## **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

$$A^{zA} + B^{zB} \rightarrow Products$$
 (1) is defined by:  $\frac{-d[A]}{dt} = k[A][B]$  (2)

The rate constant k has been determined to vary with ionic strength / according to  $I = I \frac{0.102^{A_2(A)/(B)}}{10^{1/2}}$ 

$$k = k^0 10^{2A_z(A)_z(B)I^{+2}}$$
(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:

$$aA + bB \rightarrow X^{\ddagger} \rightarrow Products$$
 (4)

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

$$K = \frac{\left[X^{\mp}\right]}{\left[A\right]^{a}\left[B\right]^{b}} \frac{\gamma_{X}}{\gamma_{A}^{a}\gamma_{B}^{b}}$$
(5)

in which  $X^{t}$  is the activated complex which is formed in the transition state,  $\gamma$ 's are the activity coefficients. Then again:

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

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

If we re-write equation (2): 
$$\frac{-d[A]}{dt} = k[A]^m [B]^n = \left(\frac{k_B T}{h}\right) [X^{\mp}]$$
(7)

The rate constant, k, in equation (7) is  $k = \frac{k_B T}{k} K$ 

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

$$k = k^0 \frac{\gamma_A^a \gamma_B^b}{\gamma_X} \tag{9}$$

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

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

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

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

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

This is known as the Brønsted equation and it predicts that the plot of log(k) versus the square root of ionic strength / 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<sup>-1</sup>) 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:

$$2I^{-} + S_2 O_8^{-2} \rightarrow I_2 + 2SO_4^{2-}$$
(15)

The reduction of free iodine to iodide also occurs:  $2S_2O_3^{2-} + I_2 \rightarrow 2I^- + S_4O_6^{2-}$ 

The second reaction (reaction 16) is fast compared to the previous (reaction15), and hence reaction 15 is the rate-determining one. The apparent rate constant,  $k_{app}$ , is hence given by

(16)

$$k_{app} = k [I^{-}]$$
 (17) and  $k_{app} = \frac{m_{s_2 O_3^{2^-}}}{m_{s_2 O_8^{2^-}} \times \Delta t}$  (18)

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

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

where  $\Delta x$  is the number of moles of thiosulphate added and  $\Delta t$  is the time taken from the mixing of the persulphate with the reagents until the appearance of the blue color.

In this reaction, the iodine formed by the slow oxidation of persulphate is quickly reduced back to iodide by  $S_2O_3^{2^2}$ . Hence, until all the  $S_2O_3^{2^2}$  has been consumed, the iodide concentration does not change and the blue starch-iodine color does not appear. When the blue color appears, then moles of  $S_2O_8^{2^2}$  reacted is the same as the initial number of  $S_2O_3^{2^2}$ .

## PROCEDURE

1. Add the reagents to the flask according to the scheme given below. The amounts indicated are in ml in each case. Make sure that potassium persulphate ( $K_2S_2O_8$ ) solution is added as the <u>final</u> ingredient to each flask.

Flask	10 <sup>-1</sup> M KI	$10^{-3}$ M Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	1 M KNO <sub>3</sub>	Solvent	Starch	$10^{-2} \text{ M K}_2\text{S}_2\text{O}_8$	
1	20	10	0	59	1	10	
2	20	10	0	44	1	25	
3	20	10	0	34	1	35	
4	20	10	1	43	1	25	
5	20	10	3	40	1	25	
6	20	10	5	38	1	25	
7	20	10	10	33	1	25	
8	20	10	20	23	1	25	
9	20	10	25	18	1	25	
10	20	10	35	8	1	25	

2. Note the start of the reaction as the minute you mix potassium persulphate  $(K_2S_2O_8)$  with the rest of the mixture. The blue starch-iodine color indicates the end of the reaction. Record the time the reaction takes (i.e. how long does the appearance of the color take?).

# CALCULATIONS

- 1. Calculate the apparent rate constant,  $k_{app}$ , and the true rate constant k for reaction 15. For this use the results you have obtained for flasks 1, 2 and 3.
- 2. Calculate the rate constant k for the reactions taking place in flasks 4 to 10. Remember that you have added KNO<sub>3</sub> into these flasks and that the ionic strength has changed.
- 3. Plot  $\log k$  versus  $l^{1/2}$  as in equation (13), using all the k values calculated. See if your results fit into the Brønsted equation.
- 4. Does the slope of your curve fit into the expected category?

# DATA SHEET:

Flask	1	2	3	4	5	6	7	8	9	10
Time(s)										