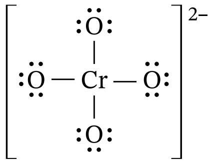
Question 2: Version J

2. Answer the following questions about the chromate ion, CrO_4^{2-}, and the dichromate ion, $Cr_2O_7^{2-}$.

Part A

The bonds between chromium and oxygen in CrO_4^{2-} can be represented as covalent bonds. One possible Lewis diagram for the CrO_4^{2-} ion is shown in Figure 1.

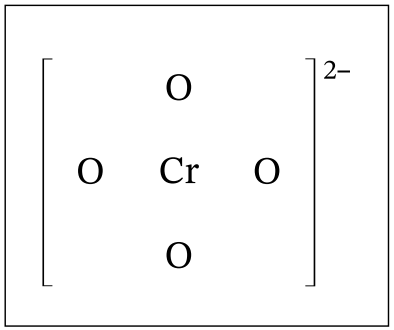
Figure 1



i. Based on VSEPR theory, **predict** the molecular geometry of the CrO_4^{2-} ion.

ii. On Figure 2, **draw** a complete Lewis diagram for a resonance structure of CrO_4^{2-} that results in a formal charge of zero on two of the O atoms and a formal charge of −1 on the other two O atoms. Your diagram should contain the same number of valence electrons as in Figure 1.

Figure 2



Part B

When reacted with a strong acid like $HNO_3(aq)$, $CrO_4^{2-}(aq)$ can be converted to $Cr_2O_7^{2-}(aq)$ and $H_2O(l)$ in a reversible reaction.

i. **Write** a balanced net ionic equation for the reaction between $CrO_4^{2-}(aq)$ and a strong acid.

ii. Is the reaction a redox reaction? **Justify** your answer based on the oxidation number of Cr.

The following information applies to parts C and D.

In acidic solutions, $Cr_2O_7^{2-}(aq)$ reacts to form $CrO_3(aq)$ according to Equation 1.

$$\text{Equation 1: } Cr_2O_7^{2-}(aq) + 2\ H_3O^+(aq) \rightarrow 2\ CrO_3(aq) + 3\ H_2O(l)$$

$CrO_3(aq)$ can be electrolyzed to plate objects with a thin layer of chromium metal according to Equation 2.

$$\text{Equation 2: } CrO_3(aq) + 6\ H^+(aq) + 6\ e^- \rightarrow Cr(s) + 3\ H_2O(l) \qquad E^\circ = -1.32\ \text{V}$$

Part C

Is the reaction represented by Equation 2 thermodynamically favorable or unfavorable under standard conditions? **Justify** your answer with a calculation of ΔG°. Show the work that leads to your answer.

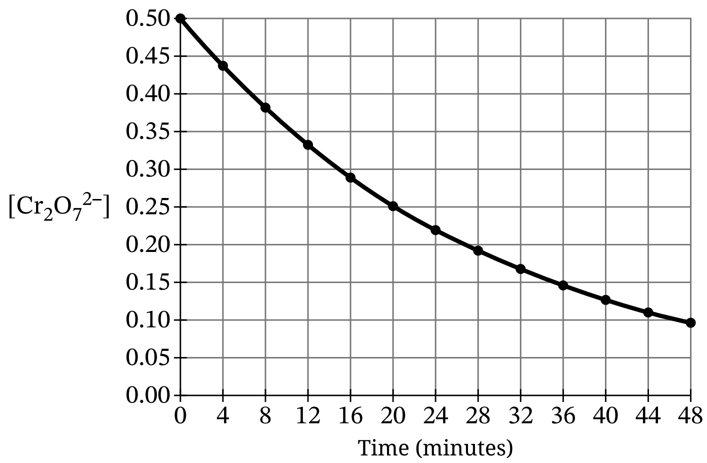
Part D

Calculate the number of grams of $Cr(s)$ that could be plated onto the surface of a steel rod when 15.0 A of current is applied for 3250 seconds. Show the work that leads to your answer.

Part E

In a separate experiment, an iron wire is placed directly in a solution of 0.50 M $Cr_2O_7^{2-}(aq)$ with pH = 1.99. The concentration of $Cr_2O_7^{2-}(aq)$ remaining is recorded over time, and the results are presented in Figure 3.

Figure 3

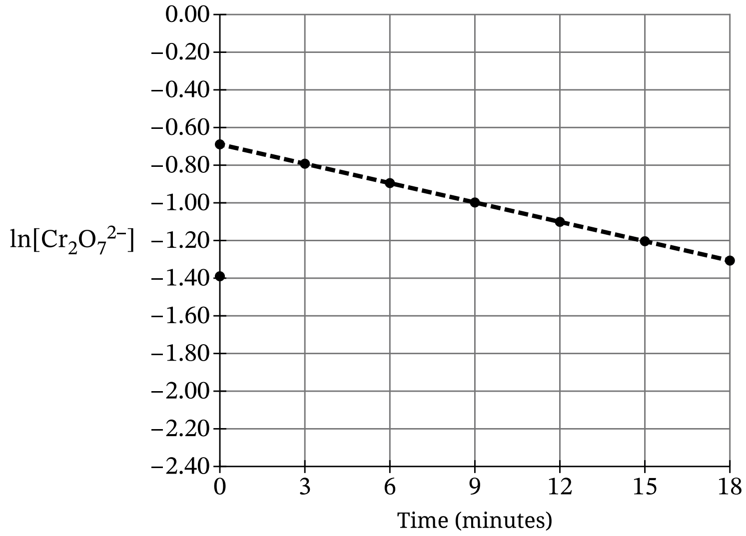


Explain how the data in Figure 3 support the conclusion that the reaction is first order with respect to $Cr_2O_7^{2-}$.

The following information applies to parts F and G.

The student creates a plot of $\ln[Cr_2O_7^{2-}]$ versus time for a trial with an initial concentration of 0.50 M $Cr_2O_7^{2-}(aq)$, as shown in Figure 4.

Figure 4



Part F

Calculate the value of the rate constant, k, for the reaction. Report your answer in units of min^{-1}. Show the work that leads to your answer.

Part G

The student then runs a second trial of the experiment under identical conditions but uses an initial concentration of 0.25 M $Cr_2O_7^{2-}(aq)$ instead of 0.50 M $Cr_2O_7^{2-}(aq)$. On Figure 4, carefully **draw** the plot of $\ln[Cr_2O_7^{2-}]$ versus time that would be expected for the second experiment. The point at time zero has already been plotted.

2. In the gas phase, $AlCl_3$ is a molecular substance. A reaction of gaseous $AlCl_3$ at high temperature is represented by the following balanced equation.

$$\text{Reaction 1: } AlCl_3(g) \rightarrow Al(g) + 3\,Cl(g) \quad \Delta H_1^\circ = ?$$

(a) How many grams of $Cl(g)$ can be formed from 1.25 mol of $AlCl_3(g)$?

Additional reactions that involve Al or Cl are shown in the following table.

Reaction Number	Equation	ΔH_{rxn}° (kJ/mol$_{rxn}$)
2	$Al(s) + \frac{3}{2} Cl_2(g) \rightarrow AlCl_3(g)$	−583
3	$Al(s) \rightarrow Al(g)$	+326
4	$Cl_2(g) \rightarrow 2\,Cl(g)$	+243

(b) Calculate the value of ΔH_1°, in kJ/mol$_{rxn}$, for reaction 1 above using reactions 2, 3, and 4.

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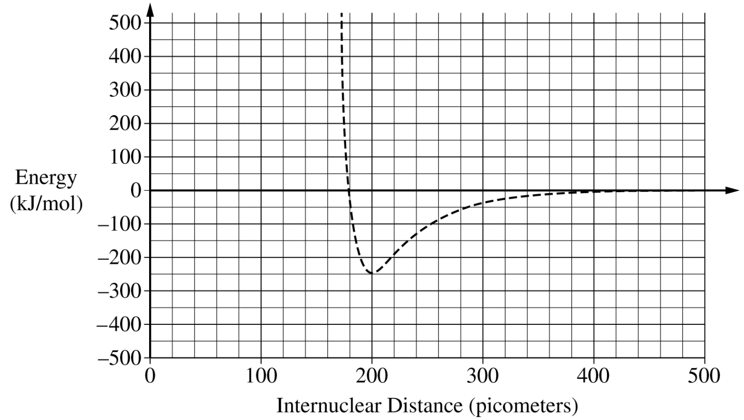
Continue your response to **QUESTION 2** on this page.

(c) A potential energy diagram for Cl_2 is shown in the following graph.



(i) Based on the graph, what is the bond length, in picometers, for Cl_2 ? ________

(ii) A student finds that the average Al − Cl bond length is 220 picometers and the average bond energy is 425 kJ/mol. Draw the potential energy curve for the average Al − Cl bond on the preceding graph.

(d) Three proposed Lewis diagrams for the $AlCl_3(g)$ molecule are shown.

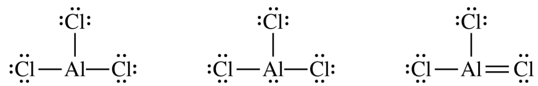


Diagram 1 Diagram 2 Diagram 3

(i) The $AlCl_3(g)$ molecule has a trigonal planar geometry. Which diagram (1, 2, or 3) can be eliminated based on geometry? Justify your choice based on VSEPR theory.

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Continue your response to **QUESTION 2** on this page.

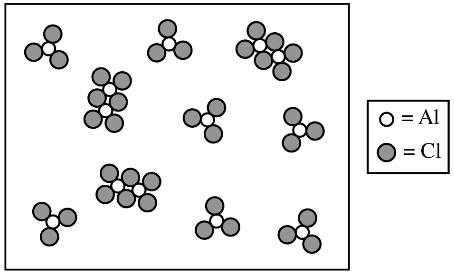
(ii) Which of the three diagrams is the best representation for the bonding in $AlCl_3$? Justify your choice based on formal charges.

$AlCl_3$ is known to dimerize reversibly in the gas phase. The dimerization equilibrium is represented by the following equation.

$$2\ AlCl_3(g) \rightleftarrows Al_2Cl_6(g)$$

(e) Write the expression for the equilibrium constant, K_p, for this reaction.

A particle-level diagram of an equilibrium mixture of $AlCl_3(g)$ and $Al_2Cl_6(g)$ at 400°C in a 25 L closed container is shown.



(f) Using the particle-level diagram, calculate the value of K_p for the reaction if the total pressure in the container is 22.1 atm.

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2. Answer the following questions about the isomers fulminic acid and isocyanic acid.

Two possible Lewis electron-dot diagrams for fulminic acid, HCNO, are shown below.

H—C≡N—Ö: H—C̈=N=Ö:

(a) Explain why the diagram on the left is the better representation for the bonding in fulminic acid. Justify your choice based on formal charges.

Fulminic acid can convert to isocyanic acid according to the equation below.

$$HCNO(g) \rightleftarrows HNCO(g)$$

fulminic acid   *isocyanic acid*

Fulminic Acid	Isocyanic Acid
H—C≡N—Ö:	H—N̈=C=Ö:

(b) Using the Lewis electron-dot diagrams of fulminic acid and isocyanic acid shown in the boxes above and the table of average bond enthalpies below, determine the value of $\Delta H°$ for the reaction of $HCNO(g)$ to form $HNCO(g)$.

Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)
N−O	201	C=N	615	H−C	413
C=O	745	C≡N	891	H−N	391

(c) A student claims that $\Delta S°$ for the reaction is close to zero. Explain why the student's claim is accurate.

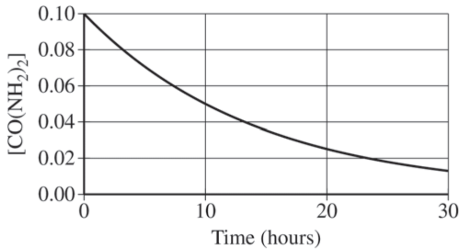
(d) Which species, fulminic acid (HCNO) or isocyanic acid (HNCO), is present in higher concentration at equilibrium at 298 K? Justify your answer in terms of thermodynamic favorability and the equilibrium constant.

The ammonium salt of isocyanic acid is a product of the decomposition of urea, $CO(NH_2)_2$, represented below.

$$CO(NH_2)_2(aq) \rightleftarrows NH_4^+(aq) + OCN^-(aq)$$

A student studying the decomposition reaction runs the reaction at 90°C. The student collects data on the concentration of urea as a function of time, as shown by the data table and the graph below.

Time (hours)	$[CO(NH_2)_2]$
0	0.1000
5	0.0707
10	0.0500
15	0.0354
20	0.0250
25	0.0177
30	0.0125



(e) The student proposes that the rate law is $rate = k[CO(NH_2)_2]$.

(i) Explain how the data support the student's proposed rate law.

(ii) Using the proposed rate law and the student's results, determine the value of the rate constant, k. Include units with your answer.

(f) The student learns that the decomposition reaction was run in a solution with a pH of 13. Briefly describe an experiment, including the initial conditions that you would change and the data you would gather, to determine whether the rate of the reaction depends on the concentration of $OH^-(aq)$.

$$NaHCO_3(s) + HC_2H_3O_2(aq) \rightarrow NaC_2H_3O_2(aq) + H_2O(l) + CO_2(g)$$

2. A student designs an experiment to study the reaction between $NaHCO_3$ and $HC_2H_3O_2$. The reaction is represented by the equation above. The student places 2.24 g of $NaHCO_3$ in a flask and adds 60.0 mL of 0.875 M $HC_2H_3O_2$. The student observes the formation of bubbles and that the flask gets cooler as the reaction proceeds.

(a) Identify the reaction represented above as an acid-base reaction, precipitation reaction, or redox reaction. Justify your answer.

(b) Based on the information above, identify the limiting reactant. Justify your answer with calculations.

(c) The student observes that the bubbling is rapid at the beginning of the reaction and gradually slows as the reaction continues. Explain this change in the reaction rate in terms of the collisions between reactant particles.

(d) In thermodynamic terms, a reaction can be driven by enthalpy, entropy, or both.

(i) Considering that the flask gets cooler as the reaction proceeds, what drives the chemical reaction between $NaHCO_3(s)$ and $HC_2H_3O_2(aq)$? Answer by drawing a circle around one of the choices below.

Enthalpy only   Entropy only   Both enthalpy and entropy

(ii) Justify your selection in part (d)(i) in terms of $\Delta G°$.

(e) The HCO_3^- ion has three carbon-to-oxygen bonds. Two of the carbon-to-oxygen bonds have the same length and the third carbon-to-oxygen bond is longer than the other two. The hydrogen atom is bonded to one of the oxygen atoms. In the box below, draw a Lewis electron-dot diagram (or diagrams) for the HCO_3^- ion that is (are) consistent with the given information.

(f) A student prepares a solution containing equimolar amounts of $HC_2H_3O_2$ and $NaC_2H_3O_2$. The pH of the solution is measured to be 4.7. The student adds two drops of 3.0 M $HNO_3(aq)$ and stirs the sample, observing that the pH remains at 4.7. Write a balanced, net-ionic equation for the reaction between $HNO_3(aq)$ and the chemical species in the sample that is responsible for the pH remaining at 4.7.