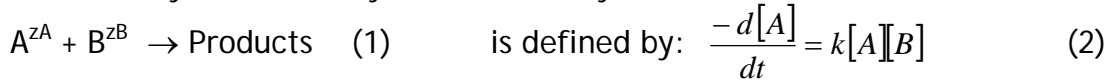


EXPERIMENT 1 - PRIMARY KINETIC SALT EFFECT

THEORY

The effect of electrolyte concentration on the rate constants of a number of reactions involving ions in aqueous solutions can be explained in terms of transition state theory and the Debye-Hückel theory. The rate constant k for the reaction



The rate constant k has been determined to vary with ionic strength I according to

$$k = k^0 10^{2Az(A)z(B)I^{1/2}} \quad (3)$$

in the low-ionic strength region where Debye-Hückel law is obeyed. In this equation A is the Debye-Hückel constant, $z(A)$ and $z(B)$ are charges on ions A and B , respectively.

If we look at the reaction above and reconsider it in terms of formation of an activated complex:



According to the transition theory, the equilibrium constant for the above reaction

$$K = \frac{[X^\ddagger]}{[A]^a [B]^b} \frac{\gamma_X}{\gamma_A^a \gamma_B^b} \quad (5)$$

in which X^\ddagger is the activated complex which is formed in the transition state, γ 's are the activity coefficients. Then again:

$$\frac{-d[A]}{dt} = k[A]^m [B]^n \times (\text{frequency}) \quad (6)$$

The frequency mentioned above is the frequency of passage of complex over barrier.

If we re-write equation (2):

$$\frac{-d[A]}{dt} = k[A]^m [B]^n = \left(\frac{k_B T}{h} \right) [X^\ddagger] \quad (7)$$

The rate constant, k , in equation (7) is

$$k = \frac{k_B T}{h} K \frac{\gamma_A^a \gamma_B^b}{\gamma_X} \quad (8)$$

where k_B is the Boltzmann constant, h is Planck's constant and T is absolute temperature. Equation (8) can be written in the form:

$$k = k^0 \frac{\gamma_A^a \gamma_B^b}{\gamma_X} \quad (9)$$

In dilute solutions the activity coefficient terms can be estimated from the Debye-Hückel theory. At 298 K

$$\log \gamma = -0.509 z_i^2 I^{1/2} \quad (10)$$

$$\log k = \log \frac{k_B T}{h} K + a \log \gamma_A + b \log \gamma_B - \log \gamma_x \quad (11)$$

$$\log k = \log \frac{k_B T}{h} K + 1.02 z_A z_B I^{1/2} \quad (12)$$

$$\log k = \log k^0 + 1.02 z_A z_B I^{1/2} \quad (13)$$

This is known as the Brønsted equation and it predicts that the plot of $\log(k)$ versus the square root of ionic strength I should be a straight line. For an aqueous solution, the slope is nearly equal to $z_A z_B$, the product of the ionic charges. Three special cases could occur:

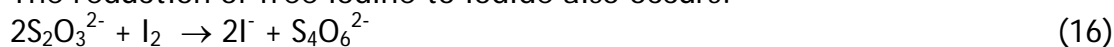
1. If z_A and z_B have the same sign, then $z_A z_B$ is positive and the rate constant increases with ionic strength.
2. If z_A and z_B have different signs, $z_A z_B$ is negative and the rate constant decreases with ionic strength.
3. If one of the reactants is uncharged, $z_A z_B$ is zero and the rate constant is independent of the ionic strength.

This change of k with I is called the **primary kinetic salt effect**. The ionic strength is calculated from $I = \Sigma(\frac{1}{2})m_i z_i^2$ (14)

where m is the concentration (in units of molality, mol kg⁻¹) of the ions. This summation is used for all the ions present in the solution, and not only for those involved in the reaction. This effect is going to be investigated for the following ionic reaction:



The reduction of free iodine to iodide also occurs:



The second reaction (reaction 16) is fast compared to the previous (reaction 15), and hence reaction 15 is the rate-determining one. The apparent rate constant, k_{app} , is hence given by

$$k_{app} = k[I^-] \quad (17) \quad \text{and} \quad k_{app} = \frac{m_{S_2O_3^{2-}}}{m_{S_2O_8^{2-}} \times \Delta t} \quad (18)$$

where m = molality. Please note that when the solutions are very dilute, molalities are replaced by molarities (M, mol L⁻¹)

The rate of the reaction is:
$$\frac{-d[S_2O_8^{2-}]}{dt} = \frac{\Delta x}{\Delta t} \quad (19)$$

