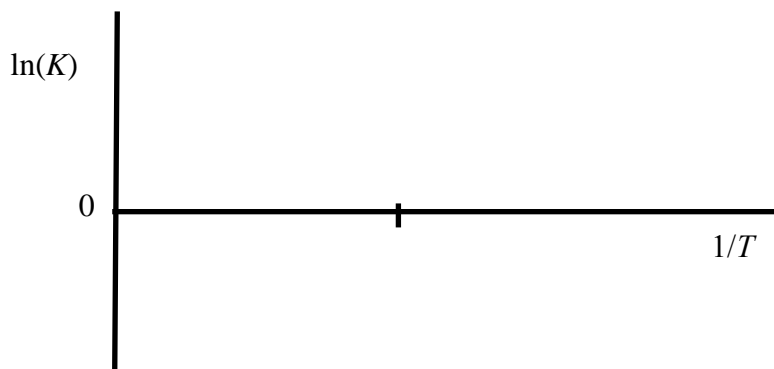


Chemistry 102 Spring 2018 Discussion #13, Chapter 17

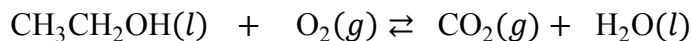
$$\Delta G = -n F E = R T \ln(Q/K) = \Delta H - T \Delta S$$

Student name _____ TA name _____ Section _____

1. A 0.01 M solution of an acid has $\text{pH} = 4$ at 300 K. At a lower temperature, the pH of the acid solution is 3. On the axes below, sketch the line of $\ln(K)$ versus $(1/T)$ for this acid.



2. A fuel cell is made based on the combustion of ethanol. The fuel cell gas pressures are $p_{\text{O}_2} = 31.5 \text{ bar}$ and $p_{\text{CO}_2} = 0.0200 \text{ bar}$. For this combustion, $\Delta_r H^\circ = -1367.51 \text{ kJ/mol}$ and $\Delta_r S^\circ = -138.58 \text{ J/(K mol)}$. Calculate the total energy available for useful work from the combustion of 1.00 kg of ethanol (46.06 g/mol) in this fuel cell at 25 °C. (Answer: -29800kJ)



3. The pH of water is 7.27 at 10.0 °C and 6.77 at 40.0 °C. Calculate the molar standard enthalpy and entropy change for the autoionization of water. (Answer: 56.6; -78.5)

Things you should know for preparation for chapter 18 not part of exam 3:

1. **Rate** = $\frac{\Delta[A]}{\Delta t}$; units: $\frac{M}{s}$

2. **Rate of chemical reactions depends on:**

- Temperature
- Catalysts
- Initial concentrations
- Magnitude of the rate constant

3. **Initial Reaction Rates:**

a. For a reaction: $aA + bB \rightarrow cC + dD$

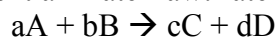
b. Initial Reaction Rate = $-\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$

c. Where $\frac{\Delta[A]}{\Delta t}$ is an individual rate of loss of A,

$$\frac{\Delta[B]}{\Delta t} = \frac{b}{a} \cdot \frac{\Delta[A]}{\Delta t}, \quad \frac{\Delta[C]}{\Delta t} = -\frac{c}{a} \frac{\Delta[A]}{\Delta t}$$

4. **Rate Law:**

a. Differential Rate Law: rate versus concentration



Rate = $k[A]^x[B]^y$ Where **k** is a rate constant $k = \frac{\text{rate}}{[A]^x \cdot [B]^y}$

Where *x* is the *order of the reaction* with respect to species A, and *y* is the *order of the reaction* with respect to species B.

b. Comparing initial rates:

$$\frac{\text{rate 1}}{\text{rate 2}} = \frac{k[A]_1^x[B]_1^y}{k[A]_2^x[B]_2^y}$$

c. Units of the rate constant depend on over all reaction order.

$$k = \frac{\left(\frac{M}{s}\right)}{M^x \cdot M^y} = \frac{M^{1-(x+y)}}{s} \text{ where } \underline{\underline{(x+y) \text{ is the order of the overall reaction.}}}$$

5. **Integrated Rate Laws: see attached table for more information**

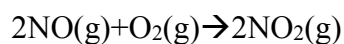
a. **Zero-Order:** $[R]_t - [R]_0 = -kt$

b. **First-Order:** $\ln \frac{[R]_t}{[R]_0} = -kt$

c. **Second-Order:** $\frac{1}{[R]_t} - \frac{1}{[R]_0} = kt$

6. Half Life $\frac{N_n}{N_0} = \left(\frac{1}{2}\right)^n$; $t_{\text{pass}} = n \cdot t_{1/2}$; $t_{1/2} = \frac{0.693}{k}$

1. A study of the reaction below gave the following result:



Fill in the missing information in the table

	[NO]	[O ₂]	$-\frac{d[\text{NO}]}{dt}$ [M/s]	Reaction rate
Ex1	0.0125	0.0185	0.020	
Ex2	0.0250	0.0185	0.080	
Ex3	0.0250	0.0370	0.160	
Ex4	0.0125	0.0370	0.040	

- What order is the reaction with respect to [NO]?
- What order is the reaction with respect to [O₂]?
- Write the rate law: $\text{rate} = k [\quad]^x [\quad]^y$
- Overall rate order =
- What are the units of *the rate constant k*?
- Calculate rate constant: $k =$
- What is the reaction rate when $[\text{NO}] = [\text{O}_2] = 0.020\text{M}$
- For each reactant, circle which plot correlating concentration with time will give you a **straight line**, and what the **sign of the slope** will be.

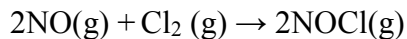
[NO] vs. time $1/[\text{NO}]$ vs. time $\ln[\text{NO}]$ vs. time

Slope: positive negative zero

[O₂] vs. time $1/[\text{O}_2]$ vs. time $\ln[\text{O}_2]$ vs. time

Slope: positive negative zero

2. A study of the reaction below gave the following result:



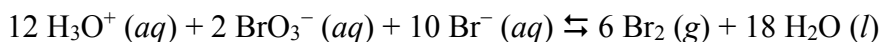
	[NO]	[Cl ₂]	$-\frac{d[\text{NO}]}{dt}$ [M/s]	RXN rate
Ex1	1.2	2.5		0.3
Ex2	4.8	2.5		0.15
Ex3	1.2	5.0		0.9

- What order is the reaction with respect to [NO]?
 - What order is the reaction with respect to [Cl₂]?
 - Fill in the table for reaction rate with respect to NO
 - Write the rate law: $\text{rate} = k [\quad]^x [\quad]^y$
 - Overall rate order =
 - What are the units of of *the rate constant k*?
3. Consider the chemical reaction: $3\text{A} + 4\text{B} \rightarrow 2\text{C} + 2\text{D}$. The experimentally determined rate law is $\text{Rate} = k[\text{A}]^2[\text{B}]$. When the initial concentrations are $[\text{A}]_i = 0.5 \text{ M}$ and $[\text{B}]_i = 0.01 \text{ M}$, the rate of consumption of B is $8 \times 10^{-5} \text{ M/s}$. Give the value of the rate constant, k , including the units.

4. Consider the reaction $\text{A} + 2\text{B} \rightarrow \text{D} + \text{C}$. Three experiments were conducted and the initial reaction rate of each reaction was determined. For each of the reactants, find the appropriate order. (Answer: 1, 0.5)

Exp	Initial conc. (mol/L)		Initial Rate (mol/L·sec)
	[A]	[B]	
#1	1.0×10^{-3}	1.0×10^{-3}	3.2×10^{-7}
#2	1.0×10^{-3}	3.0×10^{-3}	9.6×10^{-7}
#3	4.0×10^{-3}	3.0×10^{-3}	1.9×10^{-6}

5. Consider the chemical reaction: $3A + 4B \rightarrow 2C + 2D$. The experimentally determined rate law is $\text{Rate} = k [A] [B]^2$. When the initial concentrations are $[A]_i = 0.3 \text{ M}$ and $[B]_i = 0.01 \text{ M}$, the rate of consumption of B is $6 \times 10^{-4} \text{ M/s}$. Give the value of the rate constant, k , including the units.
6. Consider the comproportionation reaction of bromate and bromide to make bromine gas. Four experiments were conducted and the initial reaction rate was determined.

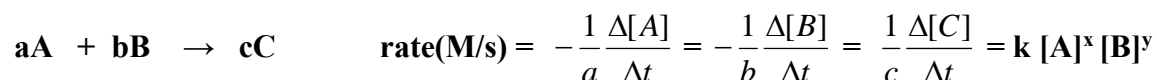


- a. Using the data, determine the order of the reaction with respect to H_3O^+ .

Exp	Initial Concentrations (mol/L)			Initial Reaction Rate (mol/L·sec)
	$[\text{BrO}_3^-]$	$[\text{Br}^-]$	$[\text{H}_3\text{O}^+]$	
#1	0.10	0.10	0.01	1.0
#2	0.20	0.10	0.01	2.0
#3	0.10	0.30	0.01	3.0
#4	0.20	0.10	0.02	8.0

- b. What is the initial rate of formation of bromine gas in experiment #1?
7. In a first order chemical reaction, the concentration of a reactant is observed to fall from 1.000 M to 0.250 M between $t = 6 \text{ s}$ and $t = 10 \text{ s}$. What is the concentration (in M) at $t = 12 \text{ s}$?
8. The first order reaction is 60.% complete after 100. seconds. What is rate constant k and $t_{1/2}$ for this reaction?
9. Fluorine-18 has a half-life of 110. minutes. After 4 half-lives, how much time has elapsed? What percentage of your original F-18 remains? What percentage has decayed? (Answer: $t_{\text{pass}}=440$. minutes, remains=6.25% , decayed=**93.75**)
10. You are trying to find the half-life of a new, meta-stable compound (X) created in your lab. You analyze the amount of X you have 30 minutes after initial production of X. You find you have 20% of the original amount. Approximately, what is $t_{1/2}$?
- 6 m. $<t_{1/2} < 7.5 \text{ m.}$ 7.5 m. $<t_{1/2} < 10 \text{ m.}$ 10 m. $<t_{1/2} < 15 \text{ m.}$ 15 m. $<t_{1/2} < 30 \text{ m.}$**
11. For another compound (Y), 94% of an original 100.0 g has decayed in 60.0 minutes. Express your answer to ONE SIGNIFICANT FIGURE.
- How many grams of Y is remaining? (Answer: 6g)
 - How many half-lives have elapsed? (Answer: $n=4$ half-lives pass)
 - What is the half-life of this compound? (Answer: $t_{1/2}=15 \text{ min}$)

Reaction Order	Differential Rate Law Conc. Dependence	Units of the rate constant, k, depend on the reaction order.	Half life, $t_{1/2}$, Integrated Rate Law	Graph Concentration versus time [A] ₀ is [A] at t = 0
Zero order reaction $x = 0, y = 0, x + y = 0$	Rate = $k[A]^0[B]^0$ Rate = k Rate is Constant Rate is independent of initial concentration.	(M/s) = units of k k = (M/s) are the units of the rate In general the units of k are a good indicator of the reaction order.	$[A]_{\text{final}} = [A]_{\text{initial}} - ak\Delta t$ When: $[A]_{\text{final}} = \frac{[A]_{\text{initial}}}{2}$ $\frac{[A]_{\text{initial}}}{2} = [A]_{\text{initial}} - akt_{1/2}$ $t_{1/2} = \frac{[A]_{\text{initial}}}{2ak}$	
First order reaction Example: $x = 1, y = 0, x + y = 1$	Rate = $k[A]^1[B]^0$ Rate = k[A] Rate depends linearly on initial concentration (ex. doubling [A] doubles the rate)	(M/s) = units of k * (M) k = (1/s)	$\ln [A]_{\text{final}} = \ln [A]_{\text{initial}} - ak\Delta t$ $\ln \frac{[A]_{\text{final}}}{[A]_{\text{initial}}} = -ak\Delta t$ When: $[A]_{\text{final}} = \frac{[A]_{\text{initial}}}{2}$ $t_{1/2} = \ln 2 / ak = 2.3 \log 2 / ak$ (half life is independent of initial concentration) $t_{1/2}$ is constant	
Second order reaction Example: $x = 2, y = 0, x + y = 2$	Rate = $k[A]^2[B]^0$ Rate = k[A]^2	(M/s) = units of k * (M) ² k = $\left(\frac{1}{M \cdot s}\right)$	$1/[A]_{\text{final}} = 1/[A]_{\text{initial}} + ak\Delta t$ When: $[A]_{\text{final}} = \frac{[A]_{\text{initial}}}{2}$ $t_{1/2} = \frac{1}{ak[A]_{\text{initial}}}$	



x and y are independent of stoichiometry and can only be determined from experimental data