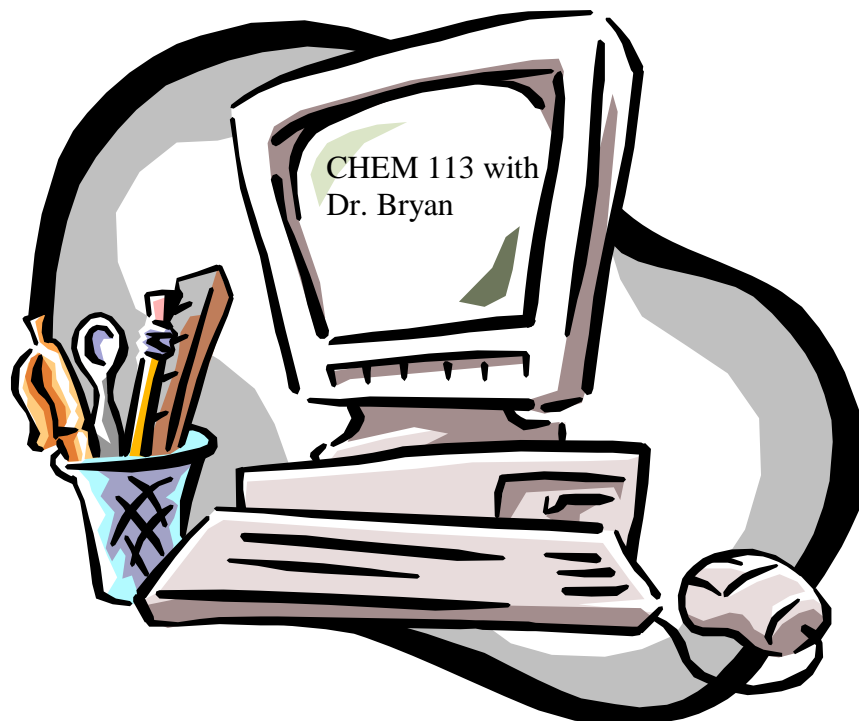


CHEMISTRY 113

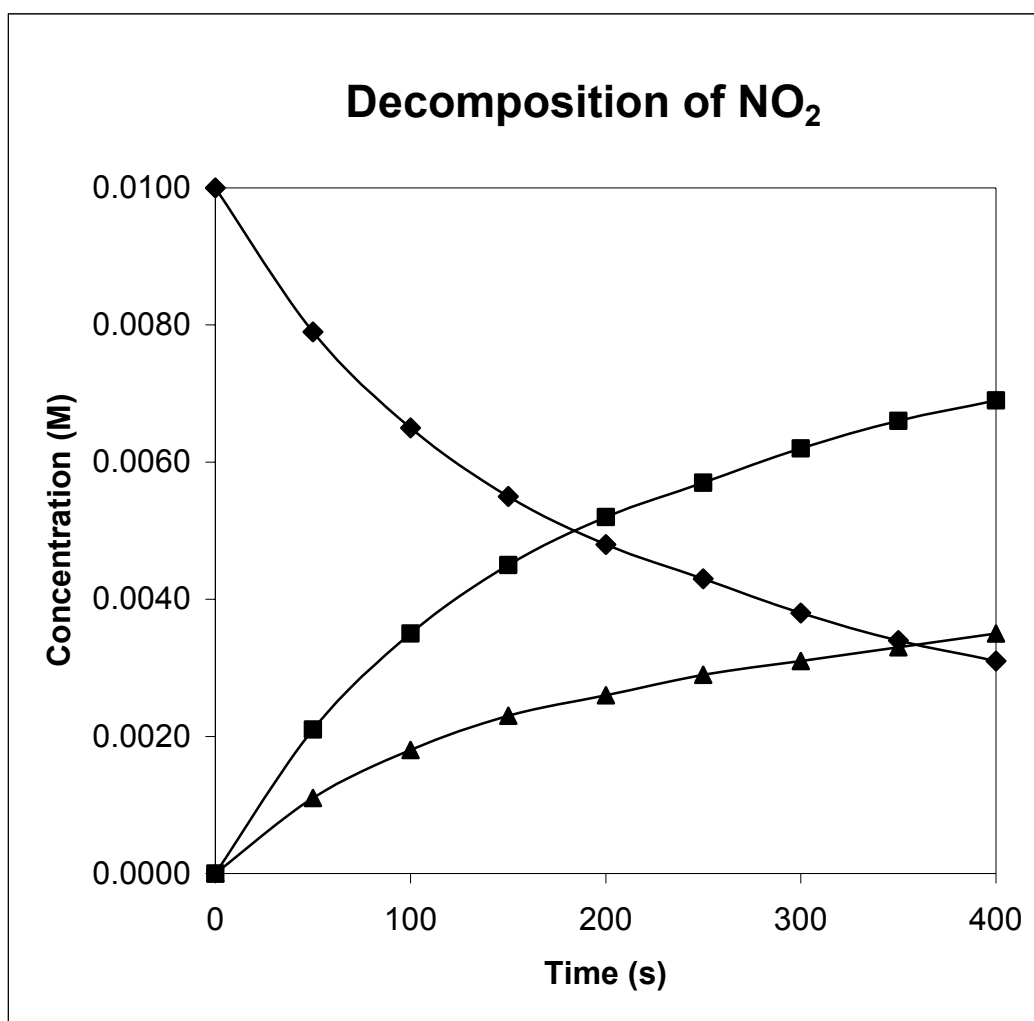
Kinetics - Summer 2005

Instructor: Dr. Andrew M. Bryan



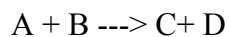
Items

- A Graph Concerning Kinetics
- Guide to Determining Rate Laws
 - A Kinetics Problem
 - Radioactivity and Kinetics
 - Power Point Slides
- Kinetics Problem Set and Key
- Sample Kinetics Test Questions – Multiple Choice.



Time (s)	$[\text{NO}_2]$, (M)	$[\text{NO}]$, (M)	$[\text{O}_2]$, (M)
0	0.0100	0	0
50	0.0079	0.0021	0.0011
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023
200	0.0048	0.0052	0.0026
250	0.0043	0.0057	0.0029
300	0.0038	0.0062	0.0031
350	0.0034	0.0066	0.0033
400	0.0031	0.0069	0.0035

CHEM 113 Determining Rate Laws • (Revised 1/2001)



$$\text{Rate} = k [A]^m [B]^n$$

m and n are the order of the reactant

k is the forward rate constant at a given temperature

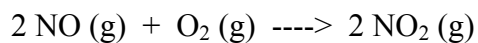
Method of initial rates

1. Perform a series of experiments
 - systematically change concentrations
 - measure the effect on rate
2. Answer the question : How does the concentration change effect rate?

A. Determining orders by inspection

Order (m or n)	If [X] is increased to [X] x 2, then rate will increase to :	If [X] is increased to [X] x 3, then rate will increase to :
0	rate x $(2)^0$	rate x $(3)^0$
1	rate x $(2)^1$	rate x $(3)^1$
2	rate x $(2)^2$	rate x $(3)^2$

B. Determining orders by math (to be shown in class)

CHEM 113 In Class Kinetics Problem (Rev. 1/2001)

Use the following data to answer the questions below:

Exp#	[NO] ₀ (M)	[O ₂] ₀ (M)	Rate of formation of N O ₂ (M/s)
1	0.01	0.01	7×10^{-6}
2	0.01	0.02	14×10^{-6}
3	0.01	0.03	21×10^{-6}
4	0.02	0.03	84×10^{-6}
5	0.03	0.03	189×10^{-6}

1. What is the order of the reaction with respect to each reactant?
2. What is the overall reaction order?
3. What is the rate constant (k)?
4. Write the rate law for the reaction.
5. Calculate the rate of formation of NO₂ when [NO]₀ = [O₂]₀ = 0.05 M

CHEM 113 Radioactivity and First Order Decay (Rev. 12/2002)**Terms:**

Alpha Decay

Beta Decay

Gamma Decay

Half- Life

Radioactive decay is a first order process In the table below are half-lives for some common isotopes (nuclides).

Nuclide	Half-life ($t_{1/2}$)
carbon-14	5730 years
uranium-238	4.51×10^9 years
iodine-131	8.04 days
radon-222	3.86 days
phosphorus-32	14.3 days

Example Calculations using Integrated Rate Law:

- Given 1.00 kg of uranium 238, how many grams will remain after 3 half-lives?
- Phosphorus-32 is used in biochemical studies to determine the pathways followed by phosphorus in living organisms.
 - What is the decay constant (rate constant) for the decay of phosphorus-32?
 - Given 1.00 mg of phosphorus-32, how many mg will remain after 57.0 days?

CHEMICAL KINETICS

CHEM 113
Dr. Bryan

What is Rate?

$$\text{Rate} = \frac{\text{Change in concentration}}{\text{Change in time}}$$

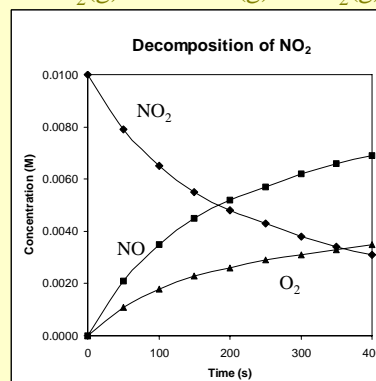
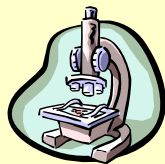
$$\text{Rate} = \frac{\Delta [A]}{\Delta t}$$

Average Rate

Instantaneous Rate

What is Kinetics?

- How long does it take?
- How fast does it go?
- Engineering . . . give me products now!
- Food Service . . . slow down bacterial growth
- Pharmacy . . . pain relief NOW!



Factors influencing rate of reaction

1. Concentration of reactants
2. Temperature
3. Physical State of Reactants
4. Catalyst



time(s)	[NO ₂]	[NO]	[O ₂]
0	0.0100	0.0000	0.0000
50	0.0079	0.0021	0.0011
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023

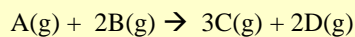


- What is the rate of change of NO_2 over the time interval from 0 to 50 seconds?
- What is the rate of formation of O_2 over that same interval?

Method of Initial Rates

1. Perform a series of experiments
 - systematically change concentrations
 - observe the effect on rate
 - How does the concentration change effect rate?
2. Determine orders by inspection (m,n)
3. Finally calculate the rate constant (k)

Relative Rates

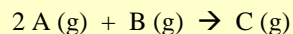


- At a given point in the reaction above, the rate of change of B is -0.150M/s , what is the rate of change of C?

Determining Order by Inspection

Order (m or n)	If [X] is increased to [X] x 2, then rate will increase to :	If [X] is increased to [X] x 3, then rate will increase to :
0	rate x $(2)^0$	rate x $(3)^0$
1	rate x $(2)^1$	rate x $(3)^1$
2	rate x $(2)^2$	rate x $(3)^2$

Differential Rate Law



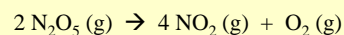
$$\text{Rate} = k_T [\text{A}]_0^m [\text{B}]_0^n$$

k_T = rate constant (temperature dependent)

m,n = orders of the reactants

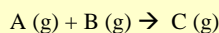
m+n = total order of reaction

Example #1



Experiment	$[\text{N}_2\text{O}_5]_0$ (M)	Rate of Loss (M/s)
#1	0.070 M	8.90×10^{-4}
#2	0.140 M	1.78×10^{-3}
#3	0.210 M	2.67×10^{-3}

Example #2



Experiment	[A] ₀ (M)	[B] ₀ (M)	Rate of Loss of A (M/s)
#1	0.100 M	0.100 M	4.0 x 10 ⁻⁵
#2	0.100 M	0.200 M	4.0 x 10 ⁻⁵
#3	0.200 M	0.100 M	16.0 x 10 ⁻⁵

Integrated Rate Law

- Simplest Case . . . Decomposition
- A → Products

$$-\frac{\Delta[A]}{\Delta t} = k[A]^m \quad \int_{A_0}^{A_t} \frac{dA}{A^m} = -k \int_0^t dt$$

Three common cases m= 0, 1, and 2!

Once you know the rate law . . .

- You can estimate rate of reaction for various concentrations.
- Example: for C + D → G
- Rate of loss of C = 3.05 M⁻¹s⁻¹ [C]²
- Calculate the rate when [C] = 0.250 M and [D] = 0.500 M.

First order decay (m=1)

$$\int_{A_0}^{A_t} \frac{dA}{A} = -k \int_0^t dt$$

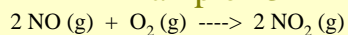
The Solution (three forms):

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

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

$$[A]_t = [A]_0 \exp(-kt)$$

Example #3



Exp#	[NO] ₀ (M)	[O ₂] ₀ (M)	Rate of formation of NO ₂ (M/s)
1	0.010	0.010	7.0 x 10 ⁻⁶
2	0.010	0.020	14 x 10 ⁻⁶
3	0.010	0.030	21 x 10 ⁻⁶
4	0.020	0.030	84 x 10 ⁻⁶
5	0.030	0.030	189 x 10 ⁻⁶

Half Life (t_{1/2})

- Time to decrease to one half the original amount.
- That is [A]_t = ½[A]₀
- For first order decay: t_{1/2} = 0.693/k

Radioactive Decay

- Alpha
- Beta
- Gamma

Calculations with the integrated rate law Example #2

Phosphorus-32 is used in biochemical studies to determine the pathways followed by phosphorus in living organisms.

- What is the decay constant (rate constant) for the decay of phosphorus-32?
- Given 1.00 mg of phosphorus-32, how many mg will remain after 57.0 days?

Half Lives of Various Isotopes

Nuclide	Half-life ($t_{1/2}$)
carbon-14	5730 years
uranium-238	4.51×10^9 years
iodine-131	8.04 days
radon-222	3.86 days
phosphorus-32	14.3 days

Zero order decay ($m=0$)

$$\int_{A_0}^{A_t} \frac{dA}{A^m} = -k \int_0^t dt$$

The Solution (when $m = 0$):

Calculations with the integrated rate law Example #1

Given 1.00 kg of uranium 238, how many grams will remain after 3 half-lives?

Second order decay ($m=2$)

$$\int_{A_0}^{A_t} \frac{dA}{A^m} = -k \int_0^t dt$$

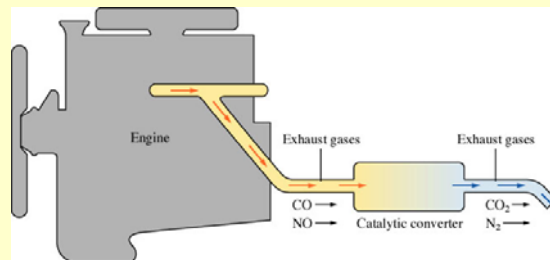
The Solution (when $m = 2$):

How do reactions occur (Collision Theory)

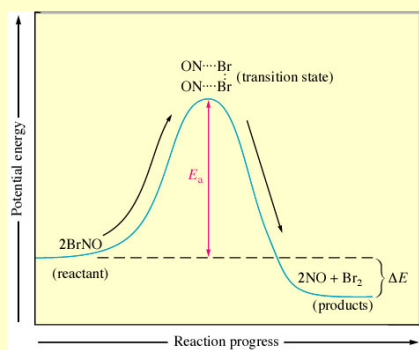
Requirements of the theory:

- Collisions must occur.
- Energy and Temperature must be appropriate.
- Orientation Factor

Example of a Catalyst



Reaction Coordinate

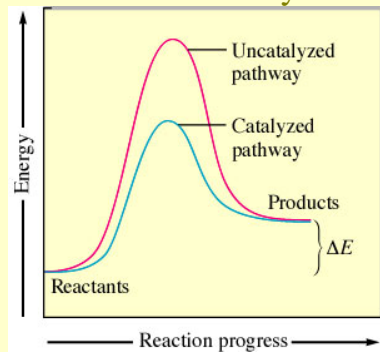


Effect of Temperature

Increasing temperature

- increases molecular motion
- increases the number of collisions
- increases the energy of the collisions
- (Rule of Thumb: rate doubles for every 10°C increase)

Effect of Catalyst



Arrhenius Rate Equation

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad \ln k = \ln A - \frac{E_a}{R} \left(\frac{1}{T}\right)$$

A = frequency factor

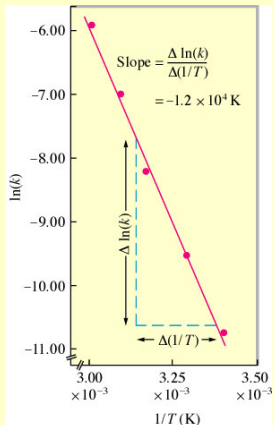
k = rate constant

R = gas constant

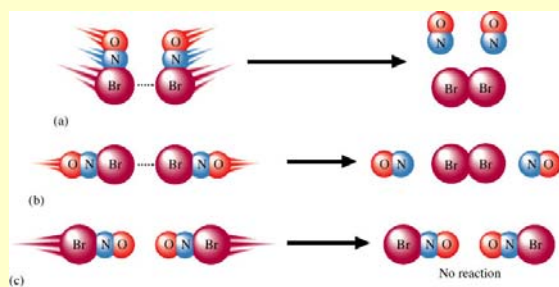
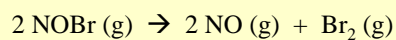
E_a = activation energy

T = temperature in Kelvin

Arrhenius Rate Plot



Orientation Effect



Mechanisms

- Determine a Rate Law experimentally
- Describe Reaction by a set of “molecular steps”
- What is the “rate determining step”?
- Are there “reaction intermediates”?
- The sum of the steps must agree with the stoichiometry!

PS#6 CHEM 113 -Chemical Kinetics - (Revised 1/2004)

Text: Zumdahl-Chapter 12 (12.1-12.5) Rate and Rate Laws, (12.6-12.8) Mechanisms

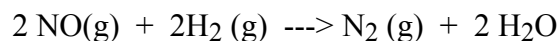
Problems: Rate and Differential Rate Law - 9,11,15,17,19,21,23,25,65

Integrated Rate Law – 27,29,33,35,37,39,41

Theory and Mechanisms - 45*,47*,49,53*,55,67*

Additional Problems:

- Define the following terms:
 formation constant, rate constant, order of reaction,
 rate law, activation energy, half-life, catalyst, intermediate
- Use the table below to answer questions concerning the reaction:



Experiment	[NO] ₀ (M)	[H ₂] ₀ (M)	Δ[N ₂]/Δt (M/s)
#1	0.60	0.15	0.076
#2	0.60	0.30	0.15
#3	0.60	0.60	0.30
#4	1.20	0.60	1.21

- Determine the orders of reaction (m and n).
- Determine the rate constant (k).
- Determine the rate law.
- What would the rate of loss of H₂ (Δ[H₂]/Δt) in experiment #2?
- What would the rate of formation of N₂ (Δ[N₂]/Δt), if [NO]₀ = 0.10 M, [H₂]₀ = 0.50 M

PS #6 Kinetics

1. For these definitions, see your book and notes!

2. a.) Rate = $k [\text{NO}]^m [\text{H}_2]^n$ where m, n are the orders of reaction

for m compare #3 } $[\text{H}_2]$ constant, $[\text{NO}] \times 2$, Rate $\times 4$
#4 } $\therefore m = 2$

for n compare #2 } $[\text{NO}]$ constant, $[\text{H}_2] \times 2$, Rate $\times 2$
#3 } $\therefore n = 1$

$\therefore \text{Rate} = k [\text{NO}]^2 [\text{H}_2]^1$ or just $\text{Rate} = k [\text{NO}]^2 [\text{H}_2]$

b.) Pick an experiment (I chose #2; it really doesn't matter!)

$$k = \frac{\text{Rate}}{[\text{NO}]^2 [\text{H}_2]} = \frac{0.15 \text{ M/s}}{[0.60 \text{ M}]^2 [0.30 \text{ M}]} = 1.39 \text{ M}^{-2} \text{ s}^{-1}$$

c.) Rate Law \Rightarrow $\boxed{\text{Rate} = 1.39 \text{ M}^{-2} \text{ s}^{-1} [\text{NO}]^2 [\text{H}_2]}$

d.) Rate given as $\frac{\Delta [\text{N}_2]}{\Delta t} = 0.15 \text{ M/s}$

from stoichiometry $-\frac{1}{2} \frac{\Delta [\text{H}_2]}{\Delta t} = \frac{\Delta [\text{N}_2]}{\Delta t} \quad \therefore \frac{\Delta [\text{H}_2]}{\Delta t} = \boxed{-0.30 \text{ M/s}}$

means loss!!

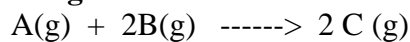
e.) Rate of formation

$$\begin{aligned} \text{Rate} = \frac{\Delta [\text{N}_2]}{\Delta t} &= 1.39 \text{ M}^{-2} \text{ s}^{-1} [\text{NO}]^2 [\text{H}_2] \\ &= 1.39 \text{ M}^{-2} \text{ s}^{-1} [0.10 \text{ M}]^2 [0.50 \text{ M}] \end{aligned}$$

$$= \boxed{6.95 \times 10^{-3} \text{ M/s}}$$

- Which of the following statements would be consistent with the "Collision Theory" of reactions between gas molecules?
 - As temperature decreases, the energy of molecular collisions increases.
 - All collisions between reactant molecules will lead to the formation of products.
 - Molecules do not have to collide with a certain orientation for a reaction to occur.
 - As temperature decreases, the number of molecular collisions decreases.
 - All of these are consistent with "Collision Theory".
- The Activation Energy of a reaction is
 - the energy difference between products and reactants.
 - the kinetic energy of gas molecules at a given temperature.
 - the minimum energy required to form a catalyst.
 - the minimum energy required for reactants to form products.
 - the minimum energy required to accelerate a gas molecule at a given temperature.
- Which of the following will generally increase the rate of a chemical reaction?
 - increasing temperature
 - adding a catalyst
 - decreasing reactant concentrations
 - Both A and B
 - A, B, and C
- The average rate of disappearance of O_3 in the reaction
$$2 O_3 (g) \rightarrow 3 O_2 (g)$$
is found to be $9.0 \times 10^{-3} \text{ M/s}$ at a given point in time. What is the rate of appearance of O_2 at that same point in time?
 - $1.4 \times 10^{-2} \text{ M/s}$
 - $9.0 \times 10^{-3} \text{ M/s}$
 - $6.0 \times 10^{-3} \text{ M/s}$
 - $3.0 \times 10^{-5} \text{ M/s}$
 - $2.7 \times 10^{-5} \text{ M/s}$
- Radioactive decay is a good example of
 - a zero order process
 - a first order process
 - a second order process
 - a third order process
 - a last order process
- Given the reaction:
$$2\text{MnO}_4^- (\text{aq}) + 5\text{H}_2\text{C}_2\text{O}_4 (\text{aq}) + 6 \text{H}^+ (\text{aq}) \rightarrow 2 \text{Mn}^{2+} (\text{aq}) + 10 \text{CO}_2 (\text{g}) + 8\text{H}_2\text{O} (\text{l})$$
At a given point in time the rate of loss of MnO_4^- is 0.328 M/s . What is the rate of loss of $\text{H}_2\text{C}_2\text{O}_4$ at this same point in time?
 - 0.164 M/s
 - 0.0656 M/s
 - 0.656 M/s
 - 0.820 M/s
 - 0.131 M/s

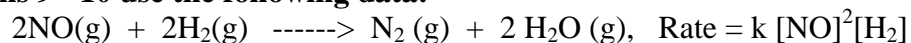
For Questions 7 - 8 use the following data:



Experiment	$[A]_0$	$[B]_0$	Rate of Loss of A
#1	0.16 M	0.15 M	8.0×10^{-2} M/s
#2	0.16 M	0.30 M	3.2×10^{-1} M/s
#3	0.080 M	0.30 M	8.0×10^{-2} M/s

7. What is the rate law for this reaction?
- A. Rate = $k[A][B]$
 B. Rate = $k[A]^2[B]$
 C. Rate = $k[A][B]^2$
 D. Rate = $k[A]^2[B]^2$
 E. Rate = $k[B]$
8. What is the numerical value for the rate constant in this reaction?
- A. 140
 B. 79
 C. 3.3
 D. 164
 E. 21

For Questions 9 - 10 use the following data:



Experiment	$[NO]_0$	$[H_2]_0$	Rate of Loss of NO
#1	0.10 M	0.20 M	1.50×10^{-2} M/s
#2	0.10 M	0.30 M	2.25×10^{-2} M/s
#3	0.20 M	0.20 M	6.00×10^{-2} M/s

9. What is the numerical value of the rate constant for this reaction?
- A. 7.5
 B. 0.0030
 C. 380
 D. 0.75
 E. 0.00030
10. What will be the rate of loss of NO (g) when $[NO]_0 = 0.30$ M and $[H_2]_0 = 0.15$ M?
- A. 1.35×10^{-2} M/s
 B. 8.00×10^{-2} M/s
 C. 1.01×10^{-1} M/s
 D. 5.13 M/s
 E. 3.38×10^{-1} M/s

11. Of the types of radioactive decay discussed in class, which of the following types of radiation was least likely to be able to pass through body tissues?
- A. alpha B. beta C. gamma D. all were about the same.

Use the following information for questions 12 through 14:

A new drug, SHAZZAM, decomposes in aqueous solution by a first order process with a rate constant of $k = 1.28 \times 10^{-3} \text{ s}^{-1}$.

12. What is the half-life of SHAZZAM in minutes?
- A. 541 min
B. 781 min
C. 25.0 min
D. 13.0 min
E. 9.02 min
13. A 500. mg tablet of SHAZZAM is placed into a beaker of water. How many mg of SHAZZAM will remain (undissolved) after 35.0 minutes?
- A. 34.0 mg
B. 62.3 mg
C. 121 mg
D. 466 mg
E. 478 mg
14. How long will it take a tablet of SHAZZAM to decay to 35.0% of its of it original amount?
- A. 128 s
B. 820 s
C. 781 s
D. 813 s
E. 273 s

-
15. Which of the following statements about equilibrium is FALSE?
- A. A system that is disturbed from equilibrium responds in a manner to restore equilibrium.
B. Equilibrium is a dynamic process, with two opposing processes balancing each other.
C. The equilibrium constant is independent of the initial mixture of reactants and products.
D. The equilibrium constant is independent of temperature.
E. None of the statements above are true.