Version A

AP* Chemistry: Kinetics

NO CALCULATORS MAY BE USED

<u>Note:</u> For all questions, assume that the temperature is 298 K, the pressure is 1.00 atmosphere, and solutions are aqueous unless otherwise specified.

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

Τ	= temperature	M = m o lar
P	= pressure	m = molal
V	= volume L,	mL = liter(s), milliliter(s)
S	= entropy	g = gram(s)
Н	= enthalpy	nm = nanometer(s)
G	= free en ergy	atm = atmosphere(s)
R	= molar gas constant .	J, kJ = joule(s), kilojoule(s)
п	= number of moles	V = volt(s)
mol	= mole(s)	

Directions: Each set of lettered choices below refers to the numbered questions or statements immediately following it. Select the one lettered choice that best answers each question or best fits each statement and then fill in the corresponding oval on the answer sheet. A choice may be used once, more than once, or not at all in each set. *Before turning in your answer sheet, count the number of questions that you have skipped and place that number next to your name ON YOUR ANSWER SHEET and circle it.*

Questions 1 refers to the following types of energy.

- A) Activation energyB) Free energyC) Ionization energyD) Kinetic energyE) Lattice energy
- 1. The energy required to form the transition state in a chemical reaction

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<u>Directions</u>: Each of the questions or incomplete statements below is followed by five suggested answers or completions. Select the one that is best in each case and then fill in the corresponding oval on the answer sheet.

2.

Step 1:
$$Ce^{4+} + Mn^{2+} \rightarrow Ce^{3+} + Mn^{3-}$$

Step 2: $Ce^{4+} + Mn^{3+} \rightarrow Ce^{3+} + Mn^{4+}$

Step 3: $Mn^{4+} + Tl^+ \rightarrow Tl^{3+} + Mn^{2+}$

The proposed steps for a catalyzed reaction between Ce⁴⁺ and Tl⁺ are represented above. The products of the overall catalyzed reaction are

- A) Ce⁴⁺ and Tl⁺
- B) Ce³⁺ and Tl³⁺
- C) Ce³⁺ and Mn³⁺
- D) Ce³⁺ and Mn⁴⁺
- E) Tl^{3+} and Mn^{2+}
- 3. Each of the following factors can affect the forward rate of a chemical reaction EXCEPT
 - A) temperature
 - B) concentration of reactants of the forward reaction
 - C) presence of a catalyst
 - D) removal of some of the products of the forward reaction
 - E) physical state or state of subdivision of solid reactants

- 4. The half-life for radioactive element X is 10.0 min. What weight of X was originally present in a sample if 40. grams is left after 60. minutes?
 - A) 320. grams
 - B) 640. grams
 - C) 1,280. grams
 - D) 2,400 grams
 - E) 2,560 grams
- 5. Which of the following has the least effect on the rate of a reaction?
 - A) adding a solid catalyst to a gas phase reaction
 - B) adding a solid catalyst to a liquid phase reaction
 - C) adding inert miscible liquid to a liquid phase reaction
 - D) adding inert gas to a gas phase reaction at constant volume
 - E) adding excess base to neutralization reaction for a nearly insoluble weak acid

Questions 6 and 7 refer to the steps of a mechanism proposed for the reaction of nitrogen(II) oxide with hydrogen.

$NO(g) + NO(g) \implies N_2O_2(g)$	fast equilibrium
$N_2O_2(g) + H_2(g) \implies N_2O(g) + H_2O(g)$	slow
$N_2O(g) + H_2(g) \implies N_2(g) + H_2O(g)$	fast

- 6. Which is the equation for the overall reaction?
 - A) $NO(g) + NO(g) \rightarrow N_2(g) + H_2O(g)$
 - B) $2 \operatorname{NO}(g) + 2 \operatorname{H}_2(g) \rightarrow \operatorname{N}_2(g) + 2 \operatorname{H}_2\operatorname{O}(g)$
 - C) $NO(g) + N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O(g)$
 - D) $2 \operatorname{NO}(g) + 2 \operatorname{H}_2(g) + \operatorname{N}_2\operatorname{O}_2(g) \rightarrow \operatorname{N}_2\operatorname{O}(g) + \operatorname{N}_2(g) + 2 \operatorname{H}_2\operatorname{O}(g)$
 - E) $NO(g) + 2 H_2(g) + N_2O_2(g) + N_2O(g) \rightarrow N_2O(g) + N_2O_2(g) + N_2(g) + 2 H_2O(g)$
- 7. Which rate law is consistent with this mechanism?
 - A) rate = $k [NO]^2$
 - B) rate = $k [NO]^2 [H_2]$
 - C) rate = $k [N_2O] [H_2]$
 - D) rate = $k [N_2O_2] [H_2]$
 - E) rate = $k [N_2O_2] [H_2] [NO]^2$

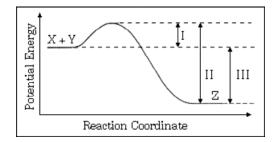
8.

$$2 \operatorname{A}(g) + \operatorname{B}(g) \leftrightarrows 2 \operatorname{C}(g)$$

When the concentration of substance B in the reaction above is doubled, all other factors being held constant, it is found that the rate of the reaction remains unchanged. The most probable explanation for this observation is that

- A) the order of the reaction with respect to substance B is 1
- B) substance B is not involved in any of the steps in the mechanism of the reaction
- C) substance B is not involved in the rate-determining step of the mechanism, but is involved in subsequent steps
- D) substance B is probably a catalyst, and as such, its effect on the rate of the reaction does not depend on its concentration
- E) the reactant with the smallest coefficient in the balanced equation generally has little or no effect on the rate of the reaction

9.



The energy diagram for the reaction $X + Y \rightarrow Z$ is shown above. The addition of a catalyst to this reaction would cause a change in which of the indicated energy differences?

- A) I only
- B) II only
- C) III only
- D) I and II only
- E) I, II, and III

- 10. The isomerization of cyclopropane to propylene is a first-order process with a half-life of 19 minutes at 500°C. The time it takes for the partial pressure of cyclopropane to decrease from 1.0 atmosphere to 0.125 atmosphere at 500°C is closest to
 - A) 38 minutes
 - B) 57 minutes
 - C) 76 minutes
 - D) 152 minutes
 - E) 190 minutes
- 11.

$$(CH_3)_3CCl(aq) + OH^- \rightarrow (CH_3)_3COH(aq) + Cl^-$$

For the reaction represented above, the experimental rate law is given as follows.

Rate =
$$k$$
 [(CH₃)₃CCl]

If some solid sodium solid hydroxide is added to a solution that is 0.010-molar in $(CH_3)_3CCl$ and 0.10-molar in NaOH, which of the following is true? (Assume the temperature and volume remain constant.)

- A) Both the reaction rate and *k* increase.
- B) Both the reaction rate and *k* decrease.
- C) Both the reaction rate and *k* remain the same.
- D) The reaction rate increases but *k* remains the same.
- E) The reaction rate decreases but *k* remains the same.

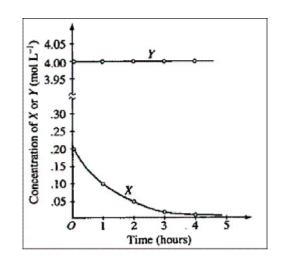
Questions 12 and 13 refer to the following reaction and its experimental data.

$$2 A + B + C \rightarrow \text{products}$$

Four trials of the reaction above were carried out in order to determine its rate law. The following data were collected.

				Initial rate
Trial	[A]	[B]	[C]	$M{ m sec^{-1}}$
1	0.02	0.02	0.02	1.6×10^{-3}
2	0.01	0.02	0.02	8.0×10^{-4}
3	0.01	0.04	0.02	1.6×10^{-3}
4	0.01	0.04	0.03	1.6×10^{-3}

- 12. As any trial of this reaction proceeds at constant temperature, the rate of the reaction
 - A) remains the same because no catalyst is added
 - B) remains the same because the temperature is constant
 - C) increases because the rate constant is a positive number
 - D) decreases because the concentrations of the reactants decrease
 - E) decreases because the effectiveness of collisions between molecules decreases
- 13. Based on these observations, what is the rate law?
 - A) Rate = $k [A]^2$
 - B) Rate = k [B][C]
 - C) Rate = k [A][B]
 - D) Rate = $k [A]^2 [B]^2$
 - E) Rate = $k [A]^2 [B][C]$
- 14. Relatively slow rates of chemical reaction are associated with which of the following?
 - A) The presence of a catalyst
 - B) High temperature
 - C) High concentration of reactants
 - D) Strong bonds in reactant molecules
 - E) Low activation energy



The graph above shows the results of a study of the reaction of X with a large excess of Y to yield Z. The concentrations of X and Y were measured over a period of time. According to the results, which of the following can be concluded about the rate law for the reaction under the conditions studied?

A) It is zero order in [X].

15.

- B) It is first order in [X].
- C) It is second order in [X].
- D) It is the first order in [Y].
- E) The overall order of the reaction is 2.

Experiment	Initial [NO] (mol L ⁻¹)	Initial [O ₂] (mol L ⁻¹)	Initial Rate of Formation of NO_2 (mol L ⁻¹ s ⁻¹)
1	0.10	0.10	2.5×10^{-4}
2	0.20	0.10	5.0×10^{-4}
3	0.20	0.40	$8.0 imes 10^{-3}$

The initial-rate data in the table above were obtained for the reaction represented below.

$$2 \text{ NO} + \text{O}_2 \rightarrow 2 \text{ NO}_2$$

What is the experimental rate law for the reaction?

- A) rate = $k[NO][O_2]$
- B) rate = $k[NO] [O_2]^2$
- C) rate = $k[NO]^2 [O_2]$
- D) rate = $k[NO]^2 [O_2]^2$
- E) rate = $k[NO] / [O_2]$

17. If 87.5 percent of a sample of pure ¹³¹I decays in 24 days, what is the half-life of ¹³¹I?

- A) 6 days
- B) 8 days
- C) 12 days
- D) 14 days
- E) 21 days

18.

Time (days)	0	1	2	3	4	5	6	7		10	 20
% Reactant remaining	100	79	63	50	40	31	25	20	-	10	1

A reaction was observed for 20 days and the percentage of the reactant remaining after each day was recorded in the table above. Which of the following best describes the order and the half-life of the reaction?

	Reaction Order	Half-life (days)
A)	First	3
B)	First	10
C)	Second	3
D)	Second	6
E)	Second	10

19.

$$\begin{aligned} & \operatorname{Cl}_2(g) \rightleftharpoons 2 \operatorname{Cl}(g) & \text{fast equilibrium} \\ & \operatorname{Cl}(g) + \operatorname{CHCl}_3(g) \to \operatorname{HCl}(g) + \operatorname{CCl}_3(g) & \text{slow} \\ & \operatorname{CCl}_3(g) + \operatorname{Cl}(g) \to \operatorname{CCl}_4(g) & \text{fast} \end{aligned}$$

The reaction between chlorine and chloroform in the gas phase which is known to proceed according to the mechanism above. According to this mechanism, what is the overall reaction?

- A) $\operatorname{Cl}_2(g) \to \operatorname{CCl}_4(g)$
- B) $\operatorname{CHCl}_3(g) + \operatorname{Cl}_2(g) \rightarrow \operatorname{HCl}(g) + \operatorname{CCl}_4(g)$
- C) $\operatorname{Cl}(g) + \operatorname{CHCl}_3(g) \rightarrow \operatorname{H}(g) + \operatorname{CCl}_4(g)$
- D) $\operatorname{Cl}(g) + \operatorname{CHCl}_3(g) \rightarrow \operatorname{HCl}(g) + \operatorname{CCl}_3(g)$

E)
$$2 \operatorname{CHCl}_3(g) + \operatorname{Cl}_2(g) \rightarrow 2 \operatorname{HCl}(g) + \operatorname{CCl}_4(g) + \operatorname{CCl}_3(g)$$

20.

Step 1	$N_2H_2O_2\leftrightarrows N_2HO_2^-+H^+$	(fast equilibrium)
Step 2	$N_2HO_2^- \rightarrow N_2O + OH^-$	(slow)
Step 3	$H^{+} + OH^{-} \rightarrow H_{2}O$	(fast)

Nitramide, $N_2H_2O_2$, decomposes slowly in aqueous solution. This decomposition is believed to occur according to the reaction mechanism above. The rate law for the decomposition of nitramide that is consistent with this mechanism is given by which of the following?

- A) Rate = $k [N_2H_2O_2]$
- B) Rate = $k [N_2H_2O_2] [H^+]$
- C) Rate = $(k [N_2H_2O_2]) / [H^+]$
- D) Rate = $(k [N_2H_2O_2]) / [N_2HO_2^-]$
- E) Rate = $k [N_2H_2O_2] [OH^-]$
- 21. Which is a correct comparison of the characteristics of a catalyzed reaction to the corresponding characteristics of the same reaction without a catalyst present?
 - I. Their energies of activation are the same.
 - II. Their enthalpies of reaction are the same.
 - III. Their free energies of reaction are the same.
 - A) I only
 - B) II only
 - C) II and III only
 - D) I and III only
 - E) I, II and III

$$2 \operatorname{NO}(g) + \operatorname{O}_2 \longrightarrow 2 \operatorname{NO}_2(g)$$

A possible mechanism for the overall reaction represented above is the following.

(1)
$$\operatorname{NO}(g) + \operatorname{NO}(g) \to \operatorname{N}_2\operatorname{O}_2(g)$$
 slow
(2) $\operatorname{N}_2\operatorname{O}_2(g) + \operatorname{O}_2(g) \to 2\operatorname{NO}_2(g)$ fast

Which of the following rate expressions agrees best with this possible mechanism?

A) Rate =
$$k[NO]^2$$

B) Rate = $k \frac{[NO]}{[O_2]}$
C) Rate = $k \frac{[NO]^2}{[O_2]}$
D) Rate = $k[NO]^2[O_2]$
E) Rate = $k[N_2O_2][O_2]$

- 23. Which of the following is most closely associated with relatively slow rates of chemical reaction?
 - A) low enthalpy of reaction
 - B) low energy of activation
 - C) the presence of a catalyst
 - D) high concentration of reactants
 - E) strong bonds in reaction molecules

24. In any first order reaction, as the reaction proceeds at constant temperature, which describes the corresponding effects on *k* (the rate constant) and *rate*?

1.		
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- A) remains the same
- B) remains the same
- C) remains the same
- D) decreasesE) decreases

decreases remains the same

- increases
- decreases

rate

remains the same

22.

Questions 25 - 26

$H_3AsO_4 + 3 I^- + 2 H_3O^+ \rightarrow H_3AsO_3 + I_3^- + H_2O$

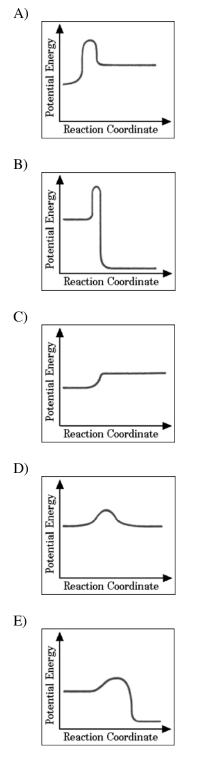
The oxidation of iodide ions by arsenic acid in acidic aqueous solution occurs according to the stoichiometry shown above. The experimental rate law of the reaction is:

Rate = $k [H_3AsO_4] [I^-] [H_3O^+]$

- 25. What is the order of the reaction with respect to $I^{-?}$
 - A) 1
 - B) 2
 - C) 3
 - D) 5
 - E) 6

- 26. According to the rate law for the reaction, an increase in the concentration of hydronium ion has what effect on this reaction?
 - A) The rate of reaction increases.
 - B) The rate of reaction decreases.
 - C) The value of the equilibrium constant increases.
 - D) The value of the equilibrium constant decreases.
 - E) Neither the rate nor the value of the equilibrium constant is changed.

27. Which of the following is a graph that describes the pathway of reaction that is endothermic and has high activation energy?



28.

Rate = $k[M][N]^2$

The rate of a certain chemical reaction between substances M and N obeys the rate law above. The reaction is first studied with [M] and [N] each 1×10^{-3} molar. If a new experiment is conducted with [M] and [N] each 2×10^{-3} molar, the reaction rate will increase by a factor of

- A) 2
- B) 4
- C) 6
- D) 8
- E) 16

- 29. Which of the following best describes the role of the spark from the spark plug in an automobile engine?
 - A) The spark decreases the energy of activation for the slow step.
 - B) The spark increases the concentration of the volatile reactant.
 - C) The spark supplies some of the energy of activation for the combustion reaction.
 - D) The spark provides a more favorable activated complex for the combustion reaction.
 - E) The spark provides the heat of vaporization for the volatile hydrocarbon.

30. The reaction between H_2 and NO occurs according to the equation

 $2 \operatorname{H}_2(g) + 2 \operatorname{NO}(g) \rightarrow 2 \operatorname{H}_2\operatorname{O}(g) + \operatorname{N}_2(g)$

Six trials of the reaction were carried out. The initial rate of change of pressure for each trial was measured and recorded.

	Initial Pressu	Initial Rate	
Trial	P _{NO}	$\mathbf{P}_{\mathbf{H}^2}$	Δ atm min -1
Ι	0.50	0.09	0.025
II	0.50	0.18	0.050
III	0.50	0.27	0.075
IV	0.09	0.80	0.0063
V	0.18	0.80	0.025
VI	0.27	0.80	0.056

Based on these results, what is the rate law for this reaction?

- A) RATE = $k (P_{NO})^0 (P_{H2})^2$
- B) RATE = $k (P_{NO})^1 (P_{H2})^2$
- C) RATE = $k (P_{NO})^2 (P_{H2})^0$
- D) RATE = $k (P_{NO})^2 (P_{H2})^1$
- E) RATE = $k (P_{NO})^2 (P_{H2})^2$

- 31. Which of the following is a correct statement about reaction order?
 - A) Reaction order can only be a whole number.
 - B) Reaction order can be determined only from the coefficients of the balanced equation for the reaction.
 - C) Reaction order can be determined only by experiment.
 - D) Reaction order increases with increasing temperature.
 - E) A second-order reaction must involve at least two different compounds as reactants.
- 32.

$$2 \text{ A} + 3 \text{ B} \rightarrow \text{F} + 2 \text{ G}$$

Each of the following expressions represents a proper expression for the rate of this reaction EXCEPT

$$\begin{array}{l} A) & \frac{-\Delta[A]}{\Delta t} \\ B) & \frac{-\Delta[B]}{3\Delta t} \\ C) & \frac{\Delta[F]}{\Delta t} \\ D) & \frac{\Delta[G]}{2\Delta t} \\ E) & \frac{-\Delta[A]}{2\Delta t} \end{array}$$

33.

rate = k[X]

For the reaction whose rate law is given above, a plot of which of the following is a straight line?

- A) [X] versus time
- B) log [X] versus time
- C) 1/[X] versus time
- D) [X] versus 1/time
- E) log [X] versus 1/time