EXAM 1
PRACTICE PROBLEMS: SOLUTIONS

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PRACTICE PROBLEM 1.1

Consider the decomposition of nitrous oxide:

Experiment	$[N_2O]_0$ (M)	Initial Rate (M/min)
1	0.387	0.00190
2	1.161	0.0171
3	1.935	0.0476

$$2\ N_2O\ (g) \rightarrow 2\ N_2\ (g) + O_2\ (g)$$

Given the following initial rates data collected at 321 K, determine the rate law for the reaction.

— answer —

Begin by constructing the generic rate law: $\qquad$ Rate $= k[N_2O]^a$

Understand that we will need to solve for the order a using the isolation method.

Let's solve for a, which is the order of the reaction with respect to $[N_2O]$. Compare experiments 2 and 1:

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[N_2O]_2^a}{k[N_2O]_1^a} \qquad \textcolor{red}{k \text{ cancels}}$$

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{[NO_2]_2^a}{[NO_2]_1^a}$$

$$\frac{0.0171\ \text{M/s}}{0.00190\ \text{M/s}} = \left(\frac{1.161\ \text{M}}{0.387\ \text{M}}\right)^a$$

$$9 = 3^a$$

$$\textcolor{red}{a = 2}$$

This means that our rate law is: $\qquad$ $\textcolor{red}{\text{Rate} = k[N_2O]^2}$

Consider the decomposition of nitrous oxide:

$$2 \, N_2O \, (g) \rightarrow 2 \, N_2 \, (g) + O_2 \, (g)$$

Determine the value and units for the rate constant k.

– answer –

Experiment	$[N_2O]_0$ (M)	Initial Rate (M/min)
1	0.387	0.00190
2	1.161	0.0171
3	1.935	0.0476

From the previous slide, our rate law is: $\text{Rate} = k[N_2O]^2$

Now that we have our rate law we can solve for the rate constant, k, by plugging in the values from any experiment.

I'll use experiment 1:
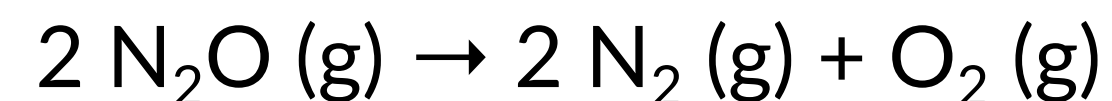
$$\text{Rate}_1 = k[N_2O]_1^2$$

$$0.00190 \, \frac{M}{s} = k(0.387 \, M)^2$$

$$k = 0.0127 \, M^{-1} \cdot s^{-1}$$

Consider the decomposition of nitrous oxide:

$$2 \text{ N}_2\text{O (g)} \rightarrow 2 \text{ N}_2 \text{ (g)} + \text{O}_2 \text{ (g)}$$

If we start with $[\text{N}_2\text{O}] = 1.00$ M, how long would it take for this reaction to go to 15% completion?

— answer —

From the previous slides, our rate law is: $\text{Rate} = k[\text{N}_2\text{O}]^2$ and $k = 0.0127 \text{ M}^{-1} \cdot \text{s}^{-1}$

Because the reaction is 2nd order with respect to $[\text{N}_2\text{O}]$, the integrated rate law is:

$$\frac{1}{[\text{N}_2\text{O}]_t} = kt + \frac{1}{[\text{N}_2\text{O}]_0}$$

Consider what it means for our reaction to go to 15% completion. This is a decomposition reaction, so being 15% complete means we have only decomposed 15% of our initial concentration. In other words,

$$[\text{N}_2\text{O}]_t = 1.00 \text{ M} - 0.15 \times 1.00 \text{ M} = 0.85 \text{ M}.$$

Now we can solve for the time it takes to get to this concentration:

$$\frac{1}{[\text{N}_2\text{O}]_t} = kt + \frac{1}{[\text{N}_2\text{O}]_0}$$

$$\frac{1}{0.85 \text{ M}} = (0.0126_9 \text{ M}^{-1} \cdot \text{s}^{-1})t + \frac{1}{1.00 \text{ M}}$$

$$t = 14 \text{ s}$$

Consider the decomposition of nitrous oxide:

$$2 \text{ N}_2\text{O (g)} \rightarrow 2 \text{ N}_2 \text{ (g)} + \text{O}_2 \text{ (g)}$$

Which of the following proposed mechanisms is <u>not valid</u>?

Justify your choice briefly.

— answer —

From the previous slides, our rate law is: $\text{Rate} = k[\text{N}_2\text{O}]^2$

To find a valid mechanism, we need the rate law for the <u>slowest elementary</u> step to <u>match</u> the <u>overall rate law</u>.

I $\text{N}_2\text{O} \rightleftharpoons \text{N}_2 + \text{O}$ (fast)
      $\text{N}_2\text{O} + \text{O} \rightarrow \text{N}_2 + \text{O}_2$ (slow)

II $2 \text{ N}_2\text{O} \rightleftharpoons \text{N}_4\text{O}_2$ (fast)
      $\text{N}_4\text{O}_2 \rightarrow 2 \text{ N}_2 + \text{O}_2$ (slow)

III $\text{N}_2\text{O} + \text{N}_2\text{O} \rightarrow 2 \text{ N}_2 + \text{O} + \text{O}$ (slow)
      $\text{O} + \text{O} \rightarrow \text{O}_2$ (fast)

Mechanism I		Elementary rate laws
Step 1: $\text{N}_2\text{O} \rightleftharpoons \text{N}_2 + \text{O}$	(fast)	$K_c = \dfrac{[\text{N}_2][\text{O}]}{[\text{N}_2\text{O}]} \Longrightarrow [\text{O}] = K_c \dfrac{[\text{N}_2\text{O}]}{[\text{N}_2]}$
Step 2: $\text{N}_2\text{O} + \text{O} \rightarrow \text{N}_2 + \text{O}_2$	(slow)	$\text{rate}_2 = k_2[\text{N}_2\text{O}][\text{O}]$
		$= k_2[\text{N}_2\text{O}]K_c \dfrac{[\text{N}_2\text{O}]}{[\text{N}_2]}$
		$= k'[\text{N}_2\text{O}]^2[\text{N}_2]^{-1}$

Mechanism III		Elementary rate laws
Step 1: $\text{N}_2\text{O} + \text{N}_2\text{O} \rightarrow 2 \text{ N}_2 + \text{O} + \text{O}$	(slow)	$\text{rate}_1 = k_1[\text{N}_2\text{O}]^2$
Step 2: $\text{O} + \text{O} \rightarrow \text{O}_2$	(fast)	

Mechanism I is <u>not</u> valid.

Mechanism II		Elementary rate laws
Step 1: $2 \text{ N}_2\text{O} \rightleftharpoons \text{N}_4\text{O}_2$	(fast)	$K_c = \dfrac{[\text{N}_4\text{O}_2]}{[\text{N}_2\text{O}]^2} \Longrightarrow [\text{N}_4\text{O}_2] = K_c[\text{N}_2\text{O}]^2$
Step 2: $\text{N}_4\text{O}_2 \rightarrow 2 \text{ N}_2 + \text{O}_2$	(slow)	$\text{rate}_2 = k_2[\text{N}_4\text{O}_2]$
		$= k_2 K_c[\text{N}_2\text{O}]^2$
		$= k'[\text{N}_2\text{O}]^2$

Some notes about rate laws:
- We can write elementary rate laws based on the stoichiometry of the elementary steps.
- The rate laws can only be depend on reactants, not products or intermediates.
- If an intermediate is present in the elementary rate law, it must be re-expressed in terms of reactants somehow. (see Mechanism I or II)
- If a prior step is in equilibrium, the reactant or product concentrations can be expressed in terms of the K_c expression. (see Mechanism I or II)

PRACTICE PROBLEM 2.1

Hypochlorous acid (HClO) is a weak acid with a $K_a = 2.98 \times 10^{-8}$ at 298 K.

What is the pH of a 100. mL solution of 2.01 M HClO?

− answer −

Step 1: Note that HClO is a weak acid because K_a is small, so we have to consider the weak acid equilibrium in water.

Step 2: Write out the balanced equilibrium expression for the weak acid dissociation and the K_a expression.

Step 3: Construct an ICE chart. Fill in the initial values, then the stoichiometric changes (x), and then equilibrium concentrations.

Step 4: We can use the equilibrium concentration values to plug into our expression for K_a.

Step 5: Finally solve for x. What is x?

Step 6: Calculate the pH.

	HClO	$\rightleftharpoons$	H⁺	+	ClO⁻
I	2.01 M		0		0
C	– x		+ x		+ x
E	2.01 – x		x		x

Because the value of K_a is very small, we know that the system will undergo very little change (x value) toward the right in order to achieve equilibrium. In other words, we can take "x" to be very small/negligible and invoke the approximation that:
2.01 – x ≈ 2.01

$$K_a = \frac{[H^+][ClO^-]}{[HClO]} = 2.98 \times 10^{-8}$$

$$2.98 \times 10^{-8} = \frac{(x)(x)}{2.01 - x}$$

$$2.98 \times 10^{-8} \approx \frac{x^2}{2.01}$$

$$x = 2.44_7 \times 10^{-4} \text{ M} = [H^+]$$

$$pH = -\log(2.44_7 \times 10^{-4}) = 3.611$$

PRACTICE PROBLEM 2.2

Hypochlorous acid (HClO) is a weak acid with a $K_a = 2.98 \times 10^{-8}$ at 298 K.

To 100. mL of 2.01 M HClO we add 0.080 moles of NaOH. What is the pH of the resulting solution?

You may assume no change in volume or temperature.

– answer –

Because NaOH is a strong base it dissociates completely: NaOH → Na$^+$ + OH$^-$

Step 1: Determine the number of moles of OH$^-$ and HClO:

$$n_{\text{HClO}} = 0.100 \text{ L} \times \frac{2.01 \text{ mol HClO}}{1 \text{ L}} = 0.201 \text{ mol HClO} \quad n_{\text{OH}^-} = 0.080 \text{ mol OH}^-$$

Step 2: Consider the reaction (not equilibrium) between HClO and OH$^-$:

Step 3: Note we are <u>not</u> at the equivalence point, so can use the Henderson-Hasselbach equation to find the pH.

	HClO	+	OH$^-$	→	ClO$^-$	+	H$_2$O
I	0.201 mol		0.080 mol		0 mol		n/a
C	– 0.080		– 0.080		+ 0.080		n/a
"E"	0.121		0		0.080		n/a

Convert to M by dividing by V$_{tot}$ = 0.100 L

| 1.21 M | 0 M | 0.80 M | n/a |

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

$$= -\log(2.98 \times 10^{-8}) + \log\frac{[0.80]}{[1.21]}$$

$$= 7.52_6 - 0.17_9$$

$$\text{pH} = 7.35$$

PRACTICE PROBLEM 2.2

Hypochlorous acid (HClO) is a weak acid with a $K_a = 2.98 \times 10^{-8}$ at 298 K.

How many grams of solid NaClO would need to be added to 100. mL of 2.01 M HClO to produce a solution with a pH = 7.60?

You may assume no change in volume or temperature.

– answer –

Understand that we are trying to make a buffer: weak acid (HClO) and a conjugate-base (ClO⁻) from a salt (NaClO).

Start with the Henderson-Hasselbach equation to solve for the concentration of ClO⁻ that would yield pH – 7.60:

$$pH = pK_a + \log\frac{[\text{ClO}^-]}{[\text{HClO}]}$$

$$7.60 = -\log(2.98 \times 10^{-8}) + \log\frac{[\text{ClO}^-]}{[2.01]}$$

$$7.60 = 7.52_6 + \log\frac{[\text{ClO}^-]}{[2.01]}$$

$$0.07_4 = \log\frac{[\text{ClO}^-]}{[2.01]}$$

$$0.07_4 = \log[\text{ClO}^-] - \log[2.01]$$

$$0.15_7 = \log[\text{ClO}^-]$$

$$[\text{ClO}^-] = 2.3_8 \text{ M}$$

Convert from the concentration of ClO⁻ to moles of ClO⁻ to moles of NaClO to mass of NaClO:

$$m_{\text{ClO}^-} = 0.100 \text{ L} \times \frac{2.3_8 \text{ mol ClO}^-}{1 \text{ L}} \times \frac{1 \text{ mol NaClO}}{1 \text{ mol ClO}^-} \times \frac{74.44 \text{ g NaClO}}{1 \text{ mol NaClO}} = 18 \text{ g NaClO}$$

PRACTICE PROBLEM 3.1

Consider the equilibrium reaction: $\quad$ Ag^+ (aq) + 2 NH_3 (aq) $\rightleftharpoons$ $[Ag(NH_3)_2]^+$ (aq) $\quad\quad$ $K_c = 1.7 \times 10^7$ (at 298 K)

If the initial solution contains only 0.10 M $[Ag(NH_3)_2]^+$, what is the equilibrium concentration of NH_3 in solution?

– answer –

Step 1: Write down the expression for the equilibrium constant.

Step 2: Prepare an ICE chart (Initial, Change, and Equilibrium)

Step 3: Use the Equilibrium (E) values to plug into the K_c expression.

Step 4: Solve for "x".

Step 5: Solve the $[NH_3]$ at equilibrium.

	Ag^+	+	2 NH_3	$\rightleftharpoons$	$[Ag(NH_3)_2]^+$
I	0 M		0 M		0.10 M
C	+ x		+ 2x		−x
E	x		2x		0.10 – x

$$[NH_3]_{eq} = 2x = 2(0.0011_4 \text{ M}) = 0.0023 \text{ M}$$

$$K_c = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}$$

$$1.7 \times 10^7 = \frac{0.10 - x}{x \cdot (2x)^2}$$

$$(4x^3)(1.7 \times 10^7) \approx 0.10 - x$$

$$(6.80 \times 10^7)x^3 = 0.10$$

$$x^3 = 1.4_7 \times 10^{-9}$$

$$x = 0.0011_4$$

It is okay to say that x is negligibly small and approximate:
$$0.10 - x \approx 0.10$$

You may be tempted not to invoke this approximation because K_c is large, but pay attention to the direction the reaction will shift. The reaction will shift left, so we are actually interested in the magnitude of the reverse process:
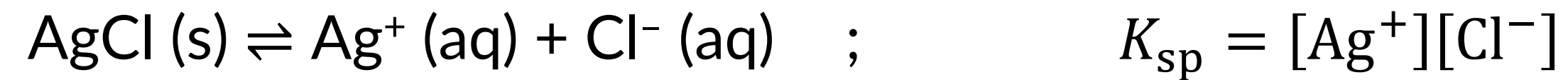
$$\frac{1}{K_c} = 5.9 \times 10^{-8}$$

PRACTICE PROBLEM 3.2

To a 0.10 M KCl solution, $AgNO_3$ is added gradually until a precipitate beings to form. If the concentration of $[Ag^+]$ at the time of precipitate formation is 1.6×10^{-9} M, what is the value of K_{sp} for AgCl?

— answer —

Step 1: Write the dissolution equilibrium and the equilibrium constant expression for K_{sp}.

$$AgCl\ (s) \rightleftharpoons Ag^+\ (aq) + Cl^-\ (aq) \quad ; \qquad K_{sp} = [Ag^+][Cl^-]$$

Step 2: Understand that at the instant of precipitation formation, the value of $Q = K_{sp}$.

Step 3: Determine the concentration of Ag^+ and Cl^- at the instant of precipitation.

$$[Ag^+] = 1.6 \times 10^{-9}\ M \quad [Cl^-] = \frac{0.10\ \text{mol KCl}}{1\ L} \times \frac{1\ \text{mol Cl}^-}{1\ \text{mol KCl}} = 0.10\ M$$

Step 4: Plug these values into the $Q = K_{sp}$ expression:

$$Q = [Ag^+][Cl^-]$$
$$= (1.6 \times 10^{-9})(0.10)$$
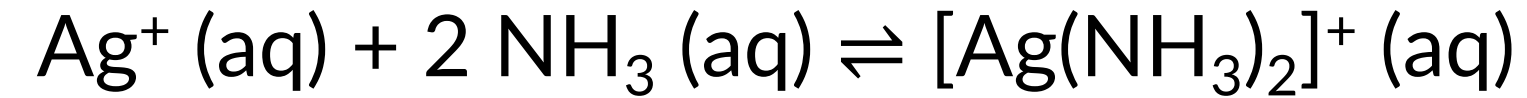$$Q = 1.6 \times 10^{-10} = K_{sp}$$

PRACTICE PROBLEM 3.3

Do you expect AgCl to be more or less soluble in a solution of pure NH_3 than in a solution of pure water? Justify your answer.

Refer to Practice Problem 3.1.

From Practice Problem 3.1: Ag^+ (aq) + 2 NH_3 (aq) $\rightleftharpoons$ $[Ag(NH_3)_2]^+$ (aq) $K_c = \dfrac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = 1.7 \times 10^7$

From the previous slide: AgCl (s) $\rightleftharpoons$ Ag^+ (aq) + Cl^- (aq) $K_{sp} = [Ag^+][Cl^-] = 1.6 \times 10^{-10}$

If we dissolved the AgCl (s) into a solution of pure NH_3, the dissociated Ag^+ ions will combine with the NH3 molecules to form the complex ion $[Ag(NH_3)_2]^+$.

Note that $[Ag(NH_3)_2]^+$ has a large K_c value, which means that $[Ag(NH_3)_2]^+$ will not dissociate back into Ag^+ and NH_3 once formed.

Therefore, AgCl (s) will have to constantly dissolve because the concentration of $[Ag^+]$ is constantly being depleted by formation of the complex ion.

So AgCl (s) is <u>more soluble</u> in NH_3.

PRACTICE PROBLEM 4.1

Consider the gaseous equilibrium: N_2 (g) + 3 H_2 (g) $\rightleftharpoons$ 2 NH_3 (g)

At 298 K, the value of K_c for this reaction is 0.060. Write an expression for K_p using K_c at 298K.

− answer −

Step 1: Write the expression for K_p for the equilibrium.

Step 2: Use the ideal gas law to related partial pressures and concentrations: $P_{N_2}V = n_{N_2}RT$

$$P_{N_2} = \frac{n_{N_2}}{V}RT$$

$$P_{N_2} = [N_2]RT$$

Step 3: Substitute the relationship from Step 2 into the expression for K_p:

Note that $\Delta n = \Sigma n_{prod} = \Sigma n_{react} = 2 \text{ mol} - 4 \text{ mol} = -2$

$$K_p = \frac{P_{NH_3}^2}{P_{N_2}P_{H_2}^3} = \frac{([NH_3]RT)^2}{([N_2]RT)^1([H_2]RT)^3} = \frac{[NH_3]^2}{[N_2]^1[H_2]^3} \cdot \frac{(RT)^2}{(RT)^4} = K_c \cdot (RT)^{\Delta n} = K_c \cdot (RT)^{-2}$$

PRACTICE PROBLEM 4.2

Which of the following aqueous salt solutions are acidic? Assume all are 1.0 M.

(a) $NaNO_2$

(b) KCH_3COO

(c) NH_4Br

(d) $BaCl_2$

— answer —

For each salt, we can write out the reaction of the ions with water to determine if it is acidic, basic, or neutral.

|	Salt	Reaction of ions with water	
(a)	$NaNO_2$	$Na^+ + H_2O \rightarrow$ no reaction $NO_2^- + H_2O \rightarrow HNO_2 + OH^-$	Basic
(b)	KCH_3COO	$K^+ + H_2O \rightarrow$ no reaction $CH_3COO^- + H_2O \rightarrow CH_3COOH + OH^-$	Basic
(c)	NH_4Br	$NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$ $Br^- + H_2O \rightarrow$ no reaction	Acidic
(d)	$BaCl_2$	$Ba^{2+} + H_2O \rightarrow$ no reaction $Cl^- + H_2O \rightarrow$ no reaction	Neutral

The following concentration-time data are plotted below for the decomposition of hydrogen peroxide (H_2O_2) at 298 K.

$$2\ H_2O_2\ (aq) \rightarrow 2\ H_2O\ (l) + O_2\ (g)$$

What is the order of the reaction with respect to [H_2O_2]?

Time (s)	[H_2O_2] (M)
0	1.00
120.	0.91
300.	0.78
600.	0.59
1200.	0.37
1800.	0.22
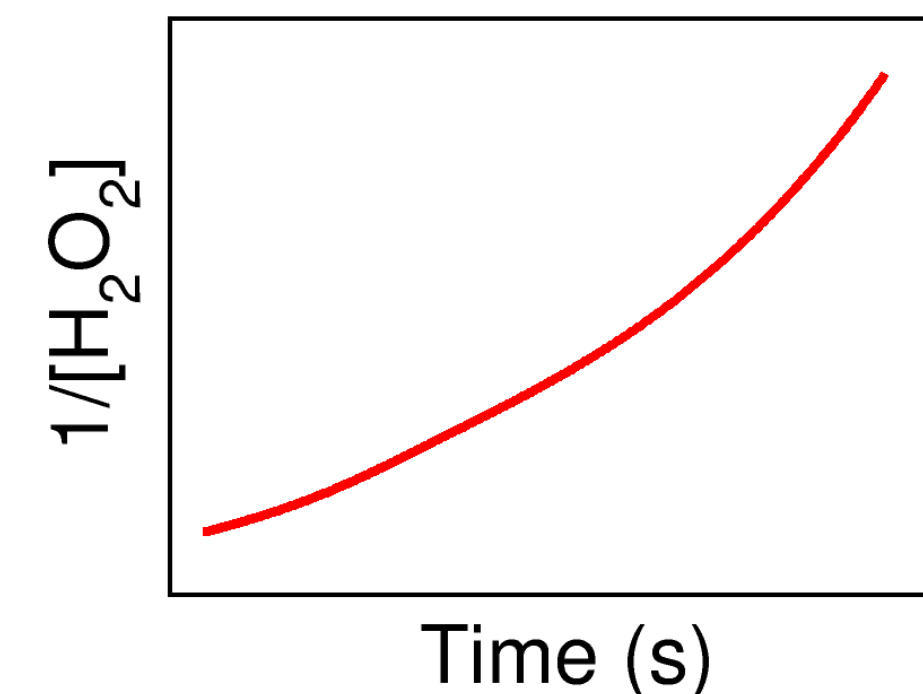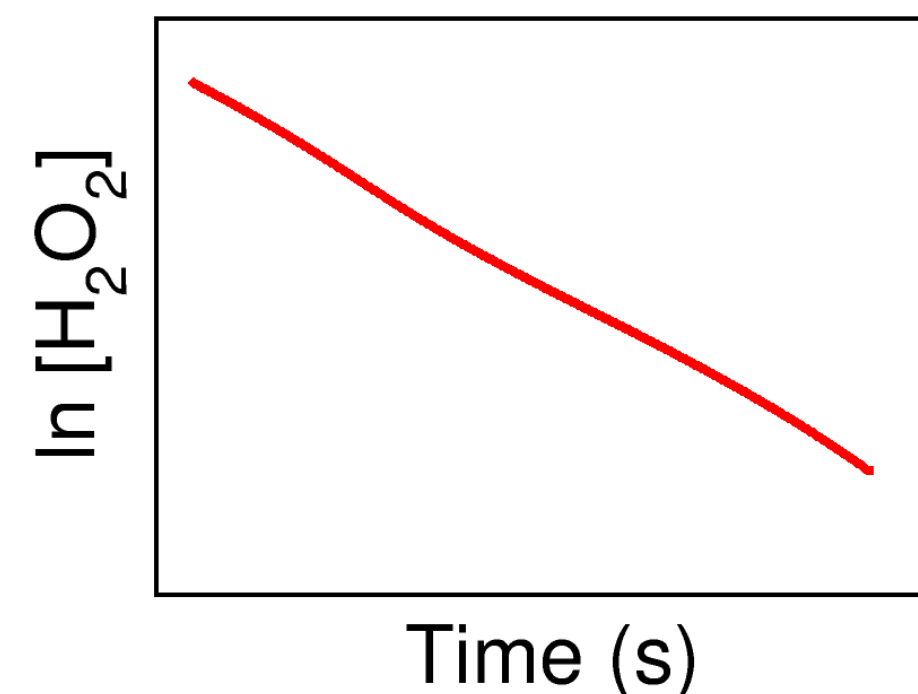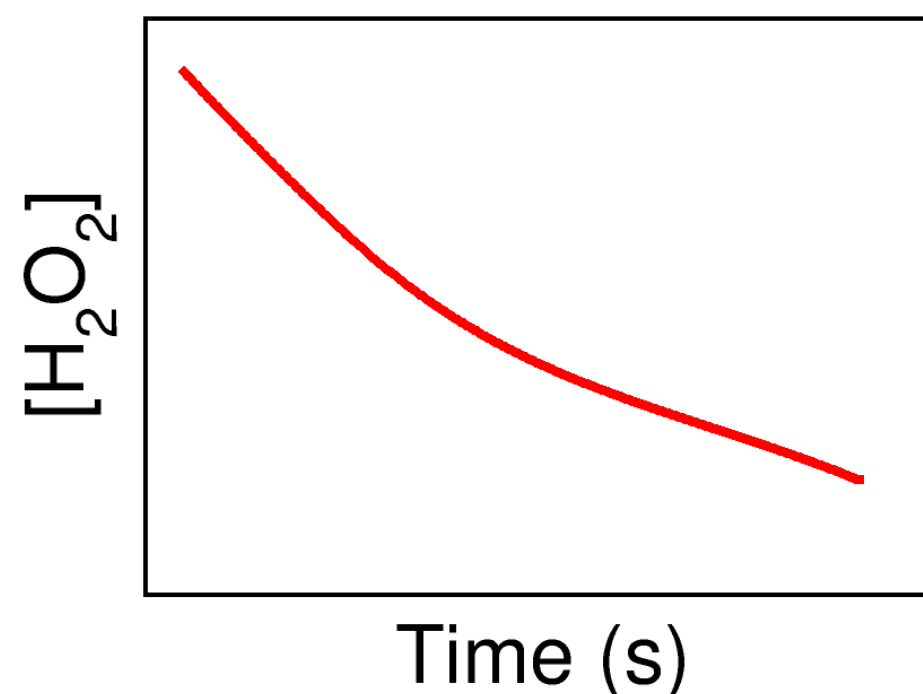
− answer −

Recall that the concentration-time plot that gives a straight line ($y = mx + b$) gives us the order of the reaction.

- If [H_2O_2] vs. time is a linear plot, then the reaction is zero-order with respect to [H_2O_2].

- If ln [H_2O_2] vs. time is a linear plot, then the reaction is first-order with respect to [H_2O_2].

- If 1/[H_2O_2] vs. time is a linear plot, then the reaction is second-order with respect to [H_2O_2].

PRACTICE PROBLEM 4.4

Which of the following changes would increase the concentration of $[Br_2]$ for the following chemical reaction?

$$2\ Br\ (g) \rightleftharpoons Br_2\ (g) \qquad ; \Delta H = -244\ kJ$$

(a) Increasing the temperature.

(b) Increasing the total pressure of the system.

(c) Increasing the volume of the container.

— *answer* —

	Change	Response of system	$[Br_2]$
(a)	Increasing the temperature	Since the reaction is exothermic ($\Delta H < 0$), we can treat heat as a product. $$2\ Br\ (g) \rightleftharpoons Br_2\ (g) + heat$$ Increasing heat would shift the reaction to the left ($Q > K$).	Decreases
(b)	Increasing the total pressure of the system	Because we are increasing the total pressure of the system, the partial pressures of the gases have to increase. As such, the system will shift to the side with a lesser number of moles of gas (right) in order to decrease the partial pressures and total pressure of the system. *However, there would be no shift if we changed the total pressure by adding an inert gas.*	Increase
(c)	Increasing the volume of the container	Increasing the volume of the container will cause the partial pressures of the gases to decrease. As such, the system will shift to the side with a greater number of moles of gas (left) in order to increase the partial pressures.	Decrease