Kinetics *(ch 14)*

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Cañada College — Chem 220

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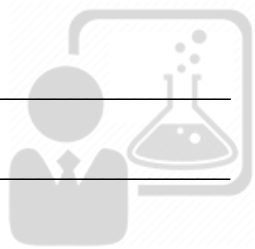


	Zero Order	First Order	Second Order
Dif Law	Rate = k	Rate = k [A]	Rate = k $[A]^2$
Int Law	$[A]_t = -k\ t + [A]_0$	$ln[A]_t = -k\ t + ln[A]_0$ $[A]_t = [A]_0\ e^{-kt}$	$1\ /[A]_t = -k\ t + (\ 1\ /[A]_0\ )$
Half Life	$[A]_0\ /\ 2k$	$0.693\ /\ k$	$1\ /\ (\ k\ [A]_0\ )$

Arrhenius Equation $k = Ae^{-Ea/RT}$ $\ln k = \ln(A) - \frac{E_a}{RT}$

R = 8.314 J/molK

(the above laws, equations & constants will be provided on the first exam)

1. Substance A and B react to form B and C by the following reaction. The initial rate of reaction is 2.0 M/s. What is the initial rate of change of A, B, C and D?

$$A + 3\ B \rightarrow 2\ C + 3\ D$$

2. Nitrogen dioxide has an initial concentration of 6.0 M. At 2, 4 and 8 hours the concentration is 4.0 M, 2.0 M and zero. What is the average rate of reaction in the first two hours (in M/hr)? What is the average rate over the last four hours? What is the instantaneous rate at 9 hours?

$$2\ N_2O \rightarrow 2\ N_2 + O_2$$

3. If the following reaction is first order what differential rate law would describe the reaction rate? If it is a second order reaction, what would be the differential rate law?

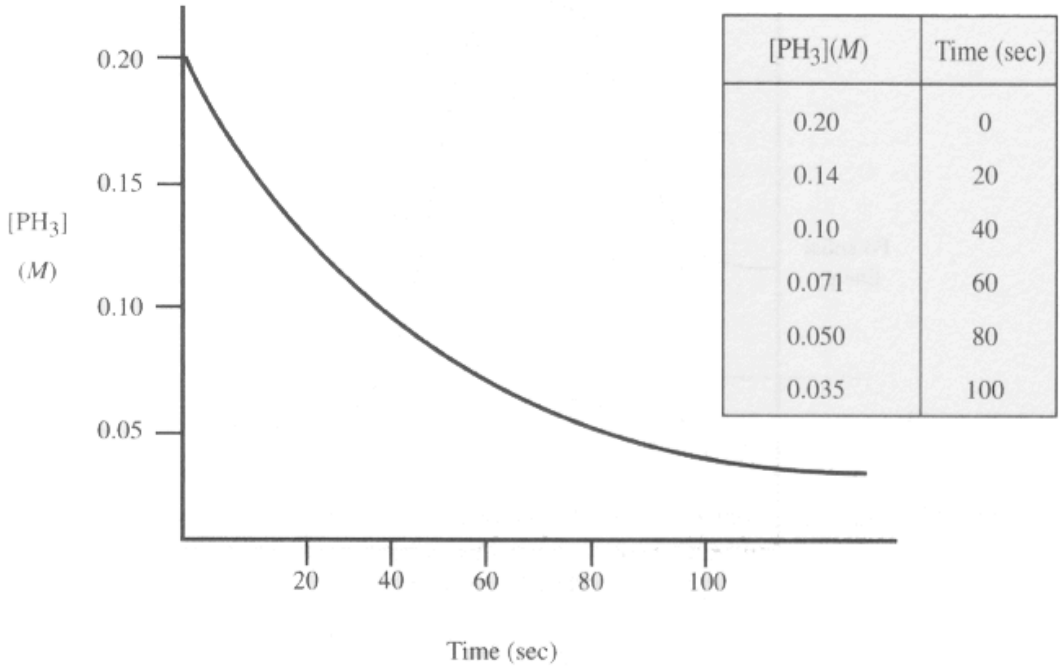
$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$$

4. The rate constant (k) for a zero order reaction is 3.981×10^{-2}. What is the reaction rate? (hint: the differential rate laws relate concentration to rate of reaction)

5. A first order reaction is 45.0% complete in 65 s. What is the rate constant (k) in s^{-1}? (hint: the integrated rate law relates concentration to time)

6. Phosphine (PH_3) decomposes via the following reaction. The concentrations of phosphine are observed at 250K over 20 second intervals (shown below).

$$4\ PH_{3\ (g)} \rightarrow P_{4\ (g)} + 6\ H_{2\ (g)}$$



$[PH_3](M)$	Time (sec)
0.20	0
0.14	20
0.10	40
0.071	60
0.050	80
0.035	100

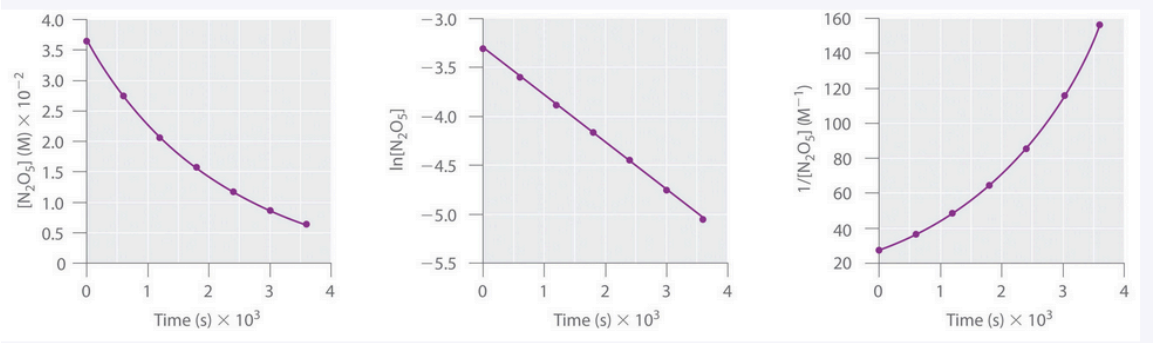
a. What is the half life of this reaction at 0.20 M? What is the half life of this reaction at 40 seconds?

b. What is the order of this reaction (justify your answer)?

c. What will be the concentration of phosphine be after 120 seconds?

7. Dinitrogen pentoxide (N_2O_5) decomposes in carbon tetrachloride according to the following reaction. To determine the rate law, a student determines the N_2O_5 concentration over time (data below) and creates three plots (below).

$$2\ N_2O_5\ (aq) \rightarrow 4\ NO_2\ (g) + O_2\ (g)$$



At 25 °C

Time (s)	$[N_2O_5]$ (M)	$\ln[N_2O_5]$	$1/[N_2O_5]$ (1/M)
0	0.0365	-3.310	27.4
600	0.0274	-3.597	36.5
1200	0.0206	-3.882	48.5
1800	0.0157	-4.154	63.7
2400	0.0117	-4.448	85.5
3000	0.00860	-4.756	116
3600	0.00640	-5.051	156

What is the rate law for this reaction?

What is *k* for this reaction?

At this temperature, what concentration would a solution initially at 0.0600 M be after 1.50 hours?

8. Four experiments are conducted to determine the rate law for the following reaction. The initial concentration and rate of each is shown as a separate line below.

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

Experiment	$[NO]_0$ (M)	$[O_2]_0$ (M)	Initial Rate (M/s)
1	0.0235	0.0125	7.98×10^{-3}
2	0.0235	0.0250	1.59×10^{-2}
3	0.0470	0.0125	3.20×10^{-2}
4	0.0470	0.0250	63.5×10^{-2}

What is rate law does this data indicate? What is *k* for this reaction?

What would be the initial rate of reaction with 0.500 M NO and 0.300 M O_2?

9. A reaction is third order in A, zero order in B and first order in C. What is the rate law? What is the overall order of this reaction?

10. In the gas phase, fluorine (F_2) can decompose by reaction with xenon (Xe), nitrogen (N_2) or ethylene (CH_2CH_2). Which reaction would you predict has the largest orientation factor (p)? Which reaction would you predict occurs the slowest?

11. Four experiments are conducted to determine the rate law for the following reaction. The initial concentration and rate of each is shown as a separate line below.

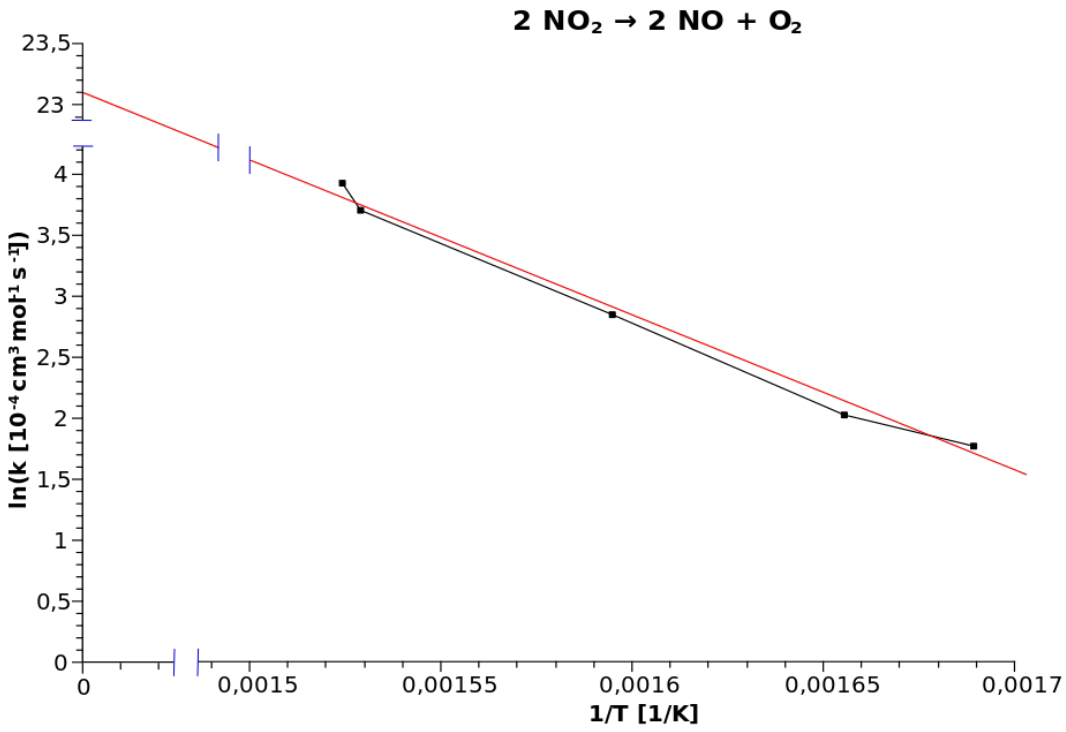
$$2\ F_2 + Xe \rightarrow XeF_4$$

Experiment	$[Xe]_0$ (M)	$[F_2]_0$ (M)	Initial Rate (M/s)
1	0.010	0.032	1.5×10^{-3}
2	0.010	0.064	3.0×10^{-3}
3	0.020	0.032	1.2×10^{-2}

What is rate law does this data indicate? What is *k* for this reaction?

12. Rate constants never change… unless you change the temperature of a reaction. A student explores the temperature dependence of the reaction below, by finding *k* at each of five different temperatures. The student creates the following plot of ln *k* verses inverse temperature. Two points on this line are:

y = 4.1 at x = 0.0015 and y = 2.2 at x = 0.00165



What is the activation energy (Ea) for this reaction? What is the pre-exponential term for this reaction (A)?

What is k for this reaction, if it occurs at 660 K?

13. Which of the following elementary steps would likely have the smaller orientation factor (explain why)? Assuming all other factors are the same, which step would occur faster?

step 1: $H_2 + ICl \rightarrow HI + HCl$

step 2: $HI + ICl \rightarrow I_2 + HCl$

14. For the following mechanism, what would be the rate law each of the three elementary steps (use intermediaries)? What would the overall law be if the first step was the slowest rate? What would the overall law be if the second step was the slowest rate? (reminder: there are no intermediaries in a the rate law for the overall reaction)

step 1: $NO + NO \xrightarrow{k_1} N_2O_2$

step 2: $N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O$

step 3: $N_2O + H_2 \xrightarrow{k_3} N_2 + H_2O$