Question 3
(9 points)

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

$Cl_2(g)$ 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 $KMnO_4(aq)$. 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 0.950 atm.

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

mol Cl^- = (0.02500 L)(0.250 *M*) = 6.25×10^{-3} 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.

$\text{mol } Cl_2 = \frac{\text{mol } Cl^-}{2} = \frac{6.25 \times 10^{-3}\text{ mol}}{2} = 3.125 \times 10^{-3}\text{ mol } Cl_2$	One point is earned for the correct number of moles of Cl_2 based on stoichiometry.
$V = \frac{nRT}{P} = \frac{(3.125 \times 10^{-3}\text{ mol } Cl_2)(0.0821\text{ L atm mol}^{-1}\text{ K}^{-1})(295\text{ K})}{0.950\text{ atm}}$ $= 0.0797\text{ L } Cl_2$	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	$[Cl^-]$	$[MnO_4^-]$	$[H^+]$	Rate of Disappearance of MnO_4^- in $M\ s^{-1}$
1	0.0104	0.00400	3.00	2.25×10^{-8}
2	0.0312	0.00400	3.00	2.03×10^{-7}
3	0.0312	0.00200	3.00	1.02×10^{-7}

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^-

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

(ii) MnO_4^-

The reaction is first order. Doubling $[MnO_4^-]$ 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_4^-.	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^+. Using this information and your answers to part (b) above, complete both of the following:

(i) Write the rate law for the reaction.

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

Question 3 (continued)

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

Using data from trial 1: $2.25 \times 10^{-8}\ M\,s^{-1} = k(0.0104\ M)^2(0.00400\ M)(3.00\ M)^3$ $k = 1.93 \times 10^{-3}\ M^{-5}s^{-1}$	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.