HANDOUT SET

GENERAL CHEMISTRY II

Periodic Table of the Elements

	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 **H** 1.00794																	2 **He** 4.00262
2	3 **Li** 6.941	4 **Be** 9.0122											5 **B** 10.811	6 **C** 12.011	7 **N** 14.0067	8 **O** 15.9994	9 **F** 18.9984	10 **Ne** 20.179
3	11 **Na** 22.9898	12 **Mg** 24.305											13 **Al** 26.98154	14 **Si** 28.0855	15 **P** 30.97376	16 **S** 32.066	17 **Cl** 35.453	18 **Ar** 39.948
4	19 **K** 39.0983	20 **Ca** 40.078	21 **Sc** 44.9559	22 **Ti** 47.88	23 **V** 50.9415	24 **Cr** 51.9961	25 **Mn** 54.9380	26 **Fe** 55.847	27 **Co** 58.9332	28 **Ni** 58.69	29 **Cu** 63.546	30 **Zn** 65.39	31 **Ga** 69.723	32 **Ge** 72.59	33 **As** 74.9216	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.80
5	37 **Rb** 85.4678	38 **Sr** 87.62	39 **Y** 88.9059	40 **Zr** 91.224	41 **Nb** 92.9064	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.9055	46 **Pd** 106.42	47 **Ag** 107.8682	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.710	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.9045	54 **Xe** 131.29
6	55 **Cs** 132.9054	56 **Ba** 137.34	57 **La*** 138.91	72 **Hf** 178.49	73 **Ta** 180.9479	74 **W** 183.85	75 **Re** 186.207	76 **Os** 190.2	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.9665	80 **Hg** 200.59	81 **Tl** 204.383	82 **Pb** 207.2	83 **Bi** 208.9804	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
7	87 **Fr** (223)	88 **Ra** 226.0254	89 **Ac**** 227.0278	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (263)	107 **Bh** (264)	108 **Hs** (265)	109 **Mt** (266)	110 (270)	111 (272)	112 ***** (277)						

*Lanthanides	58 **Ce** 140.12	59 **Pr** 140.9077	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.36	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.925	66 **Dy** 162.50	67 **Ho** 164.930	68 **Er** 167.26	69 **Tm** 168.9342	70 **Yb** 173.04	71 **Lu** 174.967
**Actinides	90 **Th** 232.038	91 **Pa** 231.0659	92 **U** 238.0289	93 **Np** 237.0482	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (260)

Mass numbers in parenthesis are the mass numbers of the most stable isotopes. As of 1997 elements 110-112 have not been named.
***Peter Armbruster and Sigurd Hofman synthesized a single atom at the Heavy-Ion Research Center in Darmstadt, Germany in 1996. The atom survived for 280 μs after which it decayed to element 110 by loss of an α-particle

Chapter 14

Chemical Kinetics

CHEMICAL KINETICS
CHAPTER 15

INTRODUCTION
A properly written chemical equation tells that a reaction may occur to yield certain products. The rate of the reaction or how fast the reaction proceeds is, however, only experimentally determined. The field of chemistry dedicated to the study of reaction rates and the mechanism by which products are formed is known as chemical kinetics and mechanisms. The focus of lecture for this chapter is on chemical kinetics.

GOALS
1. You should be able to describe the rate of reaction as a change in concentration per change in time for any species in the reaction.
2. You should be able to take graphical data and deduce average and instantaneous rates.
3. From experimental data, it is possible to derive the rate law and from the rate law calculate rates of reactions for experimental conditions.
4. Three reaction orders have been explicitly covered: zeroeth-, first-, and second-order. An understanding of the how a rate plot would look and how to analyze for each of these is important.
5. You should be comfortable with using the integrated rate law for 1st- and 2nd-order reactions and understand how to calculate and use half-life.

DEFINITIONS
You should have a working knowledge of at least these terms and any others used in lecture.

First-order reaction	Overall reaction order	Instantaneous rate
Second-order reaction	Integrated rate law	Average rate
Zeroeth-order reaction	Half-life	Initial rate
Rate law	Rate constant	Mechanism

Chemical Kinetics, Reaction Rates, and the Rate Law

1. Consider the following reaction

$$CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g)$$

The kinetic data of initial reaction rate were collected for the initial concentration conditions. The rates are average initial rates, obtained graphically from the original kinetic data. Use the method of initial rates to determine the rate law and rate constant.

	$[CO]_0$ (M)	$[NO_2]_0$ (M)	Initial Rate (M/h)
1	5.1×10^{-4}	0.35×10^{-4}	3.4×10^{-8}
2	5.1×10^{-4}	0.70×10^{-4}	6.8×10^{-8}
3	5.1×10^{-4}	0.18×10^{-4}	1.7×10^{-8}
4	1.0×10^{-3}	0.35×10^{-4}	6.8×10^{-8}
5	1.5×10^{-3}	0.35×10^{-4}	10.2×10^{-8}

2. A first-order reactions proceeds with a rate constant of 0.020/s. If the initial concentration of the reactant is 0.012 M, what will be the concentration after 30 s?

3. Referring to the previous question, what fraction of starting material remains after 15 s?

4. What is the half-life of this reaction?

5. Radioactive isotopes decay obeying a first-order kinetic rate law. Tritium, a radioactive isotope of hydrogen, has a half-life of 12.3 y. It has a natural abundance of 10^{-18} percent (by mol). What mass of tritium (atomic weight 3.016 u) is present in 1000 kg of water? After 100 years, what mass of tritium will remain?

Temperature Dependence on the Rate Constant

1. Experiment

Determine the activation energy for the reaction

$$S_2O_8^{2-} + 2\,I^- \rightarrow 2\,SO_4^{2-} + I_2$$

The rate law for the reaction is

$$\text{Rate} = k[S_2O_8^{2-}][I^-]$$

Experimental Setup:

	Temp (°C)	Volumes of Reagents (mL) 0.20 M NaI	0.010 M $Na_2S_2O_3$	2% Starch Indicator	Water	0.20 M $K_2S_2O_8$	Reaction Time (s)
1							
2							
3							
4							
5							

For reasons we won't go into here:

$$\text{Rate} = \frac{\Delta[S_2O_8^{2-}]}{t_{\text{rxn}}} = \frac{1}{2}\frac{\Delta[S_2O_3^{2-}]_0}{t_{\text{rxn}}}$$

	Rate (M/s)	Rate Constant
1		
2		
3		
4		
5		

2. The reaction to produce ethyl alcohol from ethyl iodide

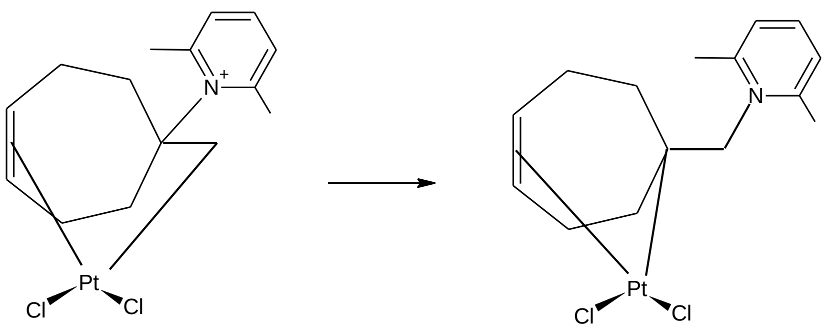
$$C_2H_5I + OH^- \rightarrow C_2H_5OH + I^-$$

was studied at several temperatures. The following rate constants for the reaction were determined:

Temperature (°C)	Rate Constant ($M^{-1}s^{-1}$)
15.83	5.03×10^{-5}
32.02	3.68×10^{-4}
59.75	6.71×10^{-3}
90.61	0.119

Determine the activation energy of the reaction graphically and by using the Arrhenius equation.

3. The following reaction is possibly important in the catalytic hydrogenation of alkene hydrocarbons. Determine the activation energy for the reaction.



What is the rate constant for the reaction at 25°C?

Data

Temp (°C)	Rate Constant (s^{-1})
-60.0	1.3×10^{-3}
-70.0	2.4×10^{-4}
-80.0	5.8×10^{-5}

Chemical Kinetics: Additional Problems

1. In the reaction

$$CH_3Br(aq) + OH^-(aq) \rightarrow CH_3OH(aq) + Br^-(aq)$$

when the OH^- concentration alone was doubled, the rate doubled; when the CH_3Br concentration alone was increased by a factor of 1.2, the rate increased by a factor of 1.2. Write the rate law for the reaction.

2. In the reaction

$$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$$

when the NO concentration alone was doubled, the rate increased by a factor of 4; when both the NO and the O_2 concentrations were increased by a factor of 2, the rate increased by a factor of 8. What is the rate law for the reaction?

3. The following kinetic data were obtained for the reaction

$$2\ ICl(g) + H_2(g) \rightarrow I_2(g) + 2\ HCl(g).$$

	Initial Concentration (mmol L^{-1})		
Experiment	$[ICl]_o$	$[H_2]_o$	Initial Rate (mmol·$L^{-1}s^{-1}$)
1	1.5	1.5	3.7×10^{-7}
2	3.0	1.5	7.4×10^{-7}
3	3.0	4.5	2.2×10^{-6}
4	4.7	2.7	?

(a) Write the rate law for the reaction.
(b) From the data, determine the value of the rate constant.
(c) Use the data to predict the reaction rate for Experiment 4.

4. The following kinetic data were obtained for the reaction

$$A(g) + 2\ B(g) \rightarrow \text{product}.$$

	Initial Concentration (mmol·L^{-1})		
Experiment	$[A]_o$	$[B]_o$	Initial Rate (mmol·$L^{-1}s^{-1}$)
1	0.60	0.30	1.6
2	0.20	0.30	1.4
3	0.60	0.10	4.2
4	0.17	0.25	?

(a) What is the order with respect to each reactant and the overall order of the reaction?
(b) Write the rate law for the reaction.
(c) From the data, determine the value of the rate constant.
(d) Use the data to predict the reaction rate for Experiment 4.

5. The following data were obtained for the reaction

$$A + B + C \rightarrow \text{products:}$$

Experiment	Initial Concentration (mmol L^{-1}) $[A]_o$	$[B]_o$	$[C]_o$	Initial Rate ((mmol A)·$L^{-1}s^{-1}$)
1	1.25	1.25	1.25	8.7
2	2.50	1.25	1.25	17.4
3	1.25	3.02	1.25	50.8
4	1.25	3.02	3.75	457
5	3.01	1.00	1.15	?

(a) Write the rate law for the reaction.
(b) What is the order of the reaction?
(c) Determine the value of the rate constant.
(d) Use the data to predict the reaction rate for Experiment 5.

6 Determine the rate constant for each of the following first- order reactions, in each case expressed for the rate of loss of A:

(a) $A \rightarrow B$, given that the concentration of A decreases to one-half its initial value in 1000 s

(b) $A \rightarrow B$, given that the concentration of A decreases from 0.67 mol L^{-1} to 0.53 mol L^{-1} in 25 s

(c) $2\ A \rightarrow B + C$, given that $[A]_o$ = 0.153 mol L^{-1} and that after 115 s the concentration of B rises to 0.034 mol L^{-1}.

7. Determine the rate constant for each of the following first- order reactions:

(a) $2\ A \rightarrow B + C$, given that the concentration of A decreases to one-fourth its initial value in 38 min

(b) $2\ A \rightarrow B + C$, given that $[A]_o$ = 0.039 mol L^{-1} and that after 75 s the concentration of B increases to 0.0095 mol L^{-1}

(c) $2\ A \rightarrow 3\ B + C$, given that $[A]_o$ = 0.040 molL and that after 8.8 min the concentration of B rises to 0.030 mol L^{-1}.

In each case, write the rate law for the rate of loss of A.

8. Dinitrogen pentoxide, N_2O_5, decomposes by first-order kinetics with a rate constant of $3.7 \times 10^{-5}\ s^{-1}$ at 298 K.
(a) What is the half-life (in hours) for the decomposition of N_2O_5 at 298 K?
(b) If $[N_2O_5]_o$ = 0.0567 mol L^{-1}, what will be the concentration of N_2O_5 after 3.5 h?
(c) How much time (in minutes) will elapse before the N_2O_5 concentration decreases from 0.0567 mol L^{-1} to 0.0135 mol L^{-1}?

9. The half-life for the first-order decomposition of A is 355 s. How much time must elapse for the concentration of A to decrease to (a) one-fourth; (b) 15% of its original value; (c) one-ninth of its initial concentration?