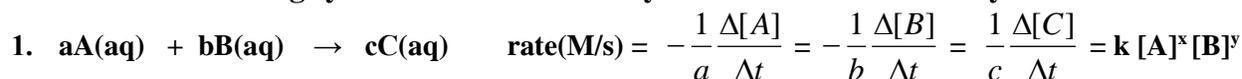
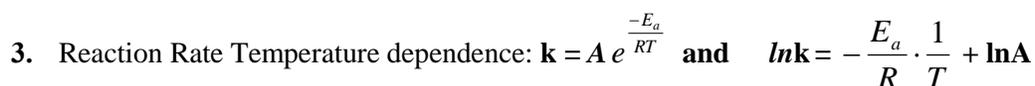


Student name _____ TA name _____ Section _____

Things you should know when you leave Discussion today:

2. Pathways or Reaction Mechanisms.

- Individual Steps
- Elementary Reactions
- Rate Determining Step
- Derivation of the Rate Law from Reaction Mechanisms



Where k is a rate constant, E_a ($\frac{J}{mol}$) is an activation energy, A is an Arrhenius Frequency Factor

4. Kinetic and Thermodynamic Connections.

Connection between Enthalpy and Activation Energy: $\Delta H^\circ_{\text{sys}} = E_a(\text{forward}) - E_a(\text{reverse})$

- If $E_a(\text{forward}) > E_a(\text{reverse})$ then $\Delta H^\circ_{\text{sys}} > 0$; Endothermic process
- If $E_a(\text{forward}) < E_a(\text{reverse})$ then $\Delta H^\circ_{\text{sys}} < 0$; Exothermic process
- If $E_a(\text{forward}) = E_a(\text{reverse})$ then $\Delta H^\circ_{\text{sys}} = 0$; no heat transferred

a. Connection between Reaction Rate and Equilibrium :

Rate_(forward) = Rate_(reverse) at Equilibrium (NOTE: $k_{\text{reverse}} \neq k_{\text{forward}}$)

b. Connection between Rate Constant (k) and Equilibrium Constant (K): $K = \frac{k_f}{k_r}$ Where k_{forward}

and k_{reverse} are the rate constants of the forward and reverse reaction respectively and K is the equilibrium constant.

At Standard Conditions:

- If $k_f < k_r$ then $K < 1$, $\ln K < 0$, $\Delta G^\circ_{\text{rxn}} = -R \cdot T \cdot \ln K > 0$, not spontaneous
- If $k_f = k_r$ then $K = 1$, $\ln K = 0$, $\Delta G^\circ_{\text{rxn}} = -R \cdot T \cdot \ln K = 0$, equilibrium
- If $k_f > k_r$ then $K > 1$, $\ln K > 0$, $\Delta G^\circ_{\text{rxn}} = -R \cdot T \cdot \ln K < 0$, spontaneous

Since Rate constant: $k = A e^{\frac{-E_a}{RT}}$ and $\ln k = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln A$

$$K = \frac{k_f}{k_r} = \frac{A_f}{A_r} e^{\frac{-(E_a(f)) - E_a(r))}{RT}} = \frac{A_f}{A_r} e^{\frac{-\Delta H_{\text{sys}}}{RT}}$$

$$\ln \frac{k_f}{k_r} = \frac{-(E_a(f) - E_a(r))}{R} \cdot \frac{1}{T} + \ln \frac{A_f}{A_r}$$

$$\ln K = \frac{-\Delta H_{sys}^\circ}{R} \cdot \frac{1}{T} + \frac{\Delta S_{sys}^\circ}{R}$$

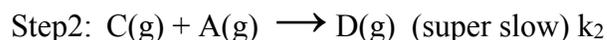
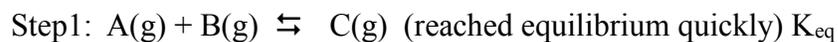
c. Connection between Entropy and Arrhenius Frequency Factor: $\frac{\Delta S_{sys}^\circ}{R} = \ln \frac{A_f}{A_r}$

$$\Delta S_{sys}^\circ = R \ln \frac{A_f}{A_r};$$

$$\ln \frac{A_f}{A_r} = \ln \frac{k_f}{k_r} \text{ at } T \rightarrow \infty$$

- If $A_f < A_r$ then $\frac{A_f}{A_r} < 1$ and $\ln \frac{A_f}{A_r} < 0$ hence $\Delta S_{sys}^\circ < 0$
- If $A_f > A_r$ then $\frac{A_f}{A_r} > 1$ and $\ln \frac{A_f}{A_r} > 0$ hence $\Delta S_{sys}^\circ > 0$
- If $A_f = A_r$ then $\frac{A_f}{A_r} = 1$ and $\ln \frac{A_f}{A_r} = 0$ hence $\Delta S_{sys}^\circ = 0$

1. Consider a reaction obeying the overall stoichiometry: $2 A(g) + B(g) \rightarrow D(g)$
Proposed mechanism is:



Net RXN:

Which step is a Rate determining step (RDS) ? Why?

Write the rate law using RDS :

What is the rate law for the overall reaction predicted by this mechanism? (Hint: Remove intermediates)?

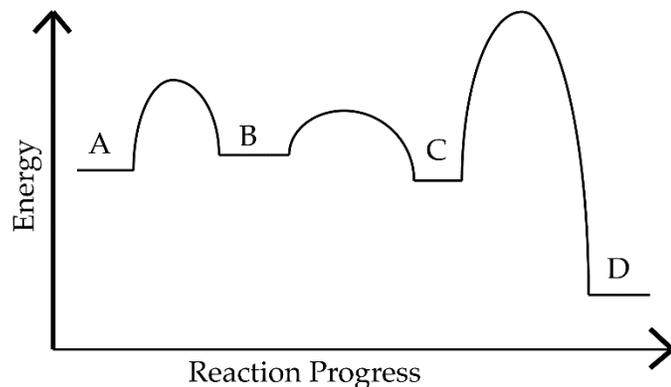
2. Consider the reaction progress diagram for $A \rightleftharpoons D$.

- a. Circle the reaction step below that corresponds to the rate limiting step (i.e. rate determining step).

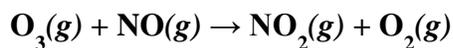


- b. Is the $A \rightleftharpoons D$ reaction endothermic or exothermic?

- c. Which step is an endothermic reaction?

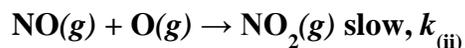
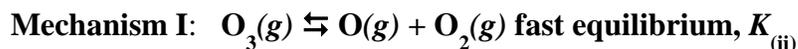


3. The net reaction of atmospheric ozone with nitric oxide and its rate law are:



$$\text{Reaction rate} = k[\text{O}_3(g)][\text{NO}(g)] \quad (\text{Predicted by an experiment})$$

Two pathways were proposed for this reaction:



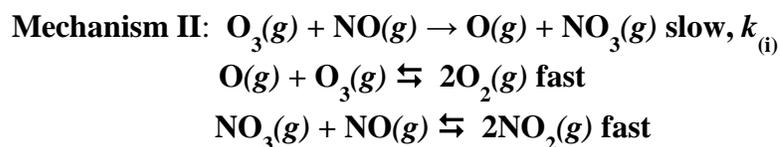
Net RXN:

Which step is a Rate determining step (RDS)? Why?

Write the rate law using RDS :

What is the rate law for the overall reaction that is predicted by this **Mechanism I** (remove intermediates)?

Sketch the reaction progress diagram for **Mechanism I** (assuming that reaction is exothermic):



Net RXN:

Which step is a Rate determining step (RDS) ? Why?

Write the rate law using RDS :

What is the rate law for the overall reaction predicted by this mechanism? How does this compare to the rate law determined with RDS? Is it different, why/why not?

Sketch the reaction progress diagram for **Mechanism II** (assuming that reaction is exothermic):

Which mechanism I or II best supported by an experiment?

4. The following reaction (elementary step) has a favored frequency factor $A_F = 5.0 \cdot 10^6/\text{M}\cdot\text{sec}$. Forward and reverse activation energies are 80. kJ/mol and 60. kJ/mol, respectively. Assume $T=25^\circ\text{C}$. (Answers: 20., 13.4,



- What is ΔH° of the reaction?
- If the reverse frequency factor is 5 times smaller than the forward frequency factor, what is ΔS° of the reaction?
- Draw the line on the graph of $\ln K$ versus $1/T$ for this reaction? And answer the following questions using two expressions below(Hint: $y=mx+b$):

d. Discuss which one of the following is true for this reaction and at what temperatures:

- $k_f < k_r$
- $k_f = k_r$
- $k_f > k_r$

e. Decide which one of the following is true for this reaction you drew and at what temperatures:

- $A_f < A_r$
- $A_f > A_r$
- $A_f = A_r$

f. Are E_a and the Arrhenius factors (A) temperature-dependent?

5. Consider the following exothermic reaction:



If the temperature is increased, what will happen to each of the quantities below?

E_a (forward) *increase* *decrease* *stay the same*

K *increase* *decrease* *stay the same*

k_f *increase* *decrease* *stay the same*

k_r *increase* *decrease* *stay the same*

A(reverse) *increase* *decrease* *stay the same*

Order of the reaction: *increase* *decrease* *stay the same*

Rate of the revers reaction: *increase* *decrease* *stay the same*

Rate of the forward reaction: *increase* *decrease* *stay the same*

Which rate constant will increase more with temperature for this reaction? k_f or k_r

6. A first order reaction is 75% complete after 100. seconds. Calculate the rate constant k and $t_{1/2}$ for this reaction. (Answer: $13.8 \cdot 10^{-3}$, 50.0)

7. The half-life of a radioactive isotope is 11 days. How long does it take for the isotope to decay by 10%? (Answer: 1.7)

8. Bromophenol blue decomposes by a first-order process with a half-life of 33 minutes. What fraction remains after 75 minutes?(Answers:21%)

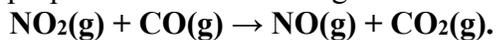
9. A certain flu virus can be thermally decomposed in humans in 6.00 days at normal body temperature, 37 °C. If a person has a fever, with temperature of 41 °C, the same virus can be decomposed in 2.00 days. What is the activation energy of the virus decomposition reaction? Express your answer in kJ/mol, to one significant figure.(Hint $k=1/\text{time}$) (Answer:222)

10. The following reaction $k_1(\text{at } T_1=350.\text{K})=9.4\cdot 10^{-6}(\text{1/s})$ and $k_2(\text{at } T_2=400.\text{K})=6.90\cdot 10^{-4}(\text{1/s})$
(Answers:100., $7.9\cdot 10^9$)



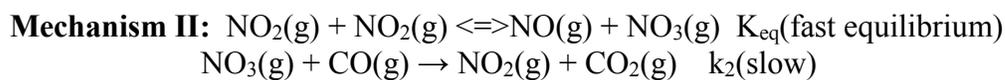
- What is the overall rate order of the reaction?
- Write an expression to solve for activation energy of the forward reaction that does not include Arrhenius factor. And then calculate it.
- What is E_a of the forward reaction?
- Write an expression to calculate Arrhenius factor of the forward reaction. What is A of the forward reaction?

11. Three different mechanisms proposed for the following reaction:



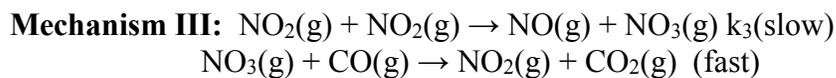
Net RXN:

What is the rate law predicted by this mechanism?



Net RXN:

What is the rate law predicted by this mechanism

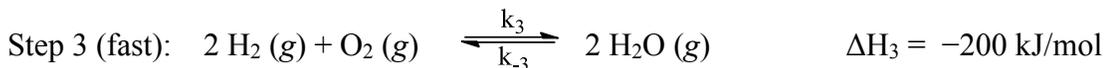
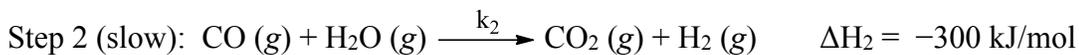
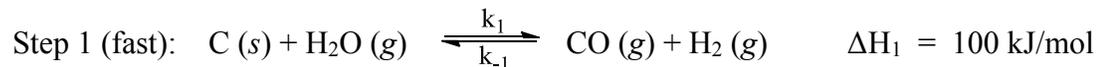


Net RXN:

What is the rate law predicted by this mechanism?

How you could experimentally distinguish between the different mechanisms?

12. Below are the proposed elementary steps and enthalpies for the mechanism of burning coal, C (s).



a. Identify each of the following molecules as either a reactant, product, intermediate, or catalyst for the net reaction.

C (s): _____ H₂O (g): _____ CO (g): _____

H₂ (g): _____ O₂ (g): _____ CO₂ (g): _____

b. Write the rate law for the reaction corresponding to the mechanism above.

c. Sketch the reaction progress profile with appropriate relative energies.

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

13. Metastable thallium-201 decays with a half-life of 48 hr by γ emission to stable thallium-201. The detected γ radiation is used to diagnose heart function. What fraction of metastable thallium-201 *remains* after 24 hr? (Answers:0.71)

14. A first order reaction is 75% complete after 100. seconds. Calculate the rate constant k and $t_{1/2}$ for this reaction. (Answer:13.9·10⁻³, 50.0)

15. The first order reaction is 20.% complete after 100. seconds. What is rate constant k and $t_{1/2}$ for this reaction? (**Hint**: what percent is remaining?) (Answers:300., 2.3·10⁻³)

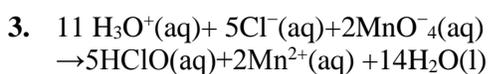
16. A sample decays 25% in 15 minutes. What is the half-life of this first-order process?(Answer:36min)

17. A first order reaction is 40.% complete in 120.s. What are the values of k and $t_{1/2}$? (Answers: $4.26 \cdot 10^{-3}$, 163)

Exam 3 Answers:

1.
 a. $9.52 \cdot 10^{-9} \text{ M}$
 b. $8.1 \cdot 10^{-7} \text{ M}$

2. $2.37 \cdot 10^{-23}$



4.
 a. $2 \text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2(\text{g}) + \text{H}_3\text{O}^+(\text{aq}) + 4\text{e}^-$
 b. 0.248V

5. $3.58 \cdot 10^{-3}/1$ or $1/279$

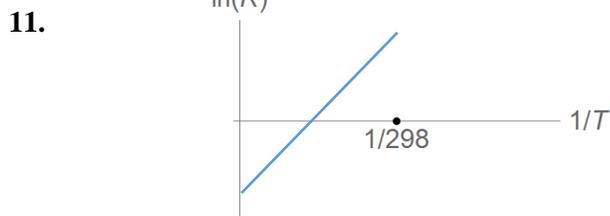
6. 21.99 J/molK; -1.992 J/molK

7. $Q > K$; $Q > 1$; $K > 1$

8. 0.434 atm

9. $S_{\text{solid}} < S_{\text{solution}}$; more information needed

10. 54kJ/mol



12. $1/70$ or $120/8400$

Here is a suggestion on how to use exam 3 as part of your final exam preparation. This coming weekend, redo your exam without looking at your work. As you do so, use the following descriptions of what each problem is about, and the corresponding background from the lectures (<http://quantum.bu.edu/courses/ch102-spring-2018/contents.html>) and the discussion packets.

If you create your own descriptions of what each problem is about, and then redo the problems for exams 1 and 2, without looking at your previous work, that will be significant additional help in your final exam preparation.

Question 1a: K_{sp} to concentration

Question 1b: Common ion; remember to take into account volume change

Question 2: Solubility to K_{sp}

Question 3: Balancing redox equations

Question 4a: Identify oxidation half-reaction

Question 4b: E_1 depends on E° and Q_1 ; E_2 depends on E° and Q_2 ; $E_2 - E_1$ eliminates the unknown E° and depends on $\log(Q_2/Q_1)$

Question 5: For concentration cell $K = 1$ and so $E^\circ = 0$. Write half-reactions so they sum to concentrated \rightarrow dilute. Use voltage to get the required value of Q .

Question 6: $\Delta S_{\text{sys}} = -\Delta H_{\text{fus}}/(273.15 \text{ K} - 22.69 \text{ K})$, $\Delta S_{\text{sur}} = +\Delta H_{\text{fus}}/(273.15 \text{ K})$

Question 7: Relations between Q , K , and 1, given ΔG and ΔG°

Question 8: Vapor pressure is due to equilibrium $X(l) \rightleftharpoons X(g)$, and so vapor pressure is the equilibrium constant $K = p_X/[X(l)] = p_X$

Question 9: Cold pack has $\Delta H_{\text{sys}} > 0$; hot pack has $\Delta H_{\text{sys}} < 0$; spontaneity requires $\Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}}$

Question 10: Slope of $\ln(K)$ vs $1/T$ is $-\Delta H/R$

Question 11: Slope of $\ln(K)$ vs $1/T$ is $-\Delta H/R$, intercept is $\Delta S/R$, if spontaneous at T , $\ln(K) > 1$ at $1/T$.

Question 12: $W_{fp}W_{fe}/W_{ip}W_{ie}$

**Chem 102 Spring final exam review will be on
Thursday May 3rd at 10am-12pm and 1pm-3pm**

Chem 102 Spring final exam review rooms and topics :

ROOM	TOPIC
CAS 211	Counting Arrangements, Entropy, (Q, K, ΔG , S), Colligative properties Exam 3
CAS 315	Equilibrium, Acid / Base, Buffers, Ksp, Solubility, Exam 2
CAS 214	Electrochemistry and Redox, Exam 3
CAS 522	Kinetics, Half Life , Mechanisms
CAS 237	MO, Gas Laws, KMT, Phace diagrams, Solution Enthaly, Exam1