

Week 21

AP Chemistry

Homework bundle for this week

本周作业合集

exercises.lol

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AP Chemistry

Name: _____ Score: _____

1. At equilibrium, the forward and reverse reaction rates are...
 - ☐ equal
 - ☐ both zero
 - ☐ increasing
2. The symbol $\rightleftharpoons$ in an equation means the reaction is...
 - ☐ reversible
 - ☐ irreversible
 - ☐ explosive
3. If $Q < K$, the reaction shifts...
 - ☐ forward (toward products)
 - ☐ backward (toward reactants)
 - ☐ it is at equilibrium
4. At equilibrium $[\text{product}] = 6$ and $[\text{reactant}] = 3$ (coefficients 1). Find K .

5. A large K (much greater than 1) means the equilibrium favours...
 - ☐ products
 - ☐ reactants
 - ☐ neither side
6. A reaction has $K = 5$. What is K for the reverse reaction? (as a decimal)

7. In an ICE table, a reactant's equilibrium amount is written as...
 - ☐ initial minus x
 - ☐ initial plus x
 - ☐ just x
8. At equilibrium, both the forward and reverse reactions have stopped.
 - ☐ True ☐ False

9. A reaction has $K = 3$. If you double every coefficient, the new K is...?

10. At equilibrium the reactant concentration reaches zero.

☐ True ☐ False

AP Chemistry

1. **equal**

Equal rates keep the concentrations constant.

2. **reversible**

A double arrow marks a reversible reaction.

3. **forward (toward products)**

Too few products means it moves forward to make more.

4. **2**

$$K = 6/3 = 2.$$

5. **products**

Large K means the reaction nearly goes to completion – product-favoured.

6. **0.2**

Reversing gives $1/K = 1/5 = 0.2$.

7. **initial minus x**

Reactants are used up, so their amount is (initial $-x$).

8. **False**

Equilibrium is dynamic – both keep running at equal rates.

9. **9**

Doubling gives $K^2 = 3^2 = 9$.

10. **False**

Both reactants and products remain present.

7.1 Introduction to Equilibrium

Name: _____ Class: _____ Date: _____

Total: 9 marks

KEY WORDS dynamic equilibrium 动态平衡 • reversible reaction 可逆反应 • chemical equilibrium 化学平衡

Objective

Build the skills to answer exam questions on **chemical equilibrium** — the dynamic balance of a reversible reaction.

You must be able to:

- describe **dynamic equilibrium** 动态平衡 (forward rate = reverse rate)
- explain that concentrations stay **constant**, not equal
- recognise the $\rightleftharpoons$ symbol

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ Dynamic equilibrium

In a closed system a reversible reaction reaches **equilibrium** when the **forward and reverse rates are equal**. Both reactions still happen — it is **dynamic**, not stopped.

■ Concentrations are constant, not equal

At equilibrium the concentrations of reactants and products stay **constant** over time, but they are usually **not equal** to each other.

■ The reversible arrow

The $\rightleftharpoons$ symbol means the reaction goes **both** ways at once. A reaction that goes essentially to completion uses a single arrow.

■ Reaching equilibrium

Starting from reactants, the forward rate is high and falls as reactants deplete; the reverse rate starts at zero and rises. They meet — that is equilibrium.

2 Practice

Now apply the methods above.

2.1 At equilibrium, how do the forward and reverse rates compare? [1]

2.2 Are reactant and product concentrations equal at equilibrium? [1]

2.3 What does “dynamic” mean in dynamic equilibrium? [1]

3 Exam-style questions

3.1 At equilibrium, the concentrations of reactants and products are [1]

- **A** equal to each other
 - **B** constant over time
 - **C** zero
 - **D** always increasing
-

3.2 A reversible reaction is placed in a closed flask starting with only reactants.

(a) Describe how the forward and reverse rates change until equilibrium. [2]

(b) State what is true of the rates at equilibrium. [1]

3.3 Explain why equilibrium is called “dynamic” even though concentrations do not change. [2]

Solutions

2.1 They are equal.

2.2 Not necessarily — they are constant, but usually not equal.

2.3 Both the forward and reverse reactions continue at the molecular level.

3.1 B — constant over time.

3.2 (a) The forward rate starts high and falls as reactants deplete; the reverse rate starts at zero and rises as products build, until they meet. (b) They are equal.

3.3 The forward and reverse reactions continue at equal rates, so molecules keep converting both ways; the concentrations stay constant only because the two rates cancel.

7.2 Direction of Reversible Reactions

Name: _____ Class: _____ Date: _____

Total: 10 marks

KEY WORDS reversible reaction 可逆反应

Objective

Build the skills to answer exam questions on the **direction of reversible reactions**.

You must be able to:

- write the **equilibrium expression** $K = \frac{[\text{products}]}{[\text{reactants}]}$ with coefficients as powers
- exclude pure solids and liquids
- write K for a given equation

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ The equilibrium expression

For $aA + bB \rightleftharpoons cC + dD$,

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}.$$

Products over reactants, each raised to its coefficient.

■ A worked expression

For $N_2 + 3H_2 \rightleftharpoons 2NH_3$:

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3}.$$

■ Leave out solids and pure liquids

Pure **solids** and pure **liquids** have constant "concentration" and are **omitted** from K . Only gases and dissolved species appear.

■ Gases can use pressures

For gas equilibria, K_p uses partial pressures in place of concentrations, with the same product-over-reactant form.

2 Practice

Now apply the methods above.

2.1 Write K for $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$. [2]

2.2 Which states are left out of an equilibrium expression? [1]

2.3 Write K for $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$. [1]

3 Exam-style questions

3.1 In the equilibrium expression, each concentration is raised to the power of its [1]

- **A** molar mass
 - **B** coefficient in the balanced equation
 - **C** oxidation number
 - **D** charge
-

3.2 For $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$:

(a) Write the equilibrium expression. [2]

(b) Explain why the solids do not appear. [1]

3.3 Write the equilibrium expression for $\text{Fe}^{3+}(aq) + \text{SCN}^{-}(aq) \rightleftharpoons \text{FeSCN}^{2+}(aq)$. [2]

Solutions

2.1 $K = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$.

2.2 Pure solids and pure liquids.

2.3 $K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$.

3.1 B — its coefficient in the balanced equation.

3.2 (a) $K = [\text{CO}_2]$. (b) The solids (CaCO_3 , CaO) have constant activity and are omitted.

3.3 $K = \frac{[\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^-]}$.

7.3 The Reaction Quotient and Equilibrium Constant

Name: _____ Class: _____ Date: _____

Total: 10 marks

KEY WORDS reaction quotient 反应商

Objective

Build the skills to answer exam questions on the **reaction quotient** Q and its comparison to K .

You must be able to:

- calculate Q with the same form as K but current (non-equilibrium) concentrations
- compare Q to K to predict the direction of shift
- state what $Q = K$ means

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ The reaction quotient

Q has the **same expression** as K but uses the **current** concentrations (not necessarily at equilibrium).

■ Comparing Q and K

- $Q < K$: too few products $\rightarrow$ shifts **forward** (toward products);
- $Q > K$: too many products $\rightarrow$ shifts **reverse** (toward reactants);
- $Q = K$: **at equilibrium**, no shift.

■ A worked comparison

If $K = 10$ and the current $Q = 2$, then $Q < K$, so the reaction proceeds **forward** to make more product until Q rises to 10.

■ Why it works

Q measures "how far along" the mixture is. The reaction always moves to bring Q toward K .

2 Practice

Now apply the methods above.

2.1 What does $Q = K$ mean? [1]

2.2 If $Q < K$, which way does the reaction shift? [1]

2.3 How does the expression for Q differ from that for K ? [1]

3 Exam-style questions

3.1 If $Q > K$, the reaction shifts [1]

- **A** forward (toward products)
 - **B** reverse (toward reactants)
 - **C** it is at equilibrium
 - **D** it stops
-

3.2 For a reaction, $K = 50$. A mixture is analyzed and $Q = 120$.

(a) Compare Q and K . [1]

(b) State the direction of shift, with a reason. [2]

3.3 For $A \rightleftharpoons B$ with $K = 4$, a mixture has $[A] = 2 \text{ M}$ and $[B] = 2 \text{ M}$. Find Q and predict the shift. [3]

Solutions

2.1 The mixture is at equilibrium.

2.2 Forward (toward products).

2.3 Q uses the current concentrations; K uses the equilibrium concentrations.

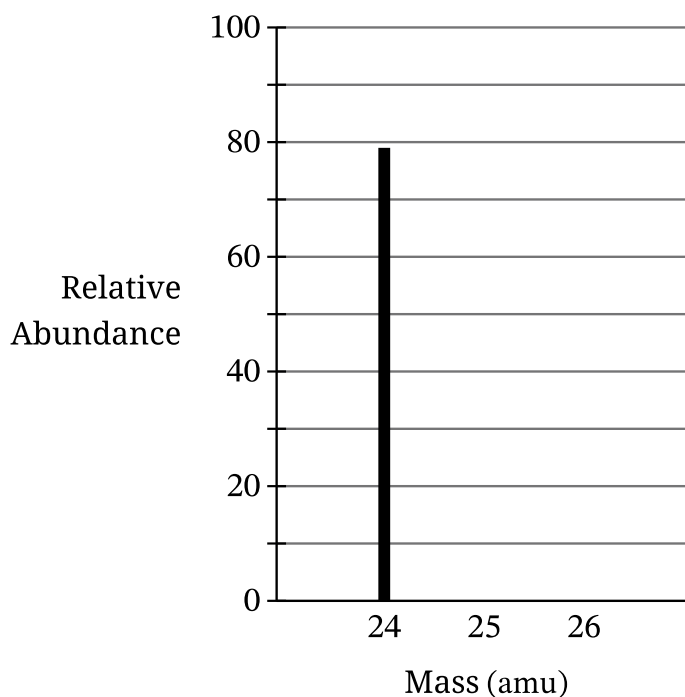
3.1 B — too many products, so it shifts reverse.

3.2 (a) $Q > K$ ($120 > 50$). (b) Shifts reverse (toward reactants), because there is more product than equilibrium allows, so Q must fall to K .

3.3 $Q = \frac{[\text{B}]}{[\text{A}]} = \frac{2}{2} = 1$; $Q < K$ ($1 < 4$), so it shifts **forward** to make more B.

1. Answer the following questions about magnesium.

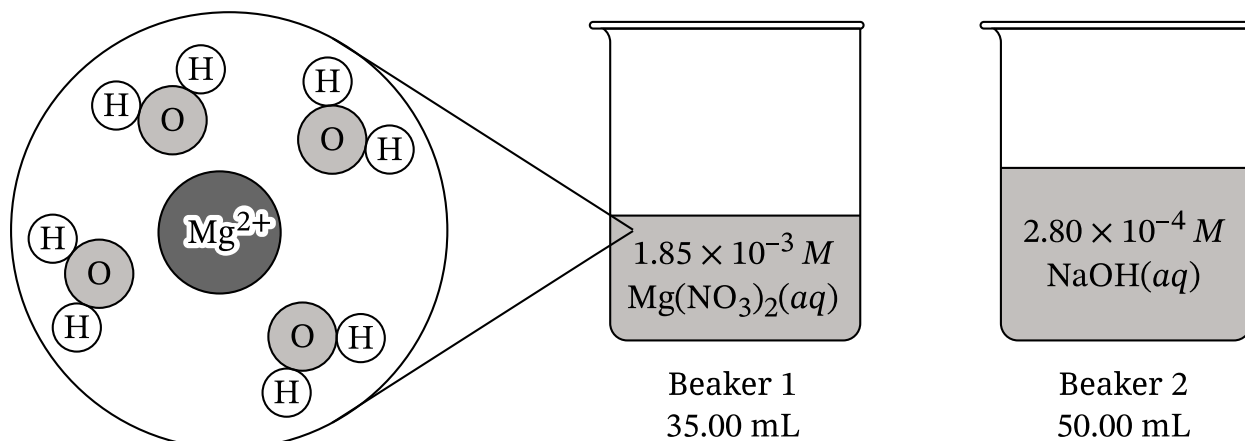
A. An incomplete mass spectrum for magnesium is shown in the diagram.



The percent abundance of magnesium-24 is 79%. The percent abundances of the other two natural isotopes of magnesium, magnesium-25 and magnesium-26, are approximately equal.

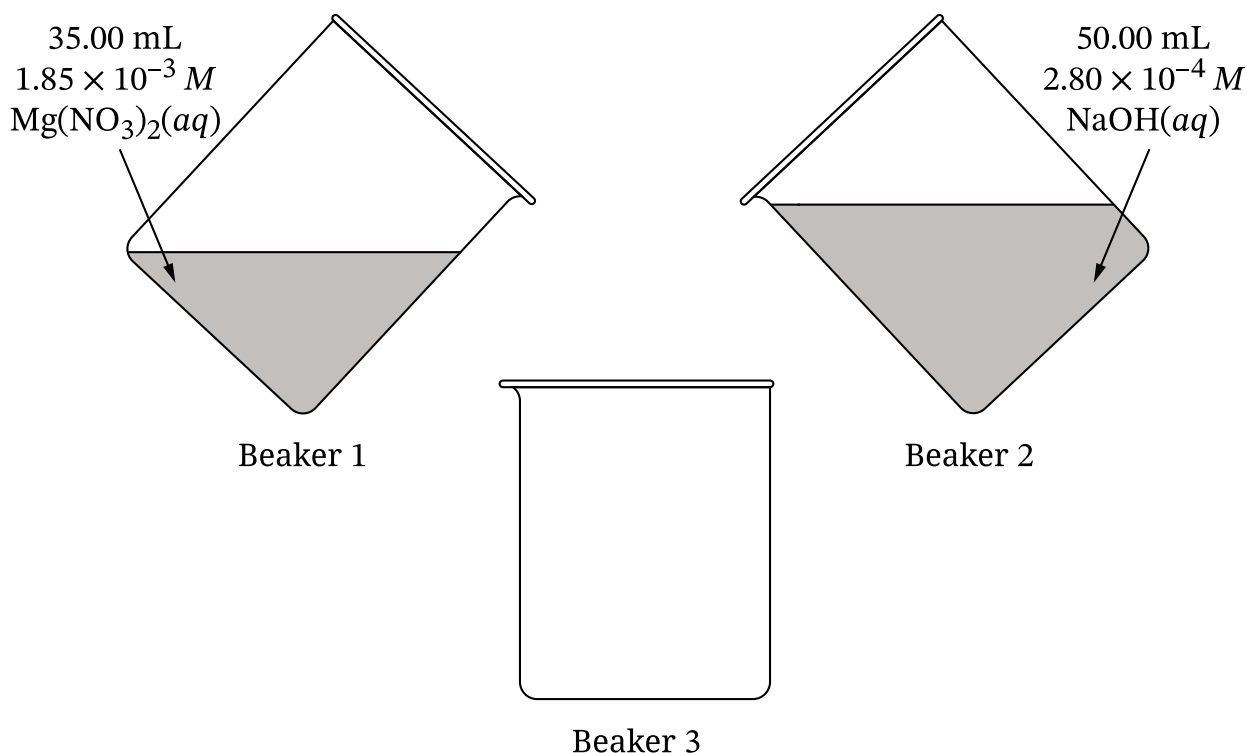
- Complete the mass spectrum in part A by drawing thick lines in the appropriate locations to represent the percent abundance of magnesium-25 and magnesium-26.
- Describe the difference in atomic structure that accounts for the difference in mass between magnesium-25 and magnesium-26.

A student prepares a $1.85 \times 10^{-3} M$ solution of $\text{Mg}(\text{NO}_3)_2(aq)$ in beaker 1 and a $2.80 \times 10^{-4} M$ solution of $\text{NaOH}(aq)$ in beaker 2, as shown.

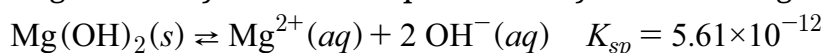


- B.** The particle diagram shown represents a magnesium ion, Mg^{2+} , in beaker 1. A sodium ion, Na^+ , in beaker 2 has a weaker attraction to water than the Mg^{2+} does. Explain this phenomenon using Coulomb's law and each of the following.
- The relative charge of the ions
 - The relative radii of the ions
- C.** Calculate the pH of the solution in beaker 2.

- D. A student combines 35.00 mL of $1.85 \times 10^{-3} M \text{Mg}(\text{NO}_3)_2(aq)$ with 50.00 mL of $2.80 \times 10^{-4} M \text{NaOH}(aq)$, as shown in the diagram. Calculate $[\text{Mg}^{2+}]$ after the two solutions are combined but before any reaction takes place. (Assume that volumes are additive.)

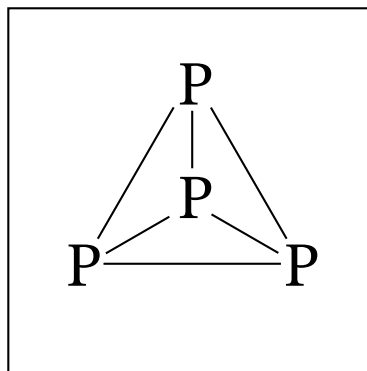
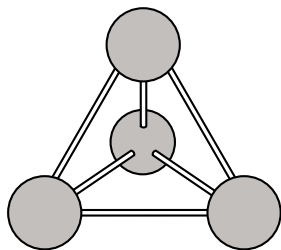


- E. The dissolution of magnesium hydroxide is represented by the following equation.

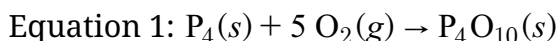


- Write the expression for the solubility product constant, K_{sp} .
 - After the two solutions are combined in beaker 3 as described in part D, but before any reaction takes place, $[\text{OH}^{-}] = 1.65 \times 10^{-4} M$. Using your answer to part D, calculate the value of the reaction quotient, Q .
 - Using the reaction quotient, Q , predict whether a precipitate should form as the mixture in beaker 3 approaches equilibrium. Justify your answer.
- F. In a separate experiment, the student adds $\text{HNO}_3(aq)$ to decrease the pH of a saturated solution containing undissolved $\text{Mg}(\text{OH})_2(s)$. Does the amount of undissolved $\text{Mg}(\text{OH})_2(s)$ increase, decrease, or remain the same as the $\text{HNO}_3(aq)$ is added? Justify your answer.

3. White phosphorus is composed of P_4 molecules with a tetrahedral structure, as shown in the diagram on the left. Each P atom is bonded to the other three P atoms by single bonds, as shown in the incomplete Lewis diagram on the right.

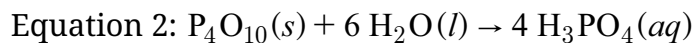


- A. In the box in part A, complete the Lewis diagram for P_4 by drawing the nonbonding electrons.
- B. The reaction of white phosphorus with oxygen to form $P_4O_{10}(s)$ is thermodynamically favorable at 298 K. The reaction is represented by equation 1.

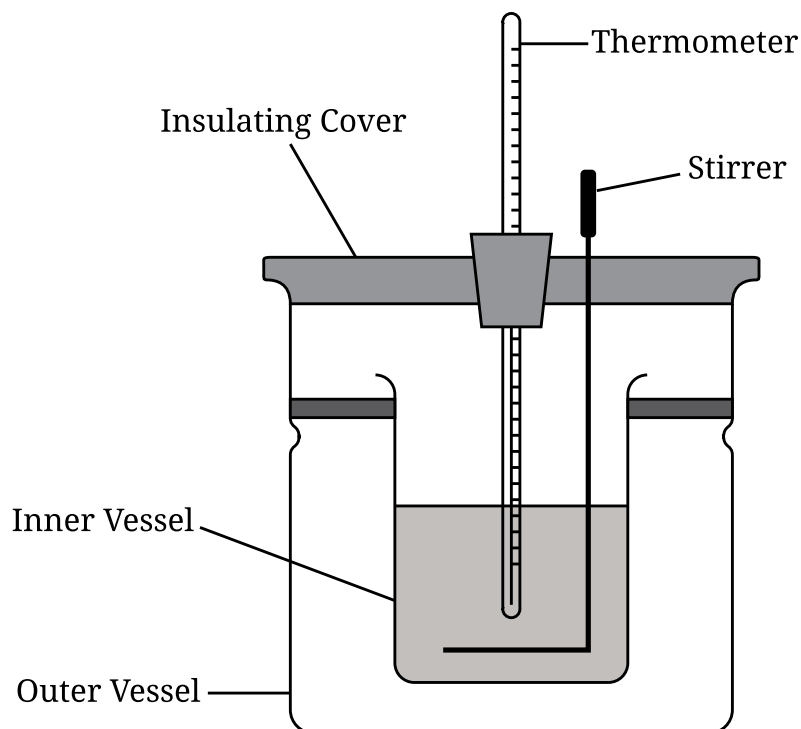


- i. The entropy change of the reaction, ΔS° , is negative. Using particle-level reasoning, explain why the entropy decreases as the reaction progresses.
- ii. The enthalpy change of the reaction, ΔH° , is also negative. A student claims that the favorability of the reaction is driven by enthalpy and **not** by entropy. Is the student's claim correct? Justify your answer by using the relationship between ΔG° , ΔH° , and ΔS° .

$\text{P}_4\text{O}_{10}(s)$ reacts exothermically with water to form phosphoric acid, as represented by equation 2.



A chemist uses a calorimetry experiment to determine the enthalpy change for the reaction, as represented by the following diagram.



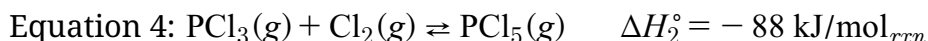
C. The chemist carries out the calorimetry experiment and records the following information.

Mass of P_4O_{10}	0.100 g
Mass of H_2O	100.0 g
Initial temperature	22.00° C
Final temperature	22.38° C
Molar mass of P_4O_{10}	283.9 g/mol
Specific heat of H_2O	4.18 J/(g·°C)

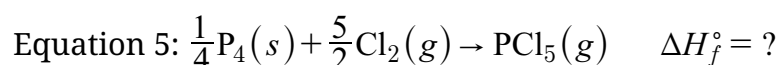
- Calculate the amount of heat, q , released during the experiment, in kJ. Assume that the specific heat of the solution is the same as that of water.
- Calculate the value of $\Delta H^\circ_{\text{rxn}}$ for equation 2 in kJ/mol_{rxn}. Include the sign in your answer.

- D. The chemist weighed out 0.100 g P_4O_{10} of and 100.0 g of H_2O to perform a second trial. In the second trial, some of the solid P_4O_{10} stuck to the weighing paper and was not transferred to the calorimeter. Given that P_4O_{10} is the limiting reactant, would ΔT for the second trial be greater than, less than, or equal to the value in the first trial? Justify your answer.

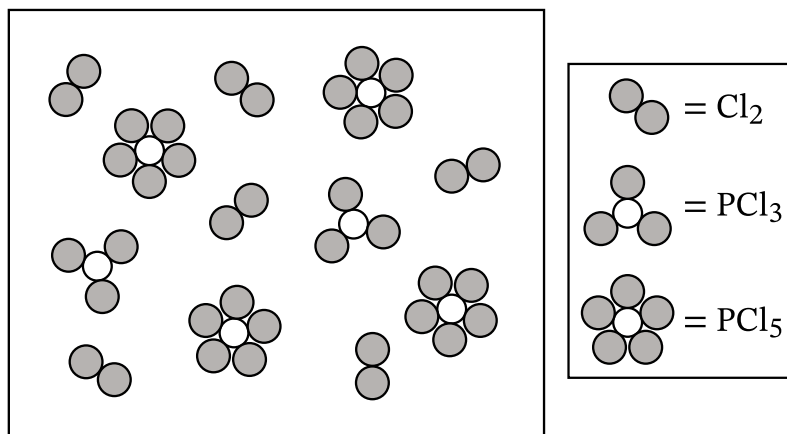
$\text{P}_4(\text{s})$ also reacts readily with $\text{Cl}_2(\text{g})$ to produce phosphorus trichloride, $\text{PCl}_3(\text{g})$, which in turn reacts with $\text{Cl}_2(\text{g})$ in an equilibrium process to produce $\text{PCl}_5(\text{g})$. The reactions are represented by equations 3 and 4.



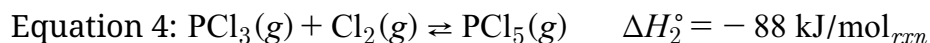
- E. Calculate the standard enthalpy of formation of $\text{PCl}_5(\text{g})$ represented by equation 5.



The following particle-level diagram represents the contents of the vessel in an equilibrium mixture at 546 K involving equation 4.



- F. Equation 4 for the reaction that occurs is shown.



- If each particle in the diagram represents a partial pressure of 1.00 atm, what is the value of K_p for the equilibrium mixture at 546 K?
- Does the value of K_p increase, decrease, or remain the same when the temperature is increased to 596 K? Justify your answer based on ΔH_2° .

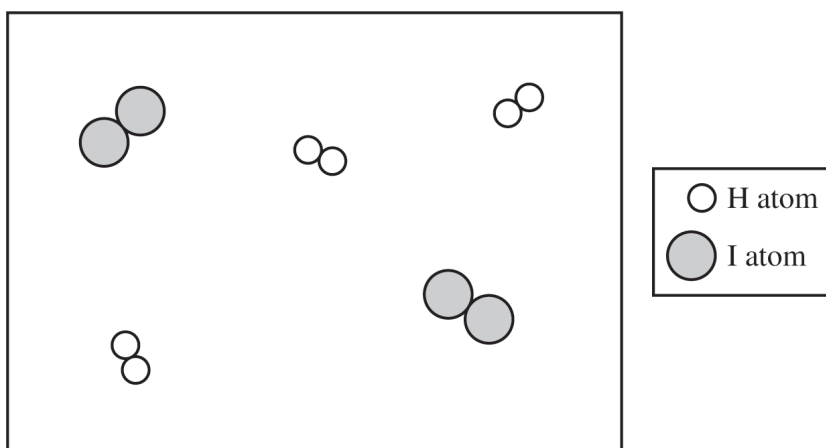
5. Hydrogen gas and iodine gas react to form hydrogen iodide at an elevated temperature, as represented by the following equation.



(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.

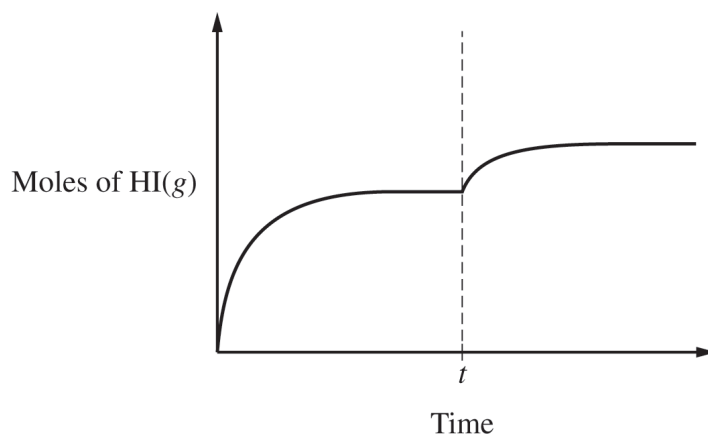
- (i) At a certain time, the value of the reaction quotient, Q , is 0.67. The following particle diagram is an incomplete representation of the system at this time. The diagram shows the relative number of $\text{H}_2(g)$ and $\text{I}_2(g)$ molecules, but the $\text{HI}(g)$ molecules are not included.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



GO ON TO THE NEXT PAGE.

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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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.



- (a) How many grams of $\text{Cl}(g)$ can be formed from 1.25 mol of $\text{AlCl}_3(g)$?

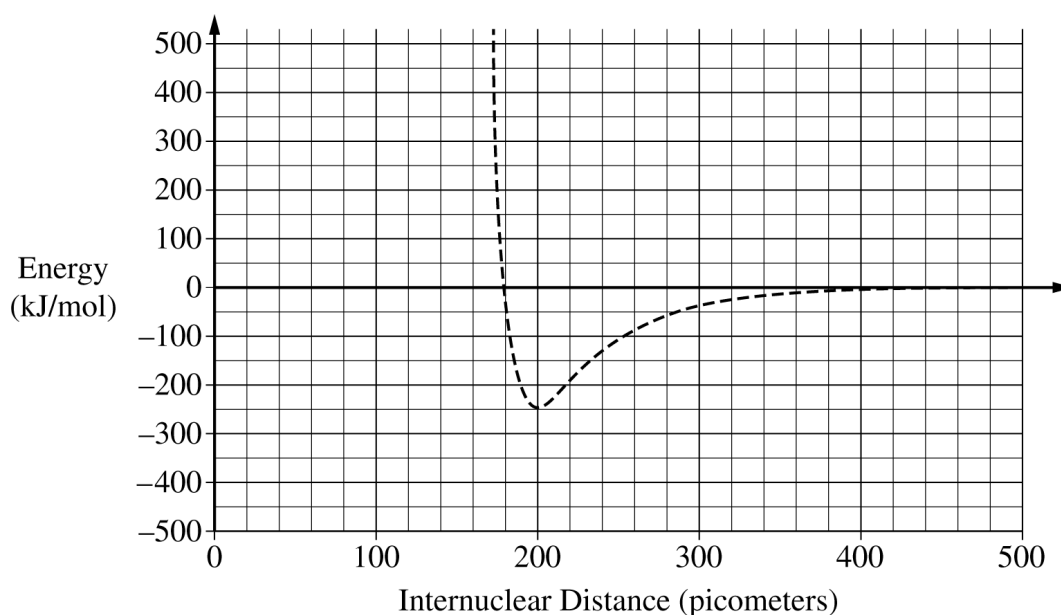
Additional reactions that involve Al or Cl are shown in the following table.

Reaction Number	Equation	ΔH_{rxn}° (kJ/mol _{rxn})
2	$\text{Al}(s) + \frac{3}{2} \text{Cl}_2(g) \rightarrow \text{AlCl}_3(g)$	-583
3	$\text{Al}(s) \rightarrow \text{Al}(g)$	+326
4	$\text{Cl}_2(g) \rightarrow 2 \text{Cl}(g)$	+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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(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 $\text{Al} - \text{Cl}$ bond length is 220 picometers and the average bond energy is 425 kJ/mol. Draw the potential energy curve for the average $\text{Al} - \text{Cl}$ bond on the preceding graph.

(d) Three proposed Lewis diagrams for the $\text{AlCl}_3(g)$ molecule are shown.

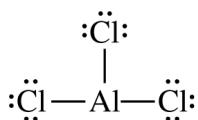


Diagram 1

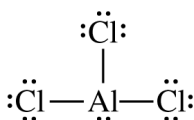


Diagram 2

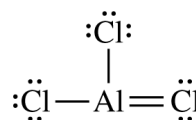


Diagram 3

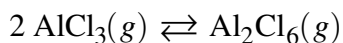
(i) The $\text{AlCl}_3(g)$ molecule has a trigonal planar geometry. Which diagram (1, 2, or 3) can be eliminated based on geometry? Justify your choice based on VSEPR theory.

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

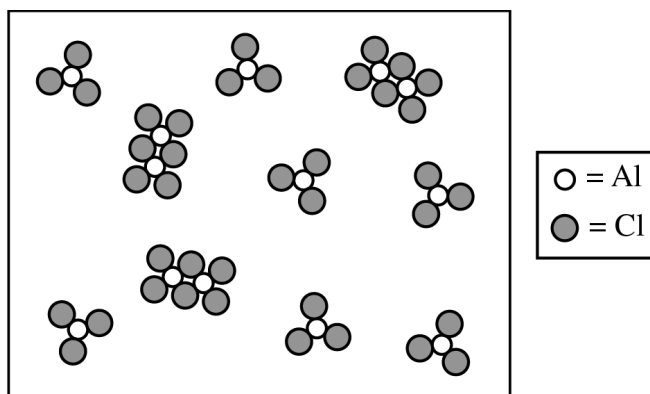
- (ii) Which of the three diagrams is the best representation for the bonding in AlCl_3 ? Justify your choice based on formal charges.

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



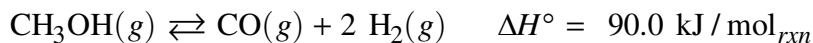
- (e) Write the expression for the equilibrium constant, K_p , for this reaction.

A particle-level diagram of an equilibrium mixture of $\text{AlCl}_3(g)$ and $\text{Al}_2\text{Cl}_6(g)$ 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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Methanol vapor decomposes to form carbon monoxide gas and hydrogen gas at high temperatures in the presence of a platinum catalyst, as represented by the balanced chemical equation given.

(a) Are the hydrogen atoms oxidized or are they reduced in the forward reaction? Justify your answer in terms of oxidation numbers.

(b) In the following box, draw the complete Lewis electron-dot diagram for the carbon monoxide molecule in which every atom obeys the octet rule. Show all bonding and nonbonding valence electrons.



(c) The values of the standard molar entropies of the compounds involved in the reaction are given in the following table.

Substance	S° (J/(K·mol))
$\text{CH}_3\text{OH}(g)$	240.
$\text{CO}(g)$	198
$\text{H}_2(g)$	131

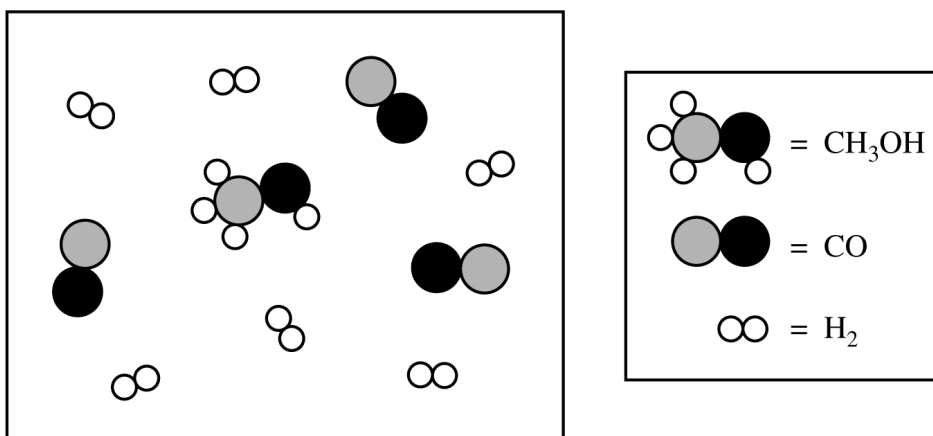
(i) Use the data in the table to calculate the value of the standard entropy change, ΔS° , in J/(K·mol_{rxn}), for the reaction.

GO ON TO THE NEXT PAGE.

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

- (ii) Calculate the value of ΔG° , in $\text{kJ/mol}_{\text{rxn}}$, for the reaction at 375 K. Assume that ΔH° and ΔS° are independent of temperature.

The following particle-level diagram shows a representative sample of the equilibrium mixture represented by the equation given.

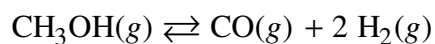


- (d) Use information from the particle diagram to calculate the partial pressure of CO at equilibrium when the total pressure of the equilibrium mixture is 12.0 atm.

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

GO ON TO THE NEXT PAGE.

Continue your response to QUESTION 2 on this page.



The reaction system represented by the equation is allowed to achieve equilibrium at a different temperature. The following table gives the partial pressure of each species in the equilibrium mixture.

Substance	Partial Pressure at Different Temperature
$\text{CH}_3\text{OH}(g)$	2.7 atm
$\text{CO}(g)$	4.2 atm
$\text{H}_2(g)$	8.4 atm

(f) Use the information in the table to calculate the value of the equilibrium constant, K_p , at the new temperature.

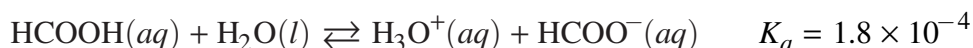
(g) The volume of the container is rapidly doubled with no change in temperature. As equilibrium is re-established, does the number of moles of $\text{CH}_3\text{OH}(g)$ increase, decrease, or remain the same? Justify your answer by comparing the value of the reaction quotient, Q , with the value of the equilibrium constant, K_p .

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CHEMISTRY**SECTION II****Time—1 hour and 45 minutes****7 Questions****YOU MAY USE YOUR CALCULATOR FOR THIS SECTION.**

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. Methanoic acid, HCOOH , ionizes according to the equation above.

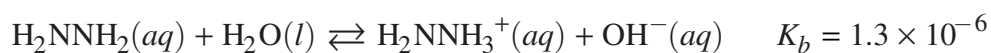
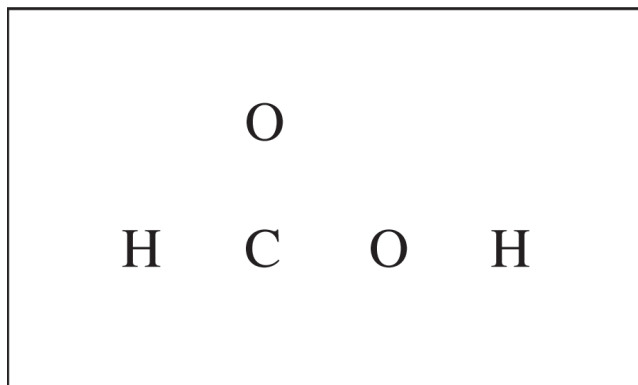
(a) Write the expression for the equilibrium constant, K_a , for the reaction.

(b) Calculate the pH of a 0.25 M solution of HCOOH .

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Use a pencil or pen with black or dark blue ink only. Do NOT write your name. Do NOT write outside the box.

(c) In the box below, complete the Lewis electron-dot diagram for HCOOH . Show all bonding and nonbonding valence electrons.



(d) In aqueous solution, the compound H_2NNH_2 reacts according to the equation above. A 50.0 mL sample of 0.25 M $\text{H}_2\text{NNH}_2(aq)$ is combined with a 50.0 mL sample of 0.25 M $\text{HCOOH}(aq)$.

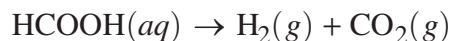
(i) Write the balanced net ionic equation for the reaction that occurs when H_2NNH_2 is combined with HCOOH .

(ii) Is the resulting solution acidic, basic, or neutral? Justify your answer.

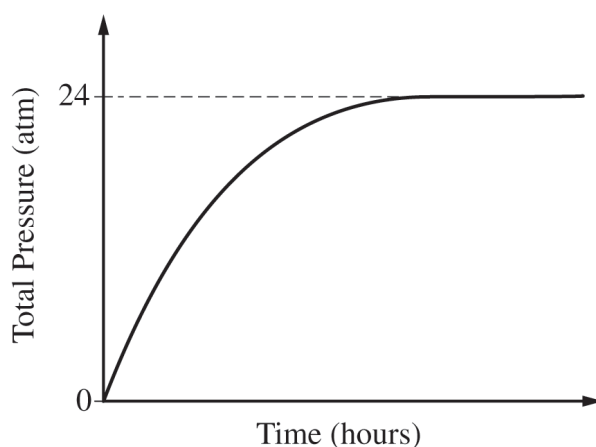
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When a catalyst is added to a solution of $\text{HCOOH}(aq)$, the reaction represented by the following equation occurs.



(e) Is the reaction a redox reaction? Justify your answer.



(f) The reaction occurs in a rigid 4.3 L vessel at 25°C , and the total pressure is monitored, as shown in the graph above. The vessel originally did not contain any gas. Calculate the number of moles of $\text{CO}_2(g)$ produced in the reaction. (Assume that the amount of $\text{CO}_2(g)$ dissolved in the solution is negligible.)

(g) After the reaction has proceeded for several minutes, does the amount of catalyst increase, decrease, or remain the same? Justify your answer.

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Use a pencil or pen with black or dark blue ink only. Do NOT write your name. Do NOT write outside the box.

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.



A chemistry teacher wants to prepare Br_2 . The teacher has access to the following three reagents: $\text{NaBr}(aq)$, $\text{Cl}_2(g)$, and $\text{I}_2(s)$.

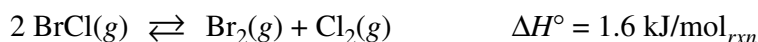
Half-Reaction	E° at 25°C (V)
$\text{Br}_2 + 2 e^- \rightarrow 2 \text{Br}^-$	1.07
$\text{Cl}_2 + 2 e^- \rightarrow 2 \text{Cl}^-$	1.36
$\text{I}_2 + 2 e^- \rightarrow 2 \text{I}^-$	0.53

- (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.

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 each substance.

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



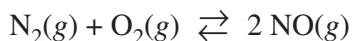
A 0.100 mole sample of pure $\text{BrCl}(g)$ is placed in a previously evacuated, rigid 2.00 L container at 298 K. Eventually the system reaches equilibrium according to the equation above.

- (d) Calculate the pressure in the container before equilibrium is established.
- (e) Write the expression for the equilibrium constant, K_{eq} , for the decomposition of BrCl .

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.
- (g) Calculate the bond energy of the Br-Cl bond, in kJ/mol, using ΔH° 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	?

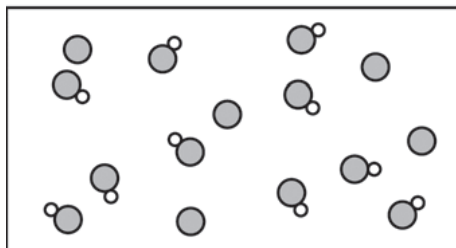
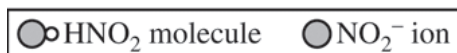


3. At high temperatures, $\text{N}_2(\text{g})$ and $\text{O}_2(\text{g})$ can react to produce nitrogen monoxide, $\text{NO}(\text{g})$, as represented by the equation above.

- (a) Write the expression for the equilibrium constant, K_p , for the forward reaction.
- (b) A student injects $\text{N}_2(\text{g})$ and $\text{O}_2(\text{g})$ into a previously evacuated, rigid vessel and raises the temperature of the vessel to 2000°C . At this temperature the initial partial pressures of $\text{N}_2(\text{g})$ and $\text{O}_2(\text{g})$ are 6.01 atm and 1.61 atm, respectively. The system is allowed to reach equilibrium. The partial pressure of $\text{NO}(\text{g})$ at equilibrium is 0.122 atm. Calculate the value of K_p .

Nitrogen monoxide, $\text{NO}(\text{g})$, can undergo further reactions to produce acids such as HNO_2 , a weak acid with a K_a of 4.0×10^{-4} and a $\text{p}K_a$ of 3.40.

- (c) A student is asked to make a buffer solution with a pH of 3.40 by using 0.100 M $\text{HNO}_2(\text{aq})$ and 0.100 M $\text{NaOH}(\text{aq})$.
- (i) Explain why the addition of 0.100 M $\text{NaOH}(\text{aq})$ to 0.100 M $\text{HNO}_2(\text{aq})$ can result in the formation of a buffer solution. Include the net ionic equation for the reaction that occurs when the student adds the $\text{NaOH}(\text{aq})$ to the $\text{HNO}_2(\text{aq})$.
- (ii) Determine the volume, in mL, of 0.100 M $\text{NaOH}(\text{aq})$ the student should add to 100. mL of 0.100 M $\text{HNO}_2(\text{aq})$ to make a buffer solution with a pH of 3.40. Justify your answer.
- (d) A second student makes a buffer by dissolving 0.100 mol of $\text{NaNO}_2(\text{s})$ in 100. mL of 1.00 M $\text{HNO}_2(\text{aq})$. Which is more resistant to changes in pH when a strong acid or a strong base is added, the buffer made by the second student or the buffer made by the first student in part (c)? Justify your answer.
- (e) A new buffer is made using $\text{HNO}_2(\text{aq})$ as one of the ingredients. A particulate representation of a small representative portion of the buffer solution is shown below. (Cations and water molecules are not shown.) Is the pH of the buffer represented in the diagram greater than, less than, or equal to 3.40? Justify your answer.



7.4 Calculating the Equilibrium Constant

Name: _____ Class: _____ Date: _____

Total: 12 marks

KEY WORDS ice table 初始 • equilibrium constant 平衡常数

Objective

Build the skills to answer exam questions on **calculating the equilibrium constant** from equilibrium concentrations.

You must be able to:

- substitute equilibrium concentrations into the K expression
- use an **ICE table** 初始-变化-平衡 (Initial, Change, Equilibrium)
- solve for K

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ Straight substitution

Given the equilibrium concentrations, put them into the K expression. For $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ with $[\text{H}_2] = 0.1$, $[\text{I}_2] = 0.1$, $[\text{HI}] = 0.8$:

$$K = \frac{(0.8)^2}{(0.1)(0.1)} = 64.$$

■ The ICE table

When only starting amounts and one change are given, use an **ICE** table: write **I**nitial, the **C**hange ($\pm x$ scaled by coefficients), and the **E**quilibrium row. Then substitute.

■ A worked ICE

$\text{A} \rightleftharpoons \text{B}$, start $[\text{A}] = 1.0$, $[\text{B}] = 0$. At equilibrium $[\text{B}] = 0.6$, so $x = 0.6$ and $[\text{A}] = 1.0 - 0.6 = 0.4$. Then $K = \frac{0.6}{0.4} = 1.5$.

■ **Watch the coefficients**

The change x is multiplied by each species' coefficient (e.g. a "2" species changes by $2x$).

2 Practice

Now apply the methods above.

2.1 For $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ with $[\text{H}_2] = [\text{I}_2] = 0.2$, $[\text{HI}] = 0.8$, find K . [2]

2.2 In an ICE table, what do I, C, and E stand for? [1]

2.3 $\text{A} \rightleftharpoons \text{B}$ starts at $[\text{A}] = 2.0$, $[\text{B}] = 0$; at equilibrium $[\text{B}] = 0.5$. Find $[\text{A}]$ at equilibrium. [1]

3 Exam-style questions

3.1 To find K , you substitute the _____ concentrations into the expression. [1]

- **A** initial
 - **B** equilibrium
 - **C** standard
 - **D** average
-

3.2 For $A \rightleftharpoons 2B$, start $[A] = 1.0 \text{ M}$, $[B] = 0$. At equilibrium $[A] = 0.6 \text{ M}$.

(a) Find $[B]$ at equilibrium (note the coefficient 2). [2]

(b) Calculate K . [2]

3.3 For $N_2 + 3H_2 \rightleftharpoons 2NH_3$, the equilibrium concentrations are $[N_2] = 0.20$, $[H_2] = 0.20$, $[NH_3] = 0.40$. Calculate K . [3]

Solutions

2.1 $K = \frac{(0.8)^2}{(0.2)(0.2)} = \frac{0.64}{0.04} = 16.$

2.2 Initial, Change, Equilibrium.

2.3 $[A] = 2.0 - 0.5 = 1.5 \text{ M}.$

3.1 B — the equilibrium concentrations.

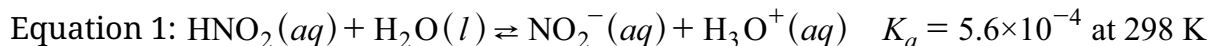
3.2 (a) A fell by 0.4, so $x = 0.4$; B rose by $2x = 0.8$, so $[B] = 0.8 \text{ M}.$ (b) $K = \frac{(0.8)^2}{0.6} = \frac{0.64}{0.6} = 1.07.$

3.3 $K = \frac{(0.40)^2}{(0.20)(0.20)^3} = \frac{0.16}{(0.20)(0.008)} = \frac{0.16}{0.0016} = 100.$

Question 3: Version J

The following information applies to all parts.

3. Nitrous acid, HNO_2 , is a weak acid that ionizes according to Equation 1.

**Part A**

Identify a conjugate acid-base pair in the equation. Be sure to clearly label which is the acid and which is the base.

Part B

A solution of $\text{HNO}_2(aq)$ with an initial concentration of 0.125 M has a pH of 2.09.

- i. **Calculate** the value of $[\text{H}_3\text{O}^+]$ in the solution. Show the work that leads to your answer.
- ii. **Calculate** $[\text{HNO}_2]$ at equilibrium. Show the work that leads to your answer.

Part C

In an experiment, the solution of 0.125 M $\text{HNO}_2(aq)$ is heated to 333 K . The new equilibrium concentrations are determined to be $[\text{HNO}_2] = 0.114 \text{ M}$, $[\text{NO}_2^-] = 0.0109 \text{ M}$, and $[\text{H}_3\text{O}^+] = 0.0109 \text{ M}$.

- i. **Calculate** the value of K_a for HNO_2 at 333 K . Show the work that leads to your answer.
- ii. Is the reaction represented by Equation 1 endothermic or exothermic? **Justify** your answer by comparing K_a values at 298 K and 333 K .

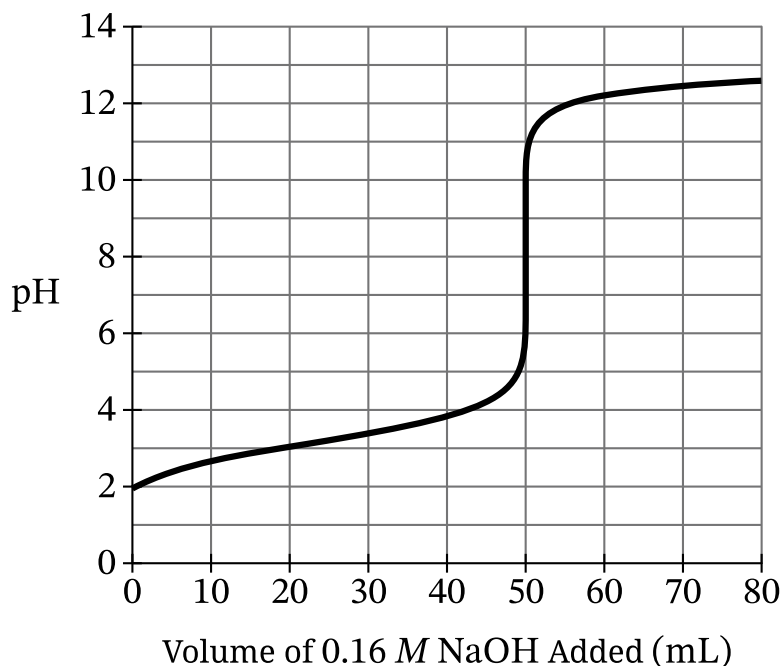
The following information applies to parts D, E, and F.

In a second experiment, a student is given a bottle containing HNO_2 with an unknown molarity. To determine the concentration of the $\text{HNO}_2(aq)$ in the bottle, the student titrates 35.0 mL of the $\text{HNO}_2(aq)$ with 0.16 M $\text{NaOH}(aq)$ at 298 K, which reacts according to Equation 2.



The results of the titration are summarized in Figure 1.

Figure 1



Part D

Using Figure 1, **identify** the pH at the equivalence point.

Part E

Using Figure 1, **calculate** the molarity $\text{HNO}_2(aq)$ of in the bottle. Show the work that leads to your answer.

Part F

Draw an X on Figure 1 to represent a point in the titration where $[\text{HNO}_2] > [\text{NO}_2^-]$ in the reaction mixture.

Part G

Equilibrium constants at 298 K are shown in Table 1 for the acid ionization reaction represented by Equation 1, K_a ; the autoionization of water, K_w ; and the neutralization reaction represented by Equation 2, K_2 .

Table 1

Chemical Equation	Equilibrium Constant
$\text{HNO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NO}_2^-(aq) + \text{H}_3\text{O}^+(aq)$	$K_a = 5.6 \times 10^{-4}$
$\text{H}_2\text{O}(l) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)$	$K_w = 1.0 \times 10^{-14}$
$\text{HNO}_2(aq) + \text{OH}^-(aq) \rightarrow \text{NO}_2^-(aq) + \text{H}_2\text{O}(l)$	$K_2 = ?$

Calculate the value of K_2 for Equation 2 at 298 K. Show the work that leads to your answer.

Part H

The student decides to repeat the experiment, this time using an indicator, and has access to the indicators in Table 2.

Table 2

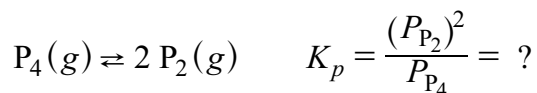
Indicator Name	Acid Color	pH Range of Color Change	Base Color
Methyl orange	Red	3.1–4.4	Yellow
Thymol blue	Yellow	8.0–9.6	Blue
Clayton yellow	Yellow	12.2–13.2	Orange

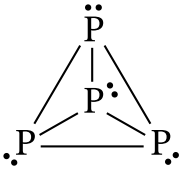
The student conducts a second titration by adding two drops of methyl orange indicator to 35.0 mL of the $\text{HNO}_2(aq)$ solution and titrating the solution with 0.16 M $\text{NaOH}(aq)$ until a color change from red to yellow occurs.

The student claims that methyl orange was the best choice for the indicator. Do you agree or disagree? **Justify** your answer.

Question 4

4. White phosphorus, $\text{P}_4(g)$, can decompose into $\text{P}_2(g)$ at elevated temperatures. A balanced chemical equation, K_p expression, and Lewis diagrams for the chemical species involved in the reaction are given.



Compound	P_4	P_2
Lewis diagram		$:\text{P} \equiv \text{P}:$

Part A

The average bond length in P_4 molecules is 221 pm, whereas the average bond length in P_2 molecules is 189 pm. **Explain** why the average bond length in P_4 is greater than the average bond length in P_2 .

Part B

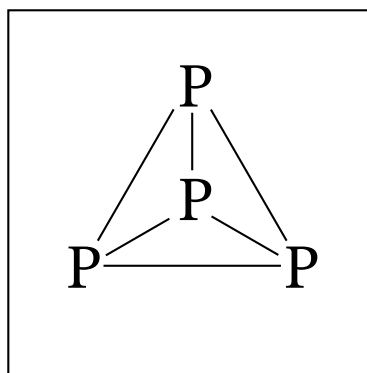
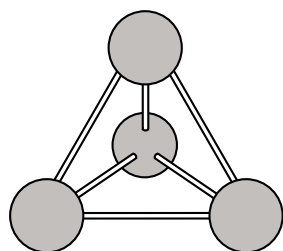
A sample of $\text{P}_4(s)$ is placed in a sealed rigid container and heated to 1600. K, at which point the initial partial pressure of $\text{P}_4(g)$ is 0.470 atm. Some of the $\text{P}_4(g)$ decomposes into $\text{P}_2(g)$ as the system reaches equilibrium. At equilibrium, the partial pressure of $\text{P}_2(g)$ is determined to be 0.630 atm.

Calculate the value of the equilibrium constant, K_p , for the reaction at 1600. K. Show the work that leads to your answer.

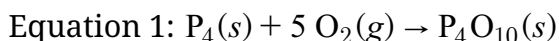
Part C

The reaction is thermodynamically favorable under standard conditions only at temperatures above 1500 K. A student claims that the reaction must be endothermic because it is favorable only at high temperatures. Do you agree or disagree? **Justify** your answer using $\Delta S_{\text{rxn}}^\circ$ and $\Delta G_{\text{rxn}}^\circ$.

3. White phosphorus is composed of P_4 molecules with a tetrahedral structure, as shown in the diagram on the left. Each P atom is bonded to the other three P atoms by single bonds, as shown in the incomplete Lewis diagram on the right.

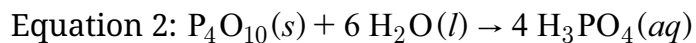


- A. In the box in part A, complete the Lewis diagram for P_4 by drawing the nonbonding electrons.
- B. The reaction of white phosphorus with oxygen to form $P_4O_{10}(s)$ is thermodynamically favorable at 298 K. The reaction is represented by equation 1.

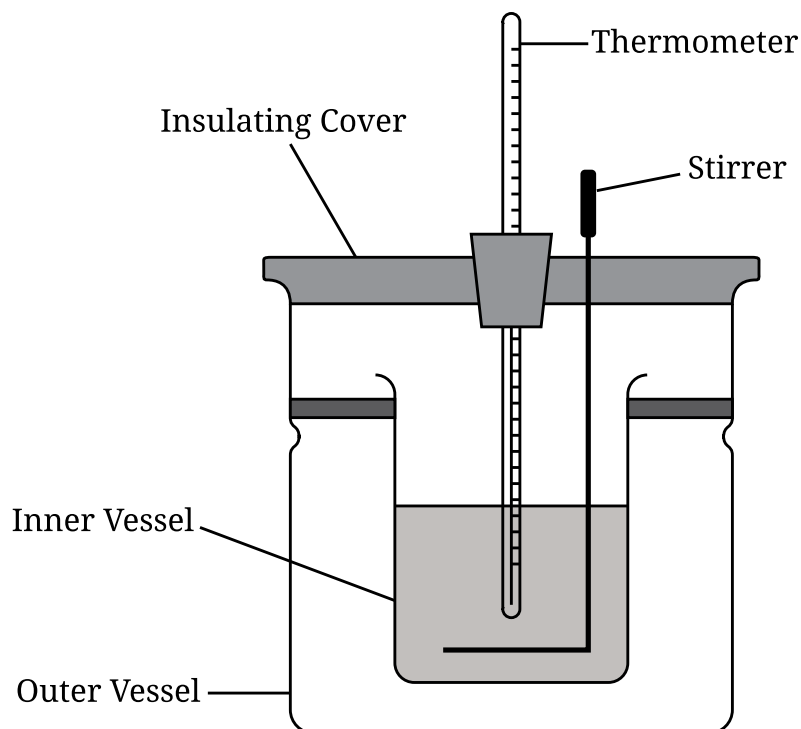


- The entropy change of the reaction, ΔS° , is negative. Using particle-level reasoning, explain why the entropy decreases as the reaction progresses.
- The enthalpy change of the reaction, ΔH° , is also negative. A student claims that the favorability of the reaction is driven by enthalpy and **not** by entropy. Is the student's claim correct? Justify your answer by using the relationship between ΔG° , ΔH° , and ΔS° .

$\text{P}_4\text{O}_{10}(s)$ reacts exothermically with water to form phosphoric acid, as represented by equation 2.



A chemist uses a calorimetry experiment to determine the enthalpy change for the reaction, as represented by the following diagram.



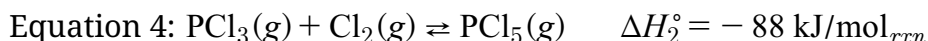
C. The chemist carries out the calorimetry experiment and records the following information.

Mass of P_4O_{10}	0.100 g
Mass of H_2O	100.0 g
Initial temperature	22.00° C
Final temperature	22.38° C
Molar mass of P_4O_{10}	283.9 g/mol
Specific heat of H_2O	4.18 J/(g·°C)

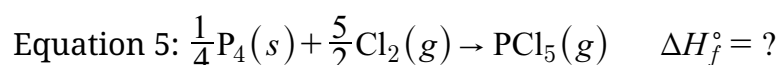
- Calculate the amount of heat, q , released during the experiment, in kJ. Assume that the specific heat of the solution is the same as that of water.
- Calculate the value of $\Delta H^\circ_{\text{rxn}}$ for equation 2 in kJ/mol_{rxn}. Include the sign in your answer.

- D. The chemist weighed out 0.100 g P_4O_{10} of and 100.0 g of H_2O to perform a second trial. In the second trial, some of the solid P_4O_{10} stuck to the weighing paper and was not transferred to the calorimeter. Given that P_4O_{10} is the limiting reactant, would ΔT for the second trial be greater than, less than, or equal to the value in the first trial? Justify your answer.

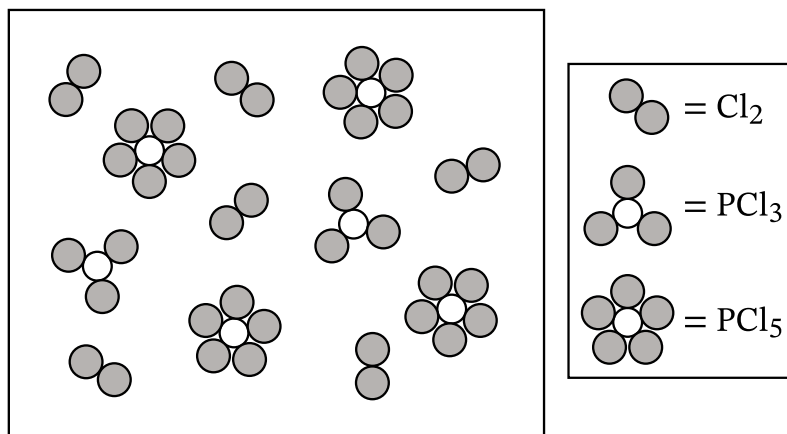
$\text{P}_4(\text{s})$ also reacts readily with $\text{Cl}_2(\text{g})$ to produce phosphorus trichloride, $\text{PCl}_3(\text{g})$, which in turn reacts with $\text{Cl}_2(\text{g})$ in an equilibrium process to produce $\text{PCl}_5(\text{g})$. The reactions are represented by equations 3 and 4.



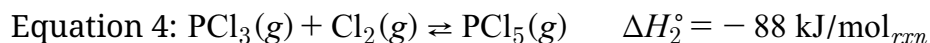
- E. Calculate the standard enthalpy of formation of $\text{PCl}_5(\text{g})$ represented by equation 5.



The following particle-level diagram represents the contents of the vessel in an equilibrium mixture at 546 K involving equation 4.



- F. Equation 4 for the reaction that occurs is shown.



- If each particle in the diagram represents a partial pressure of 1.00 atm, what is the value of K_p for the equilibrium mixture at 546 K?
- Does the value of K_p increase, decrease, or remain the same when the temperature is increased to 596 K? Justify your answer based on ΔH_2° .

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.



- (a) How many grams of $\text{Cl}(g)$ can be formed from 1.25 mol of $\text{AlCl}_3(g)$?

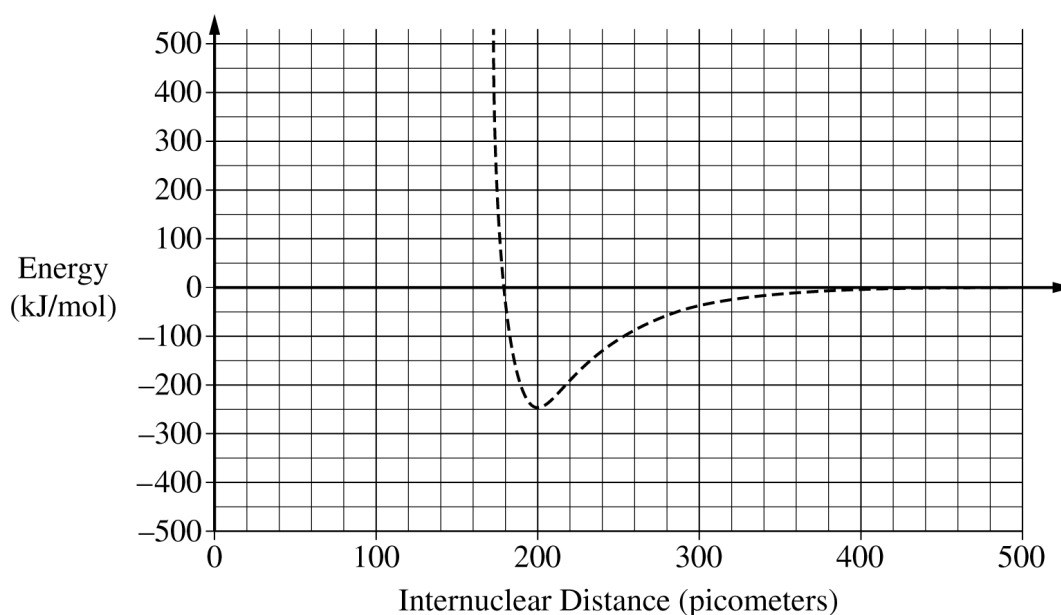
Additional reactions that involve Al or Cl are shown in the following table.

Reaction Number	Equation	ΔH_{rxn}° (kJ/mol _{rxn})
2	$\text{Al}(s) + \frac{3}{2} \text{Cl}_2(g) \rightarrow \text{AlCl}_3(g)$	-583
3	$\text{Al}(s) \rightarrow \text{Al}(g)$	+326
4	$\text{Cl}_2(g) \rightarrow 2 \text{Cl}(g)$	+243

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

GO ON TO THE NEXT 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 $\text{Al} - \text{Cl}$ bond length is 220 picometers and the average bond energy is 425 kJ/mol. Draw the potential energy curve for the average $\text{Al} - \text{Cl}$ bond on the preceding graph.

(d) Three proposed Lewis diagrams for the $\text{AlCl}_3(g)$ molecule are shown.

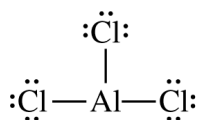


Diagram 1

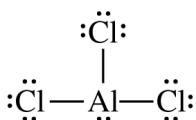


Diagram 2

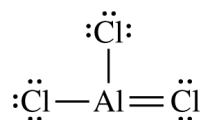


Diagram 3

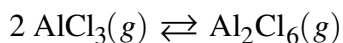
(i) The $\text{AlCl}_3(g)$ molecule has a trigonal planar geometry. Which diagram (1, 2, or 3) can be eliminated based on geometry? Justify your choice based on VSEPR theory.

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

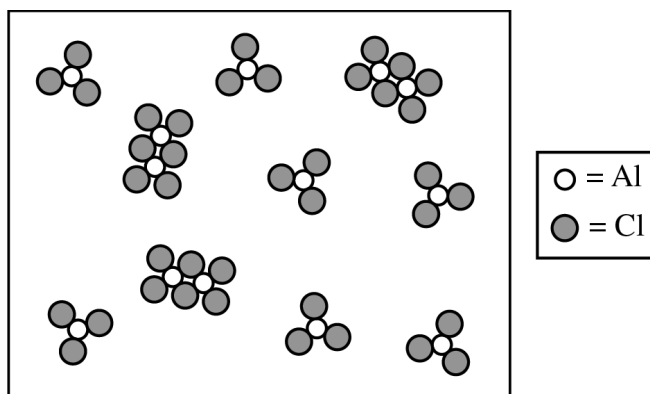
- (ii) Which of the three diagrams is the best representation for the bonding in AlCl_3 ? Justify your choice based on formal charges.

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



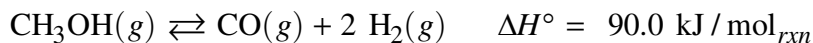
- (e) Write the expression for the equilibrium constant, K_p , for this reaction.

A particle-level diagram of an equilibrium mixture of $\text{AlCl}_3(g)$ and $\text{Al}_2\text{Cl}_6(g)$ 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.

GO ON TO THE NEXT PAGE.



Methanol vapor decomposes to form carbon monoxide gas and hydrogen gas at high temperatures in the presence of a platinum catalyst, as represented by the balanced chemical equation given.

(a) Are the hydrogen atoms oxidized or are they reduced in the forward reaction? Justify your answer in terms of oxidation numbers.

(b) In the following box, draw the complete Lewis electron-dot diagram for the carbon monoxide molecule in which every atom obeys the octet rule. Show all bonding and nonbonding valence electrons.



(c) The values of the standard molar entropies of the compounds involved in the reaction are given in the following table.

Substance	S° (J/(K·mol))
$\text{CH}_3\text{OH}(g)$	240.
$\text{CO}(g)$	198
$\text{H}_2(g)$	131

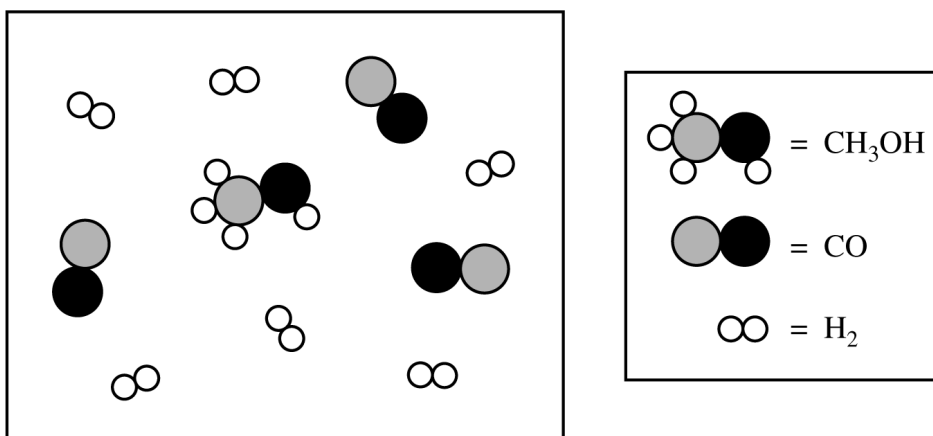
(i) Use the data in the table to calculate the value of the standard entropy change, ΔS° , in J/(K·mol_{rxn}), for the reaction.

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

- (ii) Calculate the value of ΔG° , in $\text{kJ/mol}_{\text{rxn}}$, for the reaction at 375 K. Assume that ΔH° and ΔS° are independent of temperature.

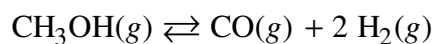
The following particle-level diagram shows a representative sample of the equilibrium mixture represented by the equation given.



- (d) Use information from the particle diagram to calculate the partial pressure of CO at equilibrium when the total pressure of the equilibrium mixture is 12.0 atm.

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

GO ON TO THE NEXT PAGE.



The reaction system represented by the equation is allowed to achieve equilibrium at a different temperature. The following table gives the partial pressure of each species in the equilibrium mixture.

Substance	Partial Pressure at Different Temperature
$\text{CH}_3\text{OH}(g)$	2.7 atm
$\text{CO}(g)$	4.2 atm
$\text{H}_2(g)$	8.4 atm

(f) Use the information in the table to calculate the value of the equilibrium constant, K_p , at the new temperature.

(g) The volume of the container is rapidly doubled with no change in temperature. As equilibrium is re-established, does the number of moles of $\text{CH}_3\text{OH}(g)$ increase, decrease, or remain the same? Justify your answer by comparing the value of the reaction quotient, Q , with the value of the equilibrium constant, K_p .

GO ON TO THE NEXT PAGE.

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.



A chemistry teacher wants to prepare Br_2 . The teacher has access to the following three reagents: $\text{NaBr}(aq)$, $\text{Cl}_2(g)$, and $\text{I}_2(s)$.

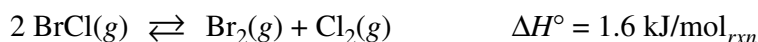
Half-Reaction	E° at 25°C (V)
$\text{Br}_2 + 2 e^- \rightarrow 2 \text{Br}^-$	1.07
$\text{Cl}_2 + 2 e^- \rightarrow 2 \text{Cl}^-$	1.36
$\text{I}_2 + 2 e^- \rightarrow 2 \text{I}^-$	0.53

- (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.

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 each substance.

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



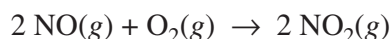
A 0.100 mole sample of pure $\text{BrCl}(g)$ is placed in a previously evacuated, rigid 2.00 L container at 298 K. Eventually the system reaches equilibrium according to the equation above.

- (d) Calculate the pressure in the container before equilibrium is established.
- (e) Write the expression for the equilibrium constant, K_{eq} , for the decomposition of BrCl .

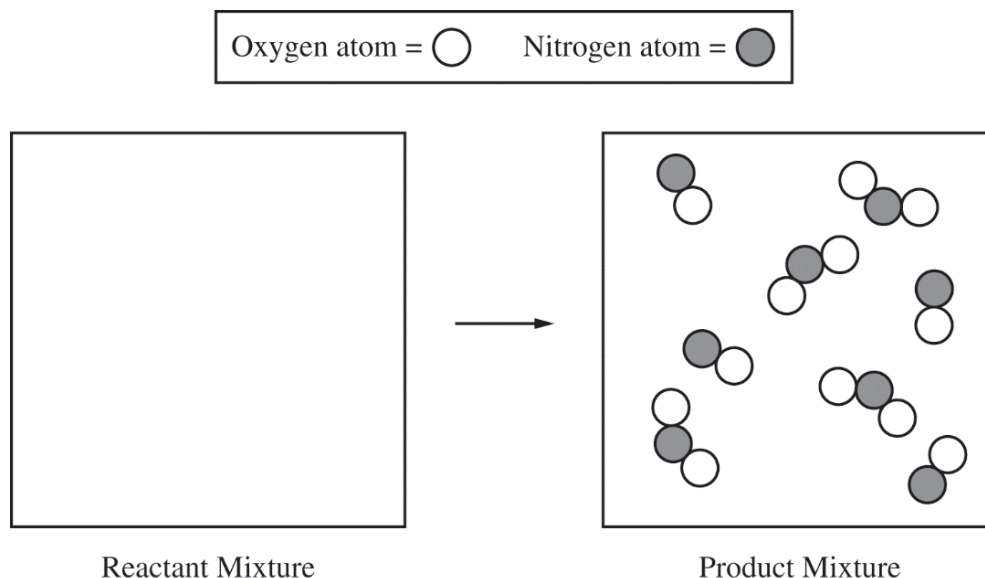
After the system has reached equilibrium, 42 percent of the original BrCl sample has decomposed.

- (f) Determine the value of K_{eq} for the decomposition reaction of BrCl at 298 K.
- (g) Calculate the bond energy of the Br-Cl bond, in kJ/mol, using ΔH° for the reaction (1.6 kJ/mol_{rxn}) and the information in the following table.

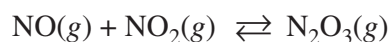
Bond	Bond Energy (kJ/mol)
Br – Br	193
Cl – Cl	243
Br – Cl	?



2. A student investigates the reactions of nitrogen oxides. One of the reactions in the investigation requires an equimolar mixture of $\text{NO}(g)$ and $\text{NO}_2(g)$, which the student produces by using the reaction represented above.
- (a) The particle-level representation of the equimolar mixture of $\text{NO}(g)$ and $\text{NO}_2(g)$ in the flask at the completion of the reaction between $\text{NO}(g)$ and $\text{O}_2(g)$ is shown below in the box on the right. In the box below on the left, draw the particle-level representation of the reactant mixture of $\text{NO}(g)$ and $\text{O}_2(g)$ that would yield the product mixture shown in the box on the right. In your drawing, represent oxygen atoms and nitrogen atoms as indicated below.



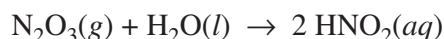
The student reads in a reference text that $\text{NO}(g)$ and $\text{NO}_2(g)$ will react as represented by the equation below. Thermodynamic data for the reaction are given in the table below the equation.



ΔH_{298}°	ΔS_{298}°	ΔG_{298}°
$-40.4 \text{ kJ/mol}_{\text{rxn}}$	$-138.5 \text{ J/(K} \cdot \text{mol}_{\text{rxn}})$	$0.87 \text{ kJ/mol}_{\text{rxn}}$

- (b) The student begins with an equimolar mixture of $\text{NO}(g)$ and $\text{NO}_2(g)$ in a rigid reaction vessel and the mixture reaches equilibrium at 298 K.
- Calculate the value of the equilibrium constant, K , for the reaction at 298 K.
 - If both P_{NO} and P_{NO_2} in the vessel are initially 1.0 atm, will $P_{\text{N}_2\text{O}_3}$ at equilibrium be equal to 1.0 atm? Justify your answer.
- (c) The student hypothesizes that increasing the temperature will increase the amount of $\text{N}_2\text{O}_3(g)$ in the equilibrium mixture. Indicate whether you agree or disagree with the hypothesis. Justify your answer.

$\text{N}_2\text{O}_3(g)$ reacts with water to form nitrous acid, $\text{HNO}_2(aq)$, a compound involved in the production of acid rain. The reaction is represented below.



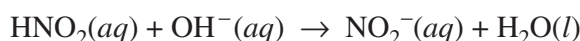
(d) The skeletal structure of the HNO_2 molecule is shown in the box below.

- (i) Complete the Lewis electron-dot diagram of the HNO_2 molecule in the box below, including any lone pairs of electrons.

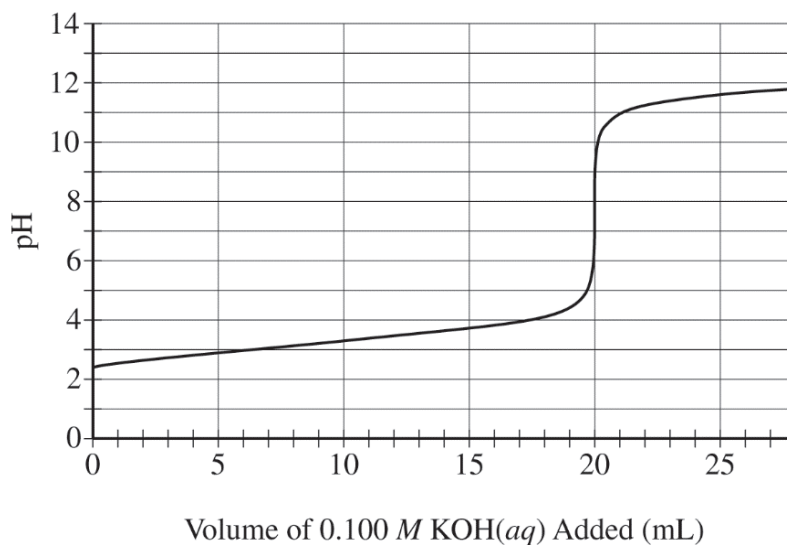


- (ii) Based on your completed diagram above, identify the hybridization of the nitrogen atom in the HNO_2 molecule.

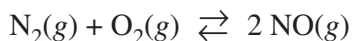
To produce an aqueous solution of HNO_2 , the student bubbles $\text{N}_2\text{O}_3(g)$ into distilled water. Assume that the reaction goes to completion and that HNO_2 is the only species produced. To determine the concentration of $\text{HNO}_2(aq)$ in the resulting solution, the student titrates a 100. mL sample of the solution with 0.100 M $\text{KOH}(aq)$. The neutralization reaction is represented below.



The following titration curve shows the change in pH of the solution during the titration.



- (e) Use the titration curve and the information above to
- determine the initial concentration of the $\text{HNO}_2(aq)$ solution
 - estimate the value of $\text{p}K_a$ for $\text{HNO}_2(aq)$
- (f) During the titration, after a volume of 15 mL of 0.100 M $\text{KOH}(aq)$ has been added, which species, $\text{HNO}_2(aq)$ or $\text{NO}_2^-(aq)$, is present at a higher concentration in the solution? Justify your answer.

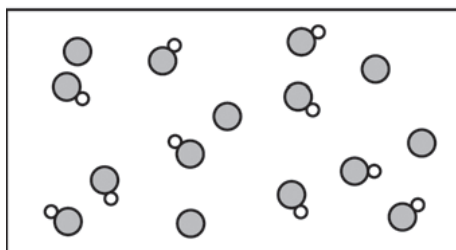
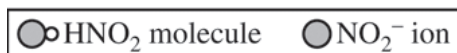


3. At high temperatures, $\text{N}_2(\text{g})$ and $\text{O}_2(\text{g})$ can react to produce nitrogen monoxide, $\text{NO}(\text{g})$, as represented by the equation above.

- (a) Write the expression for the equilibrium constant, K_p , for the forward reaction.
- (b) A student injects $\text{N}_2(\text{g})$ and $\text{O}_2(\text{g})$ into a previously evacuated, rigid vessel and raises the temperature of the vessel to 2000°C . At this temperature the initial partial pressures of $\text{N}_2(\text{g})$ and $\text{O}_2(\text{g})$ are 6.01 atm and 1.61 atm, respectively. The system is allowed to reach equilibrium. The partial pressure of $\text{NO}(\text{g})$ at equilibrium is 0.122 atm. Calculate the value of K_p .

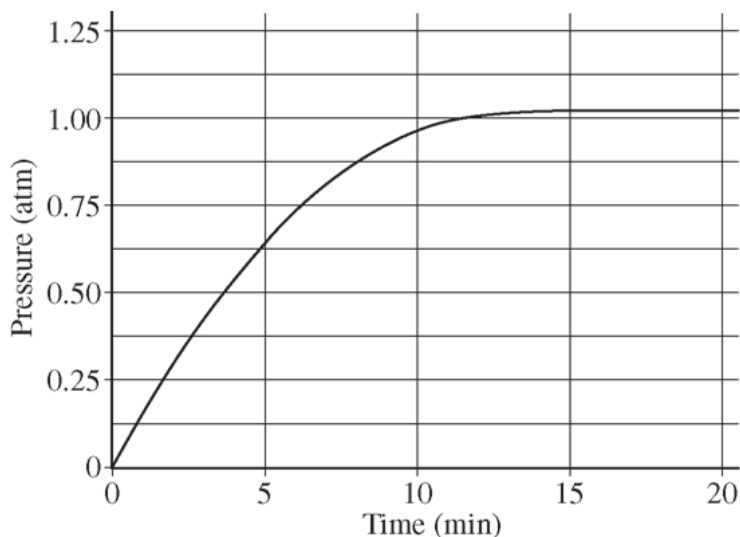
Nitrogen monoxide, $\text{NO}(\text{g})$, can undergo further reactions to produce acids such as HNO_2 , a weak acid with a K_a of 4.0×10^{-4} and a $\text{p}K_a$ of 3.40.

- (c) A student is asked to make a buffer solution with a pH of 3.40 by using 0.100 M $\text{HNO}_2(\text{aq})$ and 0.100 M $\text{NaOH}(\text{aq})$.
- (i) Explain why the addition of 0.100 M $\text{NaOH}(\text{aq})$ to 0.100 M $\text{HNO}_2(\text{aq})$ can result in the formation of a buffer solution. Include the net ionic equation for the reaction that occurs when the student adds the $\text{NaOH}(\text{aq})$ to the $\text{HNO}_2(\text{aq})$.
- (ii) Determine the volume, in mL, of 0.100 M $\text{NaOH}(\text{aq})$ the student should add to 100. mL of 0.100 M $\text{HNO}_2(\text{aq})$ to make a buffer solution with a pH of 3.40. Justify your answer.
- (d) A second student makes a buffer by dissolving 0.100 mol of $\text{NaNO}_2(\text{s})$ in 100. mL of 1.00 M $\text{HNO}_2(\text{aq})$. Which is more resistant to changes in pH when a strong acid or a strong base is added, the buffer made by the second student or the buffer made by the first student in part (c)? Justify your answer.
- (e) A new buffer is made using $\text{HNO}_2(\text{aq})$ as one of the ingredients. A particulate representation of a small representative portion of the buffer solution is shown below. (Cations and water molecules are not shown.) Is the pH of the buffer represented in the diagram greater than, less than, or equal to 3.40? Justify your answer.





4. When heated, calcium carbonate decomposes according to the equation above. In a study of the decomposition of calcium carbonate, a student added a 50.0 g sample of powdered $\text{CaCO}_3(s)$ to a 1.00 L rigid container. The student sealed the container, pumped out all the gases, then heated the container in an oven at 1100 K. As the container was heated, the total pressure of the $\text{CO}_2(g)$ in the container was measured over time. The data are plotted in the graph below.



The student repeated the experiment, but this time the student used a 100.0 g sample of powdered $\text{CaCO}_3(s)$. In this experiment, the final pressure in the container was 1.04 atm, which was the same final pressure as in the first experiment.

- Calculate the number of moles of $\text{CO}_2(g)$ present in the container after 20 minutes of heating.
- The student claimed that the final pressure in the container in each experiment became constant because all of the $\text{CaCO}_3(s)$ had decomposed. Based on the data in the experiments, do you agree with this claim? Explain.
- After 20 minutes some $\text{CO}_2(g)$ was injected into the container, initially raising the pressure to 1.5 atm. Would the final pressure inside the container be less than, greater than, or equal to 1.04 atm? Explain your reasoning.
- Are there sufficient data obtained in the experiments to determine the value of the equilibrium constant, K_p , for the decomposition of $\text{CaCO}_3(s)$ at 1100 K? Justify your answer.

7.5 Magnitude of the Equilibrium Constant

Name: _____ Class: _____ Date: _____

Total: 9 marks

KEY WORDS equilibrium constant 平衡常数

Objective

Build the skills to answer exam questions on the **magnitude of the equilibrium constant**.

You must be able to:

- interpret a **large** K (products favored) and a **small** K (reactants favored)
- relate $K \approx 1$ to comparable amounts
- reason about the position of equilibrium

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ What the size of K tells you

- $K \gg 1$: at equilibrium there are **mostly products** — the reaction "goes nearly to completion".
- $K \ll 1$: mostly **reactants** — the reaction "barely proceeds".
- $K \approx 1$: comparable amounts of reactants and products.

■ A worked interpretation

$K = 1 \times 10^8 \rightarrow$ very large $\rightarrow$ products strongly favored. $K = 1 \times 10^{-6} \rightarrow$ very small $\rightarrow$ reactants favored.

■ K is not the rate

A large K says the **position** favors products, **not** that the reaction is fast. Speed (kinetics) and extent (equilibrium) are separate ideas.

■ Comparing two reactions

The one with the **larger** K has the equilibrium lying further toward products under the same conditions.

2 Practice

Now apply the methods above.

2.1 A reaction has $K = 1 \times 10^{10}$. Are products or reactants favored? [1]

2.2 A reaction has $K = 1 \times 10^{-5}$. Are products or reactants favored? [1]

2.3 Does a large K mean the reaction is fast? [1]

3 Exam-style questions

3.1 A very large equilibrium constant means at equilibrium there are mostly [1]

- **A** reactants
 - **B** products
 - **C** equal amounts
 - **D** no molecules
-

3.2 Two reactions have $K_1 = 5 \times 10^3$ and $K_2 = 2 \times 10^{-2}$.

(a) State which favors products more. [1]

(b) Describe the equilibrium mixture for reaction 2. [2]

3.3 Explain why a large K does not tell you how quickly equilibrium is reached. [2]

Solutions

2.1 Products.

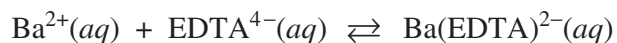
2.2 Reactants.

2.3 No.

3.1 B — mostly products.

3.2 (a) Reaction 1 (larger K). (b) Reaction 2 has a small K , so at equilibrium it is mostly reactants with little product.

3.3 K describes the extent (position) of equilibrium, which is thermodynamic; the speed of reaching it depends on kinetics (activation energy), a separate factor.



$$K = 7.7 \times 10^7$$

6. The polyatomic ion $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8^{4-}$ is commonly abbreviated as EDTA^{4-} . The ion can form complexes with metal ions in aqueous solutions. A complex of EDTA^{4-} with Ba^{2+} ion forms according to the equation above. A 50.0 mL volume of a solution that has an $\text{EDTA}^{4-}(\text{aq})$ concentration of 0.30 M is mixed with 50.0 mL of 0.20 M $\text{Ba}(\text{NO}_3)_2$ to produce 100.0 mL of solution.
- (a) Considering the value of K for the reaction, determine the concentration of $\text{Ba}(\text{EDTA})^{2-}(\text{aq})$ in the 100.0 mL of solution. Justify your answer.
- (b) The solution is diluted with distilled water to a total volume of 1.00 L. After equilibrium has been reestablished, is the number of moles of $\text{Ba}^{2+}(\text{aq})$ present in the solution greater than, less than, or equal to the number of moles of $\text{Ba}^{2+}(\text{aq})$ present in the original solution before it was diluted? Justify your answer.

7.6 Properties of the Equilibrium Constant

Name: _____ Class: _____ Date: _____

Total: 10 marks

KEY WORDS equilibrium constant 平衡常数

Objective

Build the skills to answer exam questions on the **properties of the equilibrium constant**.

You must be able to:

- **reverse** a reaction ($K \rightarrow 1/K$)
- **scale** a reaction by n ($K \rightarrow K^n$)
- **add** reactions ($K \rightarrow K_1 \times K_2$)

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ Reversing a reaction

Reversing an equation **inverts** the constant:

$$K_{\text{reverse}} = \frac{1}{K_{\text{forward}}}.$$

■ Scaling a reaction

Multiplying all coefficients by n raises K to the power n :

$$K_{\text{new}} = (K_{\text{old}})^n.$$

■ Adding reactions

If you add two reactions, you **multiply** their constants:

$$K_{\text{total}} = K_1 \times K_2.$$

■ A worked example

If $K = 4$ for a reaction, then the reverse has $K = \frac{1}{4}$; doubling the equation gives $K = 4^2 = 16$; halving gives $K = 4^{1/2} = 2$.

2 Practice

Now apply the methods above.

2.1 A reaction has $K = 100$. Find K for the reverse reaction. [1]

2.2 A reaction has $K = 3$. Find K if all coefficients are doubled. [1]

2.3 Two reactions with $K_1 = 2$ and $K_2 = 5$ are added. Find K for the sum. [1]

3 Exam-style questions

3.1 Reversing a reaction changes K to [1]

- A $-K$
 - B $1/K$
 - C K^2
 - D $2K$
-

3.2 A reaction has $K = 16$.

(a) Find K for the reaction written with all coefficients halved. [2]

(b) Find K for the reverse of the halved reaction. [2]

3.3 Given $A \rightleftharpoons B$, $K_1 = 4$, and $B \rightleftharpoons C$, $K_2 = 3$, find K for $A \rightleftharpoons C$. [2]

Solutions

2.1 $\frac{1}{100} = 0.01.$

2.2 $3^2 = 9.$

2.3 $2 \times 5 = 10.$

3.1 $B = 1/K.$

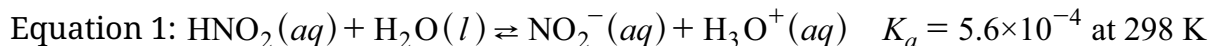
3.2 (a) $16^{1/2} = 4.$ (b) $\frac{1}{4} = 0.25.$

3.3 Adding the reactions multiplies the constants: $K = 4 \times 3 = 12.$

Question 3: Version J

The following information applies to all parts.

3. Nitrous acid, HNO_2 , is a weak acid that ionizes according to Equation 1.

**Part A**

Identify a conjugate acid-base pair in the equation. Be sure to clearly label which is the acid and which is the base.

Part B

A solution of $\text{HNO}_2(aq)$ with an initial concentration of 0.125 M has a pH of 2.09.

- i. **Calculate** the value of $[\text{H}_3\text{O}^+]$ in the solution. Show the work that leads to your answer.
- ii. **Calculate** $[\text{HNO}_2]$ at equilibrium. Show the work that leads to your answer.

Part C

In an experiment, the solution of 0.125 M $\text{HNO}_2(aq)$ is heated to 333 K . The new equilibrium concentrations are determined to be $[\text{HNO}_2] = 0.114 \text{ M}$, $[\text{NO}_2^-] = 0.0109 \text{ M}$, and $[\text{H}_3\text{O}^+] = 0.0109 \text{ M}$.

- i. **Calculate** the value of K_a for HNO_2 at 333 K . Show the work that leads to your answer.
- ii. Is the reaction represented by Equation 1 endothermic or exothermic? **Justify** your answer by comparing K_a values at 298 K and 333 K .

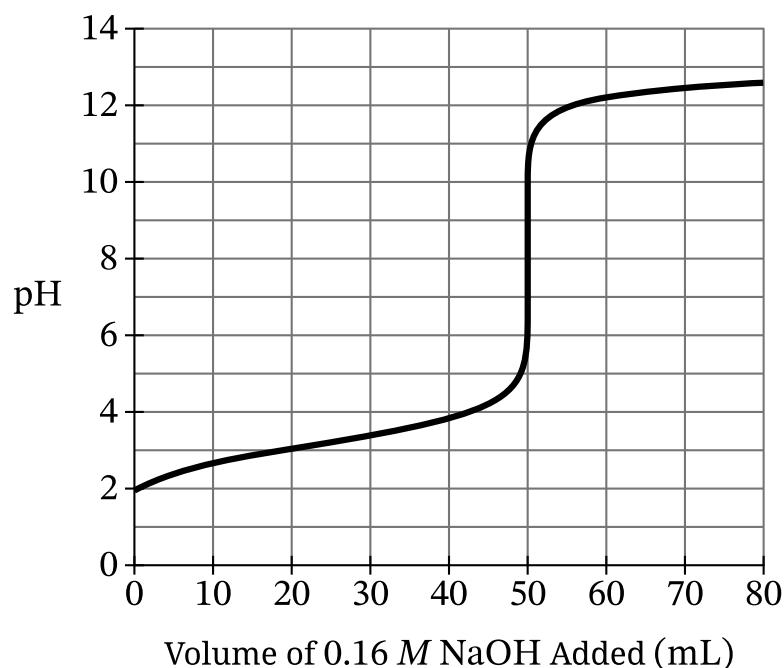
The following information applies to parts D, E, and F.

In a second experiment, a student is given a bottle containing HNO_2 with an unknown molarity. To determine the concentration of the $\text{HNO}_2(aq)$ in the bottle, the student titrates 35.0 mL of the $\text{HNO}_2(aq)$ with 0.16 M $\text{NaOH}(aq)$ at 298 K, which reacts according to Equation 2.



The results of the titration are summarized in Figure 1.

Figure 1



Part D

Using Figure 1, **identify** the pH at the equivalence point.

Part E

Using Figure 1, **calculate** the molarity $\text{HNO}_2(aq)$ of in the bottle. Show the work that leads to your answer.

Part F

Draw an X on Figure 1 to represent a point in the titration where $[\text{HNO}_2] > [\text{NO}_2^-]$ in the reaction mixture.

Part G

Equilibrium constants at 298 K are shown in Table 1 for the acid ionization reaction represented by Equation 1, K_a ; the autoionization of water, K_w ; and the neutralization reaction represented by Equation 2, K_2 .

Table 1

Chemical Equation	Equilibrium Constant
$\text{HNO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NO}_2^-(aq) + \text{H}_3\text{O}^+(aq)$	$K_a = 5.6 \times 10^{-4}$
$\text{H}_2\text{O}(l) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)$	$K_w = 1.0 \times 10^{-14}$
$\text{HNO}_2(aq) + \text{OH}^-(aq) \rightarrow \text{NO}_2^-(aq) + \text{H}_2\text{O}(l)$	$K_2 = ?$

Calculate the value of K_2 for Equation 2 at 298 K. Show the work that leads to your answer.

Part H

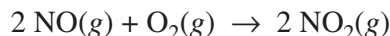
The student decides to repeat the experiment, this time using an indicator, and has access to the indicators in Table 2.

Table 2

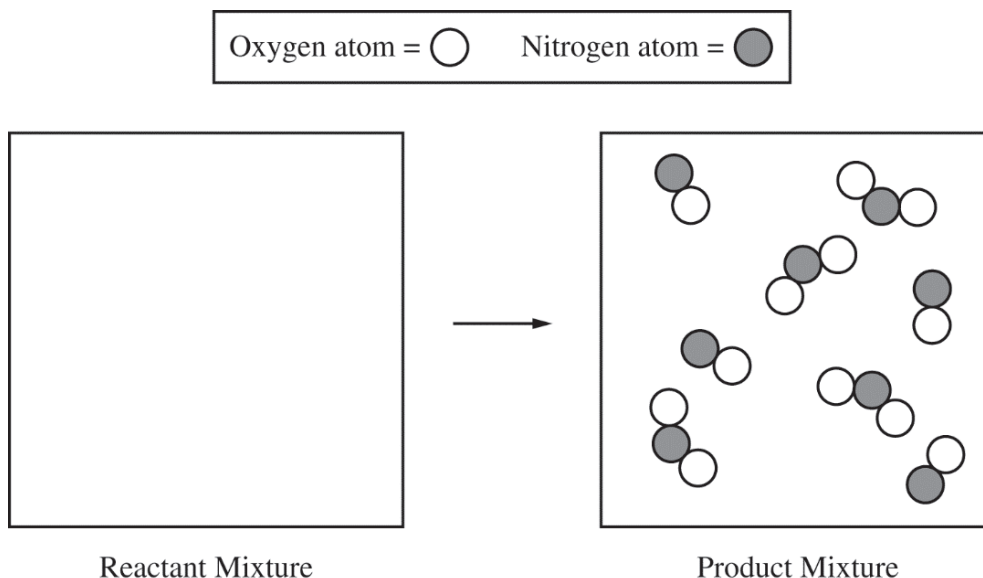
Indicator Name	Acid Color	pH Range of Color Change	Base Color
Methyl orange	Red	3.1–4.4	Yellow
Thymol blue	Yellow	8.0–9.6	Blue
Clayton yellow	Yellow	12.2–13.2	Orange

The student conducts a second titration by adding two drops of methyl orange indicator to 35.0 mL of the $\text{HNO}_2(aq)$ solution and titrating the solution with 0.16 M $\text{NaOH}(aq)$ until a color change from red to yellow occurs.

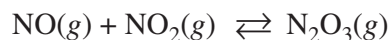
The student claims that methyl orange was the best choice for the indicator. Do you agree or disagree? **Justify** your answer.



2. A student investigates the reactions of nitrogen oxides. One of the reactions in the investigation requires an equimolar mixture of $\text{NO}(g)$ and $\text{NO}_2(g)$, which the student produces by using the reaction represented above.
- (a) The particle-level representation of the equimolar mixture of $\text{NO}(g)$ and $\text{NO}_2(g)$ in the flask at the completion of the reaction between $\text{NO}(g)$ and $\text{O}_2(g)$ is shown below in the box on the right. In the box below on the left, draw the particle-level representation of the reactant mixture of $\text{NO}(g)$ and $\text{O}_2(g)$ that would yield the product mixture shown in the box on the right. In your drawing, represent oxygen atoms and nitrogen atoms as indicated below.



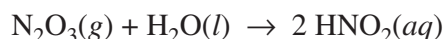
The student reads in a reference text that $\text{NO}(g)$ and $\text{NO}_2(g)$ will react as represented by the equation below. Thermodynamic data for the reaction are given in the table below the equation.



ΔH_{298}°	ΔS_{298}°	ΔG_{298}°
$-40.4 \text{ kJ/mol}_{\text{rxn}}$	$-138.5 \text{ J/(K} \cdot \text{mol}_{\text{rxn}})$	$0.87 \text{ kJ/mol}_{\text{rxn}}$

- (b) The student begins with an equimolar mixture of $\text{NO}(g)$ and $\text{NO}_2(g)$ in a rigid reaction vessel and the mixture reaches equilibrium at 298 K.
- Calculate the value of the equilibrium constant, K , for the reaction at 298 K.
 - If both P_{NO} and P_{NO_2} in the vessel are initially 1.0 atm, will $P_{\text{N}_2\text{O}_3}$ at equilibrium be equal to 1.0 atm? Justify your answer.
- (c) The student hypothesizes that increasing the temperature will increase the amount of $\text{N}_2\text{O}_3(g)$ in the equilibrium mixture. Indicate whether you agree or disagree with the hypothesis. Justify your answer.

$\text{N}_2\text{O}_3(g)$ reacts with water to form nitrous acid, $\text{HNO}_2(aq)$, a compound involved in the production of acid rain. The reaction is represented below.



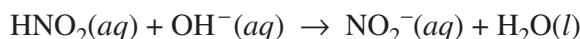
(d) The skeletal structure of the HNO_2 molecule is shown in the box below.

- (i) Complete the Lewis electron-dot diagram of the HNO_2 molecule in the box below, including any lone pairs of electrons.

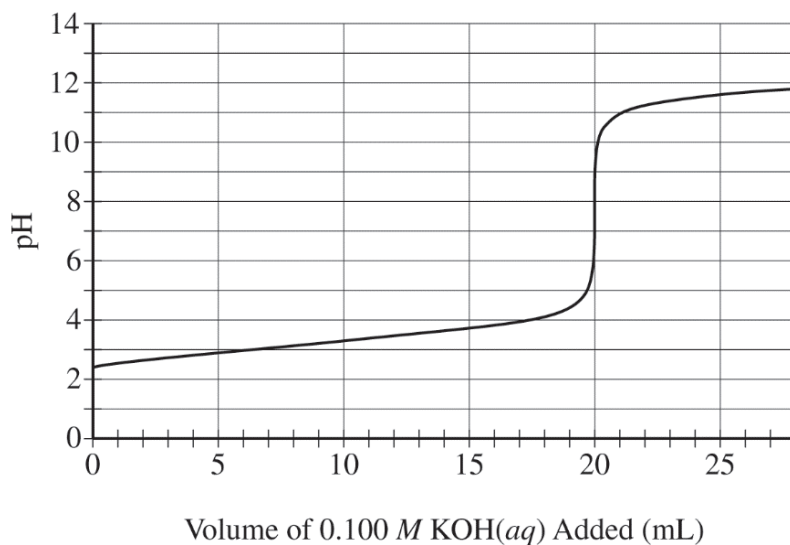


- (ii) Based on your completed diagram above, identify the hybridization of the nitrogen atom in the HNO_2 molecule.

To produce an aqueous solution of HNO_2 , the student bubbles $\text{N}_2\text{O}_3(g)$ into distilled water. Assume that the reaction goes to completion and that HNO_2 is the only species produced. To determine the concentration of $\text{HNO}_2(aq)$ in the resulting solution, the student titrates a 100. mL sample of the solution with 0.100 M $\text{KOH}(aq)$. The neutralization reaction is represented below.



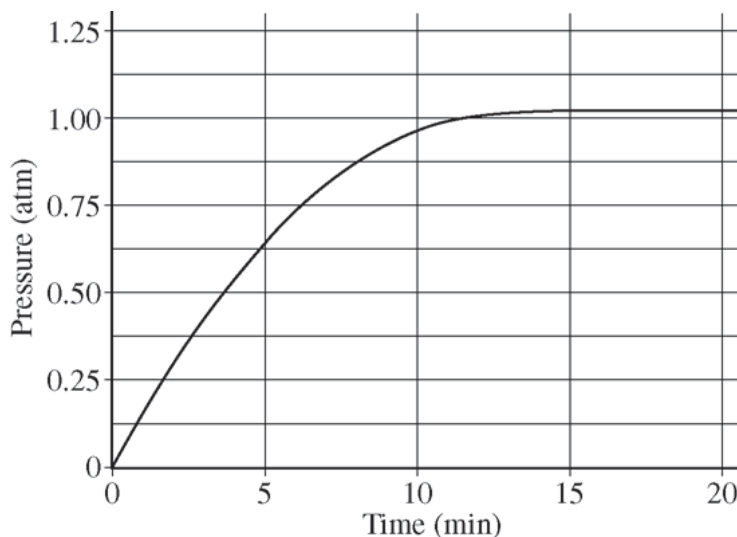
The following titration curve shows the change in pH of the solution during the titration.



- (e) Use the titration curve and the information above to
- determine the initial concentration of the $\text{HNO}_2(aq)$ solution
 - estimate the value of $\text{p}K_a$ for $\text{HNO}_2(aq)$
- (f) During the titration, after a volume of 15 mL of 0.100 M $\text{KOH}(aq)$ has been added, which species, $\text{HNO}_2(aq)$ or $\text{NO}_2^-(aq)$, is present at a higher concentration in the solution? Justify your answer.



4. When heated, calcium carbonate decomposes according to the equation above. In a study of the decomposition of calcium carbonate, a student added a 50.0 g sample of powdered $\text{CaCO}_3(s)$ to a 1.00 L rigid container. The student sealed the container, pumped out all the gases, then heated the container in an oven at 1100 K. As the container was heated, the total pressure of the $\text{CO}_2(g)$ in the container was measured over time. The data are plotted in the graph below.



The student repeated the experiment, but this time the student used a 100.0 g sample of powdered $\text{CaCO}_3(s)$. In this experiment, the final pressure in the container was 1.04 atm, which was the same final pressure as in the first experiment.

- Calculate the number of moles of $\text{CO}_2(g)$ present in the container after 20 minutes of heating.
- The student claimed that the final pressure in the container in each experiment became constant because all of the $\text{CaCO}_3(s)$ had decomposed. Based on the data in the experiments, do you agree with this claim? Explain.
- After 20 minutes some $\text{CO}_2(g)$ was injected into the container, initially raising the pressure to 1.5 atm. Would the final pressure inside the container be less than, greater than, or equal to 1.04 atm? Explain your reasoning.
- Are there sufficient data obtained in the experiments to determine the value of the equilibrium constant, K_p , for the decomposition of $\text{CaCO}_3(s)$ at 1100 K? Justify your answer.

7.7 Calculating Equilibrium Concentrations

Name: _____ Class: _____ Date: _____

Total: 12 marks

Objective

Build the skills to answer exam questions on **calculating equilibrium concentrations** with an ICE table.

You must be able to:

- set up an **ICE table** with an unknown change x
- substitute into K and solve for x
- use a valid **approximation** when K is small

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ ICE with unknown x

Write the change as x (times each coefficient), fill the equilibrium row, and substitute into K . For $A \rightleftharpoons B$, start $[A] = 1.0$, $K = 3$: equilibrium $[A] = 1 - x$, $[B] = x$;
 $\frac{x}{1 - x} = 3 \Rightarrow x = 0.75$.

■ Solving the algebra

Cross-multiply and solve. Reject any root that gives a **negative** concentration — only physically sensible values are valid.

■ The small- K approximation

When K is very small, the change x is tiny, so $[A]_{\text{start}} - x \approx [A]_{\text{start}}$. This avoids the quadratic. Check that x is under ~5% of the start.

■ A worked approximation

$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$, start $[\text{HA}] = 0.10$, $K = 1 \times 10^{-5}$: assume $0.10 - x \approx 0.10$, so $x^2/0.10 = 10^{-5}$, $x = \sqrt{10^{-6}} = 10^{-3}$.

2 Practice

Now apply the methods above.

2.1 In an ICE table, if $[A]$ decreases by x , what is $[A]$ at equilibrium (start = 0.5)? [1]

2.2 Why reject a negative value of x ? [1]

2.3 When is the small- K approximation valid? [1]

3 Exam-style questions

3.1 The small- x approximation assumes the change is [1]

- **A** large compared to the starting concentration
 - **B** small compared to the starting concentration
 - **C** exactly zero
 - **D** negative
-

3.2 For $A \rightleftharpoons B$, start $[A] = 2.0 \text{ M}$, $[B] = 0$, $K = 1.0$.

(a) Set up the ICE expression in terms of x . [2]

(b) Solve for x and give the equilibrium concentrations. [3]

3.3 A weak acid $HA \rightleftharpoons H^+ + A^-$ has $K = 4 \times 10^{-6}$ and start $[HA] = 0.10 \text{ M}$. Using the

small- x approximation, find $[\text{H}^+]$.

[3]

Solutions

2.1 $0.5 - x$.

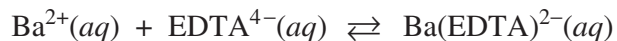
2.2 A concentration cannot be negative — it is unphysical.

2.3 When K is very small, so x is under about 5% of the starting concentration.

3.1 B — small compared to the starting concentration.

3.2 (a) $[A] = 2 - x$, $[B] = x$; $K = \frac{x}{2 - x} = 1.0$. (b) $x = 2 - x \Rightarrow 2x = 2 \Rightarrow x = 1.0$; so $[A] = [B] = 1.0$ M.

3.3 $\frac{x^2}{0.10} \approx 4 \times 10^{-6}$; $x^2 = 4 \times 10^{-7}$, $x = 6.3 \times 10^{-4}$; $[H^+] = 6.3 \times 10^{-4}$ M.



$$K = 7.7 \times 10^7$$

6. The polyatomic ion $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8^{4-}$ is commonly abbreviated as EDTA^{4-} . The ion can form complexes with metal ions in aqueous solutions. A complex of EDTA^{4-} with Ba^{2+} ion forms according to the equation above. A 50.0 mL volume of a solution that has an $\text{EDTA}^{4-}(\text{aq})$ concentration of 0.30 M is mixed with 50.0 mL of 0.20 M $\text{Ba}(\text{NO}_3)_2$ to produce 100.0 mL of solution.
- (a) Considering the value of K for the reaction, determine the concentration of $\text{Ba}(\text{EDTA})^{2-}(\text{aq})$ in the 100.0 mL of solution. Justify your answer.
- (b) The solution is diluted with distilled water to a total volume of 1.00 L. After equilibrium has been reestablished, is the number of moles of $\text{Ba}^{2+}(\text{aq})$ present in the solution greater than, less than, or equal to the number of moles of $\text{Ba}^{2+}(\text{aq})$ present in the original solution before it was diluted? Justify your answer.

7.8 Representations of Equilibrium

Name: _____ Class: _____ Date: _____

Total: 9 marks

Objective

Build the skills to answer exam questions on **representations of equilibrium** — the particle picture.

You must be able to:

- read a **particle diagram** showing an equilibrium mixture
- connect the diagram's ratio to the size of K
- recognise that amounts stay constant at equilibrium

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ Particle diagrams of equilibrium

An equilibrium particle diagram shows a **mixture** of reactant and product particles whose numbers stay **constant** over time (equal forward and reverse rates).

■ Reading K from the ratio

The ratio of product to reactant particles reflects the size of K : mostly products $\rightarrow$ large K ; mostly reactants $\rightarrow$ small K ; roughly equal $\rightarrow K \approx 1$.

■ A worked reading

A box with 8 product particles and 2 reactant particles suggests products are favored, so $K > 1$. The exact value uses the equilibrium expression.

■ Constant over time

Two diagrams at different times, both at equilibrium, should show the **same** numbers of each particle — individual molecules interconvert, but the totals hold.

2 Practice

Now apply the methods above.

2.1 At equilibrium, do the numbers of each particle change over time? [1]

2.2 A diagram shows mostly product particles. Is K large or small? [1]

2.3 A diagram shows roughly equal reactant and product particles. Estimate K . [1]

3 Exam-style questions

3.1 An equilibrium particle diagram with mostly reactant particles indicates [1]

- **A** $K > 1$
 - **B** $K < 1$
 - **C** $K = 0$
 - **D** no reaction
-

3.2 For $A \rightleftharpoons B$, a box at equilibrium shows 3 A and 9 B particles (in a fixed volume).

(a) Estimate K (treat particle counts as concentrations). [2]

(b) State whether products or reactants are favored. [1]

3.3 Explain why two particle diagrams of the same equilibrium, taken 1 minute apart, should show the same numbers of each species. [2]

Solutions

2.1 No — they stay constant.

2.2 Large.

2.3 About 1.

3.1 B — mostly reactants means $K < 1$.

3.2 (a) $K = \frac{[\text{B}]}{[\text{A}]} = \frac{9}{3} = 3$. (b) Products favored ($K > 1$).

3.3 At equilibrium the forward and reverse rates are equal, so although individual molecules keep converting, the total number of each species does not change.

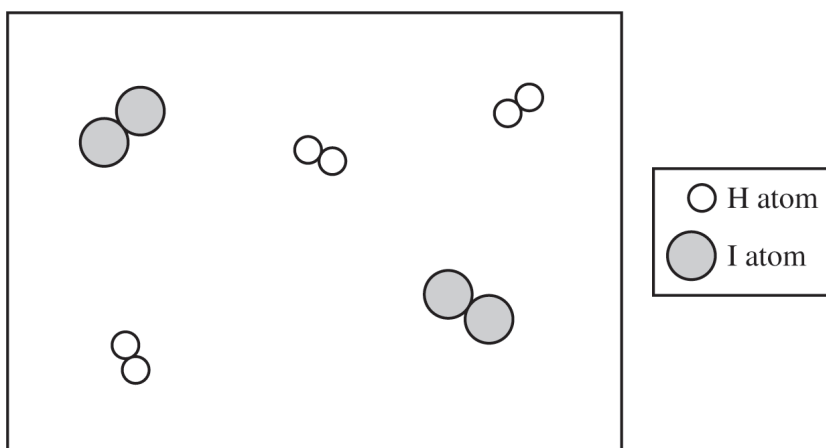
5. Hydrogen gas and iodine gas react to form hydrogen iodide at an elevated temperature, as represented by the following equation.



(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.

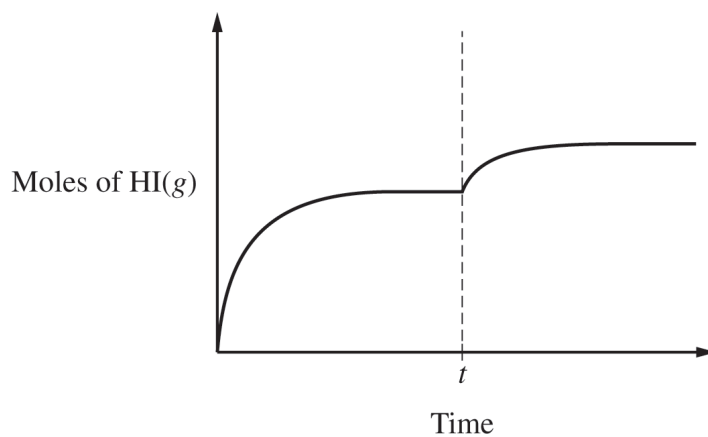
- (i) At a certain time, the value of the reaction quotient, Q , is 0.67. The following particle diagram is an incomplete representation of the system at this time. The diagram shows the relative number of $\text{H}_2(g)$ and $\text{I}_2(g)$ molecules, but the $\text{HI}(g)$ molecules are not included.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



GO ON TO THE NEXT PAGE.

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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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.



- (a) How many grams of $\text{Cl}(g)$ can be formed from 1.25 mol of $\text{AlCl}_3(g)$?

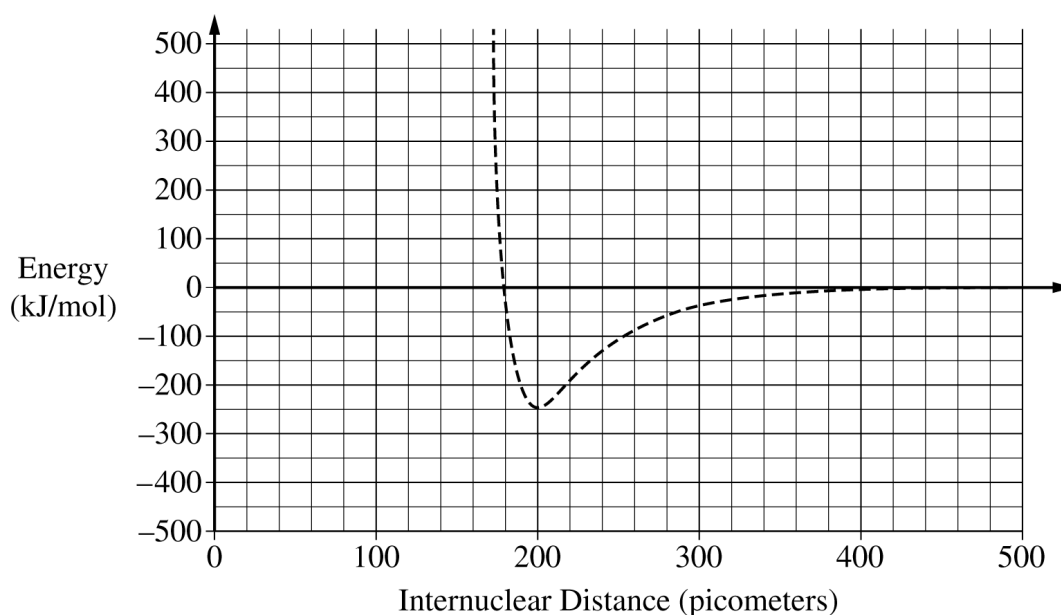
Additional reactions that involve Al or Cl are shown in the following table.

Reaction Number	Equation	ΔH_{rxn}° (kJ/mol _{rxn})
2	$\text{Al}(s) + \frac{3}{2} \text{Cl}_2(g) \rightarrow \text{AlCl}_3(g)$	-583
3	$\text{Al}(s) \rightarrow \text{Al}(g)$	+326
4	$\text{Cl}_2(g) \rightarrow 2 \text{Cl}(g)$	+243

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

GO ON TO THE NEXT 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 $\text{Al} - \text{Cl}$ bond length is 220 picometers and the average bond energy is 425 kJ/mol. Draw the potential energy curve for the average $\text{Al} - \text{Cl}$ bond on the preceding graph.

(d) Three proposed Lewis diagrams for the $\text{AlCl}_3(g)$ molecule are shown.

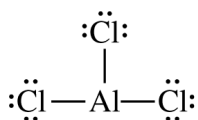


Diagram 1

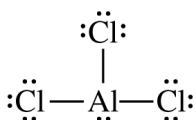


Diagram 2

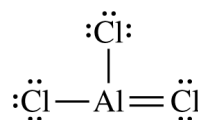


Diagram 3

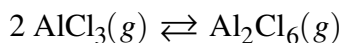
(i) The $\text{AlCl}_3(g)$ molecule has a trigonal planar geometry. Which diagram (1, 2, or 3) can be eliminated based on geometry? Justify your choice based on VSEPR theory.

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

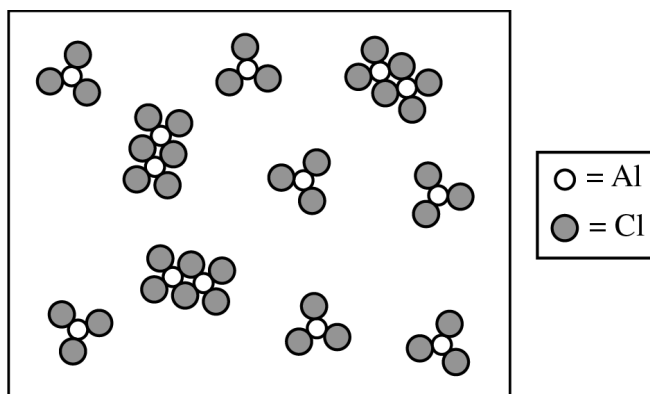
- (ii) Which of the three diagrams is the best representation for the bonding in AlCl_3 ? Justify your choice based on formal charges.

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



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

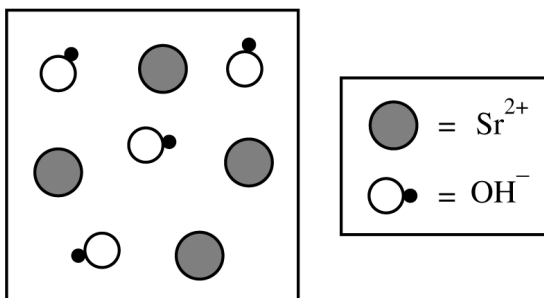
A particle-level diagram of an equilibrium mixture of $\text{AlCl}_3(g)$ and $\text{Al}_2\text{Cl}_6(g)$ at 400°C in a 25 L closed container is shown.



- (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.

GO ON TO THE NEXT PAGE.

Strontium hydroxide dissolves in water according to the following equation. The K_{sp} expression for strontium hydroxide is provided.



(a) A student draws the particulate diagram shown to represent the ions present in an aqueous solution of $\text{Sr}(\text{OH})_2$. (Water molecules are intentionally omitted.) Identify the error in the student's drawing.

(b) The student prepares a saturated solution by adding excess $\text{Sr}(\text{OH})_2(s)$ to distilled water and stirring until no more solid dissolves. The student then determines that $[\text{Sr}^{2+}] = 0.043\text{ M}$ in the solution.

(i) Calculate the value of $[\text{OH}^-]$ in the solution.

(ii) Calculate the value of K_{sp} for $\text{Sr}(\text{OH})_2$.

GO ON TO THE NEXT PAGE.

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

- (c) The student prepares a second saturated solution of $\text{Sr}(\text{OH})_2$ in aqueous $0.10\text{ }M\text{ Sr}(\text{NO}_3)_2$ instead of water. Will the value of $[\text{OH}^-]$ in the second solution be greater than, less than, or equal to the value in the first solution? Justify your answer. (Assume constant temperature.)

STOP

END OF EXAM

7.9 Introduction to Le Chatelier's Principle

Name: _____ Class: _____ Date: _____

Total: 10 marks

KEY WORDS le chatelier's principle 勒沙特列原理

Objective

Build the skills to answer exam questions on **Le Chatelier's principle**.

You must be able to:

- predict the shift when **concentration**, **pressure/volume**, or **temperature** changes
- state **Le Chatelier's principle** 勒沙特列原理
- treat a temperature change using the reaction's ΔH

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ The principle

If a stress is applied to a system at equilibrium, it shifts to **counteract** the stress and restore equilibrium.

■ Concentration

Adding a reactant shifts **toward products** (to use it up); removing a product shifts **toward products** (to replace it).

■ Pressure and volume (gases)

Increasing pressure (smaller volume) shifts toward the side with **fewer gas moles**. If both sides have equal moles, pressure has no effect.

■ Temperature

Treat heat as a reactant/product using ΔH :

- **exothermic** (heat is a product): heating shifts **toward reactants** (backward);
- **endothermic** (heat is a reactant): heating shifts **toward products** (forward).

Only temperature changes the value of K .

2 Practice

Now apply the methods above.

2.1 State Le Chatelier's principle. [1]

2.2 For $A + B \rightleftharpoons C$, which way does adding more A shift it? [1]

2.3 Which single change alters the value of K ? [1]

3 Exam-style questions

3.1 Increasing the pressure on a gas equilibrium shifts it toward the side with [1]

- **A** more gas moles
 - **B** fewer gas moles
 - **C** solids
 - **D** no change ever
-

3.2 Consider $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta H < 0$.

(a) State the shift when the pressure is increased. [2]

(b) State the shift when the temperature is increased, with a reason. [2]

3.3 For $2SO_2 + O_2 \rightleftharpoons 2SO_3$ ($\Delta H < 0$), state and explain the effect of removing SO_3 . [2]

Solutions

2.1 A system at equilibrium shifts to counteract an applied stress and restore equilibrium.

2.2 Toward products (forward).

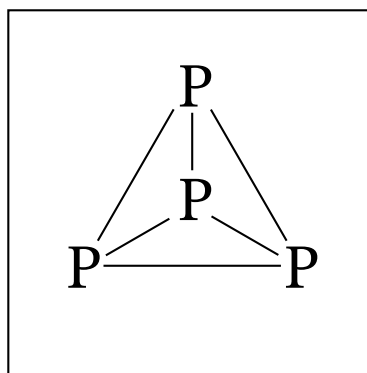
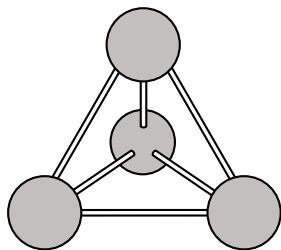
2.3 A temperature change.

3.1 B — fewer gas moles.

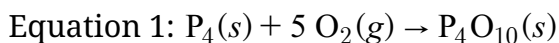
3.2 (a) There are 4 gas moles left, 2 right; increasing pressure shifts toward the fewer-mole side — **toward products**. (b) Exothermic, so heat is a product; increasing temperature shifts **toward reactants** (backward).

3.3 Removing SO_3 (a product) shifts the equilibrium **forward** to replace it, making more SO_3 .

3. White phosphorus is composed of P_4 molecules with a tetrahedral structure, as shown in the diagram on the left. Each P atom is bonded to the other three P atoms by single bonds, as shown in the incomplete Lewis diagram on the right.

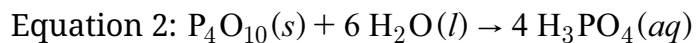


- A. In the box in part A, complete the Lewis diagram for P_4 by drawing the nonbonding electrons.
- B. The reaction of white phosphorus with oxygen to form $P_4O_{10}(s)$ is thermodynamically favorable at 298 K. The reaction is represented by equation 1.

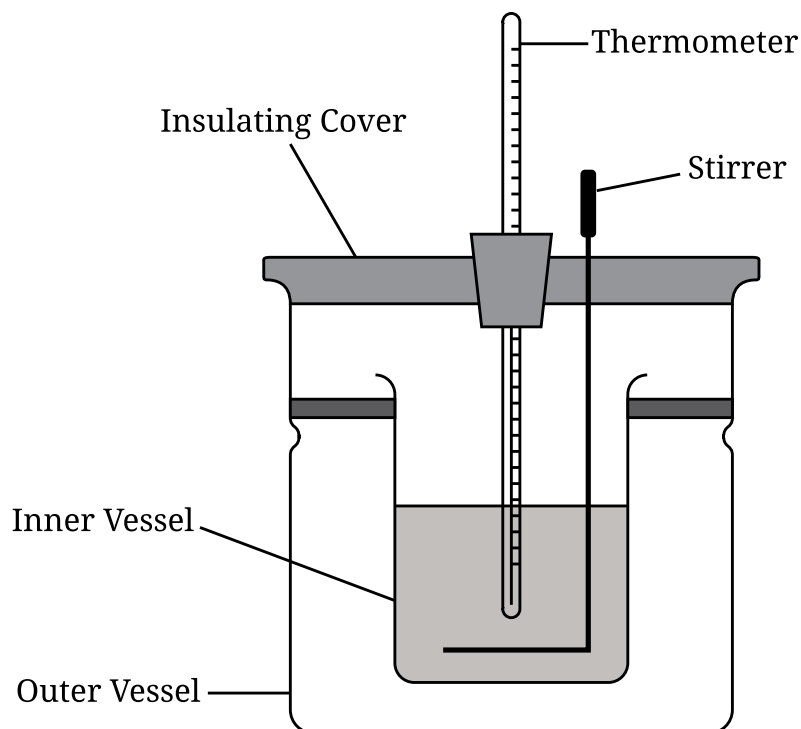


- The entropy change of the reaction, ΔS° , is negative. Using particle-level reasoning, explain why the entropy decreases as the reaction progresses.
- The enthalpy change of the reaction, ΔH° , is also negative. A student claims that the favorability of the reaction is driven by enthalpy and **not** by entropy. Is the student's claim correct? Justify your answer by using the relationship between ΔG° , ΔH° , and ΔS° .

$\text{P}_4\text{O}_{10}(s)$ reacts exothermically with water to form phosphoric acid, as represented by equation 2.



A chemist uses a calorimetry experiment to determine the enthalpy change for the reaction, as represented by the following diagram.



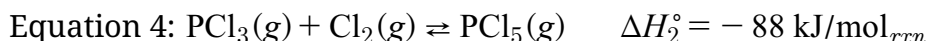
C. The chemist carries out the calorimetry experiment and records the following information.

Mass of P_4O_{10}	0.100 g
Mass of H_2O	100.0 g
Initial temperature	22.00° C
Final temperature	22.38° C
Molar mass of P_4O_{10}	283.9 g/mol
Specific heat of H_2O	4.18 J/(g·°C)

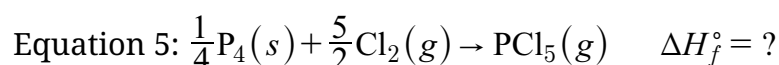
- Calculate the amount of heat, q , released during the experiment, in kJ. Assume that the specific heat of the solution is the same as that of water.
- Calculate the value of $\Delta H^\circ_{\text{rxn}}$ for equation 2 in kJ/mol $_{\text{rxn}}$. Include the sign in your answer.

- D. The chemist weighed out 0.100 g P_4O_{10} of and 100.0 g of H_2O to perform a second trial. In the second trial, some of the solid P_4O_{10} stuck to the weighing paper and was not transferred to the calorimeter. Given that P_4O_{10} is the limiting reactant, would ΔT for the second trial be greater than, less than, or equal to the value in the first trial? Justify your answer.

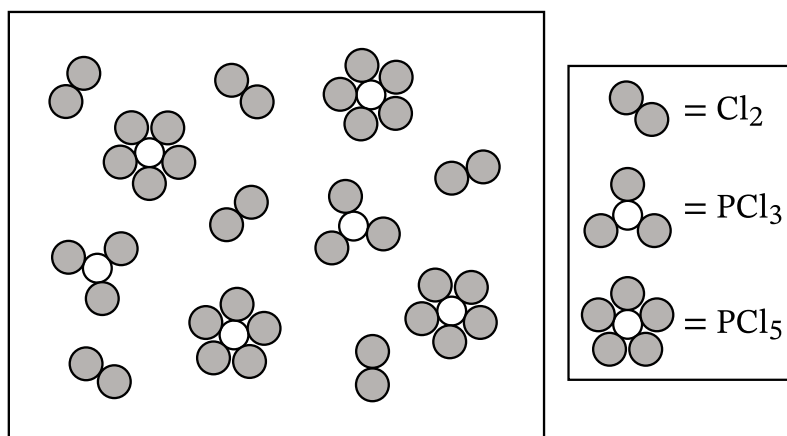
$\text{P}_4(\text{s})$ also reacts readily with $\text{Cl}_2(\text{g})$ to produce phosphorus trichloride, $\text{PCl}_3(\text{g})$, which in turn reacts with $\text{Cl}_2(\text{g})$ in an equilibrium process to produce $\text{PCl}_5(\text{g})$. The reactions are represented by equations 3 and 4.



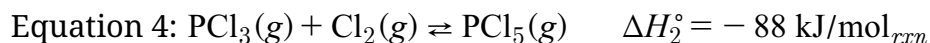
- E. Calculate the standard enthalpy of formation of $\text{PCl}_5(\text{g})$ represented by equation 5.



The following particle-level diagram represents the contents of the vessel in an equilibrium mixture at 546 K involving equation 4.



- F. Equation 4 for the reaction that occurs is shown.

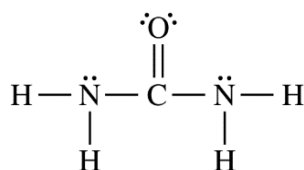


- If each particle in the diagram represents a partial pressure of 1.00 atm, what is the value of K_p for the equilibrium mixture at 546 K?
- Does the value of K_p increase, decrease, or remain the same when the temperature is increased to 596 K? Justify your answer based on ΔH_2° .

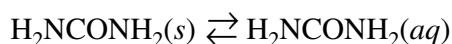
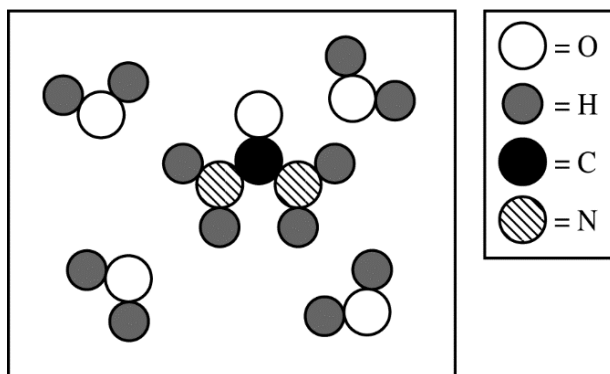
CHEMISTRY**Section II****Time—1 hour and 45 minutes****7 Questions****YOU MAY USE YOUR CALCULATOR FOR THIS SECTION.**

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.

Write your response in the space provided following each question. 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.

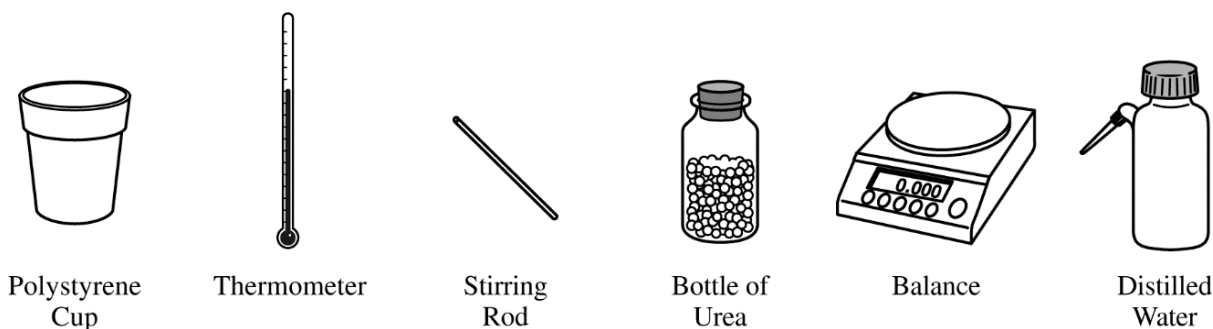


1. The compound urea, H_2NCONH_2 , is widely used in chemical fertilizers. The complete Lewis electron-dot diagram for the urea molecule is shown above.
- (a) Identify the hybridization of the valence orbitals of the carbon atom in the urea molecule.
- (b) Urea has a high solubility in water, due in 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.



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.

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



- (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.

	S° (J/(mol·K))
$\text{H}_2\text{NCONH}_2(s)$	104.6
$\text{H}_2\text{NCONH}_2(aq)$	?

- (f) The entropy change for the dissolution of urea, $\Delta S^\circ_{\text{soln}}$, 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.
- (g) Using particle-level reasoning, explain why $\Delta S^\circ_{\text{soln}}$ is positive for the dissolution of urea in water.
- (h) The student claims that ΔS° 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.

7.10 The Reaction Quotient and Le Chatelier's Principle

Name: _____ Class: _____ Date: _____

Total: 9 marks

KEY WORDS reaction quotient 反应商 • le chatelier's principle 勒沙特列原理

Objective

Build the skills to answer exam questions on **the reaction quotient and Le Chatelier's principle** — using Q vs K to explain a shift.

You must be able to:

- show how a stress changes Q relative to K
- predict the shift that restores $Q = K$
- connect the Q/K view to Le Chatelier

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ A stress changes Q

Adding or removing a species instantly changes Q but not K . The system then shifts to bring Q back to K — the quantitative reason behind Le Chatelier.

■ A worked concentration change

At equilibrium $Q = K$. **Add reactant** → the denominator grows → Q drops below K → reaction shifts **forward** until $Q = K$ again.

■ Removing a product

Remove product → the numerator shrinks → Q drops below K → shifts **forward** to remake product.

■ Why temperature is different

Concentration and pressure changes move Q toward a fixed K . A **temperature** change instead changes K **itself**, so the system shifts to reach the new K .

2 Practice

Now apply the methods above.

2.1 Adding a reactant makes Q do what (relative to K)? [1]

2.2 If $Q < K$ after a stress, which way does the reaction shift? [1]

2.3 Does adding a reactant change K ? [1]

3 Exam-style questions

3.1 Removing a product from an equilibrium causes Q to [1]

- **A** rise above K
 - **B** fall below K
 - **C** stay equal to K
 - **D** become zero
-

3.2 For $A \rightleftharpoons B$ at equilibrium, more B is suddenly added.

(a) State how Q changes relative to K . [1]

(b) State the direction of shift and explain using Q and K . [2]

3.3 Explain why a concentration change shifts the equilibrium but leaves K unchanged, whereas a temperature change alters K . [2]

Solutions

2.1 Q falls below K .

2.2 Forward (toward products).

2.3 No.

3.1 B — removing a product lowers the numerator, so Q falls below K .

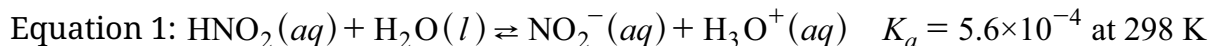
3.2 (a) Q rises above K (more product in the numerator). (b) Shifts **reverse** (toward A), because $Q > K$ so the reaction consumes B to bring Q back down to K .

3.3 Concentration changes only move the current Q ; the reaction shifts to restore the same K . Temperature changes the equilibrium position by changing K itself (since K depends on temperature).

Question 3: Version J

The following information applies to all parts.

3. Nitrous acid, HNO_2 , is a weak acid that ionizes according to Equation 1.

**Part A**

Identify a conjugate acid-base pair in the equation. Be sure to clearly label which is the acid and which is the base.

Part B

A solution of $\text{HNO}_2(aq)$ with an initial concentration of 0.125 M has a pH of 2.09.

- i. **Calculate** the value of $[\text{H}_3\text{O}^+]$ in the solution. Show the work that leads to your answer.
- ii. **Calculate** $[\text{HNO}_2]$ at equilibrium. Show the work that leads to your answer.

Part C

In an experiment, the solution of 0.125 M $\text{HNO}_2(aq)$ is heated to 333 K . The new equilibrium concentrations are determined to be $[\text{HNO}_2] = 0.114 \text{ M}$, $[\text{NO}_2^-] = 0.0109 \text{ M}$, and $[\text{H}_3\text{O}^+] = 0.0109 \text{ M}$.

- i. **Calculate** the value of K_a for HNO_2 at 333 K . Show the work that leads to your answer.
- ii. Is the reaction represented by Equation 1 endothermic or exothermic? **Justify** your answer by comparing K_a values at 298 K and 333 K .

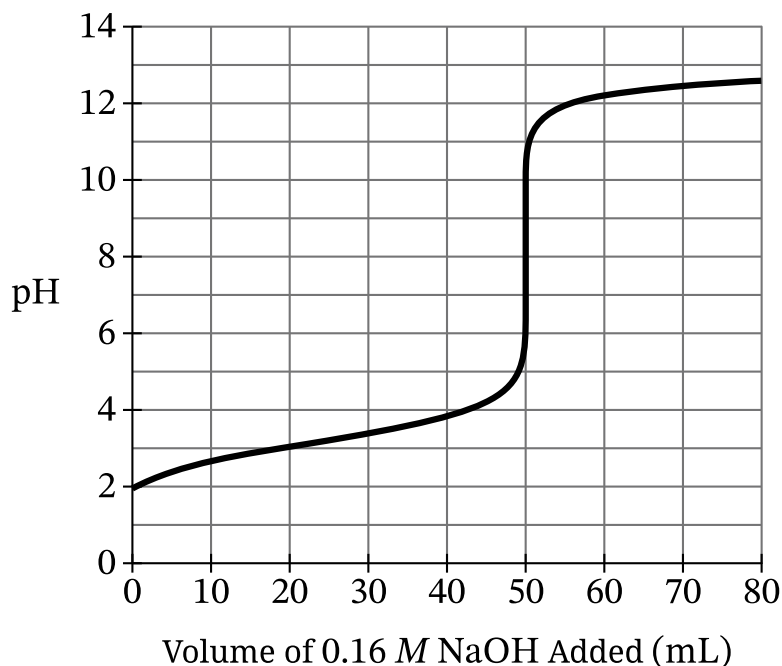
The following information applies to parts D, E, and F.

In a second experiment, a student is given a bottle containing HNO_2 with an unknown molarity. To determine the concentration of the $\text{HNO}_2(aq)$ in the bottle, the student titrates 35.0 mL of the $\text{HNO}_2(aq)$ with 0.16 M $\text{NaOH}(aq)$ at 298 K, which reacts according to Equation 2.



The results of the titration are summarized in Figure 1.

Figure 1



Part D

Using Figure 1, **identify** the pH at the equivalence point.

Part E

Using Figure 1, **calculate** the molarity $\text{HNO}_2(aq)$ of in the bottle. Show the work that leads to your answer.

Part F

Draw an X on Figure 1 to represent a point in the titration where $[\text{HNO}_2] > [\text{NO}_2^-]$ in the reaction mixture.

Part G

Equilibrium constants at 298 K are shown in Table 1 for the acid ionization reaction represented by Equation 1, K_a ; the autoionization of water, K_w ; and the neutralization reaction represented by Equation 2, K_2 .

Table 1

Chemical Equation	Equilibrium Constant
$\text{HNO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NO}_2^-(aq) + \text{H}_3\text{O}^+(aq)$	$K_a = 5.6 \times 10^{-4}$
$\text{H}_2\text{O}(l) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)$	$K_w = 1.0 \times 10^{-14}$
$\text{HNO}_2(aq) + \text{OH}^-(aq) \rightarrow \text{NO}_2^-(aq) + \text{H}_2\text{O}(l)$	$K_2 = ?$

Calculate the value of K_2 for Equation 2 at 298 K. Show the work that leads to your answer.

Part H

The student decides to repeat the experiment, this time using an indicator, and has access to the indicators in Table 2.

Table 2

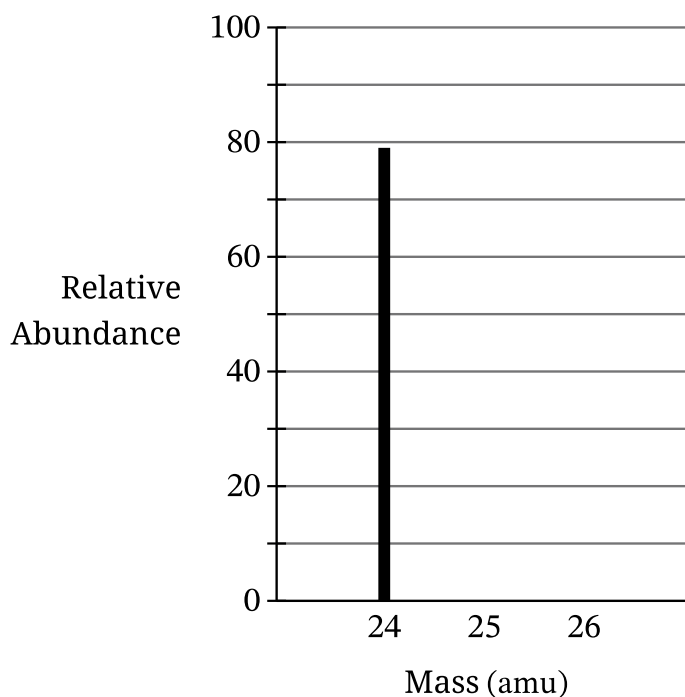
Indicator Name	Acid Color	pH Range of Color Change	Base Color
Methyl orange	Red	3.1–4.4	Yellow
Thymol blue	Yellow	8.0–9.6	Blue
Clayton yellow	Yellow	12.2–13.2	Orange

The student conducts a second titration by adding two drops of methyl orange indicator to 35.0 mL of the $\text{HNO}_2(aq)$ solution and titrating the solution with 0.16 M $\text{NaOH}(aq)$ until a color change from red to yellow occurs.

The student claims that methyl orange was the best choice for the indicator. Do you agree or disagree? **Justify** your answer.

1. Answer the following questions about magnesium.

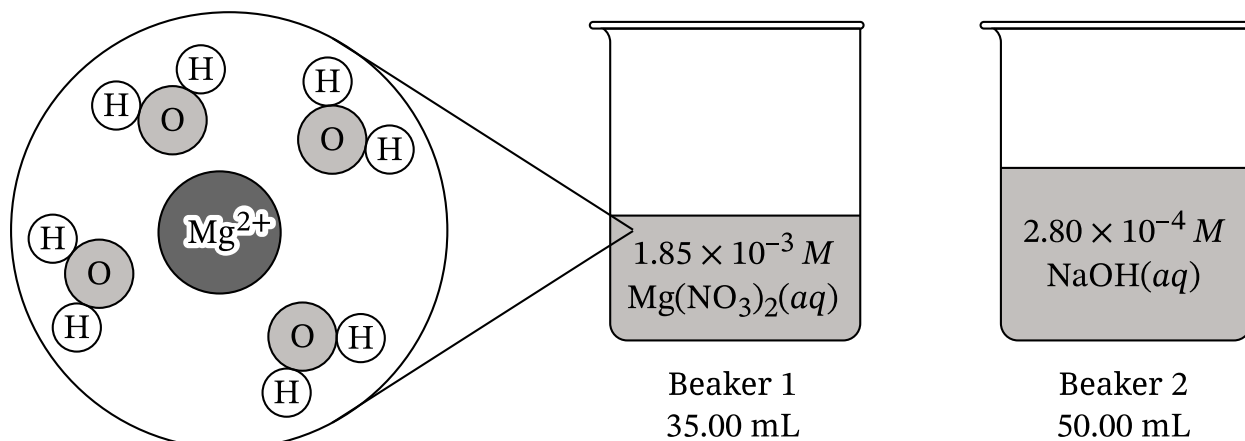
A. An incomplete mass spectrum for magnesium is shown in the diagram.



The percent abundance of magnesium-24 is 79%. The percent abundances of the other two natural isotopes of magnesium, magnesium-25 and magnesium-26, are approximately equal.

- Complete the mass spectrum in part A by drawing thick lines in the appropriate locations to represent the percent abundance of magnesium-25 and magnesium-26.
- Describe the difference in atomic structure that accounts for the difference in mass between magnesium-25 and magnesium-26.

A student prepares a $1.85 \times 10^{-3} M$ solution of $\text{Mg}(\text{NO}_3)_2(aq)$ in beaker 1 and a $2.80 \times 10^{-4} M$ solution of $\text{NaOH}(aq)$ in beaker 2, as shown.

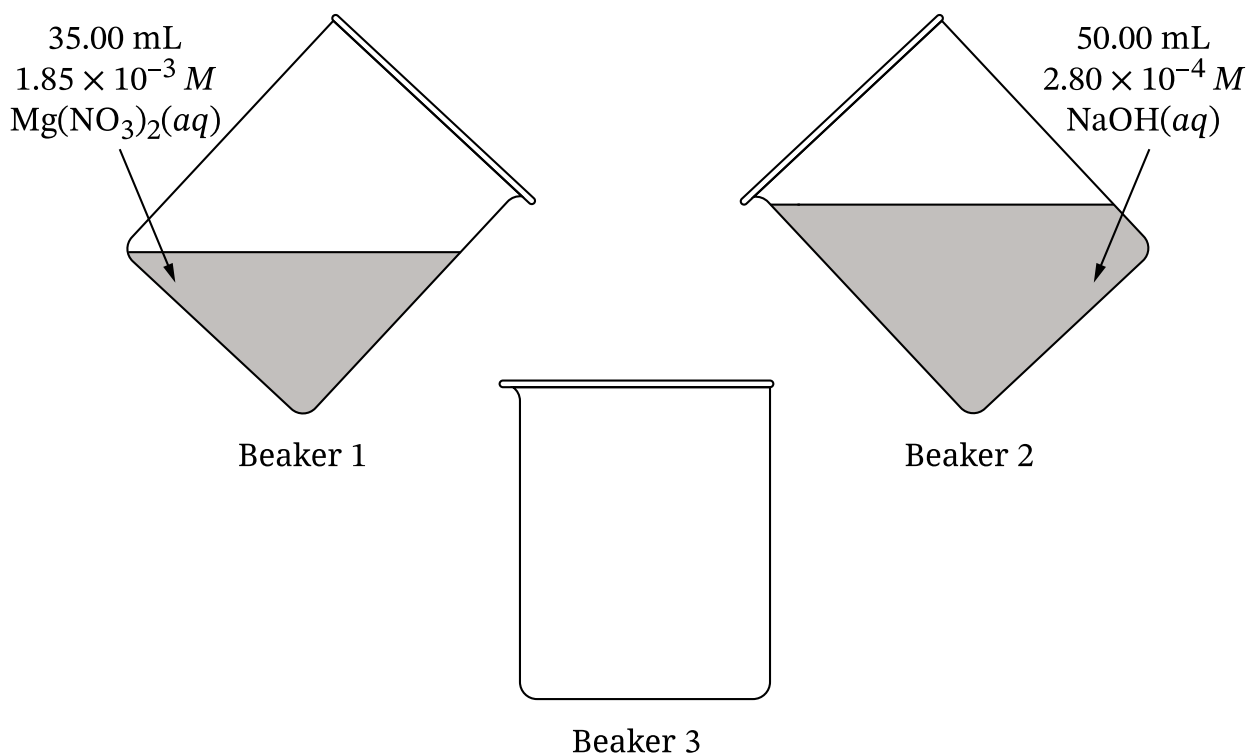


B. The particle diagram shown represents a magnesium ion, Mg^{2+} , in beaker 1. A sodium ion, Na^+ , in beaker 2 has a weaker attraction to water than the Mg^{2+} does. Explain this phenomenon using Coulomb's law and each of the following.

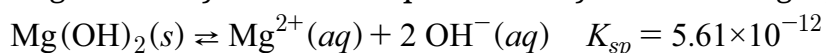
- The relative charge of the ions
- The relative radii of the ions

C. Calculate the pH of the solution in beaker 2.

- D. A student combines 35.00 mL of $1.85 \times 10^{-3} M \text{Mg}(\text{NO}_3)_2(aq)$ with 50.00 mL of $2.80 \times 10^{-4} M \text{NaOH}(aq)$, as shown in the diagram. Calculate $[\text{Mg}^{2+}]$ after the two solutions are combined but before any reaction takes place. (Assume that volumes are additive.)



- E. The dissolution of magnesium hydroxide is represented by the following equation.



- Write the expression for the solubility product constant, K_{sp} .
 - After the two solutions are combined in beaker 3 as described in part D, but before any reaction takes place, $[\text{OH}^{-}] = 1.65 \times 10^{-4} M$. Using your answer to part D, calculate the value of the reaction quotient, Q .
 - Using the reaction quotient, Q , predict whether a precipitate should form as the mixture in beaker 3 approaches equilibrium. Justify your answer.
- F. In a separate experiment, the student adds $\text{HNO}_3(aq)$ to decrease the pH of a saturated solution containing undissolved $\text{Mg}(\text{OH})_2(s)$. Does the amount of undissolved $\text{Mg}(\text{OH})_2(s)$ increase, decrease, or remain the same as the $\text{HNO}_3(aq)$ is added? Justify your answer.

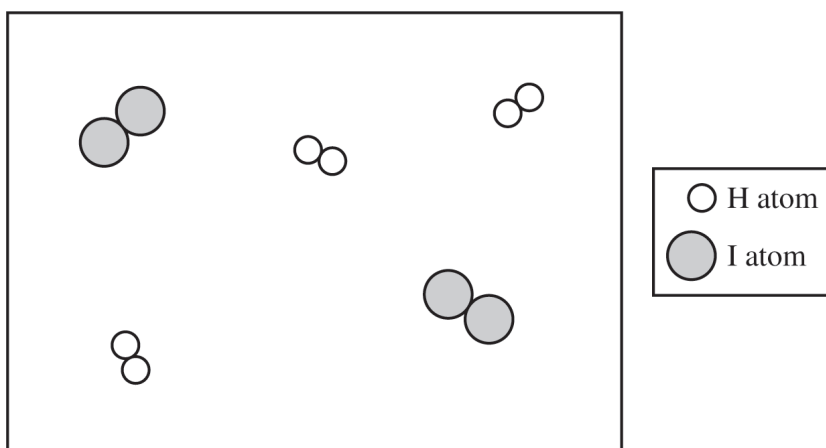
5. Hydrogen gas and iodine gas react to form hydrogen iodide at an elevated temperature, as represented by the following equation.



(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.

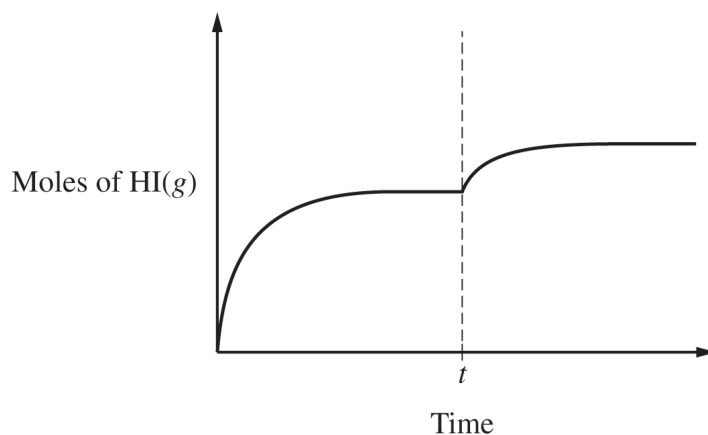
- (i) At a certain time, the value of the reaction quotient, Q , is 0.67. The following particle diagram is an incomplete representation of the system at this time. The diagram shows the relative number of $\text{H}_2(g)$ and $\text{I}_2(g)$ molecules, but the $\text{HI}(g)$ molecules are not included.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



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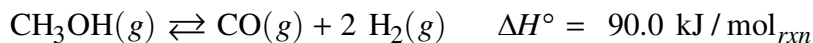
Continue your response to **QUESTION 5** on this page.

- (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.

GO ON TO THE NEXT PAGE.



Methanol vapor decomposes to form carbon monoxide gas and hydrogen gas at high temperatures in the presence of a platinum catalyst, as represented by the balanced chemical equation given.

(a) Are the hydrogen atoms oxidized or are they reduced in the forward reaction? Justify your answer in terms of oxidation numbers.

(b) In the following box, draw the complete Lewis electron-dot diagram for the carbon monoxide molecule in which every atom obeys the octet rule. Show all bonding and nonbonding valence electrons.



(c) The values of the standard molar entropies of the compounds involved in the reaction are given in the following table.

Substance	S° (J/(K·mol))
$\text{CH}_3\text{OH}(g)$	240.
$\text{CO}(g)$	198
$\text{H}_2(g)$	131

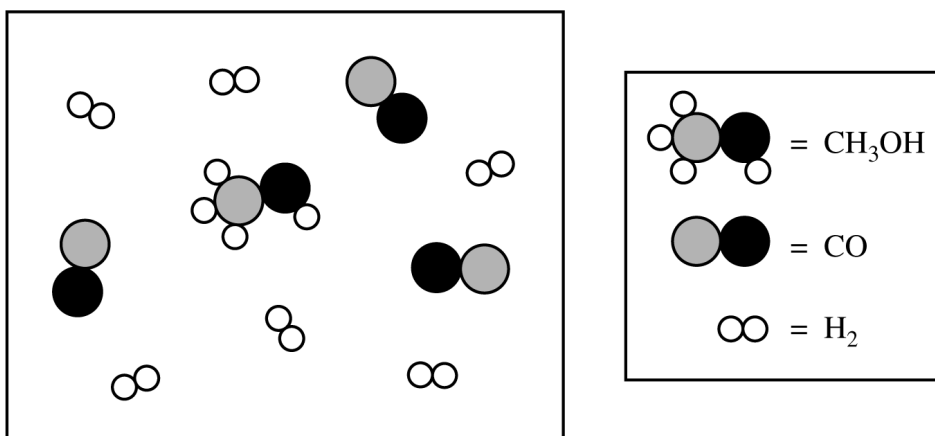
(i) Use the data in the table to calculate the value of the standard entropy change, ΔS° , in J/(K·mol_{rxn}), for the reaction.

GO ON TO THE NEXT PAGE.

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

- (ii) Calculate the value of ΔG° , in $\text{kJ/mol}_{\text{rxn}}$, for the reaction at 375 K. Assume that ΔH° and ΔS° are independent of temperature.

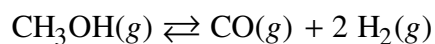
The following particle-level diagram shows a representative sample of the equilibrium mixture represented by the equation given.



- (d) Use information from the particle diagram to calculate the partial pressure of CO at equilibrium when the total pressure of the equilibrium mixture is 12.0 atm.

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

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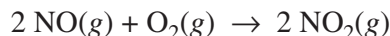
The reaction system represented by the equation is allowed to achieve equilibrium at a different temperature. The following table gives the partial pressure of each species in the equilibrium mixture.

Substance	Partial Pressure at Different Temperature
$\text{CH}_3\text{OH}(g)$	2.7 atm
$\text{CO}(g)$	4.2 atm
$\text{H}_2(g)$	8.4 atm

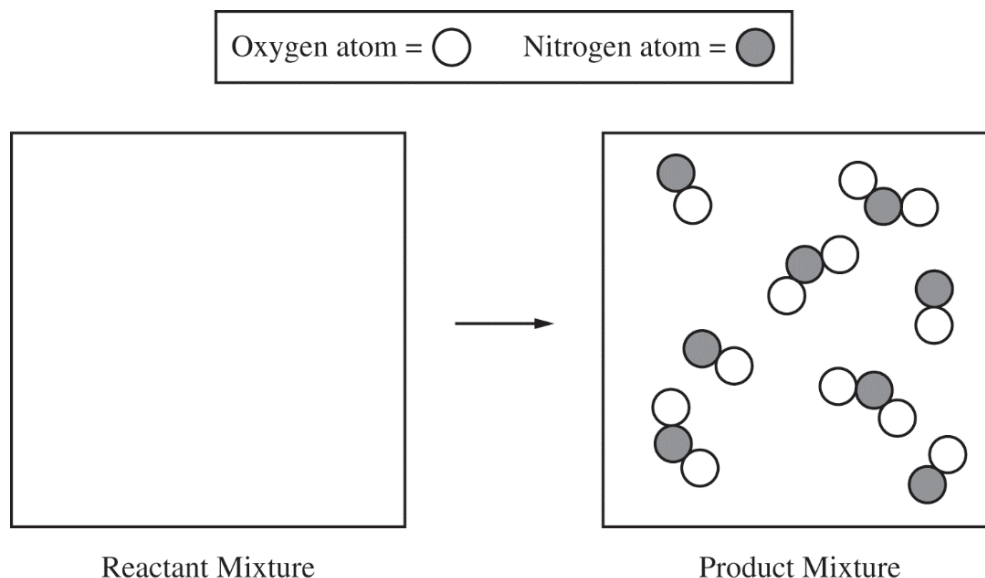
(f) Use the information in the table to calculate the value of the equilibrium constant, K_p , at the new temperature.

(g) The volume of the container is rapidly doubled with no change in temperature. As equilibrium is re-established, does the number of moles of $\text{CH}_3\text{OH}(g)$ increase, decrease, or remain the same? Justify your answer by comparing the value of the reaction quotient, Q , with the value of the equilibrium constant, K_p .

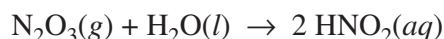
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2. A student investigates the reactions of nitrogen oxides. One of the reactions in the investigation requires an equimolar mixture of $\text{NO}(g)$ and $\text{NO}_2(g)$, which the student produces by using the reaction represented above.
- (a) The particle-level representation of the equimolar mixture of $\text{NO}(g)$ and $\text{NO}_2(g)$ in the flask at the completion of the reaction between $\text{NO}(g)$ and $\text{O}_2(g)$ is shown below in the box on the right. In the box below on the left, draw the particle-level representation of the reactant mixture of $\text{NO}(g)$ and $\text{O}_2(g)$ that would yield the product mixture shown in the box on the right. In your drawing, represent oxygen atoms and nitrogen atoms as indicated below.



$\text{N}_2\text{O}_3(g)$ reacts with water to form nitrous acid, $\text{HNO}_2(aq)$, a compound involved in the production of acid rain. The reaction is represented below.



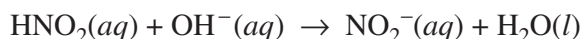
(d) The skeletal structure of the HNO_2 molecule is shown in the box below.

- (i) Complete the Lewis electron-dot diagram of the HNO_2 molecule in the box below, including any lone pairs of electrons.

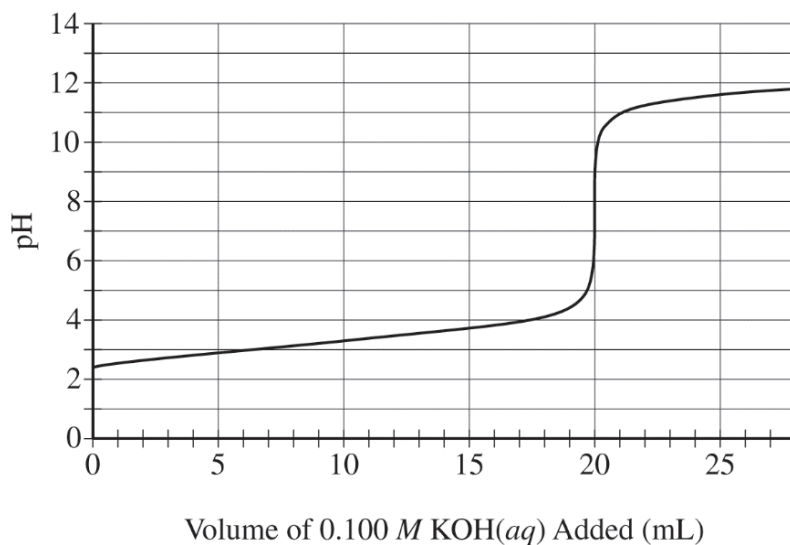


- (ii) Based on your completed diagram above, identify the hybridization of the nitrogen atom in the HNO_2 molecule.

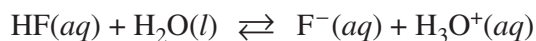
To produce an aqueous solution of HNO_2 , the student bubbles $\text{N}_2\text{O}_3(g)$ into distilled water. Assume that the reaction goes to completion and that HNO_2 is the only species produced. To determine the concentration of $\text{HNO}_2(aq)$ in the resulting solution, the student titrates a 100. mL sample of the solution with 0.100 M $\text{KOH}(aq)$. The neutralization reaction is represented below.



The following titration curve shows the change in pH of the solution during the titration.



- (e) Use the titration curve and the information above to
- determine the initial concentration of the $\text{HNO}_2(aq)$ solution
 - estimate the value of $\text{p}K_a$ for $\text{HNO}_2(aq)$
- (f) During the titration, after a volume of 15 mL of 0.100 M $\text{KOH}(aq)$ has been added, which species, $\text{HNO}_2(aq)$ or $\text{NO}_2^-(aq)$, is present at a higher concentration in the solution? Justify your answer.



5. The ionization of $\text{HF}(aq)$ in water is represented by the equation above. In a 0.0350 M $\text{HF}(aq)$ solution, the percent ionization of HF is 13.0 percent.
- (a) Two particulate representations of the ionization of HF molecules in the 0.0350 M $\text{HF}(aq)$ solution are shown below in Figure 1 and Figure 2. Water molecules are not shown. Explain why the representation of the ionization of HF molecules in water in Figure 1 is more accurate than the representation in Figure 2. (The key below identifies the particles in the representations.)

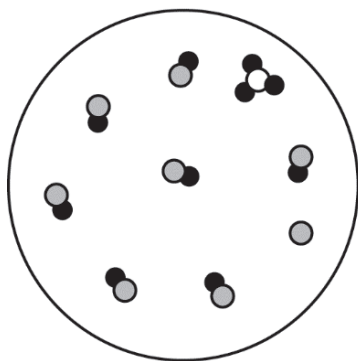
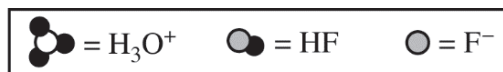


Figure 1

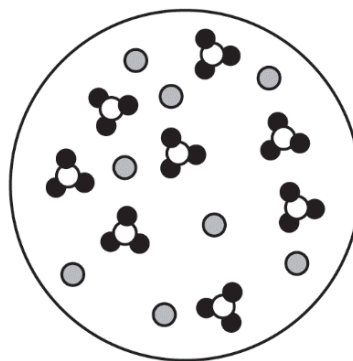
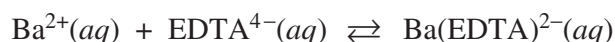


Figure 2

- (b) Use the percent ionization data above to calculate the value of K_a for HF .
- (c) If 50.0 mL of distilled water is added to 50.0 mL of 0.035 M $\text{HF}(aq)$, will the percent ionization of $\text{HF}(aq)$ in the solution increase, decrease, or remain the same? Justify your answer with an explanation or calculation.

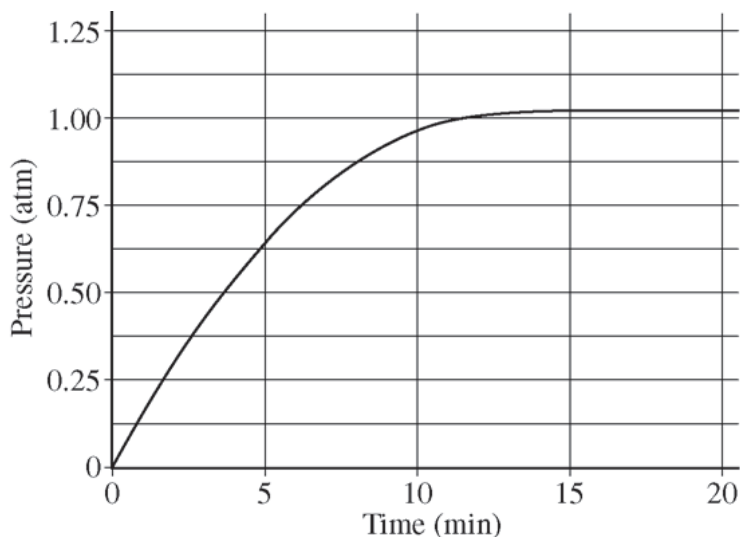


$$K = 7.7 \times 10^7$$

6. The polyatomic ion $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8^{4-}$ is commonly abbreviated as EDTA^{4-} . The ion can form complexes with metal ions in aqueous solutions. A complex of EDTA^{4-} with Ba^{2+} ion forms according to the equation above. A 50.0 mL volume of a solution that has an $\text{EDTA}^{4-}(aq)$ concentration of 0.30 M is mixed with 50.0 mL of 0.20 M $\text{Ba}(\text{NO}_3)_2$ to produce 100.0 mL of solution.
- (a) Considering the value of K for the reaction, determine the concentration of $\text{Ba}(\text{EDTA})^{2-}(aq)$ in the 100.0 mL of solution. Justify your answer.
- (b) The solution is diluted with distilled water to a total volume of 1.00 L . After equilibrium has been reestablished, is the number of moles of $\text{Ba}^{2+}(aq)$ present in the solution greater than, less than, or equal to the number of moles of $\text{Ba}^{2+}(aq)$ present in the original solution before it was diluted? Justify your answer.



4. When heated, calcium carbonate decomposes according to the equation above. In a study of the decomposition of calcium carbonate, a student added a 50.0 g sample of powdered $\text{CaCO}_3(s)$ to a 1.00 L rigid container. The student sealed the container, pumped out all the gases, then heated the container in an oven at 1100 K. As the container was heated, the total pressure of the $\text{CO}_2(g)$ in the container was measured over time. The data are plotted in the graph below.



The student repeated the experiment, but this time the student used a 100.0 g sample of powdered $\text{CaCO}_3(s)$. In this experiment, the final pressure in the container was 1.04 atm, which was the same final pressure as in the first experiment.

- (a) Calculate the number of moles of $\text{CO}_2(g)$ present in the container after 20 minutes of heating.
- (b) The student claimed that the final pressure in the container in each experiment became constant because all of the $\text{CaCO}_3(s)$ had decomposed. Based on the data in the experiments, do you agree with this claim? Explain.
- (c) After 20 minutes some $\text{CO}_2(g)$ was injected into the container, initially raising the pressure to 1.5 atm. Would the final pressure inside the container be less than, greater than, or equal to 1.04 atm? Explain your reasoning.
- (d) Are there sufficient data obtained in the experiments to determine the value of the equilibrium constant, K_p , for the decomposition of $\text{CaCO}_3(s)$ at 1100 K? Justify your answer.

7.11 Introduction to Solubility Equilibria

Name: _____ Class: _____ Date: _____

Total: 12 marks

KEY WORDS molar solubility 摩尔溶解度 • solubility product 溶度积

Objective

Build the skills to answer exam questions on **solubility equilibria** and K_{sp} .**You must be able to:**

- write the **solubility product** 溶度积 K_{sp} expression
- relate **molar solubility** 摩尔溶解度 to K_{sp}
- calculate one from the other

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ The K_{sp} expression

For a sparingly soluble salt dissolving, e.g. $\text{AgCl}(s) \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$:

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-].$$

The solid is omitted.

■ Molar solubility

Let s be the moles of salt that dissolve per litre. Each formula unit gives ions according to its formula: for AgCl , $[\text{Ag}^+] = [\text{Cl}^-] = s$, so $K_{sp} = s^2$.

■ A worked calculation

If $K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}$, then $s = \sqrt{K_{sp}} = \sqrt{1.8 \times 10^{-10}} = 1.3 \times 10^{-5} \text{ M}$.

■ Salts giving more ions

For $\text{CaF}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{F}^-$: $[\text{Ca}^{2+}] = s$, $[\text{F}^-] = 2s$, so $K_{sp} = s(2s)^2 = 4s^3$.

2 Practice

Now apply the methods above.

2.1 Write the K_{sp} expression for $\text{BaSO}_4 \rightleftharpoons \text{Ba}^{2+} + \text{SO}_4^{2-}$. [1]

2.2 For a 1:1 salt with molar solubility s , write K_{sp} in terms of s . [1]

2.3 If $K_{sp} = 4 \times 10^{-10}$ for a 1:1 salt, find s . [2]

3 Exam-style questions

3.1 For $\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$ with molar solubility s , $K_{sp} =$ [1]

- A s
 - B s^2
 - C $2s$
 - D $4s^3$
-

3.2 $\text{PbCl}_2 \rightleftharpoons \text{Pb}^{2+} + 2\text{Cl}^-$ has molar solubility s .

(a) Write $[\text{Pb}^{2+}]$ and $[\text{Cl}^-]$ in terms of s . [2]

(b) Write K_{sp} in terms of s . [2]

3.3 $K_{sp}(\text{CaF}_2) = 3.2 \times 10^{-11}$, with $K_{sp} = 4s^3$. Find the molar solubility s . [3]

Solutions

2.1 $K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$.

2.2 $K_{sp} = s^2$.

2.3 $s = \sqrt{4 \times 10^{-10}} = 2 \times 10^{-5} \text{ M}$.

3.1 B — $K_{sp} = s^2$ for a 1:1 salt.

3.2 (a) $[\text{Pb}^{2+}] = s$, $[\text{Cl}^-] = 2s$. (b) $K_{sp} = s(2s)^2 = 4s^3$.

3.3 $4s^3 = 3.2 \times 10^{-11}$; $s^3 = 8 \times 10^{-12}$; $s = 2 \times 10^{-4} \text{ M}$.

Question 1

1. A student performs a calorimetry experiment with KCl.

Part A

Consider the K^+ ion in KCl.

- Write** the complete ground-state electron configuration for the potassium ion, K^+ .
- Which has the larger radius, the K^+ ion or the K atom? **Explain** your reasoning using principles of atomic structure.

The following information applies to parts B, C, D, and E.

A student performs an experiment to determine the enthalpy of solution, ΔH_{soln} , of KCl. The student places water in a calorimeter, measures the initial temperature, adds $\text{KCl}(s)$, and stirs until the KCl dissolves completely. The temperature is continuously monitored during the experiment. Data from the experiment are given in the following table.

Mass of water	97.5 g
Mass of $\text{KCl}(s)$	6.80 g
Initial temperature of water	24.5°C
Final temperature of solution	21.1°C

Part B

Describe how the student can use the temperature readings during the experiment to determine when the dissolution is complete.

Part C

Use the data in the table to do the following.

- Calculate** the magnitude of the thermal energy, q , in joules, transferred during the dissolution. Show the work that leads to your answer. (Assume that the solution has a specific heat capacity of $3.95 \text{ J}/(\text{g}\cdot^\circ\text{C})$.)
- Calculate** the value of the molar enthalpy of solution, ΔH_{soln} , in kJ/mol , for KCl given that 0.0912 mol of KCl dissolved. Show the work that leads to your answer. Include the sign with your answer.

Part D

The calorimeter is not perfectly insulated. Would this cause the magnitude of ΔH_{soln} calculated in part C (ii) to be greater than, less than, or equal to the accepted value? **Justify** your answer.

Part E

The student performs a second experiment using the same mass of water but 6.80 g of $\text{RbCl}(s)$ instead of 6.80 g of $\text{KCl}(s)$. The magnitude of the molar enthalpy of solution, ΔH_{soln} , of RbCl is approximately equal to that of KCl .

Is the magnitude of ΔT in the RbCl experiment greater than, less than, or equal to that in the KCl experiment? **Justify** your answer. (Assume that the specific heat capacities of the solutions are equal.)

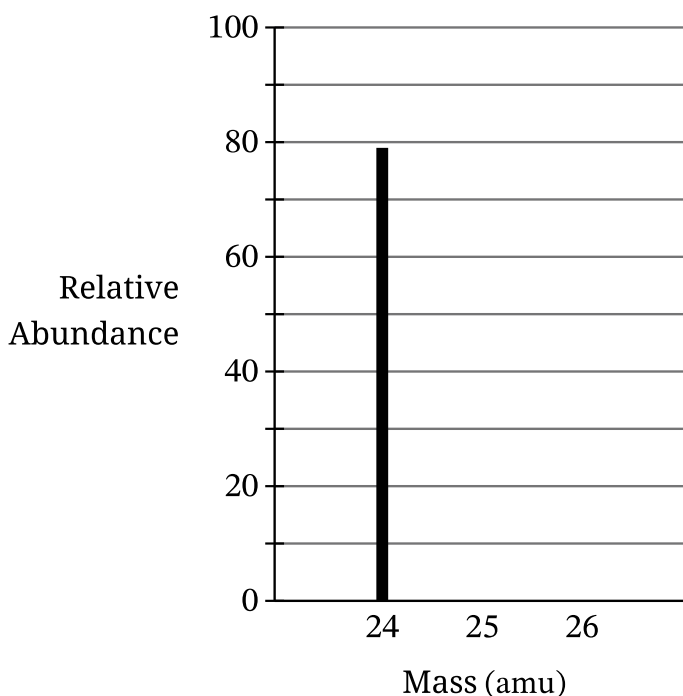
Part F

RbCl has a K_{sp} of 57 at 20°C .

- i. **Write** the net ionic equation for the dissolution of RbCl in pure water.
- ii. **Calculate** the molar solubility of RbCl in a saturated solution at 20°C . Show the work that leads to your answer.
- iii. A second saturated solution is prepared by dissolving $\text{RbCl}(s)$ in $1.0\text{ M KCl}(aq)$ at 20°C instead of in pure water. Will the molar solubility of RbCl in $1.0\text{ M KCl}(aq)$ be greater than, less than, or equal to the molar solubility calculated in part F (ii)? **Justify** your answer.

1. Answer the following questions about magnesium.

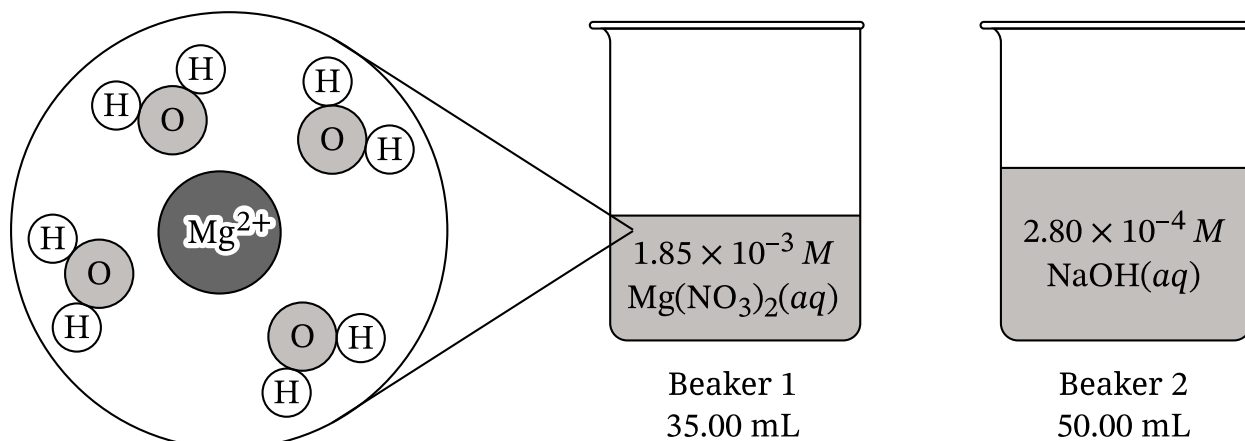
A. An incomplete mass spectrum for magnesium is shown in the diagram.



The percent abundance of magnesium-24 is 79%. The percent abundances of the other two natural isotopes of magnesium, magnesium-25 and magnesium-26, are approximately equal.

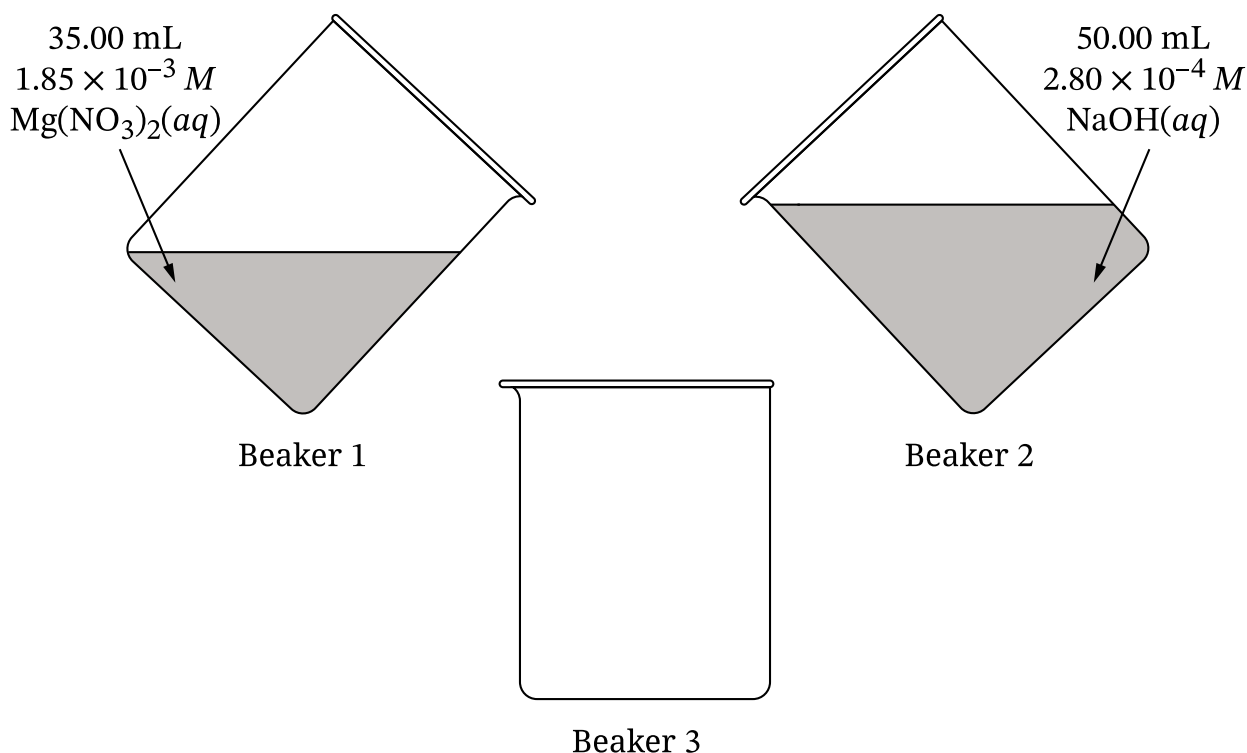
- i. Complete the mass spectrum in part A by drawing thick lines in the appropriate locations to represent the percent abundance of magnesium-25 and magnesium-26.
- ii. Describe the difference in atomic structure that accounts for the difference in mass between magnesium-25 and magnesium-26.

A student prepares a $1.85 \times 10^{-3} M$ solution of $\text{Mg}(\text{NO}_3)_2(aq)$ in beaker 1 and a $2.80 \times 10^{-4} M$ solution of $\text{NaOH}(aq)$ in beaker 2, as shown.

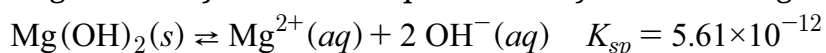


- B.** The particle diagram shown represents a magnesium ion, Mg^{2+} , in beaker 1. A sodium ion, Na^+ , in beaker 2 has a weaker attraction to water than the Mg^{2+} does. Explain this phenomenon using Coulomb's law and each of the following.
- The relative charge of the ions
 - The relative radii of the ions
- C.** Calculate the pH of the solution in beaker 2.

- D. A student combines 35.00 mL of $1.85 \times 10^{-3} \text{ M Mg(NO}_3)_2(aq)$ with 50.00 mL of $2.80 \times 10^{-4} \text{ M NaOH}(aq)$, as shown in the diagram. Calculate $[\text{Mg}^{2+}]$ after the two solutions are combined but before any reaction takes place. (Assume that volumes are additive.)

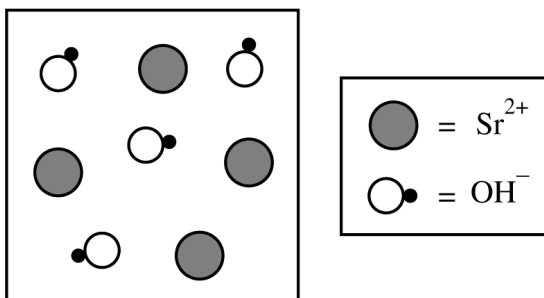


- E. The dissolution of magnesium hydroxide is represented by the following equation.



- Write the expression for the solubility product constant, K_{sp} .
 - After the two solutions are combined in beaker 3 as described in part D, but before any reaction takes place, $[\text{OH}^{-}] = 1.65 \times 10^{-4} \text{ M}$. Using your answer to part D, calculate the value of the reaction quotient, Q .
 - Using the reaction quotient, Q , predict whether a precipitate should form as the mixture in beaker 3 approaches equilibrium. Justify your answer.
- F. In a separate experiment, the student adds $\text{HNO}_3(aq)$ to decrease the pH of a saturated solution containing undissolved $\text{Mg(OH)}_2(s)$. Does the amount of undissolved $\text{Mg(OH)}_2(s)$ increase, decrease, or remain the same as the $\text{HNO}_3(aq)$ is added? Justify your answer.

Strontium hydroxide dissolves in water according to the following equation. The K_{sp} expression for strontium hydroxide is provided.



- (a) A student draws the particulate diagram shown to represent the ions present in an aqueous solution of $\text{Sr}(\text{OH})_2$. (Water molecules are intentionally omitted.) Identify the error in the student's drawing.
- (b) The student prepares a saturated solution by adding excess $\text{Sr}(\text{OH})_2(s)$ to distilled water and stirring until no more solid dissolves. The student then determines that $[\text{Sr}^{2+}] = 0.043\text{ M}$ in the solution.
- (i) Calculate the value of $[\text{OH}^-]$ in the solution.
- (ii) Calculate the value of K_{sp} for $\text{Sr}(\text{OH})_2$.

GO ON TO THE NEXT PAGE.

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

- (c) The student prepares a second saturated solution of $\text{Sr}(\text{OH})_2$ in aqueous $0.10\text{ }M\text{ Sr}(\text{NO}_3)_2$ instead of water. Will the value of $[\text{OH}^-]$ in the second solution be greater than, less than, or equal to the value in the first solution? Justify your answer. (Assume constant temperature.)

STOP

END OF EXAM

. A Lewis electron-dot diagram of the oxalate ion, $\text{C}_2\text{O}_4^{2-}$, is shown.

(a) Identify the hybridization of the valence orbitals of either carbon atom in the oxalate ion.

(b) Silver oxalate, $\text{Ag}_2\text{C}_2\text{O}_4(s)$, is slightly soluble in water. The value of K_{sp} for $\text{Ag}_2\text{C}_2\text{O}_4$ is 5.40×10^{-12} .

(i) Write the expression for the solubility-product constant, K_{sp} , for $\text{Ag}_2\text{C}_2\text{O}_4$.

(ii) Calculate the molar solubility of $\text{Ag}_2\text{C}_2\text{O}_4$ in neutral distilled water.

(iii) The molar solubility of $\text{Ag}_2\text{C}_2\text{O}_4$ increases when it is dissolved in $0.5\text{ M HClO}_4(aq)$ instead of neutral distilled water. Write a balanced, net-ionic equation for the process that occurs between species in solution that contributes to the increased solubility of $\text{Ag}_2\text{C}_2\text{O}_4(aq)$ in $\text{HClO}_4(aq)$.

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STOP

END OF EXAM

6. A student is studying the properties of CaSO_4 and PbSO_4 . The student has samples of both compounds, which are white powders.

(a) The student tests the electrical conductivity of each solid and observes that neither solid conducts electricity. Describe the structures of the solids that account for their inability to conduct electricity.

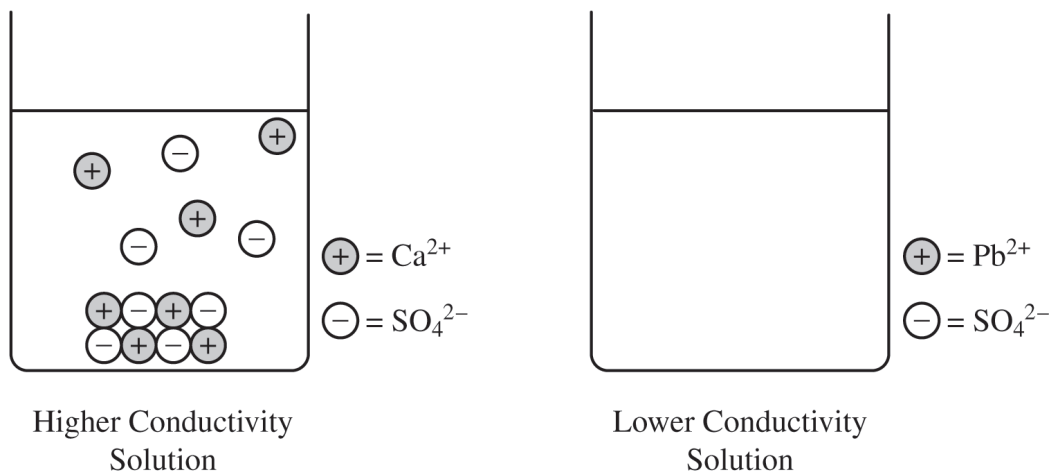
The student places excess $\text{CaSO}_4(s)$ in a beaker containing 100 mL of water and places excess $\text{PbSO}_4(s)$ in another beaker containing 100 mL of water. The student stirs the contents of the beakers and then measures the electrical conductivity of the solution in each beaker. The student observes that the conductivity of the solution in the beaker containing the $\text{CaSO}_4(s)$ is higher than the conductivity of the solution in the beaker containing the $\text{PbSO}_4(s)$.

(b) Which compound is more soluble in water, $\text{CaSO}_4(s)$ or $\text{PbSO}_4(s)$? Justify your answer based on the results of the conductivity test.

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Use a pencil or pen with black or dark blue ink only. Do NOT write your name. Do NOT write outside the box.

The left side of the diagram below shows a particulate representation of the contents of the beaker containing the $\text{CaSO}_4(s)$ from the solution conductivity experiment.



(c) Draw a particulate representation of $\text{PbSO}_4(s)$ and the ions dissolved in the solution in the beaker on the right in the diagram. Draw the particles to look like those shown to the right of the beaker. Draw an appropriate number of dissolved ions relative to the number of dissolved ions in the beaker on the left.

(d) The student attempts to increase the solubility of $\text{CaSO}_4(s)$ by adding 10.0 mL of 2 M $\text{H}_2\text{SO}_4(aq)$ to the beaker, and observes that additional precipitate forms in the beaker. Explain this observation.

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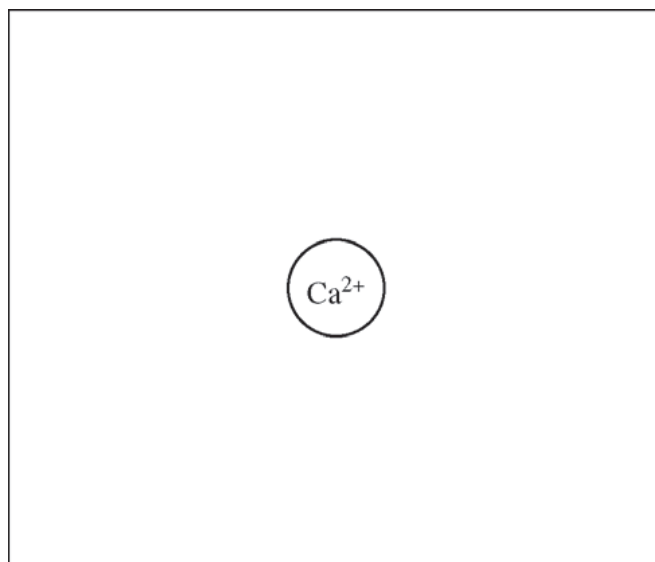
Use a pencil or pen with black or dark blue ink only. Do NOT write your name. Do NOT write outside the box.

6. Answer the following questions about Mg(OH)_2 . At 25°C , the value of the solubility product constant, K_{sp} , for $\text{Mg(OH)}_2(s)$ is 1.8×10^{-11} .
- (a) Calculate the number of grams of Mg(OH)_2 (molar mass 58.32 g/mol) that is dissolved in 100. mL of a saturated solution of Mg(OH)_2 at 25°C .
- (b) The energy required to separate the ions in the Mg(OH)_2 crystal lattice into individual $\text{Mg}^{2+}(g)$ and $\text{OH}^-(g)$ ions, as represented in the table below, is known as the lattice energy of $\text{Mg(OH)}_2(s)$. As shown in the table, the lattice energy of $\text{Sr(OH)}_2(s)$ is less than the lattice energy of $\text{Mg(OH)}_2(s)$. Explain why in terms of periodic properties and Coulomb's law.

Reaction	Lattice Energy (kJ/mol)
$\text{Mg(OH)}_2(s) \rightarrow \text{Mg}^{2+}(g) + 2 \text{OH}^-(g)$	2900
$\text{Sr(OH)}_2(s) \rightarrow \text{Sr}^{2+}(g) + 2 \text{OH}^-(g)$	2300

4. Answer the following questions about the solubility of Ca(OH)_2 ($K_{sp} = 1.3 \times 10^{-6}$).
- (a) Write a balanced chemical equation for the dissolution of $\text{Ca(OH)}_2(s)$ in pure water.
- (b) Calculate the molar solubility of Ca(OH)_2 in $0.10 \text{ M Ca(NO}_3)_2$.
- (c) In the box below, complete a particle representation diagram that includes four water molecules with proper orientation around the Ca^{2+} ion.

Represent water molecules as .



CHEMISTRY**Section II****7 Questions****Time—90 minutes****YOU MAY USE YOUR CALCULATOR FOR THIS SECTION.**

Directions: Questions 1–3 are long free-response questions that require about 20 minutes each to answer and are worth 10 points each. Questions 4–7 are short free-response questions that require about 7 minutes each to answer and are worth 4 points each.

Write your response in the space provided following each question. 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.

Mass of KI tablet	0.425 g
Mass of thoroughly dried filter paper	1.462 g
Mass of filter paper + precipitate after first drying	1.775 g
Mass of filter paper + precipitate after second drying	1.699 g
Mass of filter paper + precipitate after third drying	1.698 g

1. A student is given the task of determining the I^- content of tablets that contain KI and an inert, water-soluble sugar as a filler. A tablet is dissolved in 50.0 mL of distilled water, and an excess of $0.20\text{ M Pb}(\text{NO}_3)_2(aq)$ is added to the solution. A yellow precipitate forms, which is then filtered, washed, and dried. The data from the experiment are shown in the table above.
 - (a) For the chemical reaction that occurs when the precipitate forms,
 - (i) write a balanced, net-ionic equation for the reaction, and
 - (ii) explain why the reaction is best represented by a net-ionic equation.
 - (b) Explain the purpose of drying and weighing the filter paper with the precipitate three times.
 - (c) In the filtrate solution, is $[\text{K}^+]$ greater than, less than, or equal to $[\text{NO}_3^-]$? Justify your answer.
 - (d) Calculate the number of moles of precipitate that is produced in the experiment.
 - (e) Calculate the mass percent of I^- in the tablet.
 - (f) In another trial, the student dissolves a tablet in 55.0 mL of water instead of 50.0 mL of water. Predict whether the experimentally determined mass percent of I^- will be greater than, less than, or equal to the amount calculated in part (e). Justify your answer.

- (g) A student in another lab also wants to determine the I^- content of a KI tablet but does not have access to $Pb(NO_3)_2$. However, the student does have access to $0.20\ M\ AgNO_3$, which reacts with $I^-(aq)$ to produce $AgI(s)$. The value of K_{sp} for AgI is 8.5×10^{-17} .
- Will the substitution of $AgNO_3$ for $Pb(NO_3)_2$ result in the precipitation of the I^- ion from solution? Justify your answer.
 - The student only has access to one KI tablet and a balance that can measure to the nearest 0.01 g. Will the student be able to determine the mass of AgI produced to three significant figures? Justify your answer.

7.12 The Common-Ion Effect

Name: _____ Class: _____ Date: _____

Total: 9 marks

KEY WORDS common ion 同离子 • le chatelier's principle 勒沙特列原理

Objective

Build the skills to answer exam questions on the **common-ion effect**.

You must be able to:

- predict that a **common ion** 同离子 lowers a salt's solubility
- explain it with Le Chatelier / Q vs K_{sp}
- reason qualitatively about the shift

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ The common-ion effect

Adding an ion that is **already** part of a solubility equilibrium **decreases** the salt's solubility. The extra ion pushes the equilibrium back toward the solid.

■ A worked case

$\text{AgCl}(s) \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$. Add NaCl (a source of Cl^-): the extra Cl^- raises Q above K_{sp} , so the equilibrium shifts **left** — more AgCl precipitates, and less dissolves.

■ Le Chatelier view

Adding a product (Cl^-) stresses the system; it shifts to consume the added ion, forming more solid. The salt is **less** soluble than in pure water.

■ The practical result

You can reduce how much of a slightly soluble salt dissolves by adding a soluble salt sharing one of its ions.

2 Practice

Now apply the methods above.

2.1 Does adding a common ion increase or decrease solubility? [1]

2.2 For $\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$, name a salt that provides a common ion. [1]

2.3 Which way does the equilibrium shift when a common ion is added? [1]

3 Exam-style questions

3.1 Adding NaCl to a saturated AgCl solution makes AgCl [1]

- **A** more soluble
 - **B** less soluble
 - **C** unaffected
 - **D** a gas
-

3.2 Consider $\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+} + 2\text{F}^-$. Sodium fluoride (NaF) is added.

(a) State the effect on the solubility of CaF_2 . [1]

(b) Explain using Le Chatelier's principle. [2]

3.3 Explain, in terms of Q and K_{sp} , why adding a common ion causes precipitation. [2]

Solutions

2.1 Decrease.

2.2 NaCl (or any soluble chloride).

2.3 Toward the solid (left, toward less dissolving).

3.1 B — less soluble.

3.2 (a) It decreases. (b) Adding F^- (a product) stresses the equilibrium, which shifts left to consume it, forming more solid CaF_2 — so less dissolves.

3.3 The added common ion raises the ion product Q above K_{sp} ; the system responds by precipitating solid until Q falls back to K_{sp} .

Question 1

1. A student performs a calorimetry experiment with KCl.

Part A

Consider the K^+ ion in KCl.

- i. **Write** the complete ground-state electron configuration for the potassium ion, K^+ .
- ii. Which has the larger radius, the K^+ ion or the K atom? **Explain** your reasoning using principles of atomic structure.

The following information applies to parts B, C, D, and E.

A student performs an experiment to determine the enthalpy of solution, ΔH_{soln} , of KCl. The student places water in a calorimeter, measures the initial temperature, adds $\text{KCl}(s)$, and stirs until the KCl dissolves completely. The temperature is continuously monitored during the experiment. Data from the experiment are given in the following table.

Mass of water	97.5 g
Mass of $\text{KCl}(s)$	6.80 g
Initial temperature of water	24.5°C
Final temperature of solution	21.1°C

Part B

Describe how the student can use the temperature readings during the experiment to determine when the dissolution is complete.

Part C

Use the data in the table to do the following.

- i. **Calculate** the magnitude of the thermal energy, q , in joules, transferred during the dissolution. Show the work that leads to your answer. (Assume that the solution has a specific heat capacity of $3.95 \text{ J/(g}\cdot^\circ\text{C)}$.)
- ii. **Calculate** the value of the molar enthalpy of solution, ΔH_{soln} , in kJ/mol , for KCl given that 0.0912 mol of KCl dissolved. Show the work that leads to your answer. Include the sign with your answer.

Part D

The calorimeter is not perfectly insulated. Would this cause the magnitude of ΔH_{soln} calculated in part C (ii) to be greater than, less than, or equal to the accepted value? **Justify** your answer.

Part E

The student performs a second experiment using the same mass of water but 6.80 g of $\text{RbCl}(s)$ instead of 6.80 g of $\text{KCl}(s)$. The magnitude of the molar enthalpy of solution, ΔH_{soln} , of RbCl is approximately equal to that of KCl .

Is the magnitude of ΔT in the RbCl experiment greater than, less than, or equal to that in the KCl experiment? **Justify** your answer. (Assume that the specific heat capacities of the solutions are equal.)

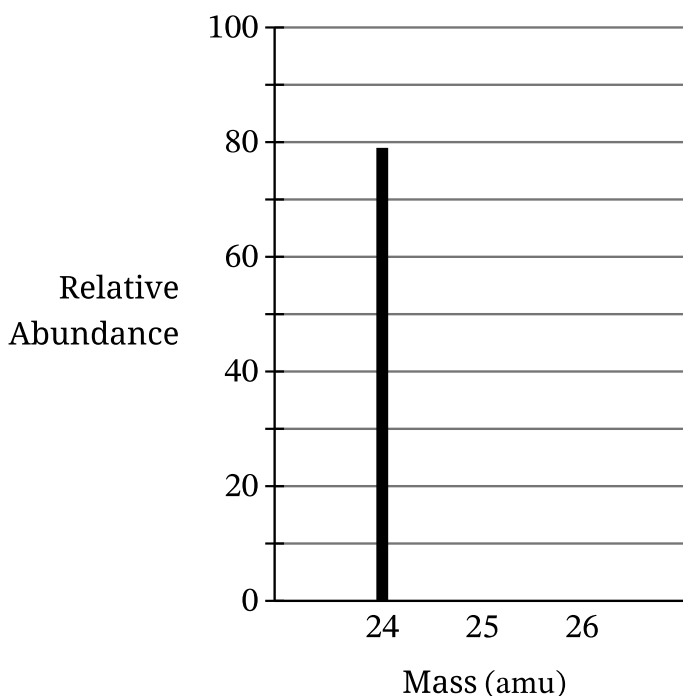
Part F

RbCl has a K_{sp} of 57 at 20°C .

- i. **Write** the net ionic equation for the dissolution of RbCl in pure water.
- ii. **Calculate** the molar solubility of RbCl in a saturated solution at 20°C . Show the work that leads to your answer.
- iii. A second saturated solution is prepared by dissolving $\text{RbCl}(s)$ in $1.0\text{ M KCl}(aq)$ at 20°C instead of in pure water. Will the molar solubility of RbCl in $1.0\text{ M KCl}(aq)$ be greater than, less than, or equal to the molar solubility calculated in part F (ii)? **Justify** your answer.

1. Answer the following questions about magnesium.

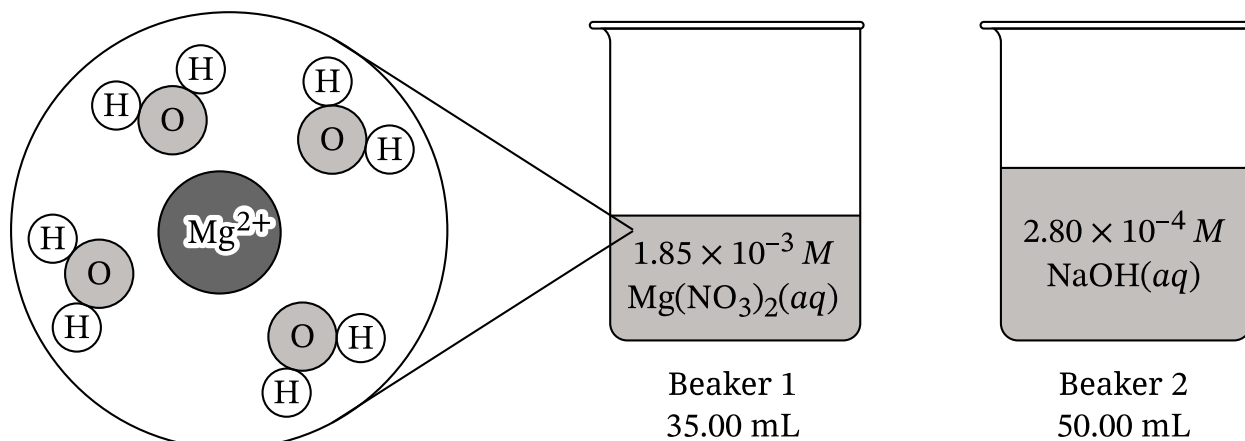
A. An incomplete mass spectrum for magnesium is shown in the diagram.



The percent abundance of magnesium-24 is 79%. The percent abundances of the other two natural isotopes of magnesium, magnesium-25 and magnesium-26, are approximately equal.

- i. Complete the mass spectrum in part A by drawing thick lines in the appropriate locations to represent the percent abundance of magnesium-25 and magnesium-26.
- ii. Describe the difference in atomic structure that accounts for the difference in mass between magnesium-25 and magnesium-26.

A student prepares a $1.85 \times 10^{-3} M$ solution of $\text{Mg}(\text{NO}_3)_2(aq)$ in beaker 1 and a $2.80 \times 10^{-4} M$ solution of $\text{NaOH}(aq)$ in beaker 2, as shown.

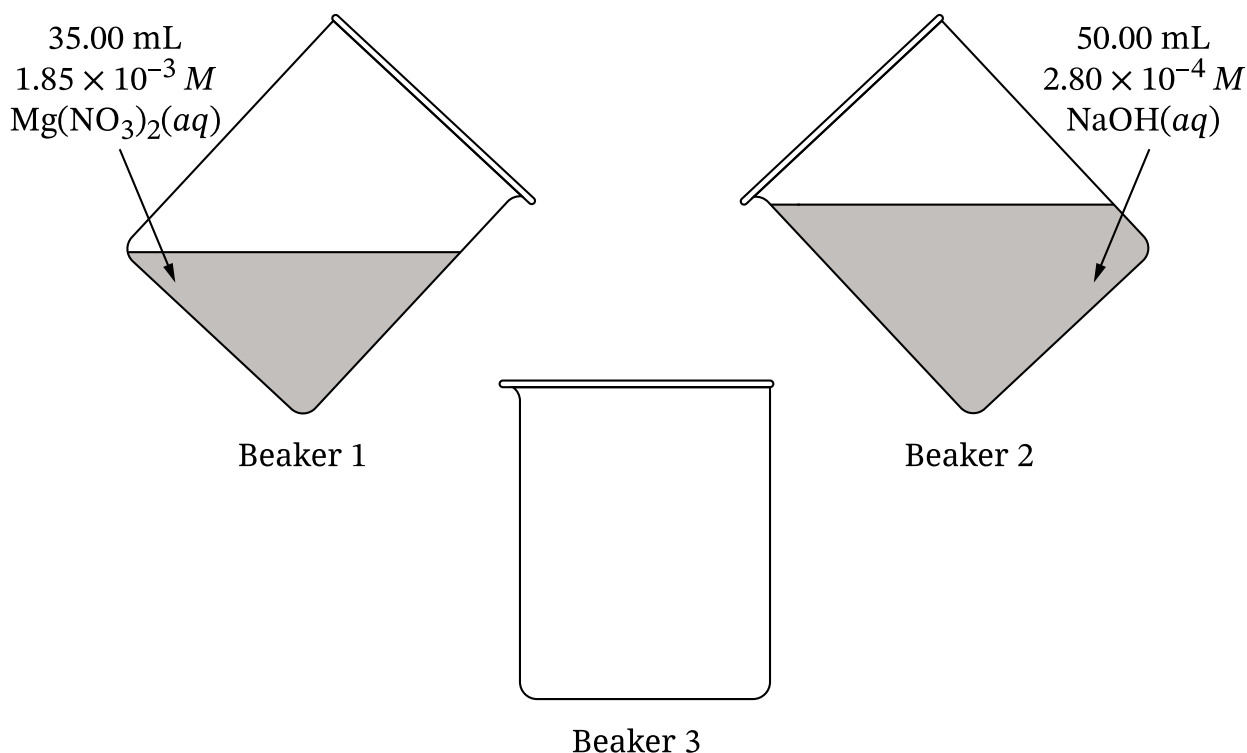


B. The particle diagram shown represents a magnesium ion, Mg^{2+} , in beaker 1. A sodium ion, Na^+ , in beaker 2 has a weaker attraction to water than the Mg^{2+} does. Explain this phenomenon using Coulomb's law and each of the following.

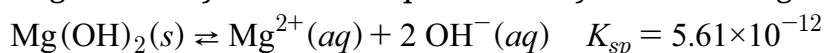
- The relative charge of the ions
- The relative radii of the ions

C. Calculate the pH of the solution in beaker 2.

- D. A student combines 35.00 mL of $1.85 \times 10^{-3} M \text{Mg}(\text{NO}_3)_2(aq)$ with 50.00 mL of $2.80 \times 10^{-4} M \text{NaOH}(aq)$, as shown in the diagram. Calculate $[\text{Mg}^{2+}]$ after the two solutions are combined but before any reaction takes place. (Assume that volumes are additive.)

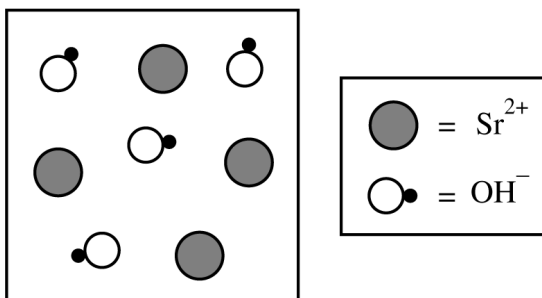


- E. The dissolution of magnesium hydroxide is represented by the following equation.



- Write the expression for the solubility product constant, K_{sp} .
 - After the two solutions are combined in beaker 3 as described in part D, but before any reaction takes place, $[\text{OH}^{-}] = 1.65 \times 10^{-4} M$. Using your answer to part D, calculate the value of the reaction quotient, Q .
 - Using the reaction quotient, Q , predict whether a precipitate should form as the mixture in beaker 3 approaches equilibrium. Justify your answer.
- F. In a separate experiment, the student adds $\text{HNO}_3(aq)$ to decrease the pH of a saturated solution containing undissolved $\text{Mg}(\text{OH})_2(s)$. Does the amount of undissolved $\text{Mg}(\text{OH})_2(s)$ increase, decrease, or remain the same as the $\text{HNO}_3(aq)$ is added? Justify your answer.

Strontium hydroxide dissolves in water according to the following equation. The K_{sp} expression for strontium hydroxide is provided.



- (a) A student draws the particulate diagram shown to represent the ions present in an aqueous solution of $\text{Sr}(\text{OH})_2$. (Water molecules are intentionally omitted.) Identify the error in the student's drawing.
- (b) The student prepares a saturated solution by adding excess $\text{Sr}(\text{OH})_2(s)$ to distilled water and stirring until no more solid dissolves. The student then determines that $[\text{Sr}^{2+}] = 0.043\text{ M}$ in the solution.
- (i) Calculate the value of $[\text{OH}^-]$ in the solution.
- (ii) Calculate the value of K_{sp} for $\text{Sr}(\text{OH})_2$.

GO ON TO THE NEXT PAGE.

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

- (c) The student prepares a second saturated solution of $\text{Sr}(\text{OH})_2$ in aqueous $0.10\text{ }M\text{ Sr}(\text{NO}_3)_2$ instead of water. Will the value of $[\text{OH}^-]$ in the second solution be greater than, less than, or equal to the value in the first solution? Justify your answer. (Assume constant temperature.)

STOP

END OF EXAM

. A Lewis electron-dot diagram of the oxalate ion, $\text{C}_2\text{O}_4^{2-}$, is shown.

(a) Identify the hybridization of the valence orbitals of either carbon atom in the oxalate ion.

(b) Silver oxalate, $\text{Ag}_2\text{C}_2\text{O}_4(s)$, is slightly soluble in water. The value of K_{sp} for $\text{Ag}_2\text{C}_2\text{O}_4$ is 5.40×10^{-12} .

(i) Write the expression for the solubility-product constant, K_{sp} , for $\text{Ag}_2\text{C}_2\text{O}_4$.

(ii) Calculate the molar solubility of $\text{Ag}_2\text{C}_2\text{O}_4$ in neutral distilled water.

(iii) The molar solubility of $\text{Ag}_2\text{C}_2\text{O}_4$ increases when it is dissolved in $0.5\text{ M HClO}_4(aq)$ instead of neutral distilled water. Write a balanced, net-ionic equation for the process that occurs between species in solution that contributes to the increased solubility of $\text{Ag}_2\text{C}_2\text{O}_4(aq)$ in $\text{HClO}_4(aq)$.

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END OF EXAM

6. A student is studying the properties of CaSO_4 and PbSO_4 . The student has samples of both compounds, which are white powders.

(a) The student tests the electrical conductivity of each solid and observes that neither solid conducts electricity. Describe the structures of the solids that account for their inability to conduct electricity.

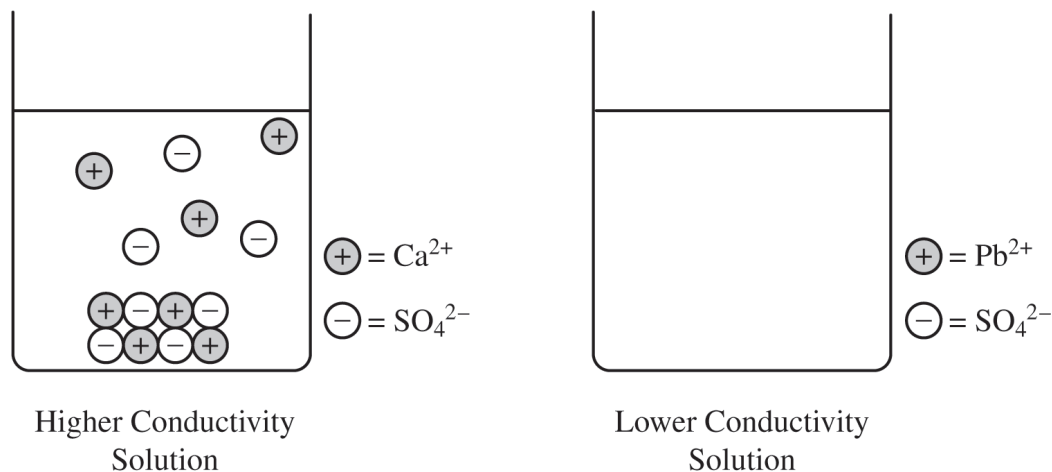
The student places excess $\text{CaSO}_4(s)$ in a beaker containing 100 mL of water and places excess $\text{PbSO}_4(s)$ in another beaker containing 100 mL of water. The student stirs the contents of the beakers and then measures the electrical conductivity of the solution in each beaker. The student observes that the conductivity of the solution in the beaker containing the $\text{CaSO}_4(s)$ is higher than the conductivity of the solution in the beaker containing the $\text{PbSO}_4(s)$.

(b) Which compound is more soluble in water, $\text{CaSO}_4(s)$ or $\text{PbSO}_4(s)$? Justify your answer based on the results of the conductivity test.

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Use a pencil or pen with black or dark blue ink only. Do NOT write your name. Do NOT write outside the box.

The left side of the diagram below shows a particulate representation of the contents of the beaker containing the $\text{CaSO}_4(s)$ from the solution conductivity experiment.



(c) Draw a particulate representation of $\text{PbSO}_4(s)$ and the ions dissolved in the solution in the beaker on the right in the diagram. Draw the particles to look like those shown to the right of the beaker. Draw an appropriate number of dissolved ions relative to the number of dissolved ions in the beaker on the left.

(d) The student attempts to increase the solubility of $\text{CaSO}_4(s)$ by adding 10.0 mL of 2 M $\text{H}_2\text{SO}_4(aq)$ to the beaker, and observes that additional precipitate forms in the beaker. Explain this observation.

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4. Answer the following questions about the solubility of $\text{Ca}(\text{OH})_2$ ($K_{sp} = 1.3 \times 10^{-6}$).

- (a) Write a balanced chemical equation for the dissolution of $\text{Ca}(\text{OH})_2(s)$ in pure water.
- (b) Calculate the molar solubility of $\text{Ca}(\text{OH})_2$ in 0.10 M $\text{Ca}(\text{NO}_3)_2$.
- (c) In the box below, complete a particle representation diagram that includes four water molecules with proper orientation around the Ca^{2+} ion.

Represent water molecules as

