CHM152/54 Exam 1   100 Pts   Spring 2005   Name: _Key_____
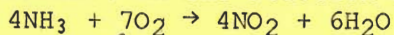MULTIPLE CHOICE

1. Of the following, only _____ are not valid units for a reaction rate.
   a) mol/L   *must have time*
   b) M/s
   c) mol/hr
   d) g/s
   e) mol/L-hr

2. Which substance in the reaction below either appears or disappears the fastest?

   $4NH_3 + 7O_2 \rightarrow 4NO_2 + 6H_2O$

   a) NH_3
   b) O_2
   c) NO_2
   d) H_2O
   e) The rates of appearance/disappearance are the same for all of these.

3. 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

4. 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?
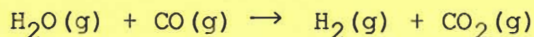   a) 1
   b) 0
   c) 2
   d) 3
   e) 4

   Look at units for k $\frac{1}{MS}$ so must be rate $= k[A]^2$

5. For a _first_ order reaction, a plot of ____ versus ____ is linear.

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

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

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

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

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

7. Suppose a reaction $A + B \rightarrow C$ 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

8. The gas phase reaction $A + B \rightarrow C$ 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.

9. 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) $M^2 \cdot s^{-1}$

$$rate = k[A]^2$$
$$\downarrow$$
$$\overline{M\,S}$$

10. A reaction is first order in X and second order in Y. Tripling the initial concentration of X and cutting the initial concentration of Y to three-fourths of its previous concentration at constant temperature causes the initial rate to _____ by a factor of _____ .

a) increase, 1.69
b) decrease, 0.19
c) increase, 1.33
d) decrease, 1.25
e) increase, 2.25

$$rate = k[x][y]^2$$
$$[3]\left[\tfrac{3}{4}\right]^2$$
$$\frac{27}{16}$$

11. Consider the following rate data for the reaction below at a particular temperature.

    $2A + 3B \longrightarrow$ Products

Experiment	Initial [A]	Initial [B]	Initial Rate of Loss of A
1	0.10 M	0.30 M	7.20 x 10^{-5} $M \cdot s^{-1}$
2	0.10 M	0.60 M	1.44 x 10^{-4} $M \cdot s^{-1}$
3	0.20 M	0.90 M	8.64 x 10^{-4} $M \cdot s^{-1}$

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

Handwritten:

for B use exp 2/1

$$\frac{1.44 \times 10^{-4}}{7.20 \times 10^{-5}} = \frac{\cancel{k}[A]^x [0.60]^y}{\cancel{k}[A]^x [0.30]^y}$$

$2 = [2]^y \quad \boxed{y = 1}$

Now for A: use 1 + 3 or 2 + 3.

$\frac{ex\ 3}{ex\ 2}$: $\frac{8.64 \times 10^{-4}}{1.44 \times 10^{-4}} = \frac{\cancel{k}[0.90]^1}{\cancel{k}[0.60]^1} \left(\frac{0.20}{0.10}\right)^x$

$4 = (2)^x \quad \boxed{x = 2}$

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

[NH_4^+]	[$NO2-$]	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

Handwritten:

For NH_4^+: $\frac{0.030}{0.020} = \left(\frac{0.015}{0.010}\right)^x$

$1.5 = (1.5)^x \quad \boxed{x = 1}$

for NO_2^-: $\frac{0.020}{0.005} = \left(\frac{0.020}{0.010}\right)^y$

$4 = (2)^x \quad \boxed{x = 2}$

13. Consider a chemical reaction involving compounds A and B, which is found to be first order in A and second order in B. At what rate will the reaction occur in experiment 2?

Experiment	Rate($M \cdot s^{-1}$)	Initial [A]	Initial [B]
1	0.10	1.0 M	0.20 M
2	?	2.0 M	0.60 M

a) 1.2 $M \cdot s^{-1}$
b) 0.20 $M \cdot s^{-1}$
c) 0.60 $M \cdot s^{-1}$
d) 1.8 $M \cdot s^{-1}$
e) none of these

Handwritten:

$rate = k[A][B]^2$

$0.10 = k[1.0][0.20]^2$

$k = 2.5\ M^{-2}s^{-1}$

So $rate = 2.5[2.0][0.60]^2 = 1.8$

14. 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

Handwritten:

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

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

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

$k = \frac{\ln 2}{1570\,s} = 4.415 \times 10^{-4}$

$\ln\left[\frac{[A]_t}{[A]_0}\right] = -4.415 \times 10^{-4}(4710) = -2.0794..$

$\left[\frac{[A]_t}{[A]_0}\right] = e^{-2.0794..} = 0.125 = \frac{1}{8}$

15. 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. 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:
1st order so: $\ln[A]_t = -kt + \ln[A]_0$ & $k = \frac{\ln 2}{t_{1/2}}$

$\ln[A]_t = -0.806(1.50) + \ln[2.00]$ $k = 0.806$

$\ln[A]_t = -0.518$

$[A]_t = e^{-0.516} = 0.597$

16. Compounds A and B react to form C and D in a reaction that is found to be <u>second-order</u>
    overall and second-order in B. The rate constant at 30°C is 0.622 liter per mole per minute.
    $A + B \rightarrow C + D$
   How many minutes does it take 4.0×10^{-2} M B (mixed with excess A) to be reduced to 3.3×10^{-2} M B?

    a) 1.4 min
    b) 3.6 min
    c) 5.0 min
    d) 6.4 min
    e) 8.5 min

Handwritten:
2nd order $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$

$\frac{1}{[3.3 \times 10^{-2}]} = 0.622(t) + \frac{1}{[4.0 \times 10^{-2}]}$

$t = 8.5$

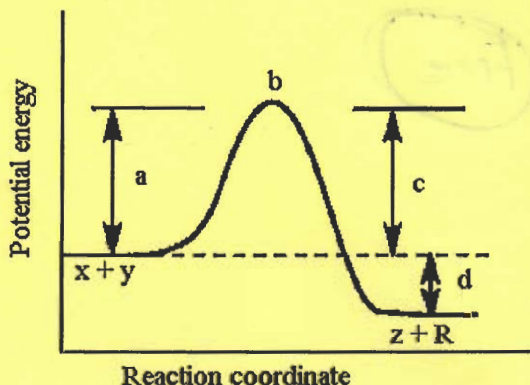17. Which one of the following statements is **false**?

    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.

18. 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
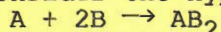   diagram best describes this reaction?
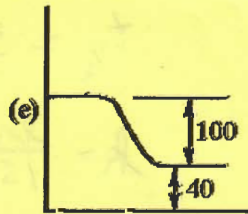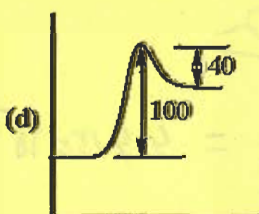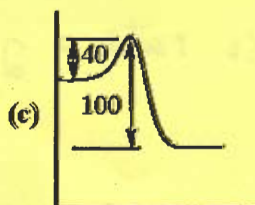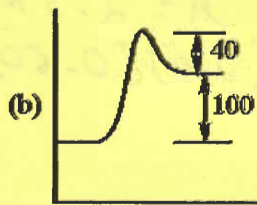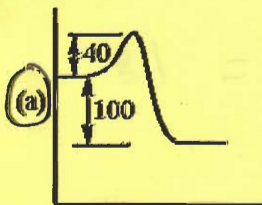
19. Given the following potential energy diagram for the one-step reaction
X + Y $\longrightarrow$ Z + R   The reaction, carried out at constant volume
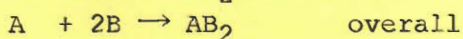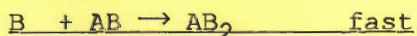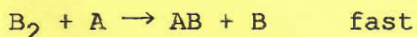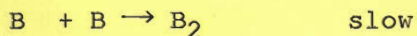and temperature, _____.

   a) releases energy
   b) absorbs energy
   c) is impossible
   d) occurs without a net change in energy
   e) may either absorb or release energy

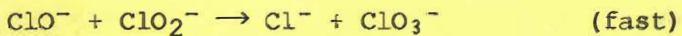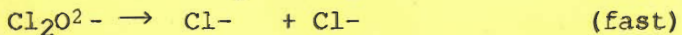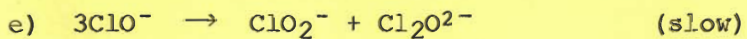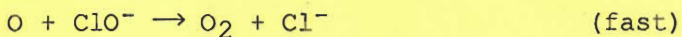20. Consider the hypothetical reaction shown below.
   A + 2B $\longrightarrow$ AB$_2$
   Assume that the following proposed mechanism is consistent with the
   rate data.

   B + B $\longrightarrow$ B$_2$ slow

   B$_2$ + A $\longrightarrow$ AB + B   fast

   B + AB $\longrightarrow$ AB$_2$ fast
   A + 2B $\longrightarrow$ 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

21. 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) $ClO^- + ClO^- \rightarrow ClO_2^- + Cl^-$ (slow)

$ClO^- + ClO_2^- \rightarrow ClO_3^- + 2Cl^-$ (fast)
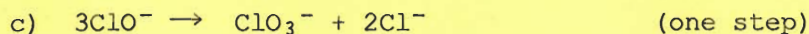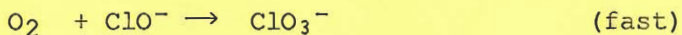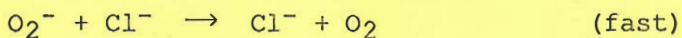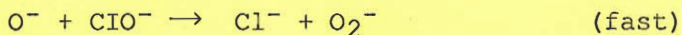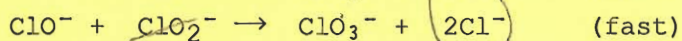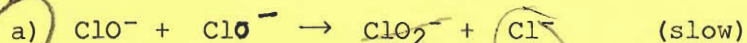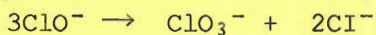
All have errors, not a good question

Free

b) $ClO^- \rightarrow Cl + O^-$ (slow)

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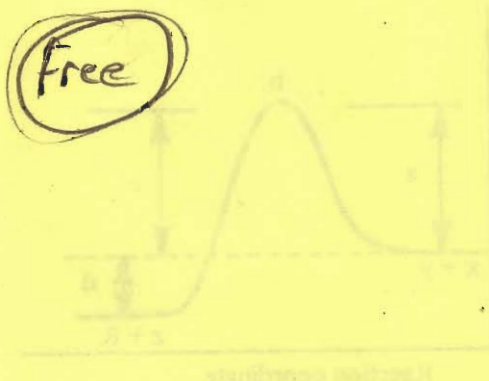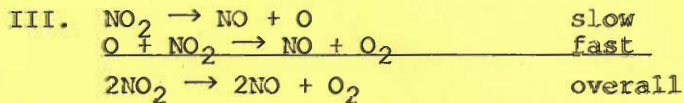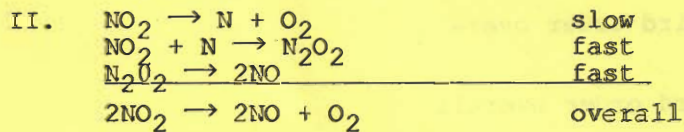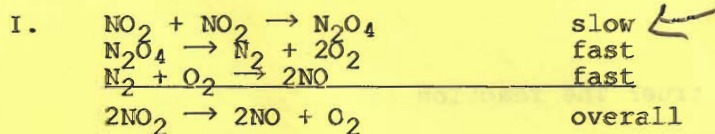
$O_2^- + Cl^- \rightarrow Cl^- + O_2$ (fast)

$O_2 + ClO^- \rightarrow ClO_3^-$ (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)

2. Consider the reaction below and its observed rate law expression. Which proposed mechanisms **are consistent** with the rate law expression?

$$2NO_2 \rightarrow 2NO + O_2 \qquad Rate = k[NO_2]^2$$

I. $NO_2 + NO_2 \rightarrow N_2O_4$ slow

$N_2O_4 \rightarrow N_2 + 2O_2$ fast

$N_2 + O_2 \rightarrow 2NO$ fast

$2NO_2 \rightarrow 2NO + O_2$ overall

II. $NO_2 \rightarrow N + O_2$ slow

$NO_2 + N \rightarrow N_2O_2$ fast

$N_2O_2 \rightarrow 2NO$ fast

$2NO_2 \rightarrow 2NO + O_2$ overall

III. $NO_2 \rightarrow NO + O$ slow

$O + NO_2 \rightarrow NO + O_2$ fast

$2NO_2 \rightarrow 2NO + O_2$ overall
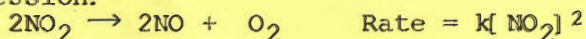
a) I

b) II

c) III

d) I and III

e) another one or another combination

23. The **principal** reason for the increase in reaction rate with increasing temperature is

    a) molecules collide more frequently at high temperatures.
    b) the pressure exerted by reactant molecules increases with increasing temperature.
    c) the activation energy increases with increasing temperature.
    d) the fraction of high energy molecules increases with increasing temperature.
    e) your instructor says so.

24. 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. 348K   298K

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

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

$$\ln \frac{11.5}{0.75} = \frac{E_a}{8.314}\left(\frac{1}{298} - \frac{1}{348}\right)$$

$$E_a = 47076 \text{ J} = 47.1 \text{ kJ}$$

25. Which response includes all the true statements and no false statements? A catalyst can
    _____.

    I.   make a nonspontaneous reaction spontaneous   F
    II.   speed up a forward reaction and slow down the reverse reaction   F
    III. lower the activation energy of the forward reaction
    IV.   lower the activation energy of the reverse reaction

    a) I and III
    b) II and II
    c) I and IV
    d) III and IV
    e) another one or another combination