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: $$\left(\frac{0.0312\ M}{0.0104\ M}\right)^x = \frac{2.03\times10^{-7}}{2.25\times10^{-8}}$$ $$3^x = 9$$ $$x = 2$$ 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: $$\left(\frac{0.00400\ M}{0.00200\ M}\right)^y = \frac{2.03\times10^{-7}}{1.02\times10^{-7}}$$ $$2^y = 2$$ $$y = 1$$ 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.

3A₁

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

3. $Cl_2(g)$ 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.

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

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}

(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^-

(ii) MnO_4^-

(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.

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

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

a) i) $(0.025)(0.25) = \boxed{0.00625 \text{ mol } Cl^-}$

ii) $(0.00625)(\frac{2}{4}) = 0.003125 \text{ mol } Cl_2$

$PV = nRT$

$(0.950)(V) = (0.003125)(0.0821)(22+273)$

$V = 0.079669 \approx \boxed{0.0797 \text{ L}}$

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b) i) $\frac{2.03 \times 10^{-7}}{2.25 \times 10^{-8}} = \frac{k[0.0312]^x[0.004]^y}{k[0.0104]^x[0.004]^y}$

$9 = 3^x$

$x = 2$ [second order]

ii) $\frac{2.03 \times 10^{-7}}{1.02 \times 10^{-7}} = \frac{[0.0312]^x[0.004]^y}{[0.0312]^x[0.002]^y}$

$2 = 2^y$ $y = 1$ [first order]

c) i) Rate $= k[H^+]^3[Cl^-]^2[MnO_4^-]$

ii) $2.25 \times 10^{-8} = k(3^3)(0.004)(0.0104)^2$

$k =$ [0.0019 $L^5/mol^5 \cdot s$]

$\frac{M}{s} = k(M^6)$

$k = \left(\frac{M}{s}\right)\left(\frac{1}{M^6}\right)$

$k = \frac{L^5}{mol^5 \cdot s}$

d) No, it is not likely the reaction will occur in a single elementary step because the rate law of that step would have to match the rate law in part c. (Rate law of reaction given does not match.) Thus, the slowest step in the pathway will occur & match the rate law of the overall reaction. (Powers do not match up to coefficients).

3B₁

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

3. $Cl_2(g)$ 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.

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

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}

   (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^-

   (ii) MnO_4^-

   (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.

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

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

3. a) $8H^+ + 4Cl^- + MnO_4^- \rightarrow 2Cl_2 + Mn^{+3} + 4H_2O$

25 mL, .25 M; xs; P: .950

i) .25 M · .025 = .00625 mols × 4 = **.025 mols Cl⁻**

ii) .025 mols Cl⁻ × $\frac{2 \text{ moles } Cl_2}{4 \text{ mols } Cl}$ = .05 moles Cl_2

PV=nRT   22°C+273=295 K

~~(.950)V=(.05)(~~ (.950 atm)(V) = (.05 mols)(.0821 atm/mol·K)(295 K)

~~V=1.27 ...~~ **V=1.27 L**

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b) i) ~~Rx~~ Rxn is 2nd order with respect to Cl^- because from Trial 1 to 2, $[Cl^-]$ triples and the rate increased by 9 times, $3^{(2)} = 9$.

ii) The reaction is 1st order with respect to MnO_4^- because from Trial 2 to 3 the $[MnO_4^-]$ halves, as does the rate of disappearance.

c) i) $Rate = k[Cl^-]^2[MnO_4^-][H^+]^3$

ii) $2.25 \times 10^{-8}\ M/s = k\,(.0104M)^2(.004M)(3M)^3$

$\boxed{k = .0019\ M^{-5}s^{-1}}$

$\frac{M/s}{M^6}$ $\quad \frac{M}{s} \cdot \frac{1}{M^6} = \frac{1}{M^5 s}$

d) The reaction does not occur in a single elementary step because the exponents of the rate law do not correspond to the coefficients in the equation for the reaction, as they would for an elementary process. Also, according the reaction equation there is more than bimolecular collisions occuring, which also cannot occur in an elementary process.

3C₁

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

3. $Cl_2(g)$ 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.

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

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}

(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^-

(ii) MnO_4^-

(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.

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

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

a) i) $\frac{.250\text{ mol } Cl^-}{L} \cdot \frac{L}{1000\text{ mL}} = 2.50 \times 10^{-4} \frac{\text{mol}}{\text{mL}} Cl^- \times 25.00\text{ mL} = 6.25 \times 10^{-3}\text{ mol } Cl^-$

ii) $PV = nRT \quad V = \frac{nRT}{P} = \frac{(6.25 \times 10^{-3}\text{ mol } Cl^-)(.0821 \frac{L\,atm}{mol\,K})(295\,K)}{.950\text{ atm}} = .159\,L$

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3C2

b) i) Cl^- is 2nd order, when $[H^+]$ and $[MnO_4^-]$ stay constant and $[Cl^-]$ increases by a factor of 3, the rate of disappearance of MnO_4^- increases by a factor of 9

ii) MnO_4^- is 1st order, when $[H^+]$ and $[Cl^-]$ stay the same and $[MnO_4^-]$ decreases by 2, the rate of disappearance of MnO_4^- decreases by 2

c) i) rate = $K[Cl^-]^2[MnO_4^-][H^+]^3$

ii) $K = \frac{(.0104M)^2(.00400M)(3.00M)^3}{2.25\times10^{-8}\ M/s} = 5.19\times10^{2}\ \frac{s}{M^3}$

d) no, many things have to break down and be formed in more than one step

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Question 3

Overview

This question assessed students' understanding of stoichiometry, the relationship among variables of state for gases, and reaction kinetics. Part (a)(i) required students to determine the moles of Cl^- ion present in a given volume of a solution of given concentration. Part (a)(ii) required students to determine the moles of $Cl_2(g)$ formed by using the balanced equation and then to determine the volume of this gas at the stated nonstandard conditions of temperature and pressure. Part (b) asked students to use given experimental data to determine the order of the reaction with respect to two of the reactants. Part (c) required students to use these orders, together with additional information, to write the rate law for the reaction and to determine the value and units of the rate constant. Part (d) asked students to assess the likelihood of the reaction occurring in a single elementary step.

Sample: 3A
Score: 9

This response earned all 9 possible points: 1 point for part (a)(i), 2 points for part (a)(ii), 1 point for part (b)(i), 1 point for part (b)(ii), 1 point for part (c)(i), 2 points for part (c)(ii), and 1 point for part (d).

Sample: 3B
Score: 7

This response earned no point for part (a)(i) because the number of moles of Cl^- is incorrect. In part (a)(ii) only 1 point was earned; although the number of moles of Cl_2 produced is not consistent with the moles of Cl^- determined in part (a)(i), the volume of dry $Cl_2(g)$ produced is consistent with the stated number of moles. Full credit was earned for parts (b), (c) and (d).

Sample: 3C
Score: 5

This response earned 1 point for part (a)(i). Only 1 point was earned for part (a)(ii) because, although the calculated number of moles of Cl_2 produced is incorrect, the volume of dry $Cl_2(g)$ produced is consistent with the stated number of moles. In part (b) 2 points were earned. In part (c)(i) 1 point was earned for a correct rate law, but no points were earned for part (c)(ii) because both the numerical value and the unit of the rate constant are incorrect. No point was earned for part (d).