{in,i} \approx \frac{E_{V,i}}{V_i}$  where  $E_{V,i}$  is the heat of vaporization of  $i$  and  $V_i$  is the molar volume. Subscript sol indicates the solvent.

For an ideal solvent all  $\Delta_{i,s}$  are zero (in practice negligibly small). If the internal pressure of the solvent is similar to that of reactants but different from that of the complex then  $k < k_o$ . If the solvent internal pressure matches that of the complex but is different than that of reactants, then  $k > k_o$ . Empirically it was found that if the internal pressure of products is lower than that of reactants the reaction is accelerated by solvents of low internal pressure. If the products have higher internal pressure than reactants, a solvent of higher internal pressure speeds the reaction.

## 7.5 Reactions Between Ions In Which Covalent Bonds Are Broken and Formed

In presence of ions electrostatic forces dominate and must be included in any theory. With this modification collision theory indicates that pre-exponential factors are increased for ions of opposite signs due to attractive forces and are decreased for ions of the same sign due to repulsive forces. We consider first simple ions with zero dipole moments.

### 7.5.1 Brief Review of Forces Between Atoms, Molecules and Ions

Clearly, attractive and repulsive forces between ions and/or neutral molecules are important in solution kinetics since they determine the way in which reactants can approach each other. These forces are short range (due to overlap of electronic orbitals in molecules) and long range (beyond the electronic orbitals and related to intermolecular/(inter nuclear distance).

Intermolecular interactions are presented in terms of potential energy  $V$  of interaction. Force  $F$  is then given by

$$F = - \frac{dV}{dr} \quad (5)$$

where  $r$  is the internuclear distance.

Coulomb's law yields the potential ( $V$ ) (erg) interaction between two ions of charges  $Z_A e$  and  $Z_B e$  separated by distance  $r = r_{AB}$  (cm)

$$V(r) = Z_A Z_B e^2 / \epsilon r \quad (6)$$

where  $\epsilon$  is the dielectric constant of the solvent and  $e$  is the charge on an electron ( $4.80 \times 10^{-10}$  esu or  $1.602 \times 10^{-19}$  Coulomb). Recall that if the charge on a capacitor is  $C_o$  in vacuum, and when we introduce our solvent between the plates the capacitance is  $C$ , then the dielectric constant of our medium is  $\epsilon = C / C_o$ . Since the charge on the plates remains unchanged this implies that the field is reduced by a factor of  $\epsilon$ .

Positive  $V$  implies repulsive forces (higher energy), negative  $V$  - attractive forces. For water  $\epsilon \approx 78$ . However, water bound to ions can have much lower  $\epsilon$  and this will be discussed later.

For interaction between an ion of charge  $Z_A$  and a polar molecule B of dipole moment  $\mu_B$  the potential is:

$$V(r) = -\frac{Z_A e \mu_B \cos \theta}{\epsilon r^2} \quad (7)$$

where  $\cos \theta$  is the angle between the direction of the dipole and  $r$  (for aligned  $r$  and dipole  $\theta = 0$ , and  $\mu_B$  is the dipole moment of the polar molecule (in esu cm or  $10^{-18}$  debyes. [A dipole consisting of charges  $\pm e$  separated by a distance of 0.1 nm would have a moment of  $4.80 \times 10^{-18}$  esu cm. The unit  $10^{-18}$  esu cm = 1 debye (D)]. Statistical averaging of eq (7) over all orientations yields  $V \propto r^{-4}$ .

The potential for ion-induced dipole interaction is

$$V(r) = -\frac{Z_A^2 e^2 \alpha_B}{2 \epsilon r^2} \quad (8)$$

where  $\alpha_B$  ( $\text{cm}^3$ ) is the polarizability of the nonpolar molecule  $B$  leading to the induced dipole of dipole moment  $\mu_B$

$$\mu_B = \frac{\alpha_B Z_A e}{\epsilon r^2} \quad (9)$$

Similar expressions can be written for attractive interactions between neutral molecules (Van der Waals forces),

$$V(r) = -\frac{2 \mu_A^2 \mu_B^2}{3 k_B T \epsilon r^6} \quad (10)$$

the potential for dipole-induced dipole interactions

$$V(r) = -\frac{\alpha_A \mu_B^2 + \alpha_B \mu_A^2}{\epsilon^2 r^6} \quad (11)$$

and the potential for induced dipole-induced dipole interactions (London dispersion forces)

$$V(r) = -\frac{3 \alpha h \nu_o}{4 \epsilon r^6} \quad (12)$$

where  $h \nu_o$  is the ionization energy (erg).

Modeling of both short range and long range interactions rests on the empirical Lennard-Jones potential

$$V(r) = 4e \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad (13)$$

where  $e$  is the minimum potential (or depth of the potential well) and  $\sigma$  is the value of  $r$  where  $V = 0$ .

## 7.5.2 Effect of Dielectric Constant-Double Sphere Model

A simple model for a reaction between two ions of charges  $Z_A e$  and  $Z_B e$  in a medium of dielectric constant  $\epsilon$  is shown in Figure 2. The two ions form a complex of total charge number  $Z_A + Z_B$  and the complex decomposes into two ions. The potential is then given by eq (6) and the force acting between the two ions is

$$F = \frac{Z_A Z_B e^2}{\epsilon r^2} \quad (14)$$

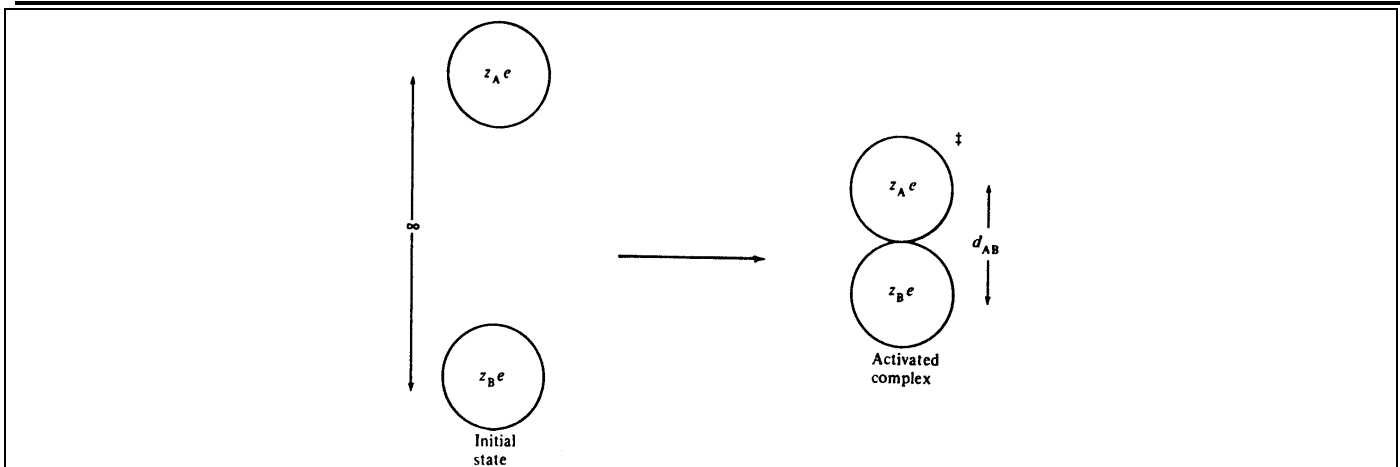
One should note that if instead of (esu) units for the electron charge, (cm) for distance  $r$ , and (dyn) for force, we want to have SI units, i.e ((N) for force, (m) for distance  $r$ , and Coulombs (C) for charge on the electron ( $1.602 \times 10^{-19}$  C) then the above eq (14) must be multiplied by  $1/4\pi\epsilon_0$  where  $\epsilon_0$  is the permittivity of vacuum ( $8.854 \times 10^{-12}$  C<sup>2</sup>N<sup>-1</sup>m<sup>-2</sup>). Hence

$$F(N) = \frac{Z_A Z_B e^2}{4\pi\epsilon_0 \epsilon r^2} \quad (14a)$$

In order for the ions to form an activated complex they must be brought from a non-interactive distance ( $r \rightarrow \infty$ ) to immediate proximity  $r = d_{AB}$ . This requires the following work

$$dw = -F dr$$

**FIGURE 2: Simple model for a reaction between two ions, of charges  $z_A e$  and  $z_B e$  in a medium of dielectric constant  $\epsilon$ . This is known as the “double-sphere” model.**



Upon integration from  $r = \infty$  to  $r = d_{AB}$  we get

$$w = \frac{Z_A Z_B e^2}{4\pi\epsilon_0 \epsilon d_{AB}} \quad (15)$$

This work is the electrostatic contribution to the Gibbs free energy (needs to be multiplied by Avogadro's constant to yield a molar quantity).

$$\Delta G_{es}^{*o} = \frac{L Z_A Z_B e^2}{4\pi \epsilon_o \epsilon d_{AB}} \quad (16)$$

The total Gibbs free energy change consists of the electrostatic and non-electrostatic contribution

$$\Delta G^{*o} = \Delta G_{es}^{*o} + \Delta G_{nes}^{*o}$$

The rate constant by transition state theory is

$$k = \frac{k_B T}{h_p} e^{-\frac{\Delta G^{*o}}{RT}} = \frac{k_B T}{h_p} e^{-\Delta G_{nes}^{*o}/RT} e^{-\left(\frac{Z_A Z_B e^2}{4\pi \epsilon_o \epsilon d_{AB} k_B T}\right)}$$

$$\text{as } R = L k_B$$

Taking logarithms yields

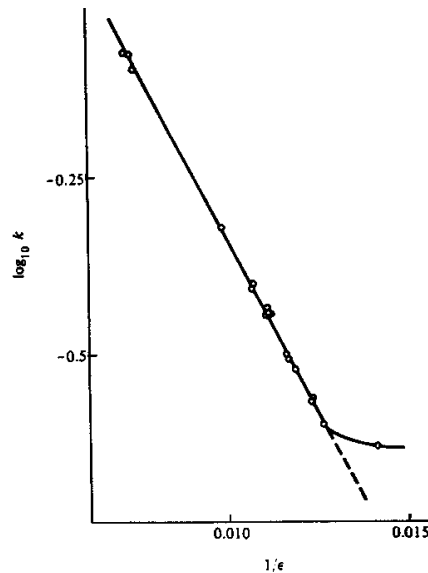
$$\ln k = \ln k^\circ - \frac{Z_A Z_B e^2}{4\pi \epsilon_o d_{AB} k_B T \epsilon} \quad (17)$$

$$\text{where } k^\circ = \frac{k_B T}{h_p} e^{-\Delta G_{nes}^{*o}/RT}$$

Hence  $k^\circ$  is the rate constant in a medium of infinite dielectric constant where the electrostatic forces are zero.

Experiments reasonably well support the theory (eq (17)) as evident from Figure 3. The slope of the line can be used to estimate  $d_{AB} = 510 \text{ pm} = 510 \times 10^{-12} \text{ m}$ .

**FIGURE 3: Plot of  $\log_{10} k$  versus the reciprocal of the dielectric constant, for the reaction between bromo-acetate and thiosulfate ions in aqueous solution.**



Using the relation between Gibbs free energy and entropy one can show



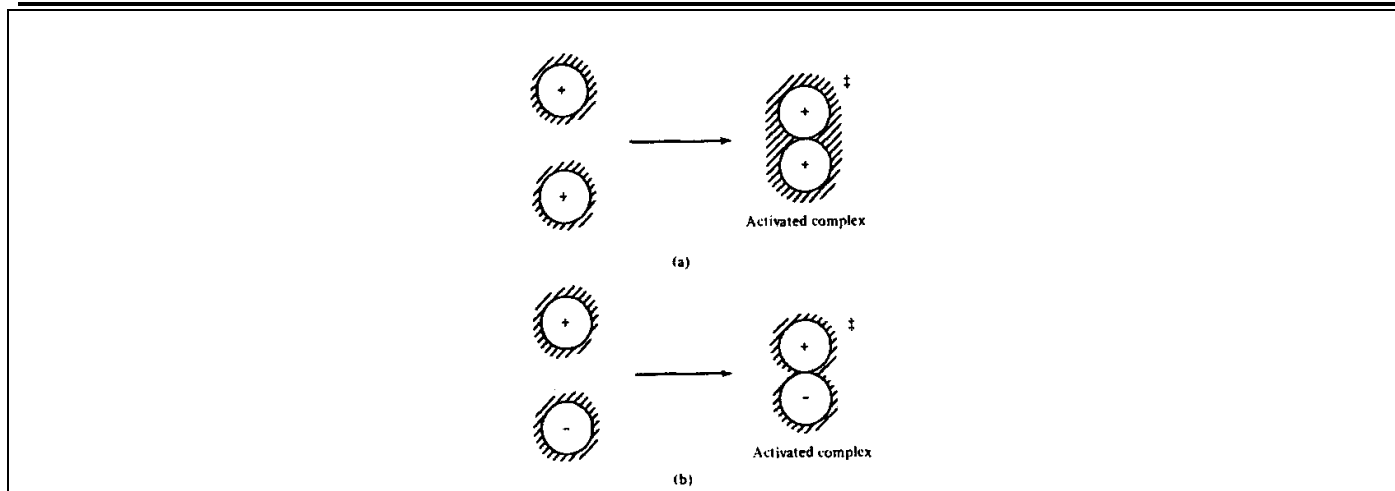
$$\Delta S_{es}^o = \frac{LZ_A Z_B e^2}{4\pi \epsilon_o d_{AB} \epsilon} \left( \frac{\partial \ln \epsilon}{\partial T} \right)_p \quad (18)$$

For water  $\epsilon \approx 78.5$  and  $(\partial \ln \epsilon / \partial T)_p = -0.0046 \text{ K}^{-1}$  over a wide range of temperature. Hence, at  $d_{AB} = 200 \text{ p m}$

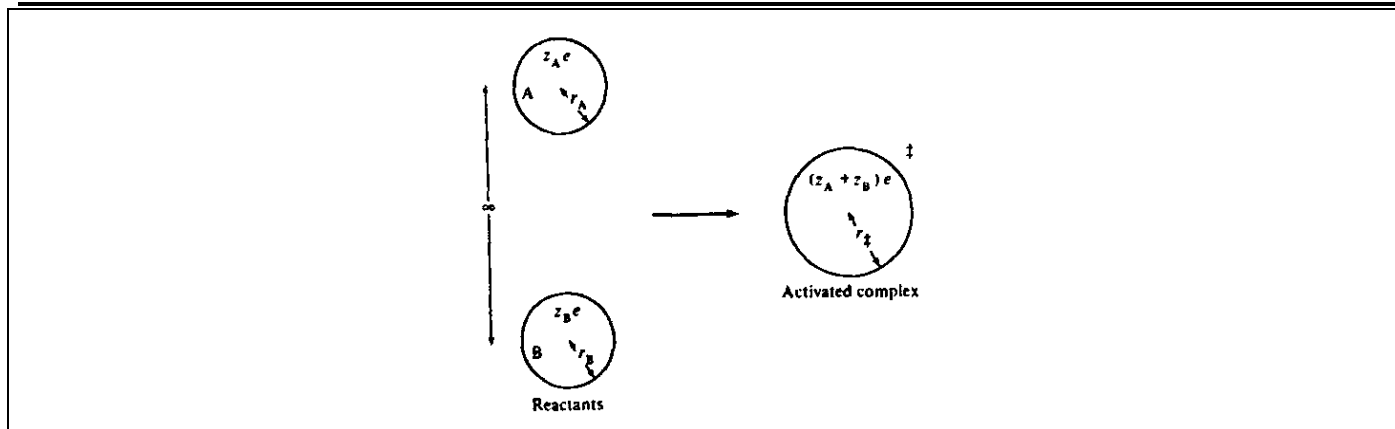
$$\Delta S_{es}^{*o} = -41 Z_A Z_B \text{ J k}^{-1} \text{ mol}^{-1} \quad (19)$$

For every unit of  $Z_A Z_B$  entropy of activation decreases by about  $-41 \text{ J K}^{-1} \text{ mol}^{-1}$  since the pre-exponential factor is  $e^{\Delta S^o/R} = 10^{\Delta S^o/2.30R}$ . The data roughly support this (Table 3). This is the solvent binding or electrostriction effect which is greater the greater the charge. (See Figure 4).

**FIGURE 4:** An interpolation of entropies of activation in terms of the electrostriction of solvent molecules. In (a) the ions are of the same sign and there is more electrostriction in the activated complex; thus, there is a decrease in entropy. In (b) there is less electrostriction in the activated complex.



**FIGURE 5:** Single-sphere model for a reaction between two ions.



**TABLE 3:** Some observed and predicted pre-exponential factors and entropies of activation.<sup>a</sup>

Reactants	Experimental		Estimated	
	$A/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$\Delta^\ddagger S^\circ/\text{J K}^{-1} \text{ mol}^{-1}$	$A/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$\Delta^\ddagger S^\circ/\text{J K}^{-1} \text{ mol}^{-1}$
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+} + \text{CNS}^-$	$\sim 10^{19}$	$\sim 126$	$10^{19}$	126
$\text{Co}(\text{NH}_3)_5\text{Br}^{2+} + \text{OH}^-$	$5 \times 10^{17}$	92	$10^{17}$	84
$\text{CH}_2\text{BrCOOCH}_3 + \text{S}_2\text{O}_3^{2-}$	$1 \times 10^{14}$	25	$10^{13}$	0
$\text{CH}_2\text{ClCOO}^- + \text{OH}^-$	$6 \times 10^{10}$	-50	$10^{11}$	-42
$\text{ClO}^- + \text{ClO}_2^-$	$9 \times 10^8$	-84	$10^{11}$	-42
$\text{CH}_2\text{BrCOO}^- + \text{S}_2\text{O}_3^{2-}$	$1 \times 10^9$	-71	$10^9$	-84
$\text{Co}(\text{NH}_3)_5\text{Br}^{2+} + \text{Hg}^{2+}$	$1 \times 10^8$	-100	$10^5$	-167
$\text{S}_2\text{O}_3^{2-} + \text{S}_2\text{O}_8^{2-}$	$2 \times 10^4$	-167	$10^5$	-167
$\text{S}_2\text{O}_3^{2-} + \text{SO}_3^{2-}$	$2 \times 10^6$	-126	$10^5$	-167

\* For references to the original literature see C. T. Burris and K. J. Laidler, *Trans. Faraday Soc.*, 15, 1497 (1955); D. T. Y. Chen and K. J. Laidler, *Can. J. Chem.*, 37, 599 (1959).

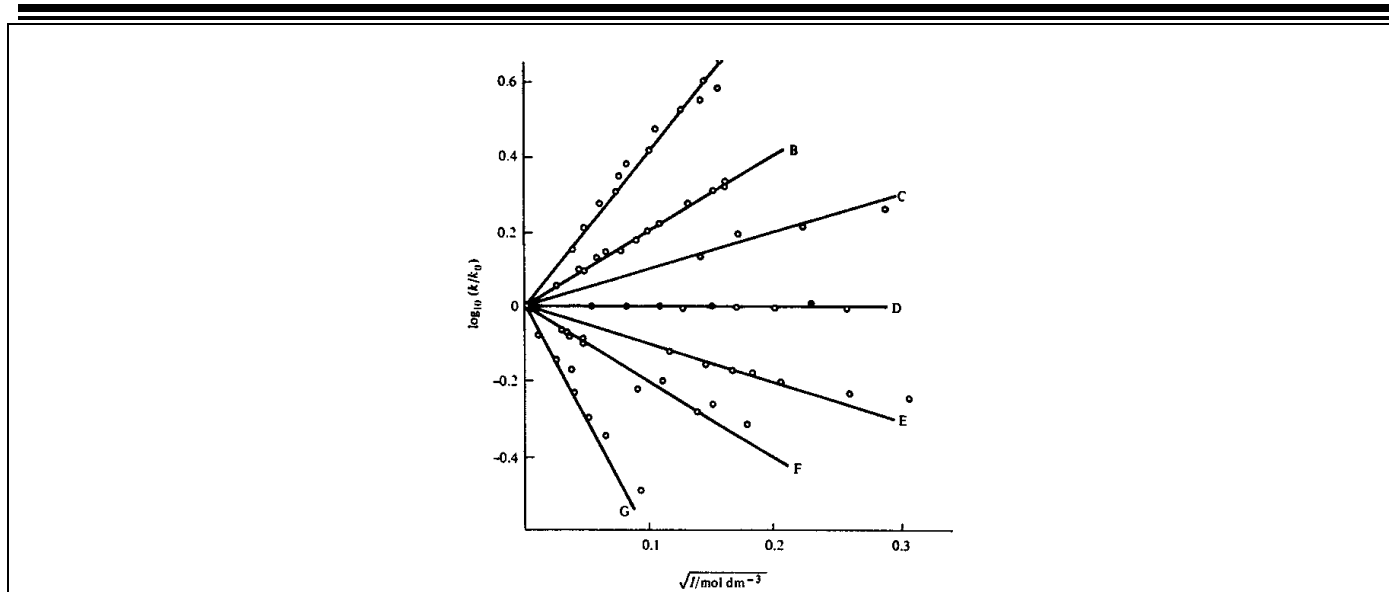
TABLE 4: Volumes and entropies of activation.<sup>a</sup>

Reaction	Solvent	$\Delta^\ddagger V^\circ/\text{cm}^3 \text{ mol}^{-1}$	$\Delta^\ddagger S^\circ/\text{J K}^{-1} \text{ mol}^{-1}$
$\text{Co}(\text{NH}_3)_5\text{Br}^{2+} + \text{OH}^- \rightarrow \text{Co}(\text{NH}_3)_5\text{OH}^{2+} + \text{Br}^-$	$\text{H}_2\text{O}$	8.5	92
$(\text{CH}_3)(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_5\text{CH}_2)\text{N}^+\text{Br}^- \rightarrow (\text{CH}_3)(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_5\text{CH}_2)\text{N} + \text{C}_2\text{H}_5\text{Br}$	$\text{H}_2\text{O}$	3.3	63
$\text{CH}_2\text{BrCOOCH}_3 + \text{S}_2\text{O}_3^{2-} \rightarrow \text{CH}_2(\text{S}_2\text{O}_5^-)\text{COOCH}_3 + \text{Br}^-$	$\text{H}_2\text{O}$	3.2	25
$\text{Sucrose} + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{glucose} + \text{fructose}$	$\text{H}_2\text{O}$	2.5	33
$\text{C}_2\text{H}_5\text{O}^- + \text{C}_2\text{H}_5\text{I} \rightarrow \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + \text{I}^-$	$\text{C}_2\text{H}_5\text{OH}^x$	-4.1	-42
$\text{CH}_2\text{ClCOO}^- + \text{OH}^- \rightarrow \text{CH}_2\text{OHCOO}^- + \text{Cl}^-$	$\text{H}_2\text{O}$	-6.1	-56
$\text{CH}_2\text{BrCOO}^- + \text{S}_2\text{O}_3^{2-} \rightarrow \text{CH}_2(\text{S}_2\text{O}_5^-)\text{COO}^- + \text{Br}^-$	$\text{H}_2\text{O}$	-4.8	-71
$\text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{COOH} + \text{CH}_3\text{OH}$	$\text{H}_2\text{O}$	-8.7	-42
$\text{CH}_3\text{CONH}_2 + \text{H}_2\text{O} \xrightarrow{\text{OH}^-} \text{CH}_3\text{COOH} + \text{NH}_3$	$\text{H}_2\text{O}$	-14.2	-142
$\text{C}_2\text{H}_5\text{N} + \text{C}_2\text{H}_5\text{I} \rightarrow \text{C}_2\text{H}_5(\text{C}_2\text{H}_5)\text{N}^+\text{I}^-$	$\text{CH}_3\text{COCH}_3$	-16.8	-146
$\text{C}_6\text{H}_5\text{CCl}_3 \rightarrow \text{C}_6\text{H}_5\text{CCl}_2 + \text{Cl}^-$	80% $\text{C}_2\text{H}_5\text{OH}$	-14.5	-146

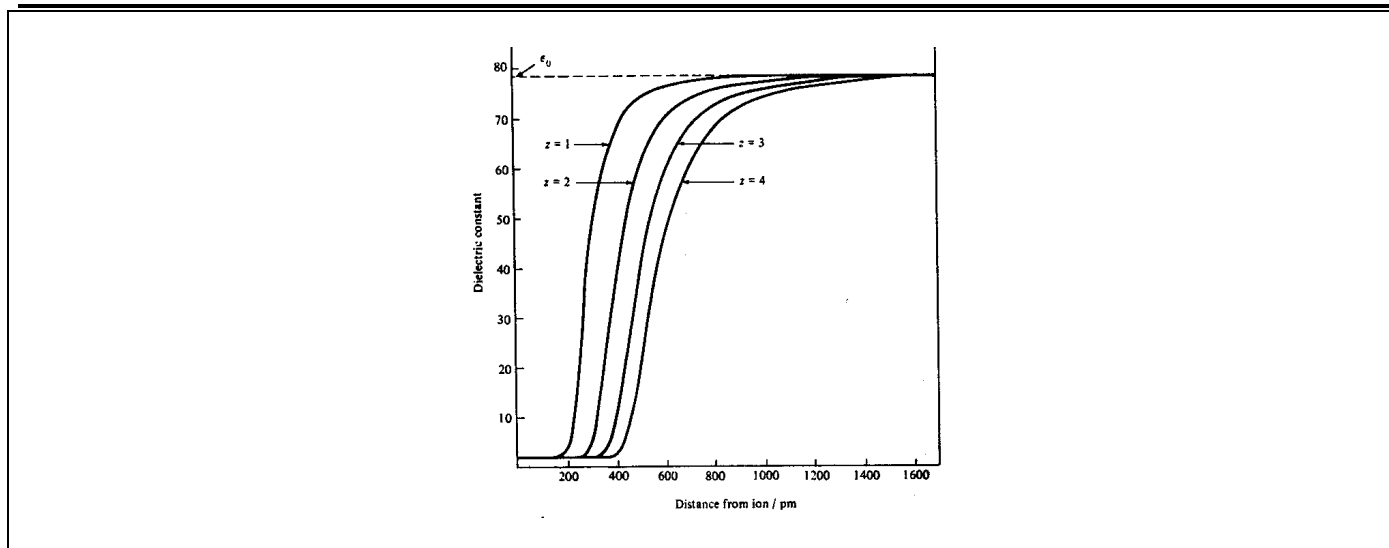
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**FIGURE 6:** Plots of  $\log_{10} (k/k_0)$  versus the square root of the ionic strength for ionic reactions of various types. The lines are drawn with slopes equal to  $z_A z_B$ . The reactants are:

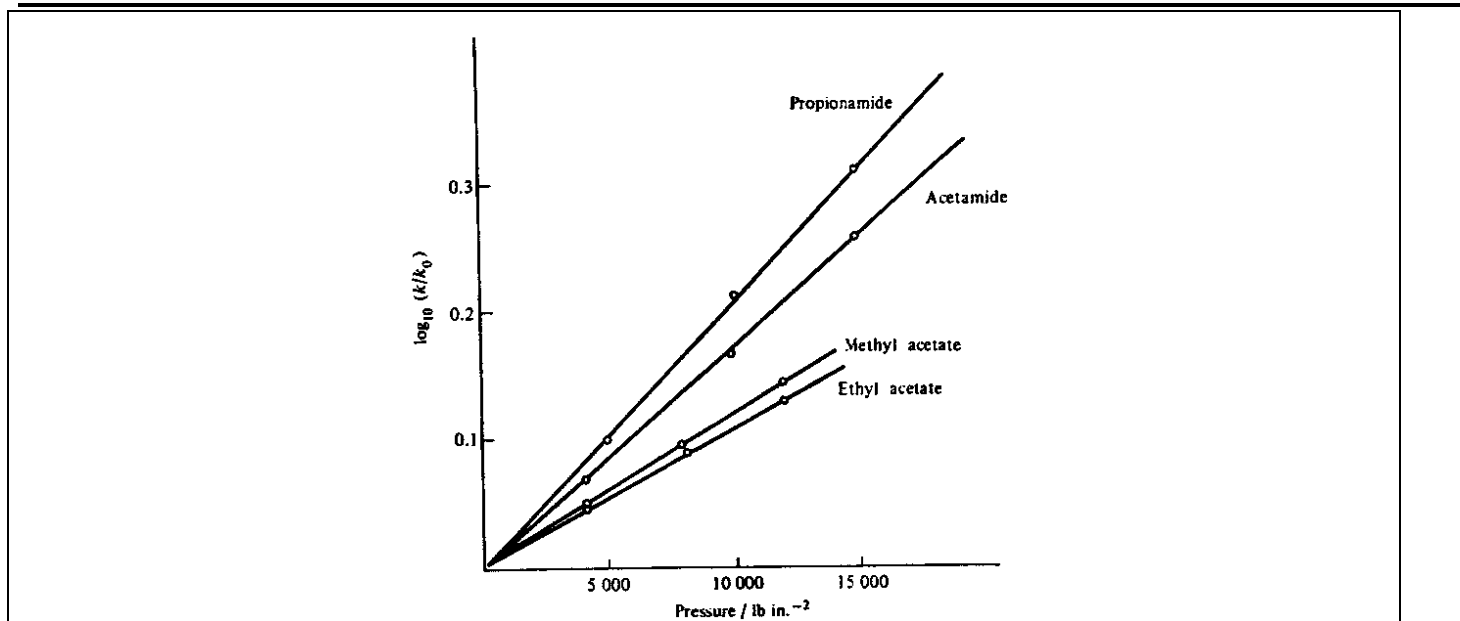
- |   |                                            |                  |
|---|--------------------------------------------|------------------|
| A | $C_o (NH_3)_5 Br^{2+} + Hg^{2+}$           | $(z_A z_B = 4)$  |
| B | $S_2O_8^{2-} + I^-$                        | $(z_A z_B = 2)$  |
| C | $CO (OC_2 H_5) N : NO_2^- + OH^-$          | $(z_A z_B = 1)$  |
| D | $[Cr (urea)_6]^{3+} + H_2O$ (open circles) | $(z_A z_B = 0)$  |
|   | $CH_3 COOC_2 H_5 + OH^-$ (closed circles)  | $(z_A z_B = 0)$  |
| E | $H^+ + Br^- + H_2O_2$                      | $(z_A z_B = -1)$ |
| F | $C_o (NH_3)_5 Br^{2+} + OH^-$              | $(z_A z_B = -2)$ |
| G | $Fe^{2+} + C_o (C_2O_4)^{3-}$              | $(z_A z_B = -6)$ |



**FIGURE 7:** Dependence of the dielectric constant of water on the distance from ions having charge numbers of 1, 2, 3 and 4.



**FIGURE 8:** Plots of  $\log_{10} (k/k_0)$  versus the hydrostatic pressure for the alkaline hydrolyses of some esters and amides. [Source: K.J. Laidler and D. Chen, *Trans. Faraday Soc.*, 54, 1020 (1958).].



### 7.5.3 Single Sphere Model

In this model (see Figure 5) the two ions collapse into a single sphere upon forming a complex. Hence, one considers charging a conducting sphere of radius  $r$  from an initial charge of zero to a final charge of  $z e$ . Charging is done incrementally by transporting an element of charge  $ed\lambda$  from  $\infty$  to  $r$  when the sphere is at charge  $\lambda e$ . The work to move  $ed\lambda$  an increment  $dr$  is

$$dw = -\frac{\lambda e^2 d\lambda dr}{4\pi \epsilon_0 r^2 \epsilon}$$

$$w = -\frac{e^2}{4\pi \epsilon_0 \epsilon} \int_0^z \lambda d\lambda \int_{\infty}^r \frac{dr}{r^2} = \frac{Z^2 e^2}{8\pi \epsilon_0 \epsilon r} \quad (20)$$

This is now applied as an increment in  $\Delta G$  for each of the original ions and for the complex.

Eventually one gets

$$\Delta^* G_{es}^o = \frac{e^2}{8\pi \epsilon_0 \epsilon} \left( \frac{(Z_A + Z_B)^2}{r^*} - \frac{Z_A^2}{r_A} - \frac{Z_B^2}{r_B} \right) \quad (21)$$

which leads to

$$\ell nk = \ell nk^o - \frac{e^2}{8\pi \epsilon_0 \epsilon k_B T} \left( \frac{(Z_A + Z_B)^2}{r^*} - \frac{Z_A^2}{r_A} - \frac{Z_B^2}{r_B} \right) \quad (22)$$

Eq (21) and eq (16) are identical when  $r^* = r_A = r_B$ .

### 7.5.4 Effect of Ionic Strength

Transition state theory combined with Debye-Huckel theory for dilute electrolyte solutions yields the dependence of the rate constant for bimolecular ionic reaction as

$$\log k = \log k_o + 2 B Z_A Z_B \sqrt{I} \quad (23)$$

Ionic strength,  $I$ , is

$$I = \frac{1}{2} \sum C_j Z_j^2 \quad (24)$$

$Z_j$  - charge number,  $C_j$  - ionic concentration of  $j$ -th ion.

$$\log \gamma_i = - B Z_i^2 I^{1/2} \quad (25)$$

where  $B = 0.51$  ( $\text{C}^{-3/2} \text{mol}^{-1/2}$ ) for aqueous solutions at  $25^\circ\text{C}$  and can in general be calculated from theory. Eq (22) is reduced for aqueous solutions at  $25^\circ\text{C}$  to

$$\log \frac{k}{k_o} = 1.02 Z_A Z_B \sqrt{I} \quad (25a)$$

Agreement with data is shown in Figure 6. The origin of eq (23) is the CTST which states

$$k = k_o \frac{\gamma_A \gamma_B}{\gamma_x}$$

Applying eq (25) to each activity coefficient produces eq (23).

Deviations occur due to breakdown of simple Debye-Huckel theory in more concentrated solutions (remedy via additional terms in eq (24)). Ion pairing and reduction in  $I$  causes deviations. Ionic pairing changes the electrostatic interactions among ions.

### 7.6 Advanced Treatments

Advanced treatments of ionic interactions consider the solvent as having a structure and examine the variation of the dielectric constant in the neighborhood of ions.

One class of advanced models still treats the solvent as a continuum but accounts for dielectric saturation - i.e the fact that solvent molecules close to an ion are subjected to a very high field and become aligned in this field which reduces the dielectric constant to a low value of 2 (characteristic of hydrocarbons and nonpolar-substances). Figure 7 shows the results of such calculation that demonstrate the dielectric constant of water of 78.5 dropping to 1.78 in the vicinity of one ion. This of course changes the force between the ions. Both Gibbs free energy and entropy change are modified by the change in dielectric saturation (e.g. repulsive forces at short distance between ions of the same sign are stronger i.e the Gibbs free energy for forming a transition state is larger).

Second class of models treats the solvent as having a molecular structure. Ions in aqueous solution are surrounded by a hydration shell - layer of tightly held water molecules. These have low  $\tilde{S}^o$  and  $\tilde{V}_i$ . Outside is

the disorder zone and only far away is water at bulk properties. In the disorder zone (arises due to electrical forces from the ion + hydrogen bonding of water)  $\tilde{S}^o$  is high.

### 7.6.1 Ion-Dipole and Dipole-Dipole Reactions

When a molecule contains atoms of different electronegativity, there is an accumulation of a negative charge on the more electronegative atom, leaving a positive charge on a more electropositive one. The bond then constitutes an electric dipole, i.e a positive and negative charge  $\pm Q$  separated by distance  $r$ . A dipole moment is a vector of magnitude  $\mu = Q r$  and the direction of the line is from the negative to the positive charge.

Many reactions occur between ions and dipolar molecules or between two dipolar molecules. The model for this situation considers the change in energy (work) for charging a sphere that has charges imbedded at several specified locations. To a first approximation for a sphere of radius  $r$ , net charge  $Z e$ , and dipole moment  $\mu$ , the work to charge it (i.e electrostatic contribution to  $\Delta G^o$ ) is:

$$\Delta G_{es}^o = \frac{Z^2 e^2}{8\pi \epsilon_o \epsilon r} + \frac{3\mu^2}{16\pi \epsilon_o \epsilon r^3} \quad (26)$$

For a bimolecular reaction  $A + B \rightarrow$  by transition state theory this yields the following contribution to the Gibbs free energy of activation.

$$\Delta^* G_{es}^o = \frac{e^2}{8\pi \epsilon_o \epsilon} \left( \frac{(Z_A + Z_B)^2}{r^*} - \frac{Z_A^2}{r_A} - \frac{Z_B^2}{r_B} \right) + \frac{3}{16\pi \epsilon_o \epsilon} \left( \frac{\mu^{*2}}{r^{*3}} - \frac{\mu_A^2}{r_A^3} - \frac{\mu_B^2}{r_B^3} \right) \quad (27)$$

leading to the rate constant:

$$\ln k = \ln k_o - \frac{e^2}{8\pi \epsilon_o k_B T \epsilon} \left( \frac{(Z_A + Z_B)^2}{r^*} - \frac{Z_A^2}{r_A} - \frac{Z_B^2}{r_B} \right) - \frac{3}{16\pi \epsilon_o k_B T \epsilon} \left( \frac{\mu^{*2}}{r^{*3}} - \frac{\mu_A^2}{r_A^3} - \frac{\mu_B^2}{r_B^3} \right) \quad (28)$$

where  $k_o$  is the hypothetical rate constant arising from nonelectrostatic contribution  $\Delta^* G_{nes}^o$  corresponding to  $\epsilon \rightarrow \infty$ .

Approximately, one takes  $d_{AB} = r^* = r_A = r_B$  which yields

$$\ln k = \ln k_o - \frac{Z_A Z_B e^2}{4\pi \epsilon_o d_{AB} k_B T \epsilon} - \frac{\mu^{*2} - \mu_A^2 - \mu_B^2}{16\pi \epsilon_o d_{AB}^3 k_B T \epsilon} \quad (29)$$

For the pre-exponential factor one can show that

$$\Delta^* S^o = -41 Z_A Z_B - 7.7 \Delta \mu_o^2 \quad (30)$$

where in aqueous solution

$$\Delta \mu_o^2 = \frac{\mu^{*2} - \mu_A^2 - \mu_B^2}{(1.602 \times 10^{-29} \text{ Cm})^2} \quad (31)$$

Here  $1.602 \times 10^{-29}$  Cm is the dipole moment of two elementary charges ( $1.602 \times 10^{-19}$  C) separated by a distance of  $10^{-10}$  m, is equal to 4.8D (debye units). The equation must be modified for non-aqueous solvents.

The effect of the ionic strength is accounted for via modified Debye-Huckel formulation for ions (given for ion A as)

$$\log \gamma_A = -BZ_A^2 \sqrt{I} + b_A I \quad (32a)$$

and by Debye-McAuley equation for the molecule with no net charge (molecule B)

$$\log \gamma_B = b_B I \quad (32b)$$

It is assumed that the activated complex has the same charge as A and its activity coefficient is given by eq (29). Then, proceeding as before we get

$$\log k = \log k_o + (b_A + b_B - b^*) I \quad (33a)$$

or

$$k = k_o e^{b'I} \approx (1 + b'I) \quad (33b)$$

and a linear dependence of k on I can now be observed.

## 7.7 Effect of Pressure

One starts with the Van't Hoff's equation

$$\frac{d \ln K_c}{dP} = - \frac{\Delta V^o}{RT} \quad (34)$$

where  $\Delta V^o$  is the overall standard molar volume change due to reaction given by:

$$\Delta V^o = V_p - V_r$$

where  $V_p$  and  $V_r$  are molal volume of products and reactants, respectively.

If  $V^*$  is the partial molar volume of the activated complex then

$$\begin{aligned} \Delta V^o &= (V^* - V_r) - (V^* - V_p) \\ &= \Delta^* V^o - \Delta^{\neq} V^o \end{aligned} \quad (35)$$

where  $\Delta^*V^o, \Delta^*V^o$  are volumes of activation for forward and reverse reaction.

Now

$$\frac{d \ln k}{dP} = - \frac{\Delta^*V^o}{RT}$$

so that

$$\ln k = \ln k_o - \frac{\Delta^*V^o}{RT} P \quad (36)$$

where  $k_o$  is the rate constant at zero pressure (usually value at 1 atm can be taken). The effect can be observed in Figure 8.

Enclosed Table 4 lists some volumes and entropies of activation.

## 7.8 Diffusion Controlled Reactions

### 7.8.1 Basic Concepts of Diffusion

Diffusion is the process of molecular mixing based on random motion due to molecular kinetic energy and velocity distribution. Molecules are constantly moving and colliding with each other. The direction of movement for an individual molecule changes with each collision and the distance travelled between collisions (the mean free path,  $\lambda$ ) depends on the conditions and type of the medium. The net effect of this random motion is the homogenization of the medium, i.e reduction of all spatial concentration gradients in a closed system to zero. We all know that if we introduce a drop of fluid ink into water in a beaker the originally small dark blue blob eventually dissipates and the whole water in the beaker becomes light blue. Hence, originally we had a region of high ink concentration, blue blob, and no ink in the water surrounding it. Hence there was a high negative concentration gradient of ink from ink blob to water. After sufficient time, the concentration of ink is uniform everywhere and there are no concentration gradients. Let us imagine that at some time  $t = 0$ , we could partition our solution into region 1, containing  $100 \times 10^6$  ink molecules per unit volume and another adjacent region 2 with  $50 \times 10^6$  ink molecules per unit volume. Since motion is random the probability of a ink molecule moving from 1 to 2 or 2 to 1 is the same. Let us assume further that both regions are the same in volume (unit volume) and are separated by a boundary of unit area. Hence, we have at time 0 a "concentration difference" of  $50 \times 10^6$  molecules/unit volume. The number that moves across the boundary dividing the two regions must then be proportional to the number of molecules in the region, i.e the number of crossings from 1 to 2 per unit time and unit boundary area is proportional to the number per unit volume in region 1; the number of crossings from 2 to 1 per unit time and unit boundary area is proportional to the number per unit volume in region 2. Let us assume that the probability is 0.1 that an ink molecule in either region crosses the unit boundary area dividing the regions during time  $\Delta t$ . At the end of  $\Delta t$  region 1 would have lost  $10 \times 10^6$  solute molecules and region 2  $5 \times 10^6$  solute molecules. However, the net gain (or loss) of a region is given by the difference between the amount of gained and loss. Hence, the net loss of region 1 is  $5 \times 10^6$  molecules, and the net gain of region 2 is  $5 \times 10^6$  molecules. This means that at the end of  $\Delta t$  the concentration difference has been reduced from  $50 \times 10^6$  to  $40 \times 10^6$  molecules/unit volume. The net rate of transfer per unit area (of dividing boundary) and unit time is  $\dot{N}$  (molecules/unit area and unit time)

$$\dot{N} = P_t (M_1 - M_2) / A \quad (37)$$



where  $P_i$  ( $\text{time}^{-1}$ ) is the probability of transfer per unit time,  $A$  (area) is the surface area between the two regions,  $M_i$  (mass) is mass of solute in region  $i$ . Defining concentration by

$$c_i = \frac{M_i}{A \Delta X}$$

we can write

$$\dot{N} = P_i \Delta x [c_1 - c_2] = P_i \Delta x [c(x) - c(x + \Delta x)]$$

and taking the limit as  $\Delta x \rightarrow 0$  and recalling that  $\lim_{\Delta x \rightarrow 0} \left[ \frac{c(x + \Delta x) - c(x)}{\Delta x} \right] = \frac{\partial c}{\partial x}$  we can write

$$\dot{N} = - [P_i (dx)^2] \frac{\partial c}{\partial x} \quad (38)$$

Net transport is always down the gradient i.e from higher to lower concentration. Since transport cannot depend on the limiting process we must have that  $P_i (dx)^2 = \text{const}$ . This has units of  $[(\text{length})^2 \text{time}^{-1}]$  and we call it diffusivity or diffusion coefficient  $D$ . Expressing now properly the flux in terms of  $(\text{mol}/\text{cm}^2 \text{ s})$  we can write Fick's First Law of Diffusion in one dimension

$$J = -D \frac{\partial C}{\partial x} \quad (39)$$

or in 3-D

$$J = -D \nabla C \quad (39a)$$

where  $C$  is molar concentration in  $(\text{mol}/\text{cm}^3)$  and  $J$  ( $\text{mol}/\text{cm}^2 \text{ s}$ ) is the molar flux. [Obviously, different units can be used and will affect the units for the flux]. One should remember that equation (39) and (39a) yields the diffusion flux relative to the mean flow velocity if our system is a flow system.

Fick's Second Law is simply the principle of conservation of mass applied to an arbitrary volume  $V$  completely surrounded by a surface boundary  $S$ .

(Rate of accumulation of the solute in  $V$ ) = (Net rate of solute transport into  $V$  by diffusion)

Assuming our medium is stagnant i.e not flowing macroscopically

$$\int_V \frac{\partial C}{\partial t} dV = D \oint_S \nabla C \cdot \underline{n} ds \quad (40)$$

where  $\underline{n}$  is the outward pointing normal on  $S$ . Using Gauss-Ostrogradski Theorem we get

$$D \oint_S \nabla C \cdot \underline{n} ds = \int_V \nabla \cdot (D \nabla C) dV$$

Substitution in eq (40) yields

$$\int_V \left( \frac{\partial C}{\partial t} - \nabla D \nabla C \right) dV = 0 \quad (41)$$

which for  $D = \text{const}$  (i.e independent of position or composition) becomes

$$\frac{\partial C}{\partial t} = D \nabla^2 C \quad (41a)$$

In 3-D Cartesian coordinates

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

and similar expressions can be written in other coordinate systems.

Let us now consider a 1D version of eq (41a) for simplicity (although what we are going to show holds for 3D also). Moreover, let us write it in terms of molecular number per unit volume  $c$  (molecules/cm<sup>3</sup>). Consider the evolution of the concentration curves when we inject  $N$  molecules at time 0 at  $x = 0$  into a medium that did not contain such molecules at  $t = 0$ .

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (42)$$

$$\begin{aligned} t = 0 & \quad c = 0 \text{ except at } x = 0 \\ x \rightarrow \infty & \quad c \rightarrow 0 \end{aligned}$$

Let  $A$  (cm<sup>2</sup>) be the cross-sectional area of the system perpendicular to direction  $x$ . Therefore, conservation of mass for the injected species requires

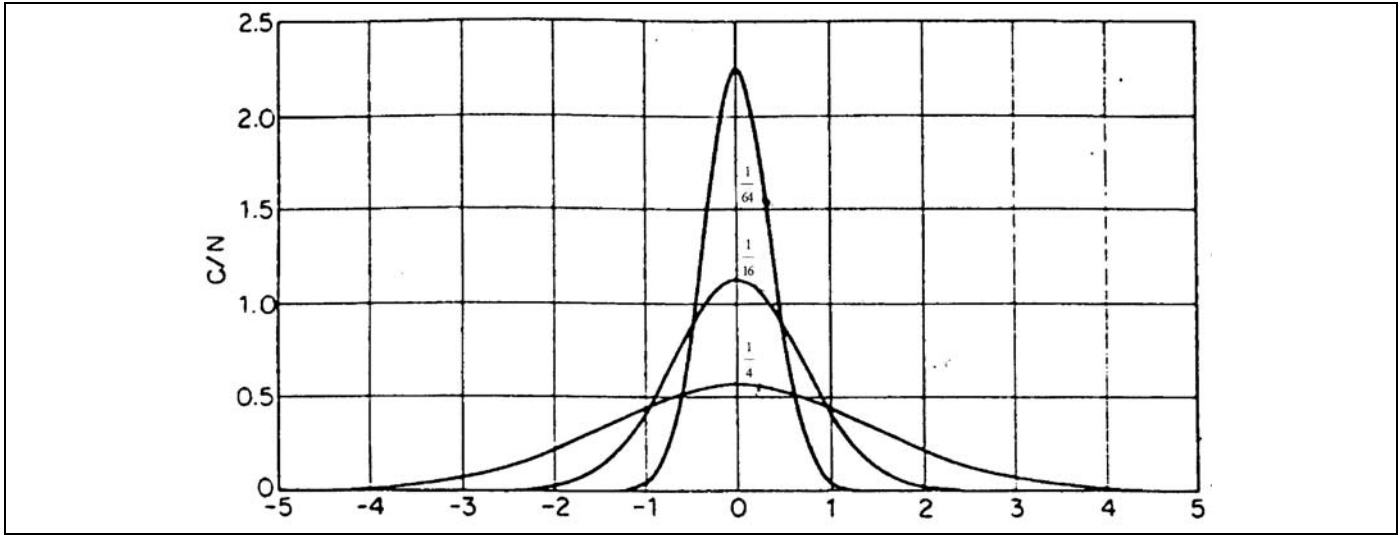
$$\int_{-\infty}^{\infty} c(x,t) dx = 2 \int_0^{\infty} c(x,t) dx = \left( \frac{N}{A} \right).$$

The solution is

$$c = \frac{(N/A)}{2\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) \quad (43)$$

The enclosed Figure 9 of  $c / (N/A)$  at different values of  $Dt$  shows how the solute spreads out to further and further distances as time passes.

**Figure 9** Concentration-distance curves for diffusion from an instantaneous plane source. Numbers on curves are values of  $Dt$ .



We can now look at the diffusion process from the view point of a single diffusing molecule. Let  $p(x) dx =$  (probability that the molecule has diffused to a region between  $x$  and  $x + dx$  at time  $t$ ) = (number of molecules between  $x$  and  $x + dx$ )/(total number in the original source).

$$p(x) dx = \frac{c(x) A dx}{N} = \frac{c(x) dx}{(N/A)} = \frac{1}{2\sqrt{\pi Dt}} \exp\left(\frac{-x^2}{4Dt}\right) dx \quad (44)$$

Now we are interested in the mean distance diffused by the molecule in time  $t$ . We cannot use  $\bar{x} = \int_{-\infty}^{\infty} x p(x) dx$  since the probability for going left and right is the same, and for one dimensional process along a line  $\bar{x} = 0$  (show that this is so). Instead, for the random walk type process like diffusion, we must consider as a measure of the mean distance the root mean square  $[\overline{x^2}]^{1/2}$  where  $\overline{x^2}$  is the mean square distance diffused by a molecule in time  $t$ .

$$\overline{x^2} = \int_{-\infty}^{\infty} x^2 p(x) dx = \frac{1}{2\sqrt{\pi Dt}} \int_{-\infty}^{\infty} x^2 e^{-(x^2/4Dt)} dx$$

By the change of variable  $\eta = \frac{x}{2\sqrt{Dt}}$

$$\begin{aligned} \overline{x^2} &= \frac{4Dt}{\sqrt{\pi}} \int_{-\infty}^{\infty} \eta^2 e^{-\eta^2} d\eta = \\ &= \frac{4Dt}{\sqrt{\pi}} \left\{ -\frac{1}{2} \eta e^{-\eta^2} \Big|_{-\infty}^{\infty} + \frac{1}{2} \int_{-\infty}^{\infty} e^{-\eta^2} d\eta \right\} = \\ &= \frac{2Dt}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-\eta^2} d\eta = \frac{2Dt}{\sqrt{\pi}} \sqrt{\pi} = 2Dt \end{aligned} \quad (45a)$$

For evaluation of the above integral see Appendix.

Equation (45)

$$\overline{x^2} = 2 D t \quad (45)$$

is used time and time again to provide a rapid estimate of mean diffusion distances in gases, liquid, solids, etc. It states that the mean square distance diffused by the molecule is the product of two times the diffusivity and time.

We can also use the above formula for an estimate of diffusivity. Consider a gas consisting of a single component A and apply the kinetic theory. Then magnitude of the mean molecular velocity is given by

$$\bar{u} = \left( \frac{8k_B T}{\pi \mu_{AA}} \right)^{1/2} \quad \text{but} \quad \mu_{AA} = \frac{m_A}{2}$$

so that we get  $\sqrt{2} \left( \frac{8k_B T}{\pi m_A} \right)^{1/2} = \sqrt{2} \bar{u}_A$

The total number of collisions per unit volume and unit time as per collision theory is given by

$$Z_{AA} = \frac{1}{2} \sqrt{2} \pi \sigma_A^2 \bar{u}_A n_A^2$$

and the number of collisions per unit volume per molecule and in unit time is:  $2 Z_{AA} / n_A$ . The mean free path that a molecule travels between collisions is

$$\lambda = \frac{\bar{u}_A}{2Z_{AA}/n_A} = \frac{\bar{u}_A}{\sqrt{2} \pi \sigma_A^2 \bar{u}_A n_A} = \frac{1}{\sqrt{2} \pi \sigma_A^2 n_A}$$

A simple representation of the mean free path is that it is an average distance over which momentum is transferred. If a macroscopic velocity gradient is  $\frac{dv}{dx}$  then the difference in velocity between the ends of the

free path is  $\lambda \frac{dv}{dx}$ . A molecule of mass  $m_A$  transports momentum  $m_A \lambda \frac{dv}{dx}$ . The number crossing up and

down per unit time is  $\frac{1}{2} n_A \bar{u}_A$ . The momentum transport is  $\frac{1}{2} n_A \bar{u}_A m_A \lambda \frac{dv}{dx}$  which is equal to the friction force per unit area

$$F = \mu \frac{dv}{dx} \quad \text{where} \quad \mu \quad \text{is viscosity.}$$

$$\mu \frac{dv}{dx} = \frac{1}{2} n_A m_A \bar{u}_A \lambda \frac{dv}{dx}$$

$$\mu = \frac{1}{2} n_A m_A \bar{u}_A \lambda = \frac{1}{2} \rho \bar{u}_A \lambda$$

Since

$$\lambda = \frac{1}{\sqrt{2} \pi \sigma_A^2 n_A}$$

$$\mu = \frac{m_A \bar{u}_A}{2\sqrt{2} \pi \sigma_A^2}$$

and gas viscosity is independent of density as proven repeatedly.

Kinematic viscosity is  $\nu = \frac{\mu}{\rho} = \frac{1}{2} \bar{u}_A \lambda$ . For an ideal gas  $Sc = \frac{\nu}{D} = 1$  so that

$$D_{AA} = \frac{1}{2} \bar{u}_A \lambda \quad (46)$$

where  $D_{AA}$  is the self diffusion coefficient .

In liquids, the force causing particle motion is the gradient of its chemical potential,  $\nabla \mu_1$ , (Gibbs free energy per molecule), the opposing force is friction given by Stokes Law  $6\pi \mu R_o V_p$  where  $\mu$  is solvent viscosity,  $R_o$  is particle (molecule) radius and  $V_p$  is the particle velocity relative to the mean velocity of the surrounding.

$$-\nabla \mu_1 = 6\pi \mu R_o V_p$$

By rules of thermodynamics

$$\begin{aligned} \mu_1 &= \mu_1^o + k_B T \ln x_1 \\ &= \mu_1^o + k_B T \ln \frac{c_1}{c_1 + c_2} \\ &= \mu_1^o + k_B T (\ln c_1 - \ln c_2) \end{aligned}$$

since solvent is much more abundant i.e  $c_2 \gg c_1$ . Then, since  $c_2 = \text{const}$

$$\begin{aligned} \nabla \mu_1 &= \frac{k_B T}{c_1} \nabla c_1 \\ -\frac{k_B T}{c_1} \nabla c_1 &= 6\pi \mu R_o V_p \end{aligned}$$

so that

$$J_1 = c_1 V_p = -\frac{k_B T}{6\pi \mu R_o} \nabla c_1 = -D \nabla c_1$$

This yields the Stokes-Einstein formula for diffusivity of a solute of diameter  $d = 2 R_o$  in liquid solvent of viscosity  $\mu$

$$D = \frac{k_B T}{3\pi \mu d} \quad (47)$$

### 7.8.2 Diffusion Limited Reaction

We assume that the two "particles" cannot co-exist. Place one (say A) of them at the center of a sphere and describe the motion of the other kind of particle (B) by the diffusion equation in spherical coordinates. All the medium at  $t = 0$  is exposed to the concentration  $C_{Bo}$  which persists at all times far away from  $r = 0$ .

$$\frac{\partial c_B}{\partial t} = \frac{D_B}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c_B}{\partial r} \right) \quad (48)$$

with

$$t = 0 \quad c_B = C_{Bo} \quad (49a)$$

$$r \rightarrow \infty \quad c_B = C_{Bo} \quad (49b)$$

$$r = 2r_A \quad c_B = 0 \quad (49c)$$

We have assumed here for simplicity that molecules of A and B are of the same size so that  $r_A = r_B$ . Once A and B touch, B ceases to exist as such at location  $r = 2r_A$  ( $c_B = 0$ ). However, we assume that A is constantly replenished at location  $r = 0$ .

Solution is given by

$$c_B(r, t) = c_{Bo} \left[ 1 - \frac{2r_A}{r} \operatorname{erfc} \left( \frac{r - 2r_A}{2\sqrt{D_B t}} \right) \right] \quad (50)$$

We define

$$\operatorname{erf} z = \frac{2}{\sqrt{\pi}} \int_0^z e^{-t^2} dt$$

$$\operatorname{erfc} z = 1 - \operatorname{erf} z = \frac{2}{\sqrt{\pi}} \int_z^\infty e^{-t^2} dt$$

The rate of arrival of these particles of species B to the particle A surface is (i.e. to the reaction surface)

$$\begin{aligned} A J_B &= \left( 4\pi r^2 D_B \frac{\partial c_B}{\partial r} \right)_{r=2r_A} = 16\pi r_A^2 D_B \left( \frac{\partial c_B}{\partial r} \right)_{r=2r_A} \\ &= 8\pi r_A D_B c_{Bo} \left( 1 + \frac{2r_A}{\sqrt{\pi D_B t}} \right) \end{aligned}$$

At steady state (i.e.  $t \rightarrow \infty$ ) the steady state rate of particles B arrival to the sphere at  $r = 2r_A$  is

$$J(4\pi r^2)_{r=2r_A} = 8\pi r_A D_B c_{Bo} \quad (51)$$

This steady state rate is obtained when  $(2r_A/\sqrt{\pi D_B t}) \ll 1$ .

Now we have to acknowledge that our particle  $A$  also moves, and we need to first find the relative diffusivity  $D_{AB}$  between  $A$  and  $B$ . As both particles undergo Brownian motion suppose that in time interval  $dt$  the displacements are  $dr_1$  and  $dr_2$ . The relative displacement is  $dr_1 - dr_2$ . The mean square relative displacement is

$$\overline{(dr_1 - dr_2)^2} = \overline{dr_1^2} + \overline{dr_2^2} - 2\overline{dr_1 \cdot dr_2}$$

Since motions of  $A$  and  $B$  are independent  $\overline{dr_1 \cdot dr_2} = 0$  so that

$$\overline{(dr_1 - dr_2)^2} = \overline{dr_1^2} + \overline{dr_2^2}$$

This implies

$$\begin{aligned} 2D_{12} dt &= 2D_1 dt + 2D_2 dt \\ D_{12} &= D_1 + D_2 \end{aligned} \quad (52)$$

and for  $D_{AB}$  we must use the sum of  $D_A$  and  $D_B$  e.g.  $D_{AB} = D_A + D_B$ .

Now we repeat our analysis for a stationary  $A$  while  $B$  diffuses with relative diffusivity  $D_A + D_B$ . The concentration  $c_B$  drops to zero at  $r = r_A + r_B$ . We now get

$$A_{r=r_A+r_B} \cdot J = 4\pi (r_A + r_B) D_{AB} c_{Bo} \left( 1 + \frac{r_A + r_B}{\sqrt{\pi D_{AB} t}} \right)$$

At steady state

$$A \cdot J = 4\pi (r_A + r_B) D_{AB} c_{Bo}$$

Total collision rate per unit volume is (with  $c_B = c_{Bo}$ )

$$\tilde{r} = 4\pi (r_A + r_B) D_{AB} c_B c_A = k_D c_B c_A \quad (53)$$

and the diffusion controlled "rate constant" is

$$k_D = 4\pi (r_A + r_B) (D_A + D_B) \quad (54)$$

### Partial Diffusion Effects

Now

$$R = k c_A c_B \quad (55)$$

where the apparent rate constant  $k$  is given by

$$k = \frac{k_{chem}}{1 + \frac{k_{chem}}{4\pi D_{AB} d_{AB}}} \quad (55a)$$

where  $d_{AB} = r_A + r_B$  .. See Figure 10. This result will be derived in full later.

Modifications are needed in case of ionic reactions in order to account for the electrostatic interactions.

Then

$$k_D = \frac{4\pi(D_A + D_B)}{\int_{d_{AB}}^{\infty} \frac{e^{u_{es}/k_B T}}{r^2} dr} \quad (56)$$

where  $U_{es} = \frac{Z_A Z_B e^2}{4\pi \epsilon_o \epsilon r}$  which then results in

$$k_D = 4\pi(D_A + D_B) d_{AB} \left( \frac{Z_A Z_B e^2 / 4\pi \epsilon_o \epsilon d_{AB} k_B T}{e^{Z_A Z_B e^2 / 4\pi \epsilon_o \epsilon d_{AB} k_B T} - 1} \right) \quad (56a)$$

### **7.8.3 Diffusion Limited Reaction (Steady State Analysis)**

#### Additional Comments

We have established that relative diffusivity of A with respect to (w.r.t.) B is

$$D_{AB} = D_A + D_B$$

Consider  $c$  (#/cm<sup>3</sup>) to be the molecular number concentration of B. Molecule of A is at  $r = 0$ .

Steady state model yields

$$\frac{d}{dr} \left( r^2 \frac{dc}{dr} \right) = 0 \quad (1)$$

$$r \rightarrow \infty \quad c = c_B \quad (2)$$

$$r = R_m \quad c = 0 \quad (3)$$

where  $c_B$  (#/cm<sup>3</sup>) is the number concentration of B away from A.

Solve (1)

$$r^2 \frac{dc}{dr} = A \rightarrow \frac{dc}{dr} = + \frac{A}{r^2}$$



$$c = B - \frac{A}{r} \quad (4)$$

Apply (2) and (3) to (4):

Then:

$$c = c_B \left( 1 - \frac{R_m}{r} \right) \quad (5)$$

$$\frac{dc}{dr} = \frac{c_B R_m}{r^2} \quad (6)$$

The diffusion flux pointing in the increasing  $r$  direction is

$$J = -D_{AB} \frac{dc}{dr} = -D_{AB} c_B \frac{R_m}{r^2} \quad (7)$$

The diffusion flux pointing inward on the surface of a sphere of radius  $r = R_m$  is

$$-J \Big|_{r=R_m} = \frac{D_{AB} c_B}{R_m} \quad (8)$$

The total number of molecules of  $B$  arriving at the surface of a sphere of radius  $R_m$  is:

$$(-J) \Big|_{R_m} \times 4\pi R_m^2 = 4\pi D_{AB} R_m c_B \quad (9)$$

Note that although the units of the above expression are (#/s) (i.e. number of molecules arrived per second) this really represents molecules of B arrived per second per molecule of A, i.e. the real units are (1/s). Multiplying this expression with the total number of molecules of A per unit volume,  $c_A$ , gives the rate of reaction in molecules of A reacted per unit volume and unit time:

$$\tilde{r} \left( \frac{\# A}{cm^3 s} \right) = [4\pi D_{AB} R_m c_B] c_A \quad (10)$$

Now introduce molar concentrations  $C_A = c_A / L$  and  $C_B = c_B / L$  where  $L$  is the Avogadro's constant.

Substitute  $c_A = L C_A$ ,  $c_B = L C_B$  into eq (10) and recall that the rate of reaction expressed in  $R$  (mol/cm<sup>3</sup>s) is  $R = \tilde{r} / L$ . So we get

$$R = 4\pi L D_{AB} R_m C_A C_B \quad (11)$$

An appropriate choice for  $R_m$  is

$$R_m = r_A + r_B \quad (12)$$

So that with

$$D_{AB} = D_A + D_B \quad (13)$$

we get

$$R = k_D C_A C_B = 4\pi L (D_A + D_B) (r_A + r_B) C_A C_B \quad (14)$$

$$k_D = 4\pi L (D_A + D_B) (r_A + r_B) \quad (15)$$

The units of  $k_D$  then are  $\left(\frac{cm^3}{mol\ s}\right)$

### 7.8.4 Partial Diffusional Effect

We will work now directly in molar quantities.

The problem can be posed (via steady state analysis) as follows:

$$\frac{d}{dr} \left( r^2 \frac{dC}{dr} \right) = 0 \quad (1)$$

$$r \rightarrow \infty \quad C = C_B \quad (2)$$

$$r = R_m \quad D_{AB} \frac{dC}{dr} \Big|_{R_m} L 4\pi R_m^2 = k_R C \quad (3)$$

Now

$$C = C_B - \frac{A}{r} \quad \frac{dC}{dr} = \frac{A}{r^2} \quad (4)$$

which satisfies eq (1) and (2).

Now from (3) we can evaluate the constant A:

$$\frac{D_{AB} A}{R_m^2} L 4\pi R_m^2 = k_R \left( C_B - \frac{A}{R_m} \right)$$

$$A = \frac{k_R C_B}{4\pi D_{AB} L + \frac{k_R}{R_m}} = \frac{k_R C_B R_m}{k_R + 4\pi D_{AB} R_m L} \quad (5)$$

where  $k_R$  is the true rate constant.

Now the flux of B is given by:

$$-J = D_{AB} \frac{dC}{dr} = D_{AB} \frac{A}{r^2} = \frac{k_R D_{AB} R_m C_B L}{r^2 (k_R + 4\pi D_{AB} R_m L)} \quad (6)$$

The rate of reaction is given by the flux of B multiplied by the area of the sphere of A on which reaction occurs

and multiplied by the concentration of A.

$$\begin{aligned}
 -R_A &= (-J)\Big|_{R_m} 4\pi R_m^2 C_A \\
 &= \frac{4\pi k_R D_{AB} R_m L C_A C_B}{k_R + 4\pi D_{AB} R_m L} \\
 &= \left[ \frac{k_R}{1 + \frac{k_R}{4\pi D_{AB} R_m L}} \right] C_A C_B = k C_A C_B
 \end{aligned} \tag{7}$$

Hence, the "apparent rate constant"  $k$  is

$$k = \frac{k_R}{1 + \frac{k_R}{4\pi D_{AB} R_m L}} = \frac{k_R}{1 + \frac{k_R}{k_D}} \tag{8}$$

where  $k_R$  is the true kinetic constant

$k_D$  is the diffusion limited rate constant.

Normally,  $R_m = d_{AB} = r_A + r_B$ . (9)

**FIGURE 10** Plot of  $k$  versus  $k_{chem}$  with  $k_D = 7.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

