CHM152   Exam 1 100 Pts FALL 2005   Name: **Key**

1. The rate constant for a particular reaction is $1.3 \times 10^{-4} M^{-1}s^{-1}$ at 100°C, and $1.1 \times 10^{-3} M^{-1}s^{-1}$ at 150°C. What is the overall order of the reaction?
   a) 1
   b) 0
   c) 2
   d) 3
   e) 4

Look at units $rate = k [A]^x$

$$\frac{M}{S} = \frac{1}{MS} [A]^2 \leftarrow order$$

2. Which one of the following statements is **false**?

   a) In order for a reaction to occur, reactant molecules must collide with each other.
   b) A catalyst alters the rate of a reaction and is neither a product nor a reactant in the overall equation.
   c) According to collision theory a three-body collision is less likely than a two-body collision.
   d) In reactions that are second order in one reactant and first order in another, the slow step generally involves a three-body collision of these reactants.
   e) The transition state is a short-lived, high energy state, intermediate between reactants and products.

3. Evaluate the specific rate constant at the temperature at which the data were collected. The rate-law expression is Rate = $k[NO]^2[H_2]$.

$$H_2(g) + NO(g) \longrightarrow N_2O(g) + H_2O(g)$$
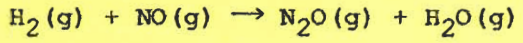
Experiment	Initial [NO] (M)	Initial [H₂] (M)	Initial Rate (M·s⁻¹)
1	0.30	0.35	2.835×10^{-3}
2	0.60	0.35	1.134×10^{-2}
3	0.60	0.70	2.268×10^{-2}

using Exp 1

   a) 9.4×10^{-3}
   b) 2.7×10^{-2}
   c) 1.6×10^{-4}
   d) 8.1×10^{-3}
   e) 9.0×10^{-2}

$rate = k[NO]^2[H_2]$

$$k = \frac{rate}{[NO]^2[H_2]} = \frac{2.835 \times 10^{-3} M \cdot s^{-1}}{[0.30]^2 [0.35]}$$

$M^{-2} s^{-1}$

4. Given the following data for the $NH_4^+ + NO_2^- \longrightarrow N_2 + 2H_2O$ reaction

[NH₄]	[NO₂⁻]	Rate
0.010 M	0.020 M	0.020 M/s
0.015	0.020	0.030
0.010	0.010	0.005

The rate law for the reaction is

   a) $R = k[NH_4^+][NO_2^-]$
   b) $R = k[NH_4^+]^2[NO_2^-]$
   c) $R = k[NH_4^+][NO_2^-]^2$
   d) $R = k[NH_4^+]^2[NO_2^-]^2$
   e) None of the above

for [NH₄⁺] use RXNs 1 & 2

$$\frac{rate_1}{Rate_2} = \frac{k[NH_4^+]^x [NO_2^-]^y}{k[NH_4^+]^x [NO_2^-]^2}$$

$$\frac{0.020}{0.030} = \left(\frac{0.010}{0.015}\right)^x$$

$$\ln\left(\frac{0.020}{0.030}\right) = x \ln\left(\frac{0.010}{0.015}\right)$$

$$\boxed{X = 1}$$

For NO_2^- using RXNs 1 & 3

$$\frac{0.020}{0.005} = \left(\frac{0.020}{0.010}\right)^y$$

$$\ln\left(\frac{0.020}{0.005}\right) = x \ln\left(\frac{0.020}{0.010}\right)$$

$$\boxed{X = 2}$$

5. The gas phase reaction $3C + 2D \rightarrow E + F$ obeys the rate-law expression
Rate = $k[D]$ and has a half-life of 0.860 s^{-1}. If 2.00 mole of D is injected into a 1.00 L
container with excess C, what concentration of D remains after 1.50 seconds?

a) 0.48 M
b) 0.60 M
c) 1.68 M
d) 1.40 M
e) 1.06 M

(handwritten)

Test 5

$t_{1/2} = \dfrac{0.693}{k}$
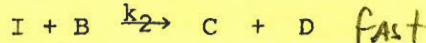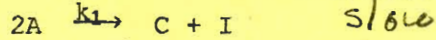
$k = \dfrac{0.693}{0.860} = 0.8058 \text{ s}^{-1}$

$\ln(A)_t = -kt + \ln[A]_0$
$= -0.8058(1.50) + \ln\left(\dfrac{2}{1}\right)$
$= -0.5156$

$[A]_t = e^{-0.5156} = 0.597 \text{ M}$

6. Consider the following proposed mechanism. If this mechanism for the
overall reaction were correct, and if k_1 were much less than k2, then
the observed rate law would be

$2A \xrightarrow{k_1} C + I$ slow

$I + B \xrightarrow{k_2} C + D$ fast

a) Rate = $k_1[A]$
b) Rate = $k_2[I][B]$
c) Rate = $k_1[A]^2$
d) Rate = $k_1[A]^2 = k_2[C][D]$
e) Rate = $k_1 k_2[A]^2[I][B]$

7. One of the reactions that is used to produce gaseous hydrogen
commercially follows. A proper expression for the rate of this
reaction could be _____ .

$$H_2O(g) + CO(g) \rightarrow H_2(g) + CO_2(g)$$
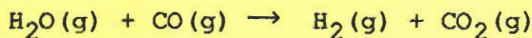
a) $\dfrac{-\Delta[CO_2]}{\Delta t}$

b) $\dfrac{-\Delta[H_2]}{\Delta t}$

c) k

d) $\dfrac{\Delta[CO]}{\Delta t}$

e) $\dfrac{-\Delta[H_2O]}{\Delta t}$

8. Which one of the following graphs shows the correct relationship between concentration and time for a reaction that is second order in [A]?

a) ln [A]

time

b) [A]

time

c) 1/[A]

time

d) [A]

time

e) [A]

time
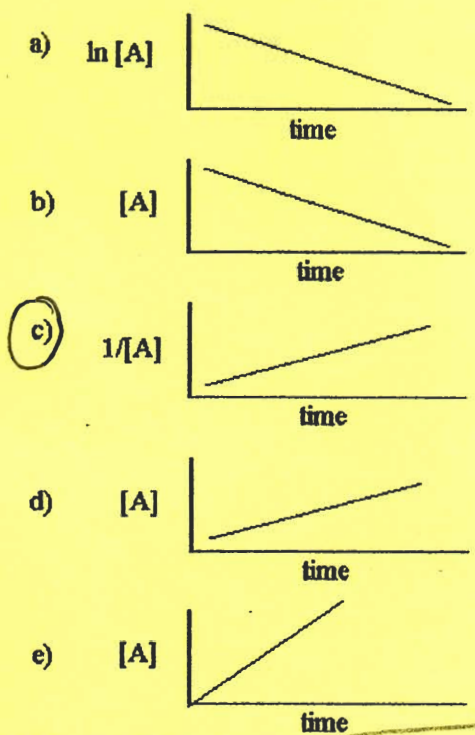
9. A reaction has an activation energy of 40 kJ and an overall energy change of reaction of (-) 100 kJ. In each of the following potential energy diagrams, the horizontal axis is the reaction coordinate and the vertical axis is potential energy in kJ. Which potential energy diagram best describes this reaction?

(a) 40 100

Exo Thermine

$\Delta E = -100 \, kJ$

(b) 40 100

(c) 40 100

(d) 40 100

(e) 100 40
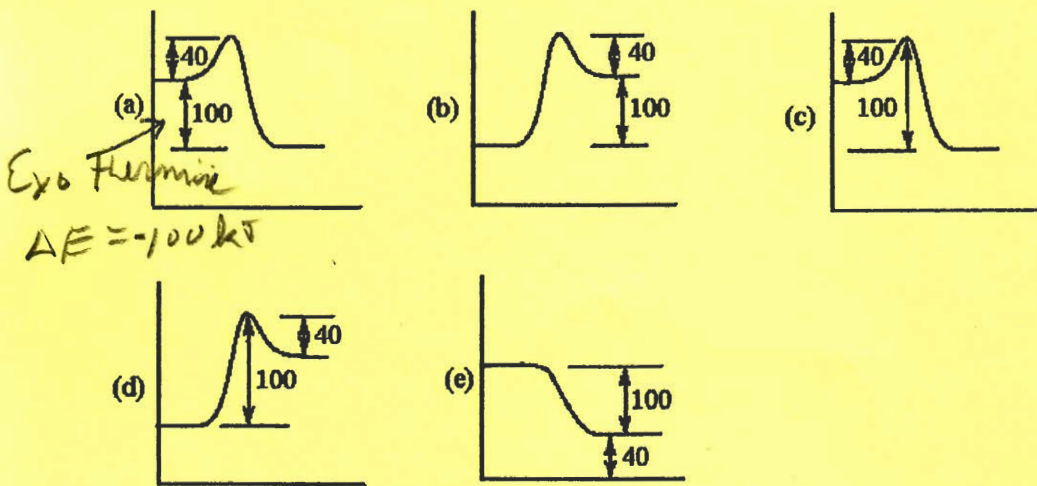
10. A catalyst _____.

a) is used up in a chemical reaction
b) changes the value of ΔG° of the reaction
c) is always a solid
d) does not influence the reaction in any way
e) changes the activation energy of the reaction

11. The gas phase reaction A + B → C has a reaction rate which is experimentally observed to follow the relationship Rate = k[A]^2[B]. Which one of the following would affect the value of the specific rate constant, k?
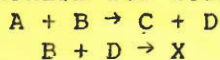
  a) decreasing the temperature
  b) changing the concentration of A
  c) changing the concentration of B
  d) changing the concentration of C
  e) letting the reaction go on for a long time

12. The oxidation of NO by O_3 is first order in each of the reactants, and its rate constant is 1.5 x 10^7 $M^{-1} \cdot s^{-1}$. If the concentrations of NO and O_3 are each 5.0 x 10^{-7} M, what is the rate of oxidation of NO in $M \cdot s^{-1}$?

  a) 3.8 x 10^{-6}
  b) 2.5 x 10^{-14}
  c) 7.5 x 10^{-7}
  d) 15
  e) 7.5

$$rate = k[NO][O_3]$$
$$= 1.5 \times 10^7 [5.0 \times 10^{-7}][5.0 \times 10^{-7}]$$

13. The mechanism for formation of the product X is:
    A + B → C + D
      B + D → X
The intermediate reactant in the reaction is _____.
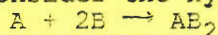 a) A
  b) B
  c) C
  d) D
  e) X

14. The reaction A + B → C + D, obeys the rate law expression Rate = k[A][B]. Which response lists all the proposed mechanisms below that are consistent with this information and none that **are inconsistent?**

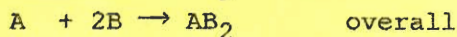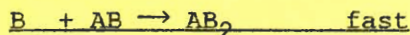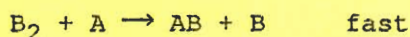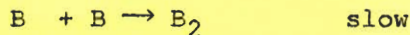 I.   A + B → C + D   one step

  II.   A + B ⇌ E   fast, equilibrium
         E → C + D   slow

  III.   A + B ⇌ E   fast, equilibrium
         A + E → C + B   slow

  a) I and II
  b) II
  c) III
  d) II and III
  e) I, II, and III

15. Consider the hypothetical reaction shown below.
    $A + 2B \rightarrow AB_2$
    Assume that the following proposed mechanism is consistent with the rate data.

    $B + B \rightarrow B_2$ slow

    $B_2 + A \rightarrow AB + B$ fast

    $\underline{B + AB \rightarrow AB_2 \quad\quad fast}$
    $A + 2B \rightarrow AB_2$ overall

    Which one of the following statements must be true? The reaction is
    _____.

    a) first order in A, second order in B, and third order overall
    b) second order in B and second order overall
    c) first order in A and first order overall
    d) second order in B, zero order in A, and third order overall
    e) second order in A and second order overall

16. One difference between first and second-order reactions is that
    a) the half-life of a first-order reaction does not depend on $[A]_0$; the half-life of a second-order reaction does depend on $[A]_0$
    b) the rate of a first-order reaction does not depend on reactant concentrations; the rate of a second-order reaction does depend on reactant concentrations
    c) the rate of a first-order reaction depends on reactant concentrations; the rate of a second-order reaction does not depend on reactant concentrations
    d) a first-order reaction can be catalyzed; a second-order reaction cannot be catalyzed
    e) the half-life of a first-order reaction depends on $[A]_0$; the half-life of a second-order reaction does not depend on $[A]_0$

17. For a first order reaction, a plot of ____ versus ____ is linear.

    a) $\ln[A]_t$, $\dfrac{1}{t}$

    b) $\ln[A]_t$, t

    c) $\dfrac{1}{[A]}$, t

    d) $[A]$, t
    e) t, $1/[A]$

18. The units of the rate constant for a second order reaction can be
    _____.

    a) $M^{-1} \cdot s^{-1}$
    b) M
    c) $M \cdot s^{-1}$
   d) s^{-1}
    e) $M^2 \cdot s^{-1}$

$rate = k\,[A]^2$

$\dfrac{M}{s} = \bigcirc\, M^2$

19. Given the following potential energy diagram for the one-step reaction
    $X + Y \rightarrow Z + R$ The arrow "d" represents the _____.

   a) energy content of products
   b) activation energy for the forward reaction
   c) energy content of reactants
   d) activation energy for the reverse reaction
   (e) the net change in energy for the reaction
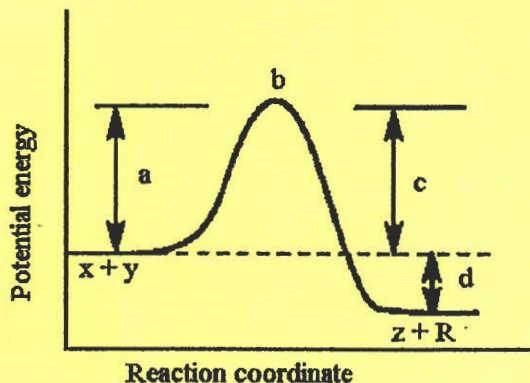
20. The disproportionation (auto-oxidation-reduction) of the hypochlorite ion to chlorate and chloride ions occurs in aqueous solution. The rate expression is found to be Rate = $k[ClO^-]^2$. Which one of the following (possible) mechanisms is consistent with this information?
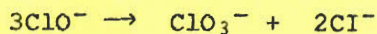
$$3ClO^- \rightarrow ClO_3^- + 2Cl^-$$

   a) $ClO^- + Cl^- \rightarrow ClO_2^- + Cl^-$ (slow)
       $ClO- + ClO_2^- \rightarrow ClO_3^- + 2Cl^-$ (fast)

   b) $ClO^- \rightarrow Cl + O^-$ (slow)
       $O^- + ClO^- \rightarrow Cl^- + O^{2-}$ (fast)
       $O^{2-} + Cl^- \rightarrow Cl^- + O_2$ (fast)
       $O_2 + ClO^- \rightarrow ClO_3^-$ (fast)

   c) $3ClO^- \rightarrow ClO_3^- + 2Cl^-$ (one step)

   d) $ClO^- \rightarrow Cl^- + O$ (slow)
       $O + ClO^- \rightarrow O_2 + Cl^-$ (fast)
       $ClO^- + O_2 \rightarrow ClO_3^-$ (fast)

   e) $3ClO^- \rightarrow ClO_2^- + Cl_2O^{2-}$ (slow)
       $Cl_2O^{2-} \rightarrow Cl^- + Cl^-$ (fast)
       $ClO^- + ClO_2^- \rightarrow Cl^- + ClO_3^-$ (fast)

ERROR so free

21. The decomposition of dimethylether at 504°C is first order with a half-life of 1570 seconds. What fraction of an initial amount of dimethylether remains after 4710 seconds?

   a) 1/3
   b) 1/6
   (c) 1/8
   d) 1/16
   e) 1/32

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

$$= -k(4710)$$

$$\ln \frac{[A]_t}{[A]_0} = -2.079$$

$$\frac{[A]_t}{[A]_0} = 0.125 \approx \frac{1}{8}$$

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

$$k = 4.414 \times 10^{-4} s^{-1}$$

22. The gas phase reaction A + B → C has a reaction rate which is experimentally observed to follow the relationship Rate = $k[A]^2[B]$. The overall order of the reaction

   a) is first.
   b) is second.
   c) is third.
   d) is zero.
   e) cannot be answered without a detailed knowledge of the reaction mechanism.

23. A reaction mechanism will usually be

   a) the only possible explanation for the reaction.
   b) difficult to verify experimentally.
   c) proven experimentally to be the balanced chemical equation.
   d) obvious from a consideration of the balanced chemical equation.
   e) obvious from a consideration of the reaction rate data.

24. The reaction A → B is first order in [A]. The concentration of A(M) is _____ M after 40.0 s.

time(s)	[A] (M)
0.0	0.20
5.0	0.14.
10.0	0.10
15.0	0.071
20.0	0.050

← this is one ½ life so $t_{1/2} = 10$ sec

and 40 sec = 4 ½-lives

$$\frac{0.20}{\left(\frac{1}{2^4}\right)} = 0.0125$$

   a) 1.2×10^{-2}
   b) 1.2
   c) 0.17
   d) 3.5×10^{-4}
   e) 0.025

25. Calculate the activation energy of a reaction if the rate constant is 0.75 s⁻¹ at 25°C and 11.5 s⁻¹ at 75°C.

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

$$\ln \frac{0.75}{11.5} = \frac{E_a}{8.314}\left(\frac{1}{273+75} - \frac{1}{273+25}\right)$$

   a) 681 J
   b) 20.4 kJ
   c) 15.8 kJ
   d) 47.1 kJ
   e) 31.4 kJ

26. A first-order reaction has a rate constant of 0.33 min⁻¹. It takes _____ min for the reactant concentration to decrease from 0.13 M to 0.088 M.

   a) 1.2
   b) 1.4
   c) 0.51
   d) 0.13
   e) 0.85

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

$$\ln [0.088] = -0.33t + \ln [0.13]$$

$$t = 1.18 \text{ min}$$

27. Suppose a reaction A + B → C occurs at some initial rate at 25°C. Which response includes all of the changes below that **could** increase the rate of this reaction?

    I.   lowering the temperature
    II. adding a catalyst
    III. increasing the initial concentration of B

    a) I
    b) II
    c) III
    d) I and II
    e) II and III

28. Which of the following does not play a part in determining the rate of a reaction?
    a) temperature
    b) the concentrations of reactants
    c) the presence of a catalyst
    d) the surface area of solid or liquid reactants
    e) the equilibrium constant

29. The half-life of a first-order reaction
   a) is the time necessary for the reactant concentration to drop to half its original value
    b) is constant
    c) can be calculated from the reaction rate constant
    d) does not depend on the initial reactant concentration
    e) all of these are correct

30. The gas phase reaction A + B → C has a reaction rate which is experimentally observed to follow the relationship Rate = k[A]^2[B] . If the concentration of A is tripled and the concentration of B is doubled, the reaction rate would be increased by a factor of

    $$rate = k [3]^2 [2] = 18$$

    a) 6
    b) 9
    c) 12
    d) 18
    e) 36

31. Consider the following rate data for the reaction below at a particular temperature.
        2A + 3B → Products
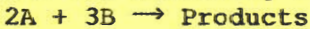
Experiment	Initial [A]	Initial [B]	Initial Rate of Loss of A
1	0.10 M	0.30 M	7.20 x 10-5 M·s^{-1}
2	0.10 M	0.60 M	1.44 x 10-4 M·s^{-1}
3	0.20 M	0.90 M	8.64 x 10-4 M·s^{-1}

show B to be 1st order

    The reaction is _____ order in A and _____ order in B.

    a) first, first
    b) second, first
    c) first, second
    d) second, second
    e) third, first

    $$rate = k [A]^x [B]^1$$
    $$rate = k [A]^x (B)^1$$
    use $\frac{2}{3}$
    use values from 1 + 3 or 2 + 3 to solve for x

32. As the temperature of a reaction is increased, the rate of the reaction increases because the _____.
    a) reactant molecules collide less frequently
    b) reactant molecules collide with greater energy per collision
    c) activation energy is lowered
    d) reactant molecules collide less frequently and with greater energy per collision
    e) reactant molecules collide more frequently with less energy per collision

33. Suppose the reaction

$$2AB + C_2 \longrightarrow A_2C + B_2C$$
occurs by the following mechanism.

Step 1 AB + $C_2 \longrightarrow AC_2$ + B   slow

Step 2 B   + $AB \longrightarrow AB_2$ fast

Step 3 AC_2 + $AB_2 \longrightarrow A_2C_2$ + B_2 fast

Step 4 A_2C_2 + $B_2 \longrightarrow A_2C$ + B_2C fast

Overall 2 AB + $C_2 \longrightarrow$ A2C   + B_2C

The rate law expression must be Rate = _____.

a) $k[AB][C_2]$
b) $k[AB]^2[C_2]$
c) $k[AB]^2$
d) $k[AB]$
e) $k[C_2]$