Key

CHM 152/54 Exam 1 Formulas

rate = k rate = k[A] rate = $k[A]^2$ $[A]_t = -kt + [A]_0$

$\ln[A]_t = -kt + \ln[A]_0$ $1/[A]_t = kt + 1/[A]_0$ $t_{1/2} = [A]_0/2k$

$t_{1/2} = 0.693/k$ $t_{1/2} = 1/k[A]_0$

$\ln(k_2/k_1) = (E_a/R)(1/T_1 - 1/T_2)$ R= 8.314 J/(mol•K) $e=mc^2$

$k = Ae^{-Ea/RT}$ PV = nRT $K = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

CHM 152/54 Exam 1 100 Pts Fall 2003 Name: Key

1. For the overall chemical reaction shown below, which one of the following statements can you rightly assume?

   $2H_2S(g) + O_2(g) \rightarrow 2S(s) + 2H_2O(l)$

   A. The reaction is second-order overall.
   B. The reaction is third-order overall.
   C. The rate law is, rate = $k[H_2S]^2[O_2]$.
   D. The rate law cannot be determined from the information given.
   E. The rate law is, rate = $k[H_2S][O_2]$.

2. The reaction $A + 2B \rightarrow$ products was found to follow the rate law: rate = $k[A]^2[B]$. Predict by what factor the rate of reaction will increase when the concentration of A is doubled and the concentration of B is tripled, and the temperature remains constant.

   A. 12
   B. 18
   C. 5
   D. 6
   E. None of the above.

   rate - $[2]^2[3] = 12$

3. The units for a first-order rate constant are

   A. 1/M•s
   B. $1/M^2$•s
   C. 1/s
   D. M/s

   rate = $k[A]$

   $\frac{M}{s} = \frac{\;}{s} M$

4. It takes 42 min for the concentration of a reactant in a first-order reaction to drop from 0.45M to 0.32M at 25°C. How long will it take for the reaction to be 90% complete?

   A. 137 min B. 13 min C. 86 min D. 284 min E. 222 min

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

$\ln[0.32] = -k(42\,\text{min}) + \ln(0.45)$

$\ln\left(\frac{0.32}{0.45}\right) = -k(42\,\text{min})$

$k = 0.008117\,\text{min}^{-1}$

then @ 90% complete $[A]_t = 0.1$ of $[A]_0$

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

$\ln(0.1) \div k = t = 284$ min

Key

5. Nitric oxide gas (NO) reacts with chlorine gas according to the equation
$NO + \frac{1}{2}Cl_2 \rightarrow NOCl$

The following initial rates of reaction have been measured for the given reagent concentrations.

Expt. #	Rate (M/hr)	NO (M)	Cl_2(M)
1	1.19	0.50	0.50
2	4.79	1.00	0.50
3	9.59	1.00	1.0

Which of the following is the rate law (rate equation) for this reaction?

A. rate = $k[NO][Cl_2]$
B. rate = $k[NO]$
C. rate = $k[NO]^2[Cl_2]$
D. rate = $k[NO][Cl_2]^{1/2}$
E. rate = $k[NO]^2[Cl_2]^2$

For NO: $\frac{Exp\,2}{Exp\,1} = \frac{rate\,2}{rate\,1} = \frac{\cancel{k}[NO]_2^x[Cl_2]_2^y}{\cancel{k}[NO]_1^x\cancel{[Cl_2]_1^y}}$

$\frac{4.79}{1.19} = \left(\frac{1.00}{0.50}\right)^x \quad 4 = (2)^x;\ x = 2$

For Cl_2: $\frac{3}{2}$; $\frac{9.79}{4.79} = \left(\frac{1.0}{0.5}\right)^y \quad 2 = (2)^y;\ \therefore y = 1$

6. At 25°C, the rate constant for the first-order decomposition of a pesticide solution is $6.40 \times 10^{-3}\ min^{-1}$. If the starting concentration of pesticide is 0.0314 M, what concentration will remain after 62.0 min at 25°C?

A. 2.11×10^{-2} M
B. -8.72.0M
C. 2.68×10^{-2} M
D. 47.4M
E. 1.14×10^{-1} M

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

$= -\frac{6.40 \times 10^{-3}}{min}(62.0\ \cancel{min}) + \ln(0.0314)$

$\ln[A]_t = -3.8577$

$[A]_t = e^{-3.8577} = 0.0211\ M$

7. A certain first-order reaction A → B is 25% complete in 42 min at 25°C. What is the half-life of the reaction?

A. 42 min B. 21 min C. 101 min D. 120 min E. 84 min

$t_{1/2} = \frac{\ln 2}{k}$, so we must find k

$\ln\frac{[A]_t}{[A]_0} = -kt$ (at 42 min $[A_t] = 0.75[A]_0$)

$\ln(0.75) = -k(42\ min)$

$k = 0.00685\ min^{-1}$

So: $t_{1/2} = \frac{\ln 2}{0.00685} = 101\ min$

repeat of 5

8. Nitric oxide reacts with chlorine to form nitrosyl chloride, NOCl. Use the following data to determine the rate equation for the reaction.

$NO + 1/2Cl_2 \rightarrow NOCl$

$rate = k[NO]^x[Cl_2]^y$

Expt. #	[NO]	$[Cl_2]$	Initial Rate
1	0.22	0.065	0.96 M/min
2	0.66	0.065	8.6 M/min
3	0.22	0.032	0.48 M/min

A. rate = $k[NO]^2[Cl_2]$
B. rate = $k[NO][Cl_2]^{1/2}$
C. rate = $k[NO][Cl_2]$
D. rate = $k[NO]^2[Cl_2]^2$
E. rate = $k[NO]$

for $NO \left(\frac{2}{1}\right)$ $9 = (3)^x$ so $x = 2$

for $Cl_2 \left(\frac{1}{3}\right)$ $2 = (2)^y$ $y = 1$

9. The isomerization of cyclopropane to form propene

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H2C — CH2
   \   /          →   CH3 – CH = CH2CH2
    CH2
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is a first-order reaction. At 760 K, 15% of a sample of cyclopropane changes to propene in 6.8 min. What is the half-life of cyclopropane at 760 K?

A. ~~2.5 min~~
B. ~~29 min~~
C. 3.4×10^{-2} min
D. 230 min
E. 23 min

$\ln(0.85) = -kt$

$k = \ln 0.85 \div 6.8\ min = 0.0239$

$t_{1/2} = \frac{\ln 2}{0.0239} = 29\ min$

10. The reaction $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$ is suspected to be second order in NO_2. Which of the following kinetic plots would be the most useful to prove whether or not the reaction is second order?

A. a plot of $[NO_2]^2$ vs. t
B. a plot of $[NO_2]^{-1}$ vs. t
C. a plot of ln $[NO_2]^{-1}$ vs. t
D. a plot of ln $[NO_2]$ vs. t
E. a plot of $[NO_2]$ vs. t

Use the following information to answer questions 11-12.
The thermal decomposition of acetaldehyde is a second-order reaction.

$CH_3CHO \rightarrow CH_4 + CO$ rate $= k[CH_3CHO]^x$

The following data were obtained at 518°C. The initial pressure of CH_3CHO is 364 mmHg.

time, s	Pressure CH_3CHO, mmHg	ln P	1/P
42	330	5.7991	0.003030
105	290	5.6699	0.003448
720	132	4.8828	0.007575

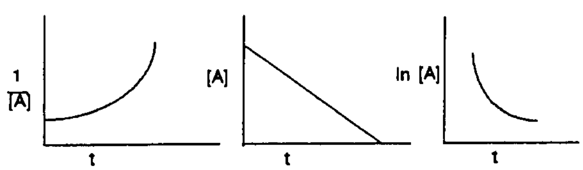
11. Calculate the rate constant for the decomposition of acetaldehyde from the above data. See graphs

A. 2.2×10^{-3}/s
B. 5.2×10^{-5}/mmHg s
C. 0.70 mmHg/s
D. 2.2×10^{-3}/mmHg s
E. 6.7×10^{-6}/mmHg s

12. Based on the data given, what is the half-life of acetaldehyde? Graph

A. 305 s B. 1.5×10^5 s C. 410 s D. 520 s E. 5.4×10^7 s

13. The graphs below all refer to the same reaction. What is the order of this reaction?



A. second order B. zero order C. first order

14. Which one of the following changes would alter the rate constant (k) for the reaction $2A + B \rightarrow$ products?

A. increasing the temperature
B. measuring k again after the reaction has run for a while
E. the rate constant will not change
C. increasing the concentration of B
D. increasing the concentration of A

15. If E_a for a certain biological reaction is 50 kJ/mol, by what factor (how many times) will the rate of this reaction increase when body temperature increases from 37°C (normal) to 40°C (fever)?

A. 1.0002 times
B. 2.0×10^5 times
C. 1.20 times
D. 2.0 times
E. 1.15 times

$$\ln \frac{k_2}{k_1} = \frac{50 \times 10^3 \text{ J/mol}}{8.314 \text{ J/mol K}} \left(\frac{1}{310 \text{ K}} - \frac{1}{313} \right)$$

$$\ln \frac{k_2}{k_1} = 0.1859$$

$$\frac{k_2}{k_1} = 1.20$$

16. The isomerization of methyl isocyanide (CH_3NC).

$CH_3NC \rightarrow CH_3CN$

follows first-order kinetics. The half-lives were found to be 161 min at 199°C, and 12.5 min at 230°C. Calculate the activation energy for this reaction.

A. 124 kJ/mol
B. 31.4 kJ/mol
C. 6.17×10^{-3} kJ/mol
D. 163 kJ/mol
E. 78.2 kJ/mol

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

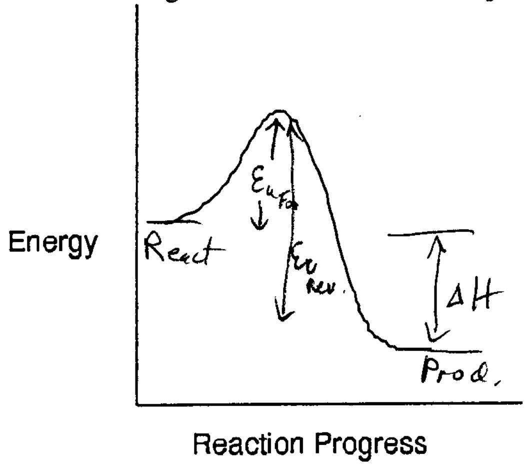
$$k_{199°C} = \frac{0.693}{161} = 4.30 \times 10^{-3} \text{ min}^{-1}$$

$$k_{230°C} = \frac{0.693}{12.5} = 5.54 \times 10^{-2} \text{ min}^{-1}$$

$$\ln \frac{4.30 \times 10^{-3}}{5.54 \times 10^{-2}} = \frac{E_a}{8.314} \left(\frac{1}{503} - \frac{1}{472} \right)$$

$$E_a = 162747 \frac{\text{J}}{\text{mol}}$$

Use the following information to answer questions 17-18.



17. For the chemical reaction system described by the diagram above, which statement is true?

   A. At equilibrium, the activation energy for the forward reaction is equal to the activation energy for the reverse reaction.
   B. The activation energy for the forward reaction is greater than the activation energy for the reverse reaction.
   C. The reverse reaction is exothermic.
   D. The activation energy for the reverse reaction is greater than the activation energy for the forward reaction.
   E. The forward reaction is endothermic.

Same

18. For the chemical reaction system described by the diagram above, which statement is true?

   If the E_a for the forward reaction is 25 kJ/mol, and the enthalpy of reaction is -95 kJ/mol, what is E_a for the reverse reaction?

   A. -70 kJ/mol
   B. 95 kJ/mol
   C. 70 kJ/mol
   D. 120 kJ/mol
   E. 25 kJ/mol

19. An increase in the temperature of the reactants causes an increase in the rate of reaction. The best explanation is: As the temperature increases,

   A. the activation energy decreases.
   B. the collision frequency increases.
   C. the fraction of collisions with total kinetic energy > E_a increases.
   D. the concentration of reactants increases.
   E. the activation energy increases.

20. According to the collision theory, all collisions do not lead to reaction. Which choice gives both reasons why all collisions between reactant molecules do not lead to reaction?

1. The total energy of two colliding molecules is less than some minimum amount of energy.
2. Molecules cannot react with each other unless a catalyst is present.
3. Molecules that are improperly oriented during collision will not react.
4. Solids cannot react with gases.

A. 2 & 3 B. 3 & 4 C. 1 & 2 D. 1 & 3 E. 1 & 4

21. The rate law for the reaction

$H_2O_2 + 2H^+ + 2I^- \rightarrow I_2 + 2H_2O$

is rate = $k[H_2O_2][I^-]$. The following mechanism has been suggested.

$H_2O_2 + I^- \rightarrow HOI + OH^-$	slow
$OH^- + H^+ \rightarrow H_2O$	fast
$HOI + H^+ + I^- \rightarrow I_2 + H_2O$	fast

Identify all intermediates included in this mechanism.

A. H^+ and I^-
B. HOI and OH^-
C. H_2O and OH^-
D. H^+ and HOI
E. H^+ only

22. The rate law for the reaction $2NO_2 + O_3 \rightarrow N_2O_5 + O_2$ is rate = $k[NO_2][O_3]$. Which one of the following mechanisms is consistent with this rate law?

A. $NO_2 + O_3 \rightarrow NO_3 + O_2$ (slow)
$NO_3 + NO_2 \rightarrow N_2O_5$ (fast)

B. $NO_2 + O_3 \rightarrow NO_5$ (fast)
$NO_5 + NO_5 \rightarrow N_2O_5 + 5/2O_2$ (slow)

C. $NO_2 + NO_2 \rightarrow N_2O_4$ (fast)
$N_2O_4 + O_3 \rightarrow N_2O_5 + O_2$ (slow)

D. $NO_2 + NO_2 \rightarrow N_2O_2 + O_2$ (slow)
$N_2O_2 + O_3 \rightarrow N_2O_5$ (fast)

23. Complete this statement: A catalyst

A. alters the reaction mechanism.
B. increases the activation energy.
C. increases the collision frequency of reactant molecules.
D. increases the average kinetic energy of the reactants.
E. increases the concentration of reactants.

24. Dinitrogen monoxide (N_2O) decomposes at 600°C according to the balanced equation

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

A reaction mechanism involving three steps is shown below. Identify all of the catalysts in the following mechanism.

$Cl_2(g) \rightarrow 2Cl(g)$
$N_2O(g) + Cl(g) \rightarrow N_2(g) + ClO(g)$ (occurs twice)
$ClO(g) + ClO(g) \rightarrow Cl_2(g) + O_2(g)$

A. ClO
B. N_2O
C. Cl_2
D. Cl
E. ClO and Cl

25. For the reaction represented below, the experimental rate law is given as follows: Rate = k $[(CH_3)_3CCl]$.

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

If some solid sodium hydroxide is added to a solution in which $[(CH_3)_3CCl] = 0.01M$ and [NaOH] = 0.10 M, which of the following would be true? (Assume the temperature and volume remain constant.)

A. The reaction rate would increase but k would remain the same.
B. Both the reaction rate and k would decrease.
C. The reaction rate would decrease but k would remain the same.
D. Both the reaction rate and k would increase.
E. Both the reaction rate and k would remain the same. , zero order w.r.t (OH^-)