Chapter 11 – Problem Set 2

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February 1, 2020

$$8\,H^+(aq) + 4\,Cl^-(aq) + MnO_4{}^-(aq) \longrightarrow 2\,Cl_2(g) + Mn^{3+}(aq) + 4\,H_2O\,(l)$$

1. $Cl_2(g)$ can be generated in the laboratory by reacting potassium permanganate with an acidified solution of sodium chloride. The net-ionic equation for the reaction is given above.

   (a) A 25[mL] sample of 0.250[M] NaCl reacts completely with excess $KMnO_4(aq)$. The $Cl_2(g)$ produced is dried and stored in a sealed container. At 22[° C] the pressure of the $Cl_2(g)$ in the container is .95[ATM]

      i. Calculate the number of moles of $Cl^-(aq)$ present before any reaction occurs.

      $$.025 \cdot .25 = 6.25 \cdot 10^{-3}[\text{mol}] \tag{1}$$

      ii. Calculate the volume, in L, of the $Cl_2(g)$ in the sealed container.

      $$\begin{aligned} V &= \frac{nRT}{P} \\ \frac{6.25 \cdot 10^{-3} \cdot .0821 \cdot 295}{.95} \cdot \frac{1}{2} &= .0797[\text{L}] \end{aligned} \tag{2}$$

   An initial-rate study was performed on the reaction system. Data for the experiment are given in the table below.

Trial	$[Cl^-]$	$[MnO_4{}^-]$	$[H^+]$	Rate of Disappearance of $MnO_4{}^-$ in $M\,s^{-1}$
1	0.0104	0.00400	3.00	$2.25 \cdot 10^{-8}$
2	0.0312	0.00400	3.00	$2.03 \cdot 10^{-7}$
3	0.0312	0.00200	3.00	$1.02 \cdot 10^{-7}$

   (b) Using the information in the table, determine the order of the reaction with respect to each of the following. Justify your answers.

i. Cl^-

$$\frac{.225}{2.03} = \left(\frac{.0104}{.0312}\right)^m \tag{3}$$
$$m = 2$$

ii. $MnO_4{}^-$

$$\frac{1.02}{2.03} = \left(\frac{.02}{.04}\right)^n \tag{4}$$
$$n = 1$$

(c) The reaction is known to be third order with respect to H^+. Using this information and your answers to part (b) above, complete both of the following:

i. Write the rate law for the reaction.

$$rate = k[Cl^-]^2[MnO_4{}^-][H^+]^3 \tag{5}$$

ii. Calculate the value of the rate constant, k, for the reaction, including appropriate units.

$$1.02 \cdot 10^{-7} = k[.0312]^2[.002][3]^3$$
$$k = .00194 \left[\frac{1}{M^5 s}\right] \tag{6}$$

(d) Is it likely that the reaction occurs in a single elementary step? Justify your answer.

No, because the orders of Cl^- and H^+ differ from those in the equation

2.
$$\begin{array}{ll} \text{Step I} & O_3 + Cl \longrightarrow O_2 + ClO \\ \text{Step II} & ClO + O \longrightarrow Cl + O_2 \end{array}$$

(a) Write a balanced equation for the overall reaction represented by Step I and Step II above.

$$O_3 + O \longrightarrow 2\,O_2$$

(b) Clearly identify the catalyst in the mechanism above. Justify your answer.

Cl drives the whole process, as it is not used up throughout the process

(c) Clearly identify the intermediate in the mechanism above. Justify your answer.

ClO is the intermediate, as it is formed in the second step, and is used up throughout the process

(d) If the rate law for the overall reaction is found to be $rate = k[O_3][Cl]$, determine the following:

i. The overall order of the reaction

The overall order is 2

ii. Appropriate units for the rate constant, k

The units are then $\left[\frac{1}{\text{M} \cdot \text{time}}\right]$

iii. The rate-determining step of the reaction, along with justification for your answer.

Step I is most likely the determining step, because the orders of O_3 and Cl match that of the rate formula