2019

AP® Chemistry

Scoring Guidelines

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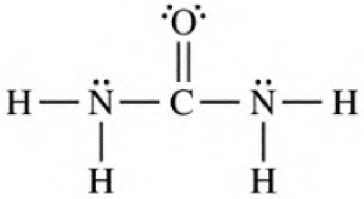
Question 1

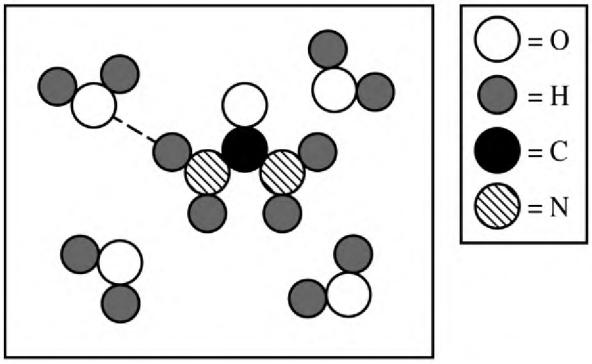


The compound urea, H_2NCONH_2, is widely used in chemical fertilizers. The complete Lewis electron-dot diagram for the urea molecule is shown above.

(a) Identify the hybridization of the valence orbitals of the carbon atom in the urea molecule.

sp^2	1 point is earned for the correct answer.

(b) Urea has a high solubility in water, due in part to its ability to form hydrogen bonds. A urea molecule and four water molecules are represented in the box below. Draw ONE dashed line (----) to indicate a possible location of a hydrogen bond between a water molecule and the urea molecule.



A dashed line should connect a hydrogen atom in water to a nitrogen or oxygen atom in urea or an oxygen atom in water to a hydrogen atom in urea. One possible correct response is shown above.	1 point is earned for a correct answer.

$$H_2NCONH_2(s) \rightleftarrows H_2NCONH_2(aq)$$

The dissolution of urea is represented by the equation above. A student determines that 5.39 grams of H_2NCONH_2 (molar mass 60.06 g/mol) can dissolve in water to make 5.00 mL of a saturated solution at 20.°C.

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Question 1 (continued)

(c) Calculate the concentration of urea, in mol/L, in the saturated solution at 20.°C.

$5.39\ \text{g}\ H_2NCONH_2 \times \dfrac{1\ \text{mol}}{60.06\ \text{g}} = 0.0897\ \text{mol}$ $\dfrac{0.0897\ \text{mol}}{0.00500\ \text{L}} = 17.9\ M$	1 point is earned for the correct number of moles of urea (may be implicit). 1 point is earned for the correct molarity.

(d) The student also determines that the concentration of urea in a saturated solution at 25°C is 19.8 M. Based on this information, is the dissolution of urea endothermic or exothermic? Justify your answer in terms of Le Chatelier's principle.

The increased solubility at the higher temperature implies that the dissolution of urea is endothermic. If a saturated solution of urea is heated, then the equilibrium system is stressed. The stress is counteracted by the endothermic dissolution of more urea.	1 point is earned for the correct answer with an appropriate justification.

(e) The equipment shown above is provided so that the student can determine the value of the molar heat of solution for urea. Knowing that the specific heat of the solution is 4.18 J/(g·°C), list the specific measurements that are required to be made during the experiment.

mass of urea, mass of water, initial temperature of water, final temperature of solution	1 point is earned for the masses. 1 point is earned for the temperatures.

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Question 1 (continued)

	$S°$ (J/(mol·K))
$H_2NCONH_2(s)$	104.6
$H_2NCONH_2(aq)$	?

(f) The entropy change for the dissolution of urea, ΔS°_{soln}, is 70.1 J/(mol·K) at 25°C. Using the information in the table above, calculate the absolute molar entropy, $S°$, of aqueous urea.

$\Delta S^\circ_{soln} = S^\circ(H_2NCONH_2(aq)) - S^\circ(H_2NCONH_2(s))$ $70.1\ \text{J/(mol·K)} = S^\circ(H_2NCONH_2(aq)) - 104.6\ \text{J/(mol·K)}$ $S^\circ(H_2NCONH_2(aq)) = 174.7\ \text{J/(mol·K)}$	1 point is earned for the correct answer.

(g) Using particle-level reasoning, explain why ΔS°_{soln} is positive for the dissolution of urea in water.

Urea molecules in solution have a greater number of possible arrangements than in solid urea. This increased number of arrangements corresponds to a positive ΔS°_{soln}.	1 point is earned for a correct explanation.

(h) The student claims that $\Delta S°$ for the process contributes to the thermodynamic favorability of the dissolution of urea at 25°C. Use the thermodynamic information above to support the student's claim.

Thermodynamic favorability for a process at standard conditions is determined by the sign of $\Delta G°$, with $\Delta G° = \Delta H° - T\Delta S°$. Since $\Delta S°$ is positive, the $T\Delta S°$ term makes the value of $\Delta G°$ smaller and thus makes the dissolution more thermodynamically favorable.	1 point is earned for the correct answer.

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Question 2

Answer the following questions relating to the chemistry of the halogens.

(a) The molecular formulas of diatomic bromine, chlorine, fluorine, and iodine are written below. Circle the formula of the molecule that has the longest bond length. Justify your choice in terms of atomic structure.

Br_2 Cl_2 F_2 I_2

I_2 has the longest bond length because the radius of the I atom is greater than the radii of the other halogen atoms. Thus, the distance between the nuclei of atoms in I_2 is greater than it is in smaller halogens.	1 point is earned for circling I_2 and providing a valid explanation.

A chemistry teacher wants to prepare Br_2. The teacher has access to the following three reagents: NaBr(aq), $Cl_2(g)$, and $I_2(s)$.

Half-Reaction	$E°$ at 25°C (V)
$Br_2 + 2\,e^- \rightarrow 2\,Br^-$	1.07
$Cl_2 + 2\,e^- \rightarrow 2\,Cl^-$	1.36
$I_2 + 2\,e^- \rightarrow 2\,I^-$	0.53

(b) Using the data in the table above, write the balanced equation for the thermodynamically favorable reaction that will produce Br_2 when the teacher combines two of the reagents. Justify that the reaction is thermodynamically favorable by calculating the value of $E°$ for the reaction.

$2\,Br^- + Cl_2 \rightarrow Br_2 + 2\,Cl^-$	1 point is earned for the correct balanced equation.
$E° = E°(\text{reduced species}) - E°(\text{oxidized species})$ $= 1.36\text{ V} - 1.07\text{ V} = +0.29\text{ V}$. Because $E°$ for the reaction has a positive value, the reaction is thermodynamically favorable.	1 point is earned for the correct calculation of $E°$.

Br_2 and Cl_2 can react to form the compound BrCl.

(c) The boiling point of Br_2 is 332 K, whereas the boiling point of BrCl is 278 K. Explain this difference in boiling point in terms of all the intermolecular forces present between molecules of <u>each</u> substance.

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Question 2 (continued)

The only intermolecular attractions in $Br_2(l)$ are London forces, while those in $BrCl(l)$ include both London forces and dipole-dipole forces. However, due to the greater polarizability of the electron cloud of Br_2 compared to that of BrCl, the London forces in $Br_2(l)$ are stronger than the combined intermolecular forces in $BrCl(l)$. Thus, the boiling point of $Br_2(l)$ is greater than that of $BrCl(l)$.	1 point is earned for identifying the intermolecular forces in each substance. 1 point is earned for a valid explanation.

The compound BrCl can decompose into Br_2 and Cl_2, as represented by the balanced chemical equation below.

$$2\ BrCl(g) \rightleftarrows Br_2(g) + Cl_2(g) \qquad \Delta H^\circ = 1.6\ \text{kJ/mol}_{rxn}$$

A 0.100 mole sample of pure $BrCl(g)$ is placed in a previously evacuated, rigid 2.00 L container at 298 K. Eventually the system reaches equilibrium according to the equation above.

(d) Calculate the pressure in the container before equilibrium is established.

$P = \dfrac{nRT}{V} = \dfrac{(0.100\ \text{mol})(0.08206\ \text{L atm mol}^{-1}\ \text{K}^{-1})(298\ \text{K})}{2.00\ \text{L}} = 1.22\ \text{atm}$	1 point is earned for a correct pressure with consistent units.

(e) Write the expression for the equilibrium constant, K_{eq}, for the decomposition of BrCl.

$K_{eq} = \dfrac{[Br_2][Cl_2]}{[BrCl]^2}$ or $K_{eq} = \dfrac{P_{Br_2}P_{Cl_2}}{(P_{BrCl})^2}$	1 point is earned for a correct equilibrium expression.

After the system has reached equilibrium, 42 percent of the original BrCl sample has decomposed.

(f) Determine the value of K_{eq} for the decomposition reaction of BrCl at 298 K.

$2\ BrCl(g) \rightleftarrows Br_2(g) + Cl_2(g)$ I: 1.22, 0, 0 C: $-2x$, $+x$, $+x$ E: 0.71, 0.26, 0.26 P_{BrCl} decomposed $= (0.42)(1.22\ \text{atm}) = 0.51\ \text{atm}$ $2x = 0.51\ \text{atm} \Rightarrow x = 0.26\ \text{atm}$ $K_{eq} = \dfrac{(0.26)(0.26)}{(0.71)^2} = 0.13$ Note: The solution is in terms of pressures. Solutions in terms of molar concentrations also earn full credit.	1 point is earned for correct stoichiometric values at equilibrium. 1 point is earned for a consistent value of K_{eq}.

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Question 2 (continued)

(g) Calculate the bond energy of the Br-Cl bond, in kJ/mol, using $\Delta H°$ for the reaction (1.6 kJ/mol$_{rxn}$) and the information in the following table.

Bond	Bond Energy (kJ/mol)
Br – Br	193
Cl – Cl	243
Br – Cl	?

$\Delta H° = \sum(\text{bond energies})_{broken} - \sum(\text{bond energies})_{formed}$ 1.6 kJ/mol = 2(Br–Cl bond energy) – (193 kJ/mol + 243 kJ/mol) (436 + 1.6) kJ/mol = 2(Br–Cl bond energy) Br–Cl bond energy = 219 kJ/mol	1 point is earned for a correct calculation of the Br–Cl bond energy.

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Question 3

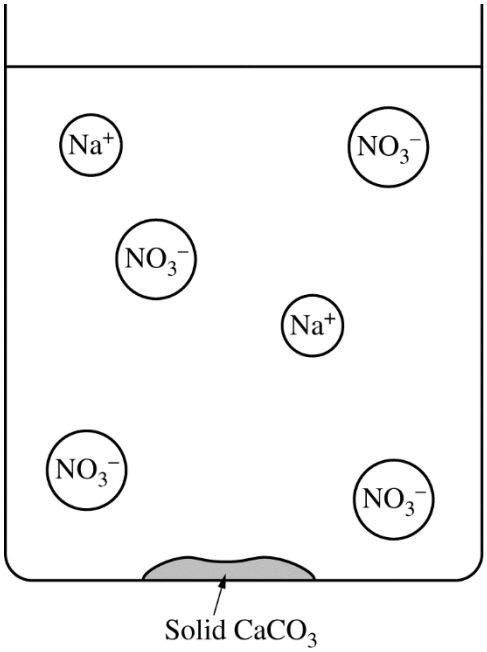
A student is given 50.0 mL of a solution of Na_2CO_3 of unknown concentration. To determine the concentration of the solution, the student mixes the solution with excess 1.0 *M* $Ca(NO_3)_2(aq)$, causing a precipitate to form. The balanced equation for the reaction is shown below.

$$Na_2CO_3(aq) + Ca(NO_3)_2(aq) \rightarrow 2\ NaNO_3(aq) + CaCO_3(s)$$

(a) Write the net ionic equation for the reaction that occurs when the solutions of Na_2CO_3 and $Ca(NO_3)_2$ are mixed.

$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$	1 point is earned for the correct equation.

(b) The diagram below is incomplete. Draw in the species needed to accurately represent the major ionic species remaining in the solution after the reaction has been completed.



The drawing shows one Ca^{2+} ion.	1 point is earned for drawing a Ca^{2+} ion.

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Question 3 (continued)

The student filters and dries the precipitate of $CaCO_3$ (molar mass 100.1 g/mol) and records the data in the table below.

Volume of Na_2CO_3 solution	50.0 mL
Volume of 1.0 *M* $Ca(NO_3)_2$ added	100.0 mL
Mass of $CaCO_3$ precipitate collected	0.93 g

(c) Determine the number of moles of Na_2CO_3 in the original 50.0 mL of solution.

$0.93 \text{ g } CaCO_3 \times \frac{1 \text{ mol } CaCO_3}{100.1 \text{ g}} = 0.0093 \text{ mol } CaCO_3$ $0.0093 \text{ mol } CaCO_3 \times \frac{1 \text{ mol } Na_2CO_3}{1 \text{ mol } CaCO_3} = 0.0093 \text{ mol } Na_2CO_3$	1 point is earned for the correct answer.

(d) The student realizes that the precipitate was not completely dried and claims that as a result, the calculated Na_2CO_3 molarity is too low. Do you agree with the student's claim? Justify your answer.

Disagree. The presence of water in the solid will cause the measured mass of the precipitate to be greater than the actual mass of $CaCO_3$. As a result, the calculated number of moles of $CaCO_3$ and moles of Na_2CO_3 will be greater than the actual moles present. Therefore the calculated concentration of $Na_2CO_3(aq)$ will be too high.	1 point is earned for the correct answer with valid justification.

(e) After the precipitate forms and is filtered, the liquid that passed through the filter is tested to see if it can conduct electricity. What would be observed? Justify your answer.

The liquid conducts electricity because ions ($Na^+(aq)$, $Ca^{2+}(aq)$, and $NO_3^-(aq)$) are present in the solution.	1 point is earned for the correct answer with valid justification.

The student decides to determine the molarity of the same Na_2CO_3 solution using a second method. When Na_2CO_3 is dissolved in water, $CO_3^{2-}(aq)$ hydrolyzes to form $HCO_3^-(aq)$, as shown by the following equation.

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq) \qquad K_b = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = 2.1 \quad 10^{\ 4}$$

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Question 3 (continued)

(f) The student decides to first determine $[OH^-]$ in the solution, then use that result to calculate the initial concentration of $CO_3^{2-}(aq)$.

(i) Identify a laboratory method (not titration) that the student could use to collect data to determine $[OH^-]$ in the solution.

Determine the pH of the solution using a pH meter.	1 point is earned for identifying a valid method.

(ii) Explain how the student could use the measured value in part (f)(i) to calculate the <u>initial</u> concentration of $CO_3^{2-}(aq)$. (Do not do any numerical calculations.)

First determine $[OH^-]$ using pOH = 14 − pH, then $[OH^-] = 10^{-pOH}$.

Then, use the K_b expression and an ICE table (see example below) to determine $[CO_3^{2-}]$ and $[HCO_3^-]$ at equilibrium. The initial concentration of CO_3^{2-}, c_i, is equal to the sum of the equilibrium concentrations of CO_3^{2-} and HCO_3^-.

	$CO_3^{2-}(aq)$ +	$H_2O(l)$	$\rightleftarrows$	$HCO_3^-(aq)$ +	$OH^-(aq)$
I	c_i	---		0	0
C	$-x$	---		$+x$	$+x$
E	$c_i - x$	---		x	x

$$K_b = \frac{(x)(x)}{c_i - x} \quad \Rightarrow \quad c_i = \frac{(x)(x)}{K_b} + x$$

1 point is earned for a valid method of determining $[OH^-]$ from the measured value.

1 point is earned for a valid method of determining the <u>initial</u> concentration of CO_3^{2-}.

(g) In the original Na_2CO_3 solution at equilibrium, is the concentration of $HCO_3^-(aq)$ greater than, less than, or equal to the concentration of $CO_3^{2-}(aq)$? Justify your answer.

Less than. The small value of K_b, 2.1×10^{-4}, indicates that the reactants are favored.	1 point is earned for the correct answer with a valid justification.

(h) The student needs to make a CO_3^{2-}/HCO_3^- buffer. Is the Na_2CO_3 solution suitable for making a buffer with a pH of 6? Explain why or why not.

No, the Na_2CO_3 solution is not suitable. The pK_a of HCO_3^- is 10.32. Buffers are effective when the required pH is approximately equal to the pK_a of the weak acid. An acid with a pK_a of 10.32 is not appropriate to prepare a buffer with a pH of 6.	1 point is earned for the correct answer with a valid explanation.

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Question 4

A student is doing experiments with $CO_2(g)$. Originally, a sample of the gas is in a rigid container at 299 K and 0.70 atm. The student increases the temperature of the $CO_2(g)$ in the container to 425 K.

(a) Describe the effect of raising the temperature on the motion of the $CO_2(g)$ molecules.

The average speed of the molecules increases as temperature increases.	1 point is earned for the correct answer.

(b) Calculate the pressure of the $CO_2(g)$ in the container at 425 K.

Both the volume and the number of molecules are constant, therefore $\frac{P_1}{T_1} = \frac{P_2}{T_2} \Rightarrow \frac{0.70 \text{ atm}}{299 \text{ K}} = \frac{P_2}{425 \text{ K}} \Rightarrow P_2 = 0.99 \text{ atm}$	1 point is earned for the correct answer.

(c) In terms of kinetic molecular theory, briefly explain why the pressure of the $CO_2(g)$ in the container changes as it is heated to 425 K.

Faster-moving gas particles collide more frequently with the walls of the container, thus increasing the pressure. OR Faster-moving gas particles collide more forcefully with the walls of the container, thus increasing the pressure.	1 point is earned for a correct explanation.

(d) The student measures the actual pressure of the $CO_2(g)$ in the container at 425 K and observes that it is less than the pressure predicted by the ideal gas law. Explain this observation.

The attractive forces between CO_2 molecules result in a pressure that is lower than that predicted by the ideal gas law.	1 point is earned for a correct explanation.

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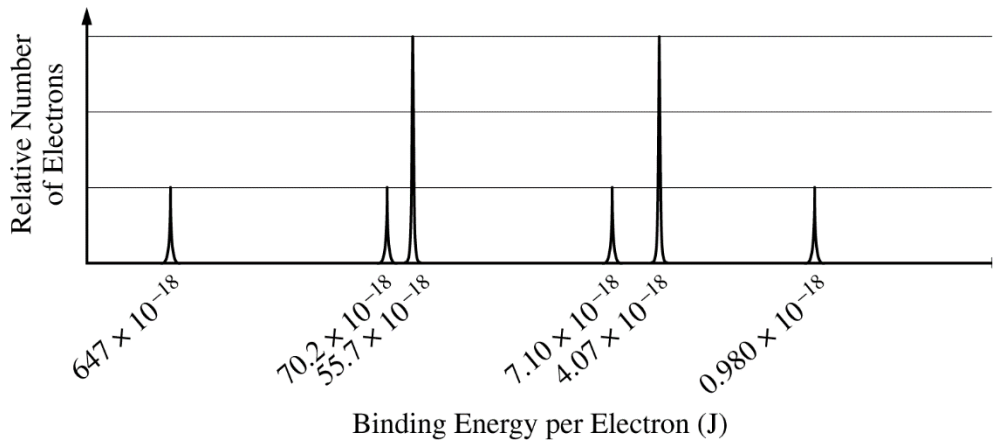
Question 5

The complete photoelectron spectrum of an element in its ground state is represented below.



(a) Based on the spectrum,

(i) write the ground-state electron configuration of the element, and

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$ or [Ar] $4s^2$	1 point is earned for the correct answer.

(ii) identify the element.

Ca	1 point is earned for the correct answer.

(b) Calculate the wavelength, in meters, of electromagnetic radiation needed to remove an electron from the valence shell of an atom of the element.

Energy (E) required = 0.980×10^{-18} J $E = h\nu = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{E}$ $\lambda = \frac{(6.626 \times 10^{-34}\ \text{Js})(2.998 \times 10^{8}\ \text{m s}^{-1})}{0.980 \times 10^{-18}\ \text{J}}$ $\lambda = 2.03 \times 10^{-7}$ m	1 point is earned for the correct identification of the energy required to remove an electron from the valence shell (may be implicit). 1 point is earned for calculating the correct wavelength.

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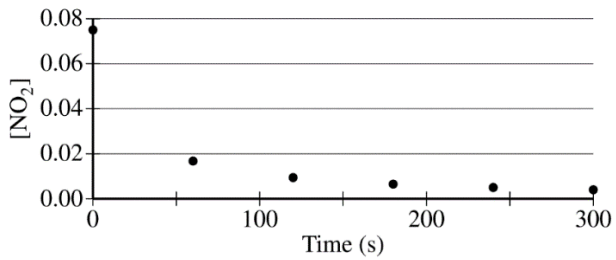
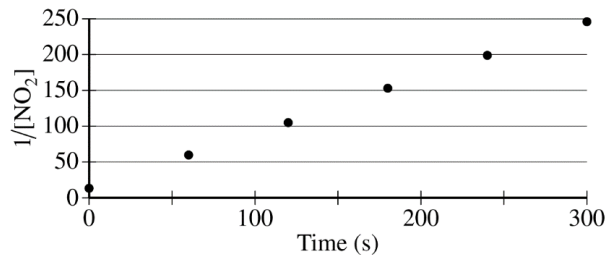
Question 6

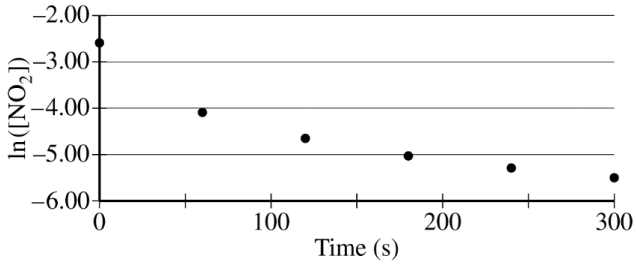
Nitrogen dioxide, $NO_2(g)$, is produced as a byproduct of the combustion of fossil fuels in internal combustion engines. At elevated temperatures $NO_2(g)$ decomposes according to the equation below.

$$2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$$

The concentration of a sample of $NO_2(g)$ is monitored as it decomposes and is recorded on the graph directly below. The two graphs that follow it are derived from the original data.







(a) Explain how the graphs indicate that the reaction is second order.

The linear graph of $\frac{1}{[NO_2]}$ vs. time indicates a second-order reaction.	1 point is earned for the correct answer.

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Question 6 (continued)

(b) Write the rate law for the decomposition of $NO_2(g)$.

rate = $k[NO_2]^2$	1 point is earned for the correct answer.

(c) Consider two possible mechanisms for the decomposition reaction.

(i) Is the rate law described by mechanism I shown below consistent with the rate law you wrote in part (b)? Justify your answer.

Mechanism I

Step 1: $NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$ *slow*

Step 2: $NO_3(g) \rightarrow NO(g) + O_2(g)$ *fast*

Yes. Step 1 is slow, therefore it is the rate-determining step of this mechanism. The rate law of this elementary reaction is rate = $k[NO_2][NO_2] = k[NO_2]^2$, which is consistent with the second-order rate law in part (b).	1 point is earned for the correct answer with justification.

(ii) Is the rate law described by mechanism II shown below consistent with the rate law you wrote in part (b)? Justify your answer.

Mechanism II

Step 1: $NO_2(g) + NO_2(g) \rightleftarrows N_2O_4(g)$ *fast equilibrium*

Step 2: $N_2O_4(g) \rightarrow 2\,NO(g) + O_2(g)$ *slow*

Yes. Step 2 is slow; therefore, it is the rate-determining step of this mechanism. The rate law of this elementary reaction is rate = $k[N_2O_4]$. Because N_2O_4 is an intermediate, it cannot appear in the rate law of the overall reaction. Because $K_{eq} = \frac{[N_2O_4]}{[NO_2]^2}$ in step 1, $[N_2O_4] = K_{eq}[NO_2]^2$. Then, substituting $K_{eq}[NO_2]^2$ for $[N_2O_4]$ in the rate law of step 2 gives rate = $(k\,K_{eq})[NO_2]^2$, which is consistent with the rate law in part (b).	1 point is earned for the correct answer with justification.

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Question 7

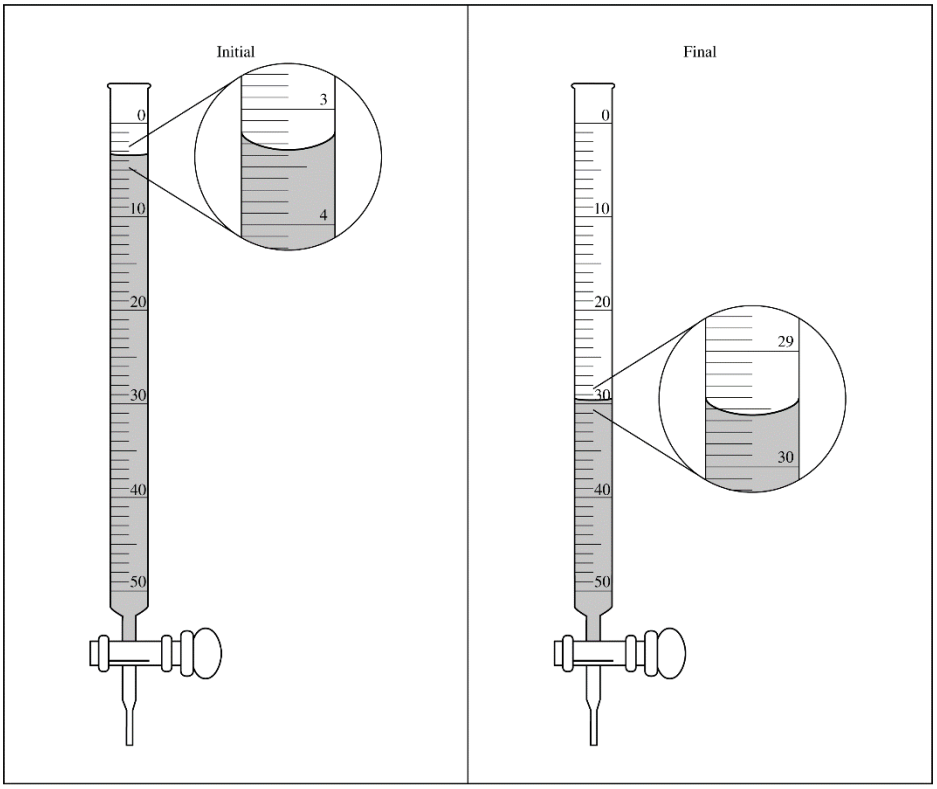
$$6\ H^+(aq) + 2\ MnO_4^-(aq) + 5\ H_2C_2O_4(aq) \rightarrow 10\ CO_2(g) + 8\ H_2O(l) + 2\ Mn^{2+}(aq)$$

A student dissolved a 0.139 g sample of oxalic acid, $H_2C_2O_4$, in water in an Erlenmeyer flask. Then the student titrated the $H_2C_2O_4$ solution in the flask with a solution of $KMnO_4$, which has a dark purple color. The balanced chemical equation for the reaction that occurred during the titration is shown above.

(a) Identify the species that was reduced in the titration reaction. Justify your answer in terms of oxidation numbers.

MnO_4^- is reduced to Mn^{2+} as the oxidation number of Mn changes from +7 to +2, indicating a gain of 5 electrons.	1 point is earned for the correct answer with justification.

(b) The student used a 50.0 mL buret to add the $KMnO_4(aq)$ to the $H_2C_2O_4(aq)$ until a faint lavender color was observed in the flask, an indication that the end point of the titration had been reached. The initial and final volume readings of the solution in the buret are shown below. Write down the initial reading and the final reading and use them to determine the volume of $KMnO_4(aq)$ that was added during the titration.



29.55 mL – 3.35 mL = 26.20 mL	1 point is earned for the correct answer.

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Question 7 (continued)

(c) Given that the concentration of $KMnO_4(aq)$ was 0.0235 *M*, calculate the number of moles of MnO_4^- ions that completely reacted with the $H_2C_2O_4$.

(0.02620 L)(0.0235 mol/L) = 0.000616 mol	1 point is earned for the correct answer.

(d) The student proposes to perform another titration using a 0.139 g sample of $H_2C_2O_4$, but this time using 0.00143 *M* $KMnO_4(aq)$ in the buret. Would this titrant concentration be a reasonable choice to use if the student followed the same procedure and used the same equipment as before? Justify your response.

No. The 0.00143 *M* titrant solution is so diluted that the volume of titrant needed to reach the end point would be much greater than the 50 mL capacity of the buret.	1 point is earned for the correct answer with appropriate justification.

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