ChE 203 - Physicochemical Systems Laboratory

EXPERIMENT 6: THE RATE OF A CHEMICAL REACTION

Before the experiment: *Read the booklet carefully. Be aware of the safety issues.*

Object

To determine the rate and the rate constant of a reaction and to observe the effect of temperature on the reaction rate

Theory

The rate of a reaction is evaluated by experimentally determining the value of a physical property, which can be related to the composition of the system as a function of time. Experimentally, it is found that the rate of a chemical reaction is dependent on the temperature, pressure and concentrations of the species involved. During the reaction, the concentration of any reactant decreases from its initial value to the equilibrium value and the concentration of any product increases from its initial value (usually zero) to the equilibrium value [1].

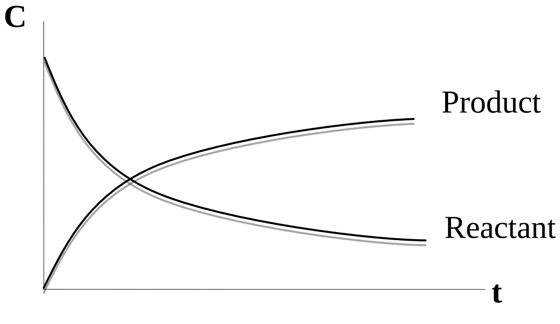

Figure 1. Variation of the concentration of reactant and product with time.

The rate of reaction may be expressed in terms of the time rate of change of concentration of any of the species involved. It can be written as the decrease in concentration of reactant(s) with time –dc/dt or as the increase of product(s) with time dc/dt. Consider a reaction of the type;

$A + B \rightarrow C + D$

$$-\frac{dc_a}{dt} = -\frac{dc_b}{dt} = f(c_a, c_b) \tag{1}$$

In many cases, the rate law has the simple form;

$$-\frac{dc}{dt} = kc_a^{\alpha} c_b^{\beta} \tag{2}$$

where k, α, β are constants. The constant k is the rate constant of the reaction. If all the concentrations were unity, k is called the specific rate of the reaction. The constant b is the reaction order with respect to B. The overall reaction order is the sum of α + β [2].

A qualitative idea of the rate equation for a reaction occurring upon the collision of two molecules can be given as follows. In such a case, the reaction rate would be proportional to A, the number of collisions per second. Furthermore, only collisions involving energy greater than some critical value of the activation energy (E_a), are effective. Then the rate of the reaction will have the form;

$$-\frac{dc}{dt} = k \cdot c^n = Aexp\left(\frac{-E_a}{RT}\right) \cdot c^n \tag{3}$$

Here n shows the overall reaction order, T is the temperature, R is the universal gas constant. This form of k is called as Arrhenius equation, and A is defined as the ‘frequency factor’[2].

Experimental Work

Apparatus and Chemicals: Beakers, Erlenmeyer flasks, pipettes, burette, water bath (50 °C)

0.05 M $Na_2S_2O_3$ (Sodium thiosulphate) (7.9 g/L)
0.1 M $K_2S_2O_8$ (Potassium persulphate) (27.0 g/L)
0.4 M KI (Potassium iodide) (66.4 g/L)

Procedure

This reaction is an oxidation reaction of iodide in neutral solution with persulphate.

$$2I^- + S_2O_8^{-2} \rightarrow 2SO_4^{-2} + I_2$$

1. Add 20 ml $Na_2S_2O_3$ solution in 180 ml water to prepare titration solution and fill the burette with this titration solution.
2. Add 20 ml $K_2S_2O_8$ solution in 80 ml water to prepare one of the reactants.
3. Divide 100 ml $K_2S_2O_8$ solution in two separate Erlenmeyer flasks.
4. Prepare two 50 ml KI solution in separate graduated cylinders.
5. Pour 50 ml KI solutions into the Erlenmeyer flasks that contain 50 ml $K_2S_2O_8$ solutions to start the reaction, and start the stopwatch.
6. Place one of the Erlenmeyer flask into the water bath at 50 °C.
7. After 3 minutes, take 10 ml sample from the Erlenmeyer flask in the room conditions by using a pipette.
8. Transfer the sample solution into another Erlenmeyer flask.
9. Titrate the sample with $Na_2S_2O_3$ solution in the burette.
10. Repeat the same procedure by taking 10 ml samples every 4 minutes (to 19 min).
11. At the end (19 min), take 10 ml sample from the flask in the water bath and titrate the sample.

Safety Issues: In this experiment, $K_2S_2O_8$ (Potassium persulphate) and KI (Potassium iodide) are used as reactants and $Na_2S_2O_3$ (Sodium thiosulphate) is used as titrant. I_2 (Iodine) is obtained as product. Potassium persulphate is very hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation, slightly hazardous in case of skin contact (corrosive, permeator). Prolonged exposure may result in skin burns and ulcerations. Over-exposure by inhalation may cause respiratory irritation. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering. Potassium iodide is slightly hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Sodium thiosulphate is hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation and prolonged or repeated skin contact may cause dermatitis. Iodine is very hazardous in case of eye contact (irritant), hazardous in case of skin contact (irritant), of ingestion, of inhalation and chronic exposure can lead to iodism characterized by salivation, nasal discharge, sneezing, conjunctivitis, fever, laryngitis, bronchitis, stomatitis, and skin rashes. Chronic exposure can affect thyroid function, which may cause kidney damage.

In case of eye or skin contact, remove any contact lenses or contaminated clothing or shoes. Immediately flush eyes or skin with plenty of cold water for at least 15 minutes. Cover the irritated skin with an emollient. In case of inhalation, remove to fresh air. If breathing is difficult get medical attention immediately. In case of ingestion, do not induce vomiting. Never give anything by mouth to an unconscious person. For further information, check MSDS of $K_2S_2O_8$ (Potassium persulphate), KI (Potassium iodide), $Na_2S_2O_3$ (Sodium thiosulphate) and I_2 (Iodine) [3, 4, 5, 6]. The solutions used in this experiment are dilute in terms of the chemicals, therefore no need to a special treatment.

Calculations

Since iodide concentration is in higher amounts, it can be assumed that it remains constant;

$$-\frac{dc_A}{dt} = kc_Ac_B = k'c_A$$

1. <u>Differential Method:</u>
   a) Plot a graph of concentration of persulphate (reactant) and I_2 (product) vs. time.
   b) Add trendline (2nd order polynomial in time) and obtain the equation of the curve by using Excel.
   c) Obtain $-dc_A/dt$ values at each time from the equation. Then, calculate the rate constant (k') by dividing these values to concentration values at each time [1].

2. Integral Method:

   Solve the rate equation as follows:

   $$\frac{dc_A}{c_A} = -k'dt$$

   After integrating it;

   $$lnc_A = lnc_{A0} - k't$$

   Draw (ln c_A) vs t, and determine k' from the slope of this line [1].

3. Half-lives Method:

   In the integrated form of the rate equation, write $c_{A0}/2$ instead of c_A and half-time ($t_{1/2}$) instead of t in the rate equation. Then, the equation can be written as:

   $$k't_{1/2} = -ln\left[\frac{\left(\frac{c_{A0}}{2}\right)}{c_{A0}}\right] = -\ln\left(\frac{1}{2}\right) = \ln(2)$$

   Calculate k' [2].

4. Compare all these k' values and discuss them.

References

[1] Fogler, S. H., *Elements of Chemical Reaction Engineering*, 4th Edition, Wiley, New York, 2006.

[2] Atkins P. and Paula J., *Atkins' Physical Chemistry*, 8th Edition, Oxford University Press, Oxford, 2006.

[3] Potassium persulphate MSDS, http://www.sciencelab.com/msds.php?msdsId=9927234.

[4] Potassium iodide MSDS, http://www.sciencelab.com/msds.php?msdsId=9927571.

[5] Sodium thiosulphate MSDS, http://www.ch.ntu.edu.tw/~genchem99/msds/exp19/Na2S2O3.pdf

[6] Iodine MSDS, http://avogadro.chem.iastate.edu/MSDS/I2.htm.