Chapter 9 – Solutions and Aqueous Reactions, Part 2

Chapter Summary:

This chapter will focus on the additional aspects of solutions, usually found in the second semester of a standard general chemistry course (whereas the first part of solutions is usually found in the first semester). Concepts discussed here and explained in example items go into more detail related to intermolecular forces associated with solution formation and properties of solutions. Reactions of solutions are discussed separately in chapters related to equilibrium.

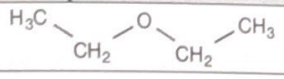
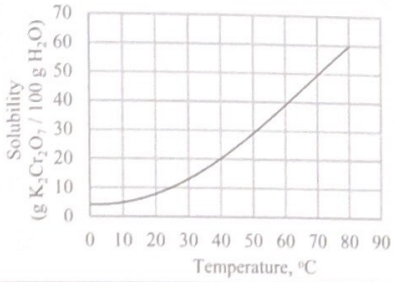
Specific topics covered in this chapter are:

- Solution formation including intermolecular forces in solutions
- Solubility as it relates to intermolecular forces
- Concentration units and conversions between
- Solubility of solids and gases, particularly in aqueous solution
- Colligative properties including freezing point depression, boiling point elevation and osmotic pressure

Previous material that is relevant to your understanding of questions in this chapter include:

- The mole and formula calculations (***Chapter 3***)
- Stoichiometry and balancing equations (***Chapter 4***)
- Molar concentrations and solution stoichiometry (***Chapter 5***)
- Lewis dot structures and polarity (***Chapter 7***)
- Intermolecular forces (***Chapter 8***)

Common representations used in questions related to this material:

Name	Example	Used in questions related to
Structures		Intermolecular forces in solutions
Graphs		Temperature dependence of solubility of solids

Where to find this in your textbook:

The material in this chapter typically aligns to a solutions chapter (could be labeled as "Physical Properties of Solutions") in your textbook. The name of your chapter may vary.

Practice exam:

There are practice exam questions aligned to the material in this chapter. Because there are a limited number of questions on the practice exam, a review of the breadth of the material in this chapter is advised in preparation for your exam.

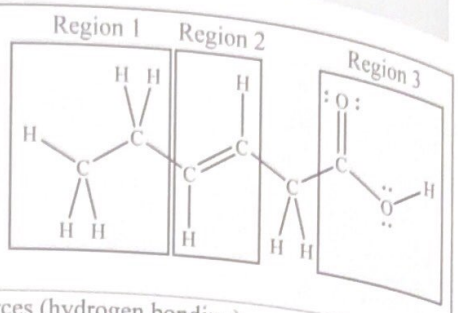
How this fits into the big picture:

The material in this chapter aligns to Intermolecular Interactions (4) as listed on page 12 of this study guide.

Study Questions (SQ)

SQ-1. Conceptual

Where is the hydrophilic (attracted to water) region of the molecule?



(A) Region 1

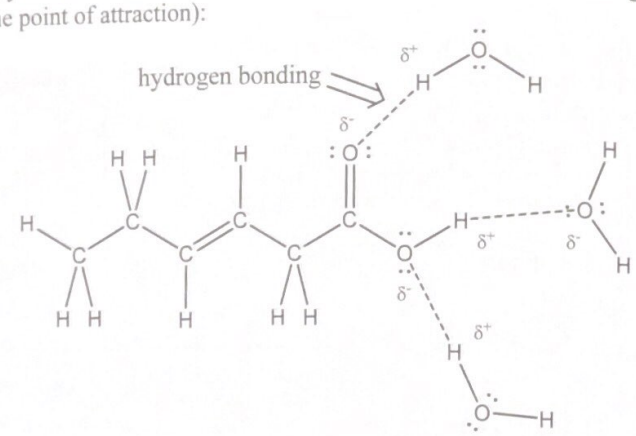
(B) Region 2

(C) Region 3

(D) The three regions are equally hydrophilic

Knowledge Required: (1) Structure of water. (2) Intermolecular forces (hydrogen bonding).

Thinking it Through: As you read this question, you realize the first step will require that you consider the structure of water in relation to the structure of the molecule because you are asked to consider how water and the shown molecule will interact. Continuing along these lines, you then compare the molecules and consider how these will interact within the context of hydrogen bonding. You know that in order to have two molecules form a hydrogen bond, you will need hydrogen bonded to N, O, or F and a lone pair of electrons on N, O, or F. In a pure substance, these will need to be present in one molecule (as all molecules are the same in a pure substance). In a solution, molecules could have only part of these requirements with the other molecules having the other components. Therefore, you draw water molecules in relation to the molecule, including the relative partial charges (to help make the point of attraction):



Therefore, water is attracted to region 3 (Choice **(C)**) and not region 1 (Choice **(A)**) or region 2 (Choice **(B)**) or all three equally (Choice **(D)**).

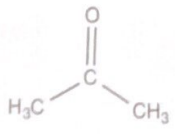
NOTE: Drawing your own representations is often an effective problem-solving strategy in chemistry.

Practice Questions Related to This: **PQ-1** and **PQ-2**

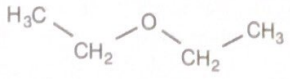
SQ-2. Conceptual

Which molecule is most soluble in water?

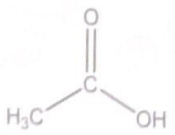
(A)



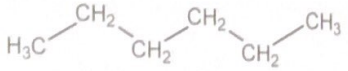
(B)



(C)



(D)

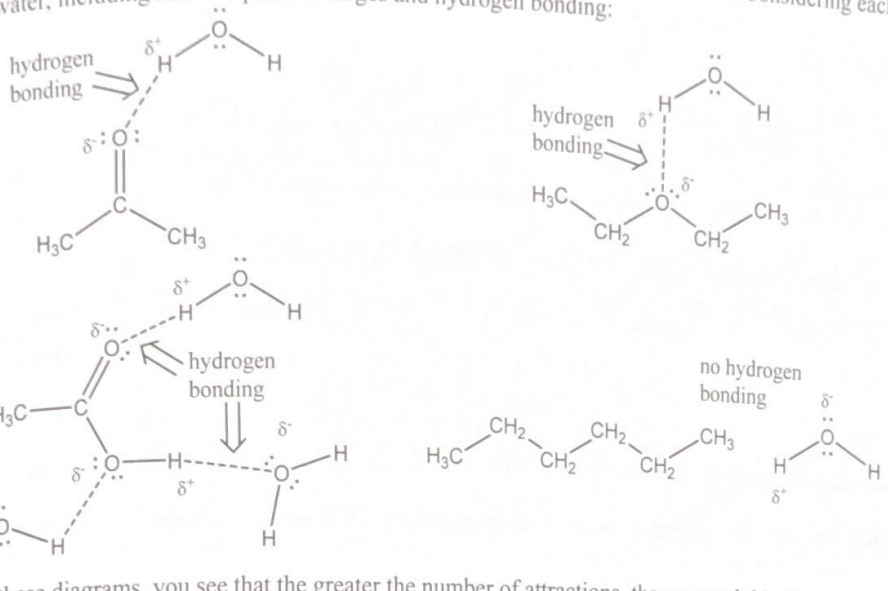


Knowledge Required: (1) Structure of water. (2) Intermolecular forces (hydrogen bonding).

Thinking it Through: Similar to the previous study question, to solve this you are going to consider each structure interacting with the structure of water, paying close attention to components that would support greater attraction due to hydrogen bonding. As a reminder again, in a solution these are:

1. Hydrogen bonded to N, O, or F
2. A lone pair of electrons on N, O, or F

Molecules interacting with water can have one or more locations for this attraction to occur. Considering each molecule with water, including relevant partial charges and hydrogen bonding:



From these diagrams, you see that the greater the number of attractions, the more soluble the molecule will be in water. Adding to this decision, you consider the relative sizes of the molecules (as solubility can be conceptualized as a "substitution" process of the solute molecules into the water molecule's location, thus needing the same relative attractions and size). You see that the molecules are reasonably the same size.

Therefore, you can see that one molecule will not hydrogen bond with water at all (Choice **(D)**), therefore this molecule will be the least soluble in water. You also see that molecules in Choices **(A)** and **(B)** have limited attractions to water making these incorrect as well. Choice **(C)** is ideal for substitution, as it has multiple opportunities for hydrogen bonding, making **(C)** or acetic acid, the correct choice.

Practice Questions Related to This: **PQ-3**, **PQ-4**, and **PQ-5**

SQ-3. A solution of NaCl in water has a concentration of 20.5% by mass. What is the molal concentration of the solution?

Molar mass / g·mol^{-1}	
NaCl	58.44

(A) 0.205 *m* **(B)** 0.258 *m* **(C)** 3.51 *m* **(D)** 4.41 *m*

Knowledge Required: (1) Concentration unit of molality. (2) Concentration unit of percent by mass.

Thinking it Through: You see this question starts by giving you percent by mass and asks you to determine molal concentration. So, to solve this, you first define both concentration units. First for percent by mass, you define this with a general definition, then for a solution and finally further define the mass of the solution as the sum of the masses of the solvent and solute:

$$\text{Percent by mass} = \frac{\text{mass of one component}}{\text{total mass}} \times 100\% = \frac{\text{mass solute}}{\text{mass solution}} \times 100\% = \frac{\text{mass solute}}{\text{mass solute} + \text{mass solvent}} \times 100\%$$

Now you define molal concentration:

$$\text{molal concentration} = \frac{\text{mol solute}}{\text{mass solvent (kg)}}$$

Before you set up your solution to the problem, you first map out what you will do:

Set your sample size to 100 g solution → Use the percent by mass of the solute to give the mass of the solute → Use molar mass to determine n_{solute} → Use the mass of solute/mass of solution to determine the mass of solvent → Calculate the molal conc

Now setup and solve the problem:

$$100.0 \text{ g solution} - 20.5 \text{ g NaCl} = 79.5 \text{ g water} \quad \Rightarrow \quad \left(\frac{(20.5 \text{ g NaCl})\left(\frac{\text{mol NaCl}}{58.44 \text{ g NaCl}}\right)}{0.0795 \text{ kg water}} \right) = 4.41m$$

Which is choice **(D)**.

Choice **(C)** uses the mass of the solution (in kg) rather than the mass of the solvent (water). Choice **(B)** omits calculating moles and use the mass of water in grams instead of kilograms. Choice **(A)** also omits calculating moles and use the mass of the solution (and not the solvent or water) in grams instead of kilograms.

Practice Questions Related to This: **PQ-6**, **PQ-7**, **PQ-8**, **PQ-9**, and **PQ-10**

SQ-4. What is the mole fraction of water in 200. g of 89% (by mass) ethanol, C_2H_5OH?

Molar mass / g·mol^{-1}	
C_2H_5OH	46

(A) 0.11 **(B)** 0.24 **(C)** 0.32 **(D)** 0.76

Knowledge Required: (1) Concentration unit of mole fraction. (2) Concentration unit of percent by mass.

Thinking it Through: Similar to the previous study question, you see this question starts by giving you percent by mass and asks you to determine mole fraction. So, again to solve this, you first define both concentration units:

$$\text{Percent by mass} = \frac{\text{mass solute}}{\text{mass solute} + \text{mass solvent}} \times 100\% \qquad \text{mole fraction}\left(X_{\text{solute}}\right) = \frac{\text{mol solute}}{\text{mol solute} + \text{mol solvent}}$$

Before you set up your solution to the problem, you first map out what you will do:

Set your sample size to 100 g solution, making: $\text{mass}_{\text{solute}}$ = % by mass and $\text{mass}_{\text{solvent}}$ = 100 – % by mass → Use molar mass (solute) to determine n_{solute} → Use molar mass (solvent) to determine $n_{solvent}$ → Calculate the mole fraction

Now setup and solve the problem (*notice the 200. g sample size is not needed*):

$$100 \text{ g solution} - 89 \text{ g } C_2H_5OH = 11 \text{ g water} \quad (89 \text{ g } C_2H_5OH)\left(\frac{\text{mol } C_2H_5OH}{46 \text{ g } C_2H_5OH}\right) = 1.9 \text{ mol } C_2H_5OH$$

$$(11 \text{ g } H_2O)\left(\frac{\text{mol } H_2O}{18 \text{ g } H_2O}\right) = 0.61 \text{ mol } H_2O \qquad X_{H_2O} = \frac{0.61 \text{ mol } H_2O}{1.9 \text{ mol } C_2H_5OH + 0.61 \text{ mol } H_2O} = 0.24$$

Which is choice **(B)**.

Choice **(D)** is the mole fraction of ethanol. Choice **(A)** is the percent by mass of water (as a fraction). Choice **(C)** uses the number of moles of solvent (ethanol) only and not the total number of moles.

Practice Questions Related to This: **PQ-6**, **PQ-7**, **PQ-8**, **PQ-9**, and **PQ-10**

SQ-5. *Conceptual*

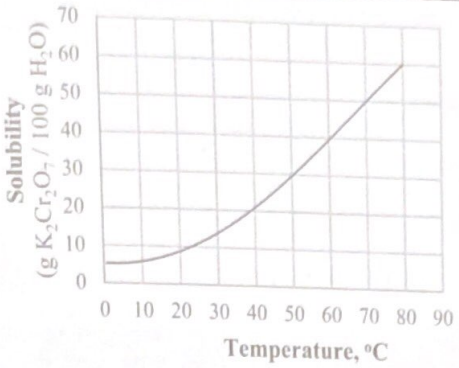
A mixture of 100 g of $K_2Cr_2O_7$ and 200 g of water is stirred at 60 °C until no more of the salt dissolves. The resulting solution is poured off into a separate beaker, leaving the undissolved solid behind. The solution is now cooled to 20 °C. What mass of $K_2Cr_2O_7$ crystallizes from the solution during the cooling?

(A) 9 g

(B) 18 g

(C) 31 g

(D) 62 g



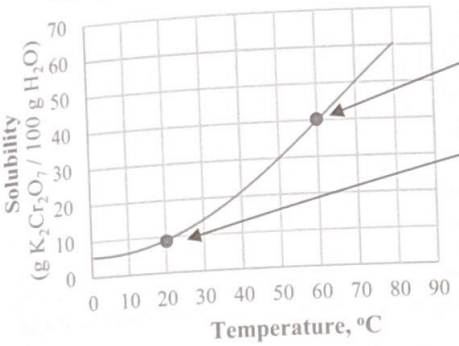
Knowledge Required: (1) Interpretation of a solubility graph. (2) Definition of solubility.

Thinking it Through: The problems provides you with both quantitative data and an associated process. You think it would be easiest to map out what is described before coordinating this with the graph:

60 °C	→	60 °C	→	20 °C
You start with: 100 g $K_2Cr_2O_7$ in 200 g water		Solution is poured off (saturated solution of $K_2Cr_2O_7$ in 200 g water)		Cooled; some mass of $K_2Cr_2O_7$ crystallizes out

↘ leaving undissolved solid

Now you coordinate this with the graph, marking the solubility of $K_2Cr_2O_7$ at 60 °C and 20 °C:



You see that:
at 60 °C, the solubility is 40 g/100 g water
so the 60 °C solution above (once poured off) contained **80 g** of $K_2Cr_2O_7$ in **200 g** of water.

at 20 °C, the solubility is 9 g/100 g water
so the 20 °C solution above (once cooled) contained **18 g** of $K_2Cr_2O_7$ in **200 g** of water in solution.

Meaning, the cooled solution had 80 g – 18 g or **62 g** of $K_2Cr_2O_7$ as a solid or crystallized from the water, which is choice **(D)**.

Choice **(B)** is incorrect because this is the mass that remained in solution. Choice **(C)** is incorrect because this is the mass that crystallized out in 100 g of water, rather than 200 g with Choice **(A)** as the incorrect choice when considering 100 g of water and the mass that remained in solution.

Practice Questions Related to This: **PQ-11** and **PQ-12**

SQ-6. *Conceptual*

Carbonated beverages have a fizz because of gas dissolved in the solution. What increases the concentration of gas in a solution?

(A) cooling the solution

(B) heating the solution

(C) increasing the volume of solution

(D) decreasing the volume of solution

Knowledge Required: (1) Solubility of gases. (2) Properties of concentration.

Thinking it Through: You recall that solubility of gases can be expressed quantitatively using Henry's law which expresses relationship of the concentration of the gas (in the solution, c), the pressure of the gas above the solution (P), and a constant for the gas (k): $c = kP$ (also written as $c = K_H P$). From this, you see that as pressure of the gas

increases, the concentration of the gas increases. You also suspect that solubility of gases vary based on their structure, and this would be expressed in the Henry's law constant, k. However, from this you also see that the volume of the solution will not change the concentration of the gas in the solution, so neither choice **(C)** or **(D)** are correct.

You do know that the Henry's law constant is a constant for a gas at a given temperature and as temperature increases, solubility of the gas decreases or k decreases. Therefore, heating the beverage will decrease the concentration of the gas (Choice **(B)**), but cooling the beverage will increase the concentration or fizziness, meaning Choice **(A)** is correct.

Practice Questions Related to This: **PQ-13** and **PQ-14**

SQ-7. When 100. g of an unknown compound was dissolved in 1.00 kg of water, the freezing point was lowered by 6.36 °C. What is the identity of this unknown compound? (K_f for water = 1.86°C·m^{-1})

(A) CsCl **(B)** KCl **(C)** LiF **(D)** NaCl

Knowledge Required: (1) Colligative properties, freezing point depression. (2) Ionic compounds and van't Hoff coefficients. (2) Molal concentration and molar mass.

Thinking it Through: As you read the question, you approach this problem by first evaluating the equation for freezing point depression (which you know is the appropriate colligative property because of the cue to this in the question): $\Delta T = K_f m$. You further examine the responses and see that all of the substances are ionic with the same 1:1 ratio of cation to anion, meaning that 2 ions form for each formula unit of the compound. Therefore, you refine the equation for freezing point depression for the van't Hoff coefficient of 2 ($i = 2$): $\Delta T = iK_f m = 2K_f m$:

$$\Delta T_f = iK_f m \qquad m = \frac{\Delta T_f}{iK_f} = \frac{6.36\ °C}{2\left(1.86\ °C \cdot m^{-1}\right)} = 1.71\ m$$

From here, you consider molal concentration and the other information provided in the problem to determine first the number of moles of solute and then (using the mass of solute), the molar mass of the solute:

$$\text{molal concentration} = \frac{\text{mol solute}}{\text{mass solvent}} \qquad \left(\frac{1.71\ \text{mol}}{\text{kg solvent}}\right)(1.00\ \text{kg water}) = 1.71\ \text{mol solute}$$

$$\left(\frac{100.\ \text{g solute}}{1.71\ \text{mol solute}}\right) = 58.5\ \text{g} \cdot \text{mol}^{-1}$$ which is NaCl or response **(D)**.

Choice **(A)** would likely be selected if the calculation of molal concentration was inverted (calculated molar mass of 170 g·mol^{-1}). Choice **(B)** may be selected if number of moles are calculated incorrectly by using the mass of solution rather than mass of solvent. Choice **(C)** may be selected if the van't Hoff coefficient was omitted (calculated molar mass of 29 g·mol^{-1}).

Practice Questions Related to This: **PQ-15**, **PQ-16**, and **PQ-17**

SQ-8. Which 0.1 molal aqueous solution will have the lowest freezing point?

Conceptual

(A) $Al(NO_3)_3$ **(B)** $CaCl_2$ **(C)** C_2H_5OH **(D)** NaCl

Knowledge Required: (1) Colligative properties, freezing point depression. (2) Ionic compounds and van't Hoff coefficients.

Thinking it Through: You know that colligative properties depend on the number of particles in solution (the molal concentration) but not the identity of the solute. You also know this is reflected in the equation for freezing point depression as noted in the previous study question. Because the concentrations are all the same (0.1 m) and the solvent is the same (water with the same freezing point depression constant, K_f), the only component that will vary will be the van't Hoff coefficient, i. So, you start by evaluating the number of particles in solution for each solute:

hydration equation	i_{calc}	hydration equation	i_{calc}
$Al(NO_3)_3(s) \rightarrow Al^{3+}(aq) + 3NO_3^-(aq)$	4	$CaCl_2(s) \rightarrow Ca^{2+}(aq) + 2Cl^-(aq)$	3
$C_2H_5OH(l) \rightarrow C_2H_5OH(aq)$	1	$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$	2

Note: i_{calc} is used here because you don't have the measured value (i_{meas}); in calculations, i_{meas} would be better than i_{calc}.

You are asked for the lowest freezing point or largest ΔT_f. Therefore, choice **(A)** is correct with a calculated van't Hoff coefficient of 4. The other choices are incorrect because the coefficients are all smaller than the value for $Al(NO_3)_3$.

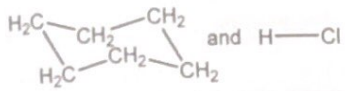
Practice Questions Related to This: **PQ-18**, **PQ-19**, and **PQ-20**

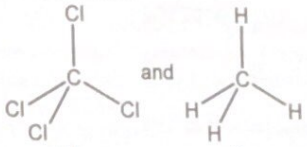
Practice Questions (PQ)

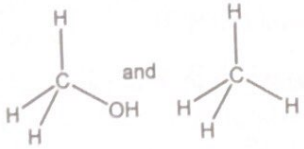
Conceptual **PQ-1.** Which pair of compounds will form hydrogen bonds with one another?

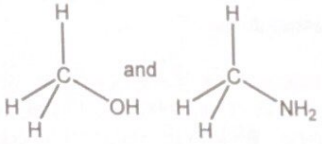
(A) CH_4 and H_2O **(B)** CH_4 and NH_3 **(C)** HF and CH_4 **(D)** H_2O and NH_3

Conceptual **PQ-2.** Which pair of compounds will form hydrogen bonds with one another?

(A)  and H—Cl

(B) 

(C) 

(D) 

Conceptual **PQ-3.** What would be expected to be the most soluble in ethanol (CH_3CH_2OH)?

(A) $CH_3CH_2CH_3$ **(B)** CO_2 **(C)** NH_3 **(D)** SF_6

Conceptual **PQ-4.** Which substance is most soluble in water?

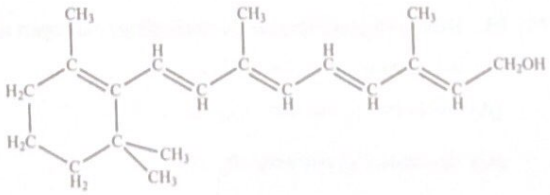
(A) ethane, CH_3CH_3

(B) ethanol, CH_3CH_2OH

(C) *n*-butane, $CH_3CH_2CH_2CH_3$

(D) 1-butanol, $CH_3CH_2CH_2CH_2OH$

Conceptual **PQ-5.** Consider the structure of Vitamin A_1 ($C_{20}H_{30}O$). Vitamin A_1 should be



(A) insoluble in water and in oil.

(B) less soluble in water than in oil.

(C) equally soluble in water and in oil.

(D) more soluble in water than in oil.

PQ-6. The mass percent of acetic acid (CH_3COOH) in a bottle of vinegar is 5.45% in water. What is the molar concentration of acetic acid in vinegar, assuming the density of vinegar is 1.005 $g \cdot mL^{-1}$?

Molar mass / $g \cdot mol^{-1}$	
CH_3COOH	60.06

(A) 0.545 M **(B)** 0.903 M **(C)** 0.908 M **(D)** 0.912 M

PQ-7. A 250-mL bottle of a sports drink solution contains 4.50% by mass of sodium chloride. What is the molal concentration of sodium chloride in this bottle of sports drink?

Molar mass / g·mol^{-1}	
NaCl	58.44

(A) 0.806 *m* **(B)** 0.770 *m* **(C)** 0.180 *m* **(D)** 0.0113 *m*

PQ-8. A 1400 g sample of stream water contains 12.2 ppm of mercury. What is the mass of Hg in the sample?

(A) 0.11 mg **(B)** 2.4 mg **(C)** 8.7 mg **(D)** 17 mg

PQ-9. What mass of water is needed to dissolve 292.5 g of NaCl to produce a 0.25 *m* aqueous solution?

Molar mass / g·mol^{-1}	
NaCl	58.44

(A) 20 kg **(B)** 5.0 kg **(C)** 0.80 kg **(D)** 0.050 kg

PQ-10. The density of a 3.539 M HNO_3 aqueous solution is 1.150 g·mL^{-1} at 20 °C. What is the molal concentration?

Molar mass / g·mol^{-1}	
HNO_3	63.02

(A) 3.077 *m* **(B)** 3.818 *m* **(C)** 3.946 *m* **(D)** 5.252 *m*

Conceptual **PQ-11.** The solubility of a substance is 60 g per 100 mL of water at 15 °C. A solution of this substance is prepared by dissolving 75 g in 100 mL of water at 75 °C. The solution is then cooled slowly to 15 °C without any solid separating. The solution is

(A) supersaturated at 75°C. **(B)** supersaturated at 15°C.

(C) unsaturated at 15°C. **(D)** saturated at 15°C.

Conceptual **PQ-12.** A student mixes 20.0 g of a salt in 100.0 g of water at 20 °C and obtains a homogeneous solution. Which salt could this be and why?

Solubility at 20 °C in 100.0 g of water	
KCl	10.0 g
KNO_3	30.0 g

(A) KCl because it is saturated. **(B)** KCl because it is unsaturated.

(C) KNO_3 because it is saturated. **(D)** KNO_3 because it is unsaturated.

PQ-13. The solubility of carbon dioxide in water is very low in air (1.05×10^{-5} M at 25 °C) because the partial pressure of carbon dioxide in air is only 0.00030 atm. What partial pressure of carbon dioxide is needed to dissolve 100.0 mg of carbon dioxide in 1.00 L of water?

(A) 0.0649 atm **(B)** 2.86 atm **(C)** 28.6 atm **(D)** 64.9 atm

Conceptual **PQ-14.** How will you increase the solubility of oxygen in water? The partial pressure of oxygen (P_{O_2}) is 0.21 atm in air at 1 atm (P_{ext}).

(A) increase P_{O_2} but keep P_{ext} constant **(B)** decrease P_{O_2} but keep P_{ext} constant

(C) increase P_{ext} but keep P_{O_2} constant **(D)** decrease P_{ext} but keep P_{O_2} constant

PQ-15. A 2.50 g sample of naphthalene, $C_{10}H_8$, was dissolved in 100 g of benzene. What is the freezing point of the benzene solution? The freezing point of pure benzene is 5.45 °C; $K_f = 5.07$ °C·m^{-1}.

Molar mass / g·mol^{-1}	
$C_{10}H_8$	128.17

(A) −0.989 °C **(B)** 0.989 °C **(C)** 4.46 °C **(D)** 6.44 °C

PQ-16. A technician has the measured osmotic pressure of a solution to determine the molar mass of a covalent solute. Which other information would need to be measured in order to determine the molar mass?

I.	Temperature
II.	Volume of solution
III.	Mass of solute

(A) Only **I** **(B)** Only **III** **(C)** Only **I** and **II** **(D)** **I**, **II**, and **III**

PQ-17. A solution was made by adding 800 g of ethanol, C_2H_5OH, to 8.0×10^3 g of water. How much would this lower the freezing point

	K_f / °C·m^{-1}
H_2O	1.86

(A) 3.2 °C **(B)** 4.1 °C **(C)** 8.2 °C **(D)** 16 °C

Conceptual **PQ-18.** Which aqueous solution will have the lowest osmotic pressure?

(A) 0.04 M $MgCl_2$ **(B)** 0.05 M KBr **(C)** 0.1 M LiCl **(D)** 0.2 M Na_2SO_4

Conceptual **PQ-19.** Consider pure water separated from an aqueous sugar solution by a semipermeable membrane. After some time has passed, what (if anything) will happen to the concentration of the sugar solution?

(A) It will decrease. **(B)** It will increase.

(C) It will remain the same. **(D)** It cannot be determined.

Conceptual **PQ-20.** Which solution has the higher boiling point?

Solution:	**Molar mass / g·mol^{-1}**
(1) 200.0 g glucose dissolved in 1.00 kg of water	glucose, 180
(2) 200.0 g sucrose dissolved in 1.00 kg of water	sucrose, 342

(A) solution **1**

(B) solution **2**

(C) Both would boil at the same temperature as pure water.

(D) Both would boil at the same temperature, but above that of pure water.

Answers to Study Questions

1. C
2. C
3. D
4. B
5. D
6. A
7. D
8. A

Answers to Practice Questions

1. D
2. D
3. C
4. B
5. B
6. D
7. A
8. D
9. A
10. B
11. B
12. D
13. A
14. A
15. C
16. D
17. B
18. B
19. A
20. A

Chapter 10 – Kinetics

Chapter Summary:
This chapter will focus on chemical kinetics. This includes the topics of reaction rate and rate laws. Methods of determining the rate laws will be presented and calculations with integrated rate laws will be reviewed. The collision theory of chemical kinetics and reaction mechanisms will be reviewed.

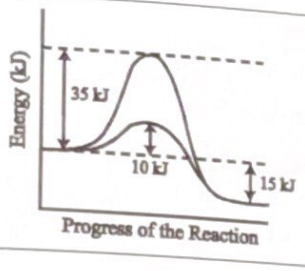
Specific topics covered in this chapter are:

- Determining a rate law from plots of data
- Method of initial rates
- Solving problems using integrated rate laws
- Half-life problems
- Collision theory and reaction energy diagrams
- Calculation of activation energy for a reaction
- Reaction mechanisms
- Relationship of kinetics to equilibrium

Previous material that is relevant to your understanding of questions in this chapter include:

- Significant figures (***Toolbox***)
- Scientific notation (***Toolbox***)
- Equilibrium ***(Chapter 11)***
- Enthalpy ***(Chapter 6)***

Common representations used in questions related to this material:

Name	Example	Used in questions related to
Compound units	$M \cdot s^{-1}$; $L \cdot mol^{-1} \cdot s^{-1}$	rates and rate constants
Energy diagrams		activation energy

Where to find this in your textbook:
The material in this chapter typically aligns to "Kinetics" or "Chemical Kinetics" in your textbook. The name of your chapter may vary.

Practice exam:
There are practice exam questions aligned to the material in this chapter. Because there are a limited number of questions on the practice exam, a review of the breadth of the material in this chapter is advised in preparation for your exam.

How this fits into the big picture:
The material in this chapter aligns to the Big Idea of Kinetics (7) as listed on page 12 of this study guide.

Study Questions (SQ)

SQ-1. What is the rate law of this reaction?

$$2H_2(g) + 2NO(g) \rightarrow N_2(g) + 2H_2O(g)$$

Trial #	$[H_2]_0$ /M	$[NO]_0$ / M	Initial rate / $M \cdot s^{-1}$
1	1.0×10^{-3}	1.0×10^{-3}	2.0×10^{3}
2	2.0×10^{-3}	2.0×10^{-3}	1.60×10^{4}
3	2.0×10^{-3}	1.0×10^{-3}	4.0×10^{3}

(A) rate = $k[H_2]^2[NO]$ **(B)** rate = $k[H_2][NO]^2$

(C) rate = $k[H_2]^2[NO]^2$ **(D)** rate = $k[N_2][H_2O]^2/[H_2]^2[NO]^2$

Knowledge Required: (1) Definition of rate law. (2) How to use the method of initial rates to determine the rate law.

Thinking it Through: You are given data with varying starting amounts (initial concentration noted as the "0" subscript, i.e. $[H_2]_0$) of each reactant and the reaction rate that was measured. You write the generic rate law for the reaction as:

$$\text{rate} = k[H_2]^x[NO]^y$$

To find the value of each exponent, you select a pair of trials that holds one concentration constant and allows you to see the effect on the rate by changing the other concentration. You select Trials 1 and 3 to determine the value of x. Taking the ratio of the trials you find: (NOTE: The k will cancel out.)

$$\frac{\text{rate}_3}{\text{rate}_1} = \frac{k[H_2]^x[NO]^y}{k[H_2]^x[NO]^y}$$

$$\frac{4.0\times10^{3}}{2.0\times10^{3}} = \frac{k(2.0\times10^{-3})^x(1.0\times10^{-3})^y}{k(1.0\times10^{-3})^x(1.0\times10^{-3})^y} \qquad 2 = \frac{(2.0\times10^{-3})^x(1.0\times10^{-3})^y}{(1.0\times10^{-3})^x(1.0\times10^{-3})^y} = 2^x$$

$$x = 1$$

The order of the reaction with respect H_2 is 1.

Repeating this process for Trials 2 and 3 to find the value of y.

$$\frac{\text{rate}_2}{\text{rate}_3} = \frac{k[H_2]^x[NO]^y}{k[H_2]^x[NO]^y}$$

$$\frac{1.6\times10^{4}}{4.0\times10^{3}} = \frac{k(2.0\times10^{-3})^x(2.0\times10^{-3})^y}{k(2.0\times10^{-3})^x(1.0\times10^{-3})^y} \qquad 4 = \frac{(2.0\times10^{-3})^x(2.0\times10^{-3})^y}{(2.0\times10^{-3})^x(1.0\times10^{-3})^y} = 2^y$$

$$y = 2$$

The order of the reaction with respect NO is 2.
The rate law for this reaction is rate = $k[H_2][NO]^2$. This is choice **(B)**.
Choice **(A)** is incorrect because it reverses the exponents.
Choice **(C)** is incorrect because it uses the coefficients from the balanced equation.
Choice **(D)** is incorrect because it is the equilibrium constant expression for the reaction.

Practice Questions Related to This: **PQ-1**, **PQ-2**, and **PQ-3**

SQ-2. *Conceptual* The rate law for the reaction

$$A + B \rightarrow C + D$$

is first order in [A] and second order in [B]. If [A] is halved and [B] is doubled, the rate of the reaction will

(A) remain the same. **(B)** be increased by a factor of 2.

(C) be increased by a factor of 4. **(D)** be increased by a factor of 8.

Knowledge Required: (1) The meanings of the terms rate law, first order, and second order. (2) The ability to use the rate law expression.

Thinking it Through: You are told the order of the reaction with respect to each reactant. You recognize that this is telling you the exponents in the rate expression. The exponent for [A] is 1 and the exponent for [B] is 2. You write the rate expression for the reaction:

$$\text{rate} = k[A][B]^2$$

You realize the problem is asking you to determine the effect of changing the initial concentrations of both reactants on the rate of the reaction. This is a similar problem to **SQ-1**, where you were given the initial amounts and the rates but were asked to find the exponents. Here you know the exponents and the amounts and are being asked to find the ratio of the rates. As before you set this up as a ratio of the two rates (for two reaction trials noted by "1"and "2" subscripts):

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{k[A]_2[B]_2^2}{k[A]_1[B]_1^2}$$

Where rate_1, $[A]_1$, and $[B]_1$ are the rate, concentration of A, concentration of B for trial #1 and rate_2, $[A]_2$, and $[B]_2$ are the rate, concentration of A, concentration of B for trial #2. The ratio of the rates is what you need to find.

You also know the relationship between $[A]_1$ and $[A]_2$ and $[B]_1$ and $[B]_2$ from the information in the question:

$[A]_2 = \frac{1}{2}[A]_1$ (because "[A] is halved")

and $[B]_2 = 2[B]_1$ (because "[B] is doubled")

Substituting these into the expression you get:

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{k[A]_2[B]_2^2}{k[A]_1[B]_1^2} = \frac{k\left(\frac{1}{2}[A]_1\right)(2[B]_1)^2}{k[A]_1[B]_1^2} = \frac{k\left(\frac{1}{2}[A]_1\right)4[B]_1^2}{k[A]_1[B]_1^2}$$

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{\left(\frac{1}{2}\right)4}{(1)(1)} = 2$$

The correct answer is choice **(B).**

Choice **(A)** is incorrect because the 2 was not squared in the expression $(2[B])^2$. Choice **(C)** is incorrect because it omitted the ½ term. Choice **(D)** is incorrect because the ½ term was mistakenly put in the denominator rather than the numerator.

Practice Questions Related to This: **PQ-4** and **PQ-5**

SQ-3. The half-life for the first order conversion of cyclobutene to ethylene,

$$C_4H_8(g) \rightarrow 2C_2H_4(g)$$

is 22.7 s at a particular temperature. How many seconds are needed for the partial pressure of cyclobutane to decrease from 100 mmHg to 10 mmHg?

(A) 0.101 s **(B)** 52.0 s

(C) 75.5 s **(D)** 5233 s

Knowledge Required: (1) The relationship between half-life and the rate constant for first-order reaction. (2) The ability to use the half-life equation and the integrated first-law equation.

Thinking it Through: You are given a reaction and told that it is first-order. You need to select and use the first-order integrated rate law to find the amount of time needed for the pressure to fall from 100 mmHg to 10 mmHg. You realize that you are not given a value for the rate constant, k. You recognize that because you know the half-life, you can find the value of the rate constant. Because the reaction is first-order you use the half-life expression for a first-order reaction:

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

Rearranging and substituting the given half-life you calculate the value of k.

$$k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{22.7\,\text{s}} = 0.0305\ \text{s}^{-1}$$

You then use this value of k in the first-order integrated rate law.

$$\ln[C_4H_8] = -kt + \ln[C_4H_8]_o$$

$$t = -\frac{\ln[C_4H_8] - \ln[C_4H_8]_o}{k} = -\frac{\ln(10) - \ln(100)}{0.0305\,\text{s}^{-1}} = 75.5\,\text{s}$$ which is choice **(C)**.

Choice **(A)** is incorrect because it used the value of the half-life as the rate constant.
Choice **(B)** is incorrect because it used 1/half-life as the rate constant, instead of ln2/half-life.
Choice **(D)** is incorrect because it used the expression for the second order half-life to find the value of k.

Practice Questions Related to This: **PQ-6** and **PQ-7**

SQ-4. The half-life for the first-order radioactive decay of ^{32}P is 14.2 days. How many days would be required for a sample of a radiopharmaceutical containing ^{32}P to decrease to 20.0% of its initial activity?

(A) 33.0 d **(B)** 49.2 d **(C)** 71.0 d **(D)** 286 d

Knowledge Required: (1) The knowledge that radioactive decay is first-order. (2) The ability to use the integrated form of the first-order rate law. (3) Relationship between half-life and rate constant.

Thinking it Through: You are being asked to find the time for a process to occur. You know that you have to use the integrated rate law. You also know that nuclear decay is a first-order process. To use the first-order integrated rate law you need a value for the rate constant. You use the relationship for the first-order half-life:

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

Solving for k you get: $k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{14.2\,\text{d}} = 0.0488\ \text{d}^{-1}$

The question is asking you for the time required for the sample to decrease to 20.0% of its original activity. This is different from other problems that give you specific amounts of initial and final concentrations. To solve the problem, you realize that you can pick any initial amount and the final amount will be 20.0% of that initial value. To keep the math simple, you assume you started with 100.0%. You then need to find the time required for the amount to decrease to 20.0% of 100%, or 0.200*1.000 = 0.200. You now know:

$$[^{32}P]_o = 1.00;\ [^{32}P] = 0.20;\ k = 0.0488\ \text{d}^{-1}$$

You then use the integrated first-order rate law to find the time needed.

$$\ln[^{32}P] = -kt + \ln[^{32}P]_o$$

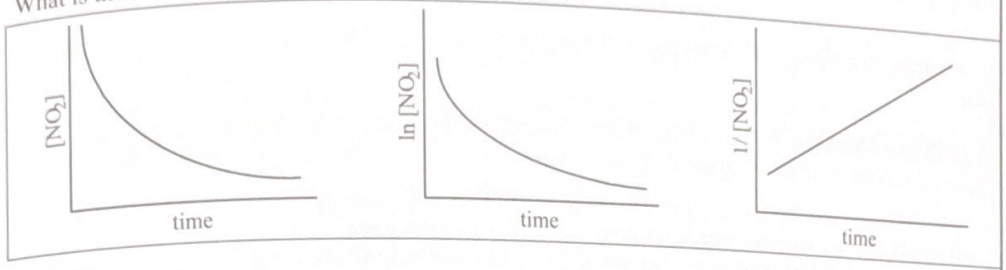
$$t = -\frac{\ln[^{32}P] - \ln[^{32}P]_o}{k} = -\frac{\ln(0.200) - \ln(1.00)}{0.0488\ d^{-1}} = 33.0\ d$$ which is choice **(A)**.

Choice **(B)** is incorrect because it represents 5 half-lives multiplied by ln(2).
Choice **(C)** is incorrect because it assumes it took 5 half-lives to get to 20.0% left.
Choice **(D)** is incorrect because it is 20 half-lives.

Practice Questions Related to This: **PQ-8** and **PQ-9**

SQ-5. ***Conceptual***

Plots are shown for the reaction $NO_2(g) \rightarrow NO(g) + \frac{1}{2} O_2(g)$.
What is the rate law for the reaction?



(A) rate = k

(B) rate = $k \times \frac{1}{[NO_2]}$

(C) rate = $k[NO_2]$

(D) rate = $k[NO_2]^2$

Knowledge Required: (1) Definition of rate law. (2) Ability to interpret integrated rate law equations.

Thinking it Through: You are given three plots of the concentration versus time data for a reaction. Each plot differs in how it plots the concentration of NO_2. You recall the three common integrated rate law expressions for reactions with a single reactant: $X \rightarrow P$

Order	Rate Law	Integrated Rate Law	Linear Plot
zero	rate = k	$[X]_t = -kt + [X]_o$	[X] vs time
first	rate = $k[X]^1$	$\ln[X]_t = -kt + \ln[X]_o$	ln[X] vs time
second	rate = $k[X]^2$	$1/[X]_t = kt + 1/[X]_o$	1/[X] vs time

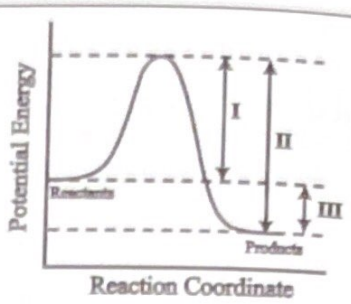
Each of the integrated rate laws has the form of a y = mx + b equation. When you examine the plots provided, you notice that the plot of $1/[NO_2]$ vs time is linear and the others are nonlinear. You decide that this means the rate law is a second order rate law: rate = $k[NO_2]^2$ which is choice **(D).**

Choice **(A)** is incorrect because this is the zero-order rate law and the plot of $[NO_2]$ is not linear.
Choice **(B)** is incorrect because this is taken directly from the plot with $1/[NO_2]$ on the y-axis.
Choice **(C)** is incorrect because this is a first-order rate law and the plot of $\ln[NO_2]$ is not linear.

Practice Questions Related to This: **PQ-10** and **PQ-11**

SQ-6. Conceptual

What changes when a catalyst is added to the reaction described by this energy diagram?



(A) I and II **(B)** I and III

(C) I only **(D)** III only

Knowledge Required: (1) Interpretation of reaction energy diagrams. (2) Meaning of catalyst and activation energy.

Thinking it Through: You are being asked to interpret a reaction energy diagram. Several parts of the diagram have been labeled. Examining the diagram, you recall what each labeled portion represents.

I is the activation energy for the reaction in the forward direction.
II is the activation energy for the reaction in the reverse direction.
III is the difference in energy of the reactants and products, which is the ΔH for the reaction.

The question asks you to determine which of these is affected by the addition of the catalyst. You remember that a catalyst provides an alternative pathway for the reaction. This alternative pathway has a lower activation energy. The presence of a catalyst does not affect the value of ΔH for the reaction. Because arrows **I** and **II** represent activation energies, these will be affected by the addition of a catalyst. The correct answer is choice **(A)**.

Choice **(B)** and **(D)** are incorrect because a catalyst does not affect the value of the enthalpy change, **III**. Choice **(C)** is incorrect because a catalyst will affect the activation energy for both the forward and reverse reactions.

Practice Questions Related to This: **PQ-12, PQ-13,** and **PQ-14**

SQ-7. Conceptual

Which statement regarding chemical reactions is true according to collision theory?

(A) All molecular collisions result in chemical reactions.

(B) Catalysts make individual collisions more effective, increasing reaction rates.

(C) Proper orientation of molecules is required for collision to result in chemical reactions.

(D) Increasing the temperature of a reaction decreases the kinetic energy of molecules, making collisions more effective.

Knowledge Required: (1) Understanding of the collision theory of chemical reactions. (2) Knowledge of what factors influence the rate of chemical reactions.

Thinking it Through: The question asks you to evaluate a series of statements about chemical reactions and collision theory. You decide to evaluate each option individually.

You know that for a collision to lead to a chemical reaction it must satisfy two criteria. The collision must have sufficient energy for the reaction to occur. Also, the molecules must be in the proper orientation for the collision to be effective. Therefore, not all collisions result in a chemical reaction. Therefore choice **(A)** is incorrect.

The presence of a catalyst does increase the rate of a reaction. However, the way a catalyst increases the rate of a reaction is not by making the collisions more effective. Instead a catalyst increases the rate of a reaction by providing an alternative route from reactants to products that has a smaller activation energy. Processes with smaller activation energies result in a faster reaction rate. Therefore choice **(B)** is incorrect.

You know that one of the two requirements for a collision to lead to a chemical reaction is that the reactants must collide with the proper orientation. Therefore choice **(C)** is correct.

Increasing the temperature **often** leads to an increase in the rate of a reaction. However, the reason is because as the temperature increases the average kinetic energy of the reactants increases. This can increase the rate of a reaction in two ways. First, there are more collisions that have the minimum energy needed for a reaction to occur. Second, the higher kinetic energy increases the number of collisions, which means the odds of a collision having the proper orientation increases. This increases the rate of a reaction. Therefore choice **(D)** is incorrect.

Practice Questions Related to This: **PQ-15, PQ-16, PQ-17, PQ-18, PQ-19, PQ-20, PQ-21, PQ-22, PQ-23,** and **PQ-24**

SQ-8. The activation energy for a particular reaction is 83.1 $kJ \cdot mol^{-1}$. By what factor will the rate constant increase when the temperature is increased from 50.0 °C to 60.0 °C?

(A) 2.53 **(B)** 1.00 **(C)** 0.927 **(D)** 0.395

Knowledge Required: (1) How to use the Arrhenius equation. (2) The relationship between activation energy and the value of the rate constant.

Thinking it Through: You are being asked to determine the relative change in the value of the rate constant when the temperature changes. You recall the Arrhenius equation which relates the value of the activation energy, the temperature, and the rate constant. You also remember that all the temperature values must by in kelvin:

$$k = Ae^{-E_a/RT}$$

An alternative form of the equation is: $$\ln k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln(A)$$

This form of the equation is useful if you have measured values of k at different temperatures. You recognize that this equation is in the form: $y = mx + b$. If you plot $\ln(k)$ versus $1/T$ the slope of this plot is equal to $(-E_a/R)$.

Another form of this equation, often called the two-point form, is used when you only have two values of k or temperature values. You get this form of the equation by subtracting the equation at the first temperature, T_1, from that at the second temperature, T_2:

$$\ln k_2 - \ln k_1 = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T_2}\right) - \left(\frac{-E_a}{R}\right)\left(\frac{1}{T_1}\right) + \ln(A) - \ln(A)$$

$$\ln k_2 - \ln k_1 = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \ln\left(\frac{k_2}{k_1}\right) = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

You recognize that the ratio of k_2/k_1 is what the problem is asking for and you substitute the given values into the equation. **Note**: you are careful to make sure the units of R and E_a match and the temperature is in kelvin:

$$\ln\left(\frac{k_2}{k_1}\right) = \left(\frac{-83.1\,kJ \cdot mol^{-1}}{8.314\,J \cdot mol^{-1} \cdot K^{-1}}\right)\left(\frac{1000\ J}{1\ kJ}\right)\left(\frac{1}{333.15\ K} - \frac{1}{323.15\ K}\right)$$

$$\ln\left(\frac{k_2}{k_1}\right) = 0.927 \qquad \frac{k_2}{k_1} = e^{0.927} = 2.53$$

The correct answer is choice **(A)**.

Choice **(B)** is not correct because it is the answer if the units of E_a are not converted to J. Choice **(C)** is not correct because it is the natural log (ln) of the ratio of the rate constants. Choice **(D)** is not correct because it is the ratio k_1/k_2.

Practice Questions Related to This: **PQ-25** and **PQ-26**

SQ-9. Consider the reaction

$$2NO_2(g) + F_2(g) \rightleftharpoons 2NO_2F(g)$$

A proposed mechanism for the reaction is

$$NO_2 + F_2 \rightleftharpoons NO_2F + F \quad \text{(slow)}$$

$$NO_2 + F \rightleftharpoons NO_2F \quad \text{(fast)}$$

What is the rate law for this mechanism?

(A) $\text{rate} = k\dfrac{[NO_2F]}{[NO_2]^2[F_2]}$ **(B)** $\text{rate} = k[NO_2]^2[F_2]$

(C) $\text{rate} = k[NO_2][F_2]$ **(D)** $\text{rate} = k[NO_2][F]$

Knowledge Required: (1) The fact that the slowest step in the reaction mechanism determines the rate law for the reaction. (2) Being able to write a rate law expression from an elementary step.

Thinking it Through: You are given a mechanism and are asked to write the rate law for the proposed mechanism. The slowest step in a reaction mechanism is the step with the highest activation energy and the species involved in this step determine the rate law for the reaction. You note that you are told the first step is the slowest. You know that you can write the rate law for this elementary step using the coefficients from the elementary step as the exponents in the rate law.

You write the rate law for the slow step as: $rate = k[NO_2][F_2]$ which is choice **(C)**.

Choice **(A)** is not correct because it is the equilibrium expression for the reaction, not a rate law. Choice **(B)** is not correct because it uses the stoichiometry of the overall reaction. Choice **(D)** is not correct because it is not the derived from the slowest step.

Practice Questions Related to This: **PQ-27, PQ-28,** and **PQ-29**

SQ-10. **Conceptual**

Consider this equilibrium:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

The forward reaction is proceeding at a certain rate at some temperature and pressure. When the pressure is increased, what might we expect for the forward reaction?

(A) a greater rate of reaction and a greater yield of SO_3 at equilibrium

(B) a greater rate of reaction and a same yield of SO_3 at equilibrium

(C) a lesser rate of reaction and a smaller yield of SO_3 at equilibrium

(D) a lesser rate of reaction and a greater yield of SO_3 at equilibrium

Knowledge Required: (1) How to use LeChatlier's principle. (2) Qualitative understanding of rate laws.

Thinking it Through: You need to predict what will happen to an equilibrium system when it is subjected to a change. You know that a change in pressure may shift the equilibrium and depends on the moles of gaseous substances as reactants and products. An increase in pressure will shift the equilibrium in the direction that minimizes the increase in pressure. This is the side that has the fewest moles of gas. For this reaction, the side with fewer moles of gas is the product side. You realize that this means that an increase in pressure will cause the rate of the reaction producing SO_3 to increase. The correct answer is choice **(A)**.

Choices **(B)** and **(C)** is incorrect because SO_3 will increase. Choice **(D)** is incorrect because the rate of the reaction will increase.

Practice Questions Related to This: **PQ-30**

Practice Questions (PQ)

Conceptual **PQ-1.** When the reaction:

$CH_3Cl(g) + H_2O(g) \rightarrow CH_3OH(g) + HCl(g)$

was studied, the tabulated data were obtained. Based on these data, what are the reaction orders?

Exp	$[CH_3Cl]_0$ / M	$[H_2O]_0$ / M	Initial Rate / $M \cdot s^{-1}$
1	0.100	0.100	0.182
2	0.200	0.200	1.45
3	0.200	0.400	5.81

(A) CH_3Cl: first order H_2O: first order **(B)** CH_3Cl: first order H_2O: second order

(C) CH_3Cl: second order H_2O: first order **(D)** CH_3Cl: second order H_2O: second order

PQ-2. The reaction between acetone and bromine in acidic solution is represented by the equation:

$CH_3COCH_3(aq) + Br_2(aq) + H_3O^+(aq) \rightarrow$ products

The tabulated kinetic data were gathered. Based on these data, the experimental rate law is

Exp	$[CH_3COCH_3]_0$ / M	$[Br_2]_0$ / M	$[H_3O^+]_0$ / M	Initial Rate / $M \cdot s^{-1}$
1	0.30	0.050	0.050	5.8×10^{-5}
2	0.30	0.100	0.050	5.8×10^{-5}
3	0.30	0.050	0.100	1.2×10^{-4}
4	0.40	0.050	0.200	3.2×10^{-4}

(A) rate = $k[CH_3COCH_3][Br_2][H_3O^+]$ **(B)** rate = $k[CH_3COCH_3][H_3O^+]$

(C) rate = $k[H_3O^+]^2$ **(D)** rate = $k[CH_3COCH_3][Br_2]$

PQ-3. Initial rate data for the reaction

$2H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

are given in the table. What is the rate law for the reaction?

Exp	$[H_2]_0$ / M	$[Cl_2]_0$ / M	Initial Rate / $M \cdot s^{-1}$
1	0.0020	0.0050	2.5×10^{-3}
2	0.0020	0.0025	1.3×10^{-3}
3	0.0015	0.0025	1.3×10^{-3}
4	0.0050	0.0010	0.5×10^{-3}

(A) rate = $k[Cl_2]^2$ **(B)** rate = $k[Cl_2]$ **(C)** rate = $k[H_2]$ **(D)** rate=$k[H_2][Cl_2]$

Conceptual **PQ-4.** The gas phase reaction, $A_2 + B_2 \rightarrow 2AB$, proceeds by bimolecular collisions between A_2 and B_2 molecules. The rate law is rate = $k[A_2][B_2]$

If the concentrations of both A_2 and B_2 are doubled, the reaction rate will change by a factor of

(A) ½. **(B)** $\sqrt{2}$. **(C)** 2. **(D)** 4.

Conceptual **PQ-5.** For the reaction of chorine and nitric oxide,

$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$

doubling the concentration of chlorine doubles the rate of reaction. Doubling the concentration of both reactants increases the rate of reaction by a factor of eight. The reaction is

(A) first order in both NO and Cl_2.

(B) first order on NO and second order in Cl_2.

(C) second order in NO and first order in Cl_2.

(D) second order in both NO and Cl_2.

PQ-6. The decomposition of NOCl is second order.

$$2NOCl(g) \rightarrow 2NO(g) + Cl_2(g)$$

The initial concentration of the reactant is 0.050 M. The rate constant equals 0.020 $L \cdot mol^{-1} \cdot s^{-1}$, what will the concentration be after 45 min?

(A) 0.048 M **(B)** 0.029 M **(C)** 0.014 M **(D)** 0.0054 M

PQ-7. If the half-life of a reaction is independent of concentration, the reaction can be

I first order	II second order	III zero order

(A) I and II only **(B)** II and III only **(C)** I only **(D)** II only

PQ-8. The activity of a radioisotope is 3000 counts per minute at one time and 2736 counts per minute 48 hours later. What is the half-life, in hours, of the radioisotope?

(A) 831 hr **(B)** 521 hr **(C)** 361 hr **(D)** 1.44 hr

PQ-9. After 55 years, what mass (in g) remains of a 200.0 g sample of a radioactive isotope with a half-life of 10.0 years?

(A) 0.22 g **(B)** 4.4 g **(C)** 51 g **(D)** 170 g

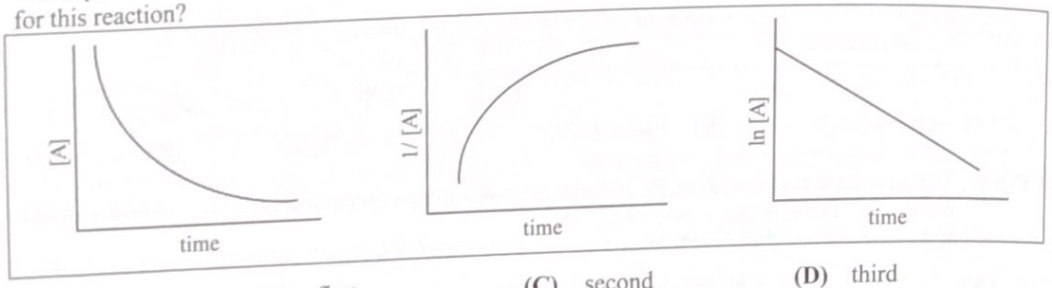
PQ-10. If the reaction

$O_3(g) \rightarrow O_2(g) + O(g)$

is first order in O_3, which plot will be linear?

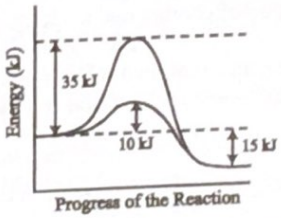
(A) $[O_3]$ vs. time **(B)** $1/[O_3]$ vs. time **(C)** $[O_3]^2$ vs. time **(D)** $\ln[O_3]$ vs. time

PQ-11. The experimental data from a certain reaction gives these three graphs. What is the most likely order for this reaction?



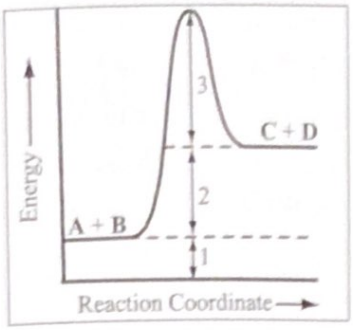
(A) zero **(B)** first **(C)** second **(D)** third

PQ-12. Consider the reaction potential energy diagram. What describes the catalyzed forward reaction pathway?



	E_a	ΔH
(A)	10 $kJ \cdot mol^{-1}$	−15 $kJ \cdot mol^{-1}$
(B)	10 $kJ \cdot mol^{-1}$	15 $kJ \cdot mol^{-1}$
(C)	25 $kJ \cdot mol^{-1}$	−15 $kJ \cdot mol^{-1}$
(D)	25 $kJ \cdot mol^{-1}$	15 $kJ \cdot mol^{-1}$

PQ-13. Which line segment represents the activation energy for the reaction between **C** and **D** to form **A** and **B**?



(A) 1, 2, & 3 (B) 2 (C) 2 & 3 (D) 3

PQ-14. A certain reaction has $\Delta H = -75\ \text{kJ·mol}^{-1}$ and an activation energy of $40\ \text{kJ·mol}^{-1}$. A catalyst is found that lowers the activation energy of the forward reaction by $15\ \text{kJ·mol}^{-1}$. What is the activation energy of the reverse reaction in the presence of the same catalyst?

(A) $25\ \text{kJ·mol}^{-1}$ (B) $60\ \text{kJ·mol}^{-1}$ (C) $90\ \text{kJ·mol}^{-1}$ (D) $100\ \text{kJ·mol}^{-1}$

Conceptual PQ-15. Which statement best explains why the activation energy is changed by adding a catalyst?

(A) The catalyst changes the reaction mechanism.

(B) The catalyst changes the free energy of reaction.

(C) The catalyst increases the kinetic energy of the reactants.

(D) The catalyst lowers the reaction volume, increasing the concentration of reactants.

Conceptual PQ-16. Which reaction rate is more affected by a change in temperature?

	Reaction	E_a / kJ·mol^{-1}
I	$H_2(g) + I_2(g) \rightarrow 2HI(g)$	173
II	$CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$	356

(A) reaction **I** because the activation energy is lower

(B) reaction **I** because the number of moles of gas stays the same

(C) reaction **II** because number of moles of gases increases as reaction goes forward

(D) reaction **II** because the activation energy is higher

PQ-17. What will increase the value of the rate constant for an elementary step?

(A) adding a catalyst

(B) raising the temperature

(C) increasing the concentration of products

(D) increasing the concentration of reactants

Conceptual **PQ-18.** The Arrhenius equation describes the relationship between the rate constant, k, and the energy of activation, E_a. $k = Ae^{-E_a/RT}$ In this equation, A is an empirical constant, R is the ideal-gas constant, e is the base of natural logarithms, and T is the absolute temperature. According to the Arrhenius equation,

(A) at constant temperature, reactions with lower activation energies proceed more rapidly.

(B) at constant temperature, reactions with lower activation energies proceed less rapidly.

(C) at constant energy of activation, reactions at lower temperatures proceed more rapidly.

(D) at constant energy of activation, reactions with smaller values of A proceed more rapidly.

Conceptual **PQ-19.** What will be the effect of increasing the temperature of reactants that are known to undergo an endothermic reaction?

(A) Both the rate of reaction and the value of the equilibrium constant increases.

(B) The rate of reaction increases and the value of the equilibrium constant decreases.

(C) The rate of reaction decreases and the value of the equilibrium constant increases.

(D) The rate of reaction increases and the value of the equilibrium constant is unchanged.

Conceptual **PQ-20.** The change in temperature from 10 °C to 20 °C is found to double the rate of a particular chemical reaction. How did the change in temperature affect the reaction?

(A) The number of molecules with sufficient energy to react increased.

(B) The number of molecules with sufficient energy to react decreased.

(C) The activation energy increased.

(D) The activation energy decreased.

Conceptual **PQ-21.** The value for the rate constant of a reaction can generally be expected to

(A) decrease with increasing temperature.

(B) increase with increasing temperature.

(C) decrease with increasing temperature only when the reaction is exothermic.

(D) increase with increasing temperature only when the reaction is exothermic.

Conceptual **PQ-22.** Two reactions with different activation energies have the same rate at room temperature. Which statement correctly describes the rates of these two reactions at the same, higher temperature?

(A) The reaction with the larger activation energy will be faster.

(B) The reaction with the smaller activation energy will be faster.

(C) The two reactions will continue to occur at the same rates.

(D) A prediction cannot be made without additional information.

Conceptual **PQ-23.** A catalyst increases the rate of a reaction by

(A) changing the mechanism of the reaction.

(B) increasing the activation energy of the reaction.

(C) increasing the concentration of one or more reactants.

(D) decreasing the difference in relative energy of the reactants and products.

Conceptual **PQ-24.** Which statement most accurately describes the behavior of a catalyst?

(A) A catalyst increases ΔG of a reaction and hence the forward rate.

(B) A catalyst reduces the ΔH of a reaction and hence the temperature needed to produce products.

(C) A catalyst reduces the activation energy for a reaction and increases the rate of a reaction.

(D) A catalyst increases the equilibrium constant and final product concentrations.

PQ-25. The rate constants for a specific reaction at two different temperatures are given in the table.
What is the activation energy for the reaction?

Temperature	Rate constant
127 °C	3.0×10^{-4} s^{-1}
227 °C	6.0×10^{-2} s^{-1}

(A) -88.1 kJ·mol^{-1} **(B)** -12.7 kJ·mol^{-1} **(C)** 12.7 kJ·mol^{-1} **(D)** 88.1 kJ·mol^{-1}

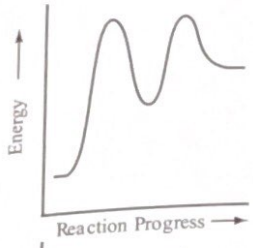
PQ-26. Activation energy can be experimentally determined from the slope of the plot of

(A) k versus $1/T$. **(B)** k versus $\ln T$. **(C)** $\ln k$ versus T. **(D)** $\ln k$ versus $1/T$.

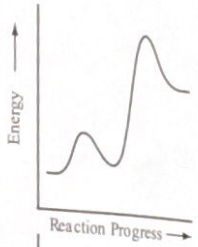
Conceptual **PQ-27.** Which energy diagram best matches the proposed mechanism for this exothermic reaction?

$E + S \rightleftharpoons ES$ (fast)
$ES \rightarrow E + P$ (slow)

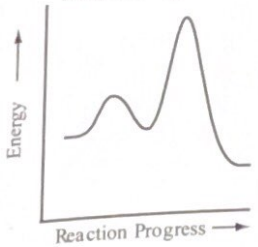
(A)



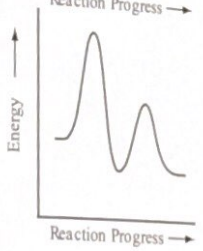
(B)



(C)



(D)



PQ-28. Consider the reaction

$$Cl_2(g) + H_2S(aq) \rightarrow S(s) + 2H^+(aq) + 2Cl^-(aq)$$

The rate equation for this reaction is

$$\text{rate} = k[Cl_2][H_2S]$$

Which mechanisms is (or are) consistent with this rate equation (if any)?

I	$Cl_2 + H_2S \rightarrow H^+ + Cl^- + Cl^+ + HS^-$ $Cl^+ + HS^- \rightarrow H^+ + Cl^- + S$	(slow) (fast)
II	$H_2S \rightarrow H^+ + HS^-$ $Cl_2 + HS^- \rightarrow 2Cl^- + H^+ + S$	(fast) (slow)

(A) **I** only **(B)** **II** only **(C)** Both **I** and **II** **(D)** Neither **I** or **II**

PQ-29. The decomposition of hydrogen peroxide in the presence of iodide ion is believed to occur via this mechanism.

$$H_2O_2(aq) + I^-(aq) \rightarrow H_2O(l) + IO^-(aq)$$
$$H_2O_2(aq) + IO^-(aq) \rightarrow H_2O(l) + O_2(g) + I^-(aq)$$

In this mechanism, $I^-(aq)$ is

(A) a catalyst.

(B) a reactant in the overall reaction.

(C) the activated complex.

(D) a product of the overall reaction.

PQ-30. What is the relationship between the equilibrium constant (K_c) of a reaction and the rate constants for the forward (k_f) and reverse (k_r) reactions in a single step reaction?

(A) $K_c = k_f k_r$ **(B)** $K_c = k_f / k_r$ **(C)** $K_c = 1/(k_f k_r)$ **(D)** $K_c = k_f - k_r$