Chem 2 AP Homework #13-2: Problems pg. 575 #14, 15, 17, 18, 19, 20, pg. 580 #87

9 **Explain what is meant by the rate law of a reaction.**
The rate law is the relationship of the rate of a reaction to the rate constant (k) and the concentrations of the reactants raised to some powers. Generically, for a reaction with reactants A and B,

$$\text{rate} = k\,[A]^x[B]^y$$

Note that x and y are not necessarily the coefficients in the balanced equation and must be determined experimentally.

10 **What is meant by the order of a reaction?**
The order of a reaction is the sum of the exponents to which all reactant concentrations in the rate law are raised. For the rate law in problem 9, the reaction order is x in reactant A and y in reactant B for an overall order of $(x + y)$.

11 **What are the units for the rate constants of first-order and second-order reactions?**
Since the rate of a reaction always has the unit of M time^{-1} or mol L^{-1} time^{-1}, the units of k must be such that when multiplied by the concentrations of reactants raised to their orders, this unit is obtained.

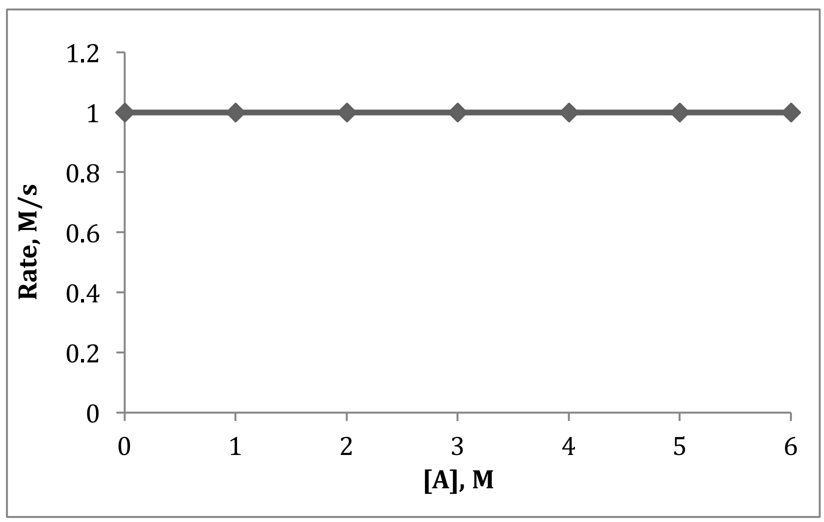
First Order: In an overall 1st order reaction, M time^{-1} = $k \times$ M, so k has the unit of time^{-1}.

Second Order: Here, M time^{-1} = $k \times$ M^2, so k has the unit of M^{-1} time^{-1}.

12 **Consider the zero-order reaction A → product**
(a) A zero-order reaction does not depend on the concentrations of the reactants, so

$$\text{rate} = k.$$

(b) Since the units for rate are M s^{-1}, the rate constant will have the same units.
(c) The plot will be a straight line, constant rate, and independent of concentration [A]:



14 **On which properties does the rate constant of a reaction depend?**
The rate constant, k, depends on both **(b) the nature of the reactants** and **(c) the temperature**, but is independent of (a) reactant concentrations.

15 **The rate law for the reaction, $NH_4^+(aq) + NO_2^-(aq) \rightarrow N_2(g) + H_2O(l)$ is given by rate = $k[NH_4^+][NO_2^-]$. At 25°C, the rate constant is $3.0\times10^{-4}/M\cdot s$. Calculate the rate of the reaction at this temperature if $[NH_4^+] = 0.26\ M$ and $[NO_2^-] = 0.080\ M$.**
rate = $k[NH_4^+][NO_2^-]$ = $(3.0 \times 10^{-4}\ /M\cdot s)(0.26\ M)(0.080\ M)$ = $\mathbf{6.2 \times 10^{-6}\ M/s}$

17 Consider the reaction A + B → products. From the following data obtained at a certain temperature, determine the order of the reaction and calculate the rate constant.

Expt.	[A] (*M*)	[B] (*M*)	Rate (*M*/s)
1	1.50	1.50	3.20×10^{-1}
2	1.50	2.50	3.20×10^{-1}
3	3.00	1.50	6.40×10^{-1}

Comparing expt 1 & 2, the rate is unchanged by changing [B], so the reaction is 0 order in B. Comparing expt. 1 & 3, when [A] doubles, rate doubles, so the reaction is first order in A: **rate = *k*[A]**

From the first set of data, 3.20×10^{-1} *M*/s = *k*(1.50 *M*), so ***k* = 0.213 s^{-1}**

What would be the value of *k* if you had used the second or third set of data? Should *k* be constant?

18 Consider the reaction X + Y → Z. The following data were obtained at 360 K.

Rate of disappearance of X	[X]	[Y]
0.053	0.10	0.50
0.127	0.20	0.30
1.02	0.40	0.60
0.254	0.20	0.60
0.509	0.40	0.30

To determine the order of the reaction, we need to find the rate law for the reaction. We assume that the rate law takes the form

$$\text{rate} = k[X]^x[Y]^y$$

(a) Determine the order of the reaction.
Experiments 2 and 5 show that when we double the concentration of X at constant concentration of Y, the rate quadruples, so the reaction is 2nd order in X

Experiments 2 and 4 indicate that doubling [Y] at constant [X] doubles the rate. That is, the reaction is first order in Y. Hence, the rate law is given by:

$$\text{rate} = k[X]^2[Y]$$

The order of the reaction is (2 + 1) = **3**. The reaction is *3rd-order*.

(b) Determine the initial rate of disappearance of X when the concentration of X is 0.30 *M* and that of Y is 0.40 *M*

$$k = \frac{\text{rate}}{[X]^2[Y]} = \frac{0.053\ \boldsymbol{M}/\text{s}}{(0.10\ M)^2(0.50\ M)} = 10.6\ \boldsymbol{M}^{-2}s^{-1}$$

Next, using the known rate constant and substituting the concentrations of X and Y into the rate law, we can calculate the initial rate of disappearance of X.

$$\textbf{rate} = (10.6\ M^{-2}\text{s}^{-1})(0.30\ M)^2(0.40\ M) = \mathbf{0.38}\ \boldsymbol{M}\textbf{/s}$$

19 Determine the overall orders of the reactions to which the following rate laws apply:

(a) rate = k[NO_2]^2 second order
(b) rate = k zero order
(c) rate = k[H_2][Br_2]$^{1/2}$ 1.5 order
(d) rate = k[NO]^2[O_2] third order

20 Consider the reaction A →B. The rate of the reaction is 1.6×10^{-2} *M*/s when the concentration of A is 0.35 M. Calculate the rate constant if the reaction is:

(a) first-order in A:

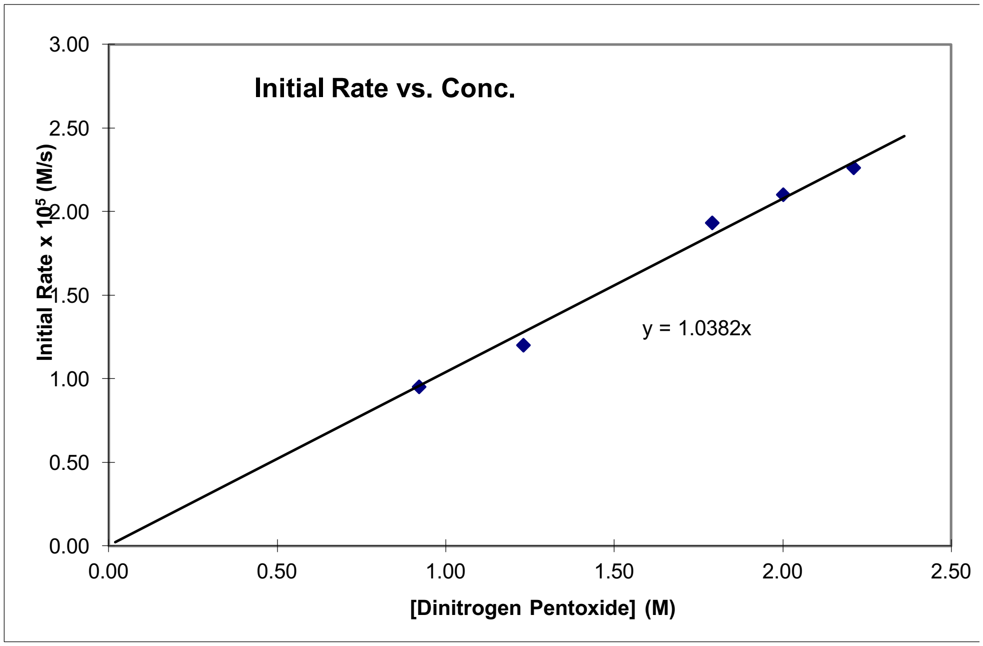
Rate = *k*[A], so 1.6×10^{-2} *M*/s = *k*(0.35 *M*) and ***k* = 0.046 s^{-1}**

(b) second-order in A:

Rate = *k*[A]^2, so 1.6×10^{-2} *M*/s = *k*(0.35 *M*)^2 and ***k* = 0.13 *M*$^{-1}$s^{-1}**

87 The decomposition of N_2O_5: $2N_2O_5 \rightarrow 4NO_2 + O_2$ in CCl_4 yields the following data:

$[N_2O_5]$, M	Initial Rate (M/s)
0.92	0.95×10^{-5}
1.23	1.20×10^{-3}
1.79	1.93×10^{-5}
2.00	2.10×10^{-5}
2.21	2.26×10^{-5}



The data are linear, with the initial rate directly proportional to the concentration of N_2O_5. Thus, the reaction is first order and the rate law is:

Rate = $k[N_2O_5]$

The rate constant k can be determined from the slope of the graph or by using any set of data, so $\boldsymbol{k = 1.0 \times 10^{-5}\ s^{-1}}$

Note that the rate law is ***not*** Rate = $k[N_2O_5]^2$, as we might expect from the balanced equation. In general, the order of a reaction must be determined by experiment; it cannot be deduced from the coefficients in the balanced equation.