

AP® Chemistry

Free-Response Questions



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AP® CHEMISTRY EQUATIONS AND CONSTANTS

Throughout the exam the following symbols have the definitions specified unless otherwise noted.

L, mL = liter(s), milliliter(s)	mm Hg = millimeters of mercury
g = gram(s)	J, kJ = joule(s), kilojoule(s)
nm = nanometer(s)	V = volt(s)
atm = atmosphere(s)	mol = mole(s)

ATOMIC STRUCTURE

$$E = h\nu$$

$$c = \lambda\nu$$

$$E = \text{energy}$$

$$\nu = \text{frequency}$$

$$\lambda = \text{wavelength}$$

$$\text{Planck's constant, } h = 6.626 \times 10^{-34} \text{ J s}$$

$$\text{Speed of light, } c = 2.998 \times 10^8 \text{ m s}^{-1}$$

$$\text{Avogadro's number} = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$\text{Electron charge, } e = -1.602 \times 10^{-19} \text{ coulomb}$$

EQUILIBRIUM

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}, \text{ where } a \text{ A} + b \text{ B} \rightleftharpoons c \text{ C} + d \text{ D}$$

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_b = \frac{[OH^-][HB^+]}{[B]}$$

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

$$= K_a \times K_b$$

$$\text{pH} = -\log[H^+], \text{ pOH} = -\log[OH^-]$$

$$14 = \text{pH} + \text{pOH}$$

$$\text{pH} = \text{p}K_a + \log \frac{[A^-]}{[HA]}$$

$$\text{p}K_a = -\log K_a, \text{ p}K_b = -\log K_b$$

Equilibrium Constants

$$K_c \text{ (molar concentrations)}$$

$$K_p \text{ (gas pressures)}$$

$$K_a \text{ (weak acid)}$$

$$K_b \text{ (weak base)}$$

$$K_w \text{ (water)}$$

KINETICS

$$[A]_t - [A]_0 = -kt$$

$$\ln[A]_t - \ln[A]_0 = -kt$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$t_{1/2} = \frac{0.693}{k}$$

$$k = \text{rate constant}$$

$$t = \text{time}$$

$$t_{1/2} = \text{half-life}$$

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GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

$$P_A = P_{\text{total}} \times X_A, \text{ where } X_A = \frac{\text{moles A}}{\text{total moles}}$$

$$P_{\text{total}} = P_A + P_B + P_C + \dots$$

$$n = \frac{m}{M}$$

$$K = ^\circ\text{C} + 273$$

$$D = \frac{m}{V}$$

$$KE_{\text{molecule}} = \frac{1}{2}mv^2$$

$$\text{Molarity, } M = \text{moles of solute per liter of solution}$$

$$A = \epsilon bc$$

$$P = \text{pressure}$$

$$V = \text{volume}$$

$$T = \text{temperature}$$

$$n = \text{number of moles}$$

$$m = \text{mass}$$

$$M = \text{molar mass}$$

$$D = \text{density}$$

$$KE = \text{kinetic energy}$$

$$\nu = \text{velocity}$$

$$A = \text{absorbance}$$

$$\epsilon = \text{molar absorptivity}$$

$$b = \text{path length}$$

$$c = \text{concentration}$$

$$\text{Gas constant, } R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$= 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$= 62.36 \text{ L torr mol}^{-1} \text{ K}^{-1}$$

$$1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr}$$

$$\text{STP} = 273.15 \text{ K and } 1.0 \text{ atm}$$

$$\text{Ideal gas at STP} = 22.4 \text{ L mol}^{-1}$$

THERMODYNAMICS/ELECTROCHEMISTRY

$$q = mc\Delta T$$

$$\Delta S^\circ = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}$$

$$\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -RT \ln K$$

$$= -nFE^\circ$$

$$I = \frac{q}{t}$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln Q$$

$$q = \text{heat}$$

$$m = \text{mass}$$

$$c = \text{specific heat capacity}$$

$$T = \text{temperature}$$

$$S^\circ = \text{standard entropy}$$

$$H^\circ = \text{standard enthalpy}$$

$$G^\circ = \text{standard Gibbs free energy}$$

$$n = \text{number of moles}$$

$$E^\circ = \text{standard reduction potential}$$

$$I = \text{current (amperes)}$$

$$q = \text{charge (coulombs)}$$

$$t = \text{time (seconds)}$$

$$Q = \text{reaction quotient}$$

$$\text{Faraday's constant, } F = 96,485 \text{ coulombs per mole of electrons}$$

$$1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}}$$

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Begin your response to **QUESTION 1** on this page.

CHEMISTRY

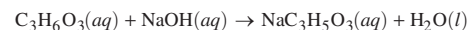
SECTION II

Time—1 hour and 45 minutes

7 Questions

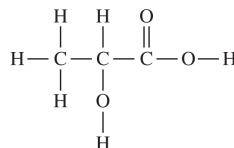
Directions: Questions 1–3 are long free-response questions that require about 23 minutes each to answer and are worth 10 points each. Questions 4–7 are short free-response questions that require about 9 minutes each to answer and are worth 4 points each.

For each question, show your work for each part in the space provided after that part. Examples and equations may be included in your responses where appropriate. For calculations, clearly show the method used and the steps involved in arriving at your answers. You must show your work to receive credit for your answer. Pay attention to significant figures.



1. A student is studying the reaction between lactic acid, $\text{C}_3\text{H}_6\text{O}_3$, and sodium hydroxide, NaOH , as represented in the balanced equation above.

(a) The structural formula of lactic acid is shown in the following diagram. Circle the hydrogen atom that most readily participates in the chemical reaction with sodium hydroxide.

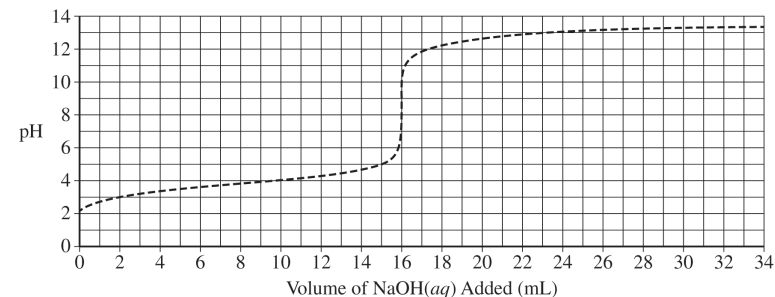


- (b) The student begins the experiment by dissolving 10.22 g of sodium hydroxide (molar mass 40.00 g/mol) in enough water to produce 500. mL of solution. Calculate the molarity of the sodium hydroxide solution.

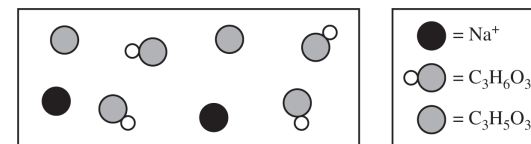
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Continue your response to **QUESTION 1** on this page.

The student uses the sodium hydroxide solution from part (b), a buret, a pH meter, and a 100 mL Erlenmeyer flask to titrate a 25.0 mL sample of lactic acid solution. The student's data are shown in the following graph.



- (c) Use the information in the graph to determine the approximate $\text{p}K_a$ of lactic acid. _____



- (d) The preceding diagram represents the relative amounts of major species in a sample of the solution in the flask at one point during the titration. (Note that water molecules are omitted.)

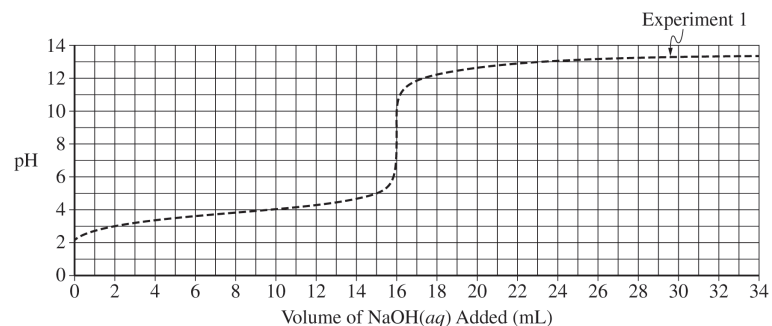
- (i) Draw an X on the preceding titration curve at a point in the titration where the reaction mixture would be represented by this diagram.
(ii) Justify your answer.

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Continue your response to **QUESTION 1** on this page.

Experiment	Mass of NaOH(s) (grams)	Volume of Solution (mL)	Titration Curve
1	10.22	500.	Already shown on graph
2	20.44	500.	?

- (iii) The student repeats the experiment but uses a solution of NaOH(aq) with twice the concentration, as shown in the preceding table. On the following graph, draw the titration curve that would be expected for experiment 2.



- (e) In a third experiment, the student investigates the enthalpy of the reaction between lactic acid and sodium hydroxide. The student combines 100.0 mL of a 0.500 M lactic acid solution at 20.0°C with 100.0 mL of a 0.500 M NaOH solution at 20.0°C in a calorimeter. The final temperature of the resulting combined solution is 23.2°C. Assume that the density of each solution before combining is 1.00 g/mL and that the specific heat capacity of the combined solution is 4.2 J/(g · °C).

- (i) Calculate the quantity of heat produced in the reaction, in J.

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Continue your response to **QUESTION 1** on this page.

- (ii) Calculate the molar enthalpy of reaction, in kJ/mol_{rxn}. Include the sign in your answer.

- (iii) The student claims that if heat is lost from the calorimeter to the surrounding air during the reaction, then the experimental value of the molar enthalpy of reaction will be smaller in magnitude than the actual value. Do you agree or disagree with the student's claim? Justify your answer.

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

2. A chemical reaction between maleic acid ($\text{H}_2\text{C}_4\text{H}_2\text{O}_4$) and sodium bicarbonate (NaHCO_3) occurs in the presence of water to produce carbon dioxide and sodium maleate ($\text{Na}_2\text{C}_4\text{H}_2\text{O}_4$), as represented by the following equation.



- (a) A student combines equal masses of $\text{H}_2\text{C}_4\text{H}_2\text{O}_4(s)$ chunks and $\text{NaHCO}_3(s)$ chunks with sufficient water at 20.0°C . The student determines that 0.0114 mol of $\text{CO}_2(g)$ is produced after the reaction goes to completion.

(i) Calculate the number of grams of $\text{CO}_2(g)$ produced.

(ii) The $\text{CO}_2(g)$ produced from the reaction at 20.0°C was collected and found to have a pressure of 1.25 atm . Calculate the volume of $\text{CO}_2(g)$, in liters.

- (b) The student performs a second experiment that is identical to the first except that the student grinds the chunks of $\text{H}_2\text{C}_4\text{H}_2\text{O}_4(s)$ and $\text{NaHCO}_3(s)$ into powder before combining the powder with water.

(i) What happens to the surface area of the reactants when the student grinds the chunks into powder?

(ii) The rate-determining step for the overall reaction is the dissolving of the solids. Would the time required for the dissolving of the solids in the second experiment be longer than, shorter than, or the same as the time required in the first experiment? Justify your answer based on the collisions between particles.

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

- (iii) When the reaction is complete, will the volume of $\text{CO}_2(g)$ at the end of the second experiment be greater than, less than, or equal to the volume at the end of the first experiment? Justify your answer.

The student conducts additional trials of the experiment and produces the following data table.

Trial	Mass of $\text{H}_2\text{C}_4\text{H}_2\text{O}_4$ (grams)	Mass of NaHCO_3 (grams)	Moles of CO_2 Produced (mol)
3	1.543	1.251	0.01489
4	1.543	1.686	0.02007

- (c) Based on the student's data, identify the limiting reactant in trial 3. Justify your answer.

- (d) The reaction has a value of ΔS° greater than zero. Using particle-level reasoning, explain why the entropy increases as the reaction progresses.

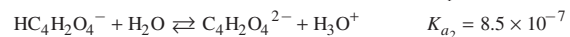
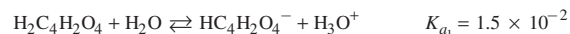
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Continue your response to **QUESTION 2** on this page.

The student notices that the temperature of the reaction mixture decreases as the reaction takes place and correctly determines that the reaction is endothermic.

- (e) The student claims that the reaction is thermodynamically favorable at all temperatures because $\Delta S_{rxn}^\circ > 0$ and the reaction is endothermic. Do you agree or disagree with the student's claim? Justify your answer.

Next, the student investigates the acid-base behavior of maleic acid. The student notes that maleic acid is a diprotic acid. The two acid dissociation processes that occur are represented by the following equations.



- (f) Calculate the $\text{p}K_{a2}$ value for the $\text{HC}_4\text{H}_2\text{O}_4^-$ ion.

- (g) A buffer solution with a pH of 7.00 is prepared using $\text{C}_4\text{H}_2\text{O}_4^{2-}$ and $\text{HC}_4\text{H}_2\text{O}_4^-$. Calculate the ratio

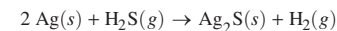
$$\frac{[\text{C}_4\text{H}_2\text{O}_4^{2-}]}{[\text{HC}_4\text{H}_2\text{O}_4^-]}$$

in this solution.

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Begin your response to **QUESTION 3** on this page.

3. Sterling silver is an alloy that is commonly used to make jewelry and consists of 92.5% silver and 7.5% other metals, such as copper, by mass. Over time, the alloy can form a tarnish of $\text{Ag}_2\text{S}(s)$ when it reacts with hydrogen sulfide, as represented by the following equation.



- (a) What are the oxidation numbers of silver in $\text{Ag}(s)$ and $\text{Ag}_2\text{S}(s)$?



- (b) The following table contains the atomic radii for silver and copper.

Element	Silver (Ag)	Copper (Cu)
Atomic radius (pm)	165	145

- (i) Explain why sterling silver is better classified as a substitutional alloy than as an interstitial alloy.

- (ii) Using principles of atomic structure and Coulomb's law, explain why silver has a larger atomic radius than copper does.

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Continue your response to **QUESTION 3** on this page.

The Ag_2S tarnish on sterling silver can be removed until only sterling silver remains. A student weighs a tarnished sterling silver sample both before and after removing the $\text{Ag}_2\text{S}(s)$ (molar mass 247.80 g/mol) and records the data in the following table.

	Before Tarnish Removal	After Tarnish Removal
Mass	409.21 g	398.94 g

(c) Assuming that only $\text{Ag}_2\text{S}(s)$ is removed, calculate the number of moles of silver atoms removed.

Rhodium plating is a process used to protect sterling silver from tarnishing. This involves electroplating (depositing) solid rhodium, $\text{Rh}(s)$, onto the surface of the metal from an acidified solution of $\text{Rh}_2(\text{SO}_4)_3(aq)$. Oxygen gas is produced during this process.

(d) A table of half-reactions related to the overall reaction is provided.

Half-Reaction	E° (V)
$\text{Rh}^{3+}(aq) + 3 e^- \rightarrow \text{Rh}(s)$	+0.80
$\text{O}_2(g) + 4 \text{H}^+(aq) + 4 e^- \rightarrow 2 \text{H}_2\text{O}(l)$	+1.23

(i) Write the balanced net ionic equation for plating $\text{Rh}(s)$ from the acidified $\text{Rh}_2(\text{SO}_4)_3(aq)$ solution.

(ii) Calculate the value of E°_{cell} for the reaction in part (d)(i).

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Continue your response to **QUESTION 3** on this page.

(iii) Based on your answer to part (d)(ii), explain why this process requires the use of an external power source.

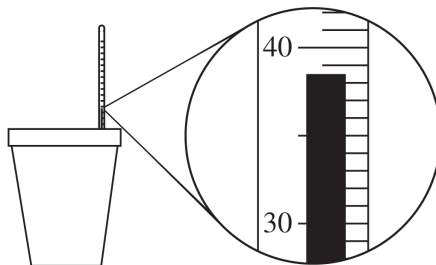
(e) Calculate the length of time, in seconds, required to plate 2.8 g of $\text{Rh}(s)$ onto a piece of sterling silver if 2.0 C/s of current is applied.

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Begin your response to **QUESTION 4** on this page.

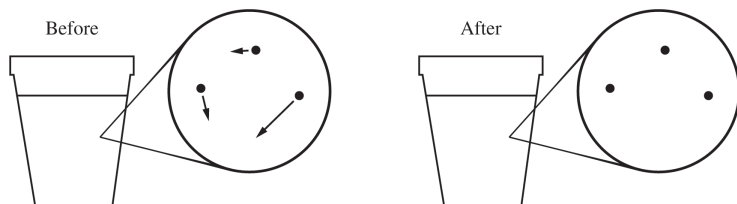
4. A student performs an experiment to determine the specific heat capacity of a metal. The student places a cube of the metal in boiling water so its temperature will be 100.0°C . The student then places the metal cube into a calorimeter that contains water and records the highest temperature of the water. A data table and a diagram of the thermometer at the highest temperature are shown.

Mass of metal cube	98.1 g
Mass of water	52.0 g
Initial temperature of metal cube	100.0°C
Initial temperature of water	25.0°C
Highest temperature of water	?



- (a) What should the student report as the highest temperature of the water? _____

- (b) A particle-level representation of water molecules in the calorimeter before and after the metal cube was added is shown. The length of the arrows in the Before diagram represents the speed of the water molecules in the system. In the After diagram, draw an arrow for each molecule to indicate how the speed of each of the molecules changes after the metal cube is added.



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Continue your response to **QUESTION 4** on this page.

- (c) Assuming the metal transfers 2940 J of thermal energy to the water, calculate the specific heat of the metal in $\text{J}/(\text{g}\cdot^{\circ}\text{C})$.
- (d) In a second experiment, 2940 J of thermal energy is transferred from 98.1 g of aluminum, which has a specific heat capacity of $0.897 \text{ J}/(\text{g}\cdot^{\circ}\text{C})$. Explain how the magnitude of the temperature change of the aluminum, ΔT_{Al} , compares with the magnitude of the temperature change of the metal in the original experiment.

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Begin your response to **QUESTION 5** on this page.

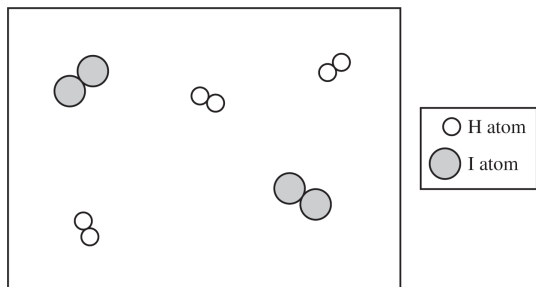
5. Hydrogen gas and iodine gas react to form hydrogen iodide at an elevated temperature, as represented by the following equation.



(a) Write the expression for the equilibrium constant, K_c , for this reaction.

(b) $\text{H}_2(g)$ and $\text{I}_2(g)$ are added to a previously evacuated container and allowed to react.

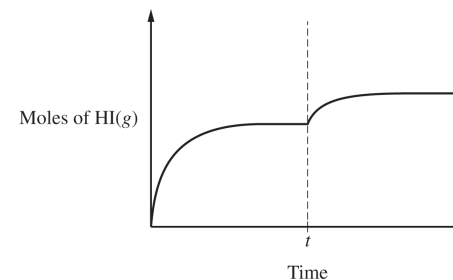
- (i) At a certain time, the value of the reaction quotient, Q , is 0.67. The following particle diagram is an incomplete representation of the system at this time. The diagram shows the relative number of $\text{H}_2(g)$ and $\text{I}_2(g)$ molecules, but the $\text{HI}(g)$ molecules are not included. Draw the number of $\text{HI}(g)$ molecules needed to complete the diagram so that it accurately represents the system.



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Continue your response to **QUESTION 5** on this page.

- (ii) A student monitors the number of moles of $\text{HI}(g)$ over time. Hypothesize an experimental change that could have been applied to the system in the rigid container at time t to result in the change in the number of moles of $\text{HI}(g)$ shown in the graph. Assume that the student did not add more $\text{HI}(g)$ to the system.

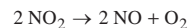


- (iii) After equilibrium is established, the mixture is transferred to a larger container at constant temperature. As a result, would the number of moles of $\text{HI}(g)$ increase, decrease, or remain the same? Justify your answer.

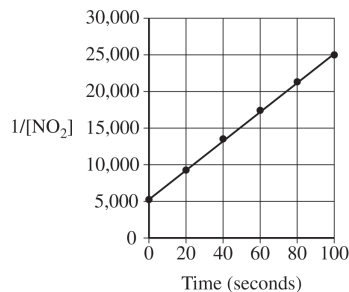
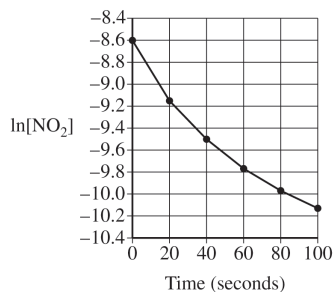
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Begin your response to **QUESTION 6** on this page.

6. At elevated temperatures, NO_2 undergoes decomposition in the gas phase, forming NO and O_2 as represented by the following equation.



A scientist measures the change in $[\text{NO}_2]$ over the first 100. s of the reaction at 546°C . The scientist uses the data collected from the experiment to generate the following two graphs.



Based on these data, the scientist makes the claim that the rate law for the reaction is $\text{rate} = k[\text{NO}_2]^2$.

- (a) Explain how the graphs indicate that the reaction is second order with respect to NO_2 .

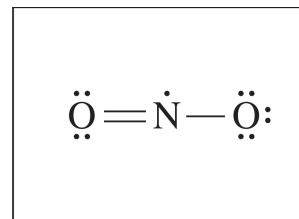
- (b) At a certain point in the reaction, the rate of disappearance of NO_2 is determined to be $6.52 \times 10^{-7} \text{ M/s}$.

Determine the rate of appearance, in M/s , of O_2 at this same point in the reaction.

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Continue your response to **QUESTION 6** on this page.

- (c) NO_2 is a molecule that contains an odd number of electrons and can be oxidized to form the NO_2^+ ion. In NO_2 , the unpaired electron is presumed to be localized on the nitrogen atom, as shown in the Lewis diagram in the box on the left.



- (i) In the box on the right, complete the Lewis diagram for NO_2^+ . Be sure to show all bonding and nonbonding electrons.
- (ii) A student makes the claim that the bond angles in NO_2 and NO_2^+ are different from each other. Do you agree or disagree with the student's claim? Justify your answer.

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Begin your response to **QUESTION 7** on this page.

7. A student conducts a chromatography experiment and needs to prepare 100.0 mL of 0.340 *M* NaCl(*aq*) to use as the solvent.

(a) Calculate the mass of solid NaCl (molar mass 58.44 g/mol) needed to prepare the 100.0 mL of 0.340 *M* NaCl(*aq*).

(b) In the following table, briefly list the additional steps necessary to prepare the 100.0 mL of 0.340 *M* NaCl(*aq*) solution using only materials selected from the choices given. Assume that all appropriate safety measures are already in place. Not all materials in the list may be needed.

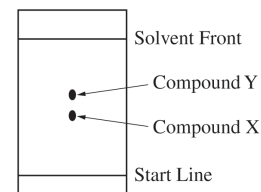
- | | | |
|--------------|-----------------------------|------------------------------|
| • Solid NaCl | • Distilled water | • Weighing paper and scoop |
| • Balance | • 100.0 mL volumetric flask | • 50.0 mL graduated cylinder |
| • Pipet | • 150 mL beakers | • Chromatography paper |

Step	Step Description and Materials Used
1.	Use the weighing paper and scoop to measure the correct mass of solid NaCl on the balance.
2.	
3.	Swirl the mixture to dissolve the solid NaCl.
4.	
5.	Stopper and invert the mixture several times to ensure that the mixture is homogeneous.

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Continue your response to **QUESTION 7** on this page.

The student uses the NaCl(*aq*) solvent to separate a mixture of compounds X and Y in a chromatography experiment. After 30 minutes, the student removes the chromatography paper from the chamber. The results of the experiment are shown.



(c) A second student conducts the same chromatography experiment but removes the chromatography paper from the chamber after 15 minutes instead of 30 minutes. Predict the effect, if any, this would have on the separation distance between compounds X and Y in the new experiment. Explain your reasoning.

STOP

END OF EXAM