## AP® CHEMISTRY 2010 SCORING GUIDELINES

# Question 3 (9 points)

$$8 \text{ H}^+(aq) + 4 \text{ Cl}^-(aq) + \text{MnO}_4^-(aq) \rightarrow 2 \text{ Cl}_2(g) + \text{Mn}^{3+}(aq) + 4 \text{ H}_2\text{O}(l)$$

 $Cl_2(g)$  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 25.00 mL sample of 0.250 M NaCl reacts completely with excess KMnO<sub>4</sub>(aq). The Cl<sub>2</sub>(g) produced is dried and stored in a sealed container. At 22°C the pressure of the Cl<sub>2</sub>(g) in the container is 0.950 atm.
  - (i) Calculate the number of moles of  $Cl^{-}(aq)$  present before any reaction occurs.

mol Cl<sup>-</sup> = 
$$(0.02500 \text{ L})(0.250 \text{ M}) = 6.25 \times 10^{-3} \text{ mol}$$
 One point is earned for the correct numerical value.

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

mol Cl<sub>2</sub> = 
$$\frac{\text{mol Cl}^{-}}{2}$$
 =  $\frac{6.25 \times 10^{-3} \text{ mol}}{2}$  =  $3.125 \times 10^{-3} \text{ mol Cl}_2$  One point is earned for the correct number of moles of Cl<sub>2</sub> based on stoichiometry.

$$V = \frac{nRT}{P} = \frac{\left(3.125 \times 10^{-3} \text{ mol Cl}_2\right)\left(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}\right)(295 \text{ K})}{0.950 \text{ atm}}$$
One point is earned for the correct number of moles of Cl<sub>2</sub> based on stoichiometry.

One point is earned for substitution into ideal gas law and correct numerical result.

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

Trial	[Cl <sup>-</sup> ]	[MnO <sub>4</sub> <sup>-</sup> ]	$[\mathrm{H}^+]$	Rate of Disappearance of $MnO_4^-$ in $Ms^{-1}$
1	0.0104	0.00400	3.00	$2.25 \times 10^{-8}$
2	0.0312	0.00400	3.00	$2.03 \times 10^{-7}$
3	0.0312	0.00200	3.00	$1.02 \times 10^{-7}$

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#### **Question 3 (continued)**

- (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<sup>-</sup>

The reaction is second order. Tripling [Cl $^-$ ] between trials 1 and 2 with no change in [MnO $_4$  $^-$ ] results in a nine-fold increase in the rate:

$$\left(\frac{0.0312 \ M}{0.0104 \ M}\right)^{x} = \frac{2.03 \times 10^{-7}}{2.25 \times 10^{-8}}$$
$$3^{x} = 9$$
$$x = 2$$

Thus the order of the reaction must be 2 with respect to Cl<sup>-</sup>.

One point is earned for the correct order of reaction with justification.

(ii) MnO<sub>4</sub>

The reaction is first order. Doubling [MnO<sub>4</sub> $^-$ ] between trials 3 and 2 with no change in [Cl $^-$ ] results in a doubling of the rate:

$$\left(\frac{0.00400 M}{0.00200 M}\right)^{y} = \frac{2.03 \times 10^{-7}}{1.02 \times 10^{-7}}$$
$$2^{y} = 2$$
$$y = 1$$

Thus the order of the reaction must be 1 with respect to MnO<sub>4</sub><sup>-</sup>.

One point is earned for the correct order of reaction with justification.

- (c) The reaction is known to be third order with respect to H<sup>+</sup>. Using this information and your answers to part (b) above, complete both of the following:
  - (i) Write the rate law for the reaction.

rate = $k[Cl^-]^2[MnO_4^-][H^+]^3$
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One point is earned for the correct rate law.

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#### Question 3 (continued)

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

Using data from trial 1:

$$2.25 \times 10^{-8} M \text{ s}^{-1} = k(0.0104 M)^2 (0.00400 M)(3.00 M)^3$$
  
$$k = 1.93 \times 10^{-3} M^{-5} \text{s}^{-1}$$

One point is earned for the correct numerical result.

One point is earned for the correct units.

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

It is not likely that the reaction occurs in a single step because the orders of the reaction with respect to the reactants do not correspond to the coefficients in the balanced equation

#### OR

It is not likely that the reaction occurs in a single step because the reaction requires the collision of many (13) reactant particles and the frequency of a 13-particle collision is negligible. One point is earned for the correct answer with justification.