Answers to Review #5: Reaction Rates

1. Know the meanings of, and be able to apply, the following terms:

Collision Theory	reaction intermediate	rate-determining step
reaction rate	activation energy	reaction order
reaction mechanism	activated complex	catalyst

2. Use Collision Theory to explain why the following factors usually increase the rate of a reaction:

a) increasing concentration of reactants
- when the concentration of the reactants is increased, it basically means that the reactants are more crowded in the same amount of space. This means that there will be more collisions between the reactants so reaction rate will increase

b) increasing temperature (two reasons)
- when temperature is increased, it means that the reactants will more faster
- because they are moving faster, they will collide with each other more often, which will increase the reaction rate
- because the reactants are moving faster, they will collide with more energyThe chances of an effective collision (one that meets or exceeds the Ea) is increased, which will increase the reaction rate

c) increasing surface area
- if a reactant is either solid or liquid, collisions can only happen at the exposed surface (the particles in the middle of a lump of reactant are covered up so they are not available to react)
- if a solid or liquid is spread out or ground up into smaller pieces, the surface area of the substance is increased. This means that more of the reactant is exposed and available to react.

3. With respect to the ***nature of the reactants***, which of the following reactions will probably have the fastest reaction rate? Why?

a) $S\,(s) + O_2\,(g) \rightarrow SO_2\,(g)$

b) $OH^-\,(aq) + H_3O^+\,(aq) \rightarrow 2\,H_2O\,(l)$

c) $2\,Ca\,(s) + H_2O\,(l) \rightarrow 2\,Ca(OH)_2\,(aq)$

d) $Ba(OH)_2\,(s) + 2\,NH_4Cl\,(s) \rightarrow BaCl_2\,(s) + 2\,H_2O\,(l) + NH_3\,(g)$

Reaction "b" will have the fastest rate of reaction. The reactants are small, charged particles in solution so they are free to move around and get into the correct orientation. Also, they are attracted to one another by their charges, so they will collide frequently. For both of these reasons, the reaction rate is very fast. (remember, and reactions with solid reactants will be slow because the reaction is limited by the surface area of the solid)

4. What are the "general rules" about the effect of the nature of the reactants on reaction rate?
- small, charged ions in solution will react very quickly so precipitation and neutralization reactions take place very quickly
- small, simple gas particles are also very free to move so they have relatively fast reaction rates
- large "bulky" molecules react more slowly because they are not often in the correct orientation
- solid and liquid reactants generally react slowly because the reaction rate is limited by the amount of exposed surface area available for reaction
- as an extension of the last point, homogeneous gas or aqueous systems react the fastest because they have the largest exposed surface area

5. For the reaction: $Ba(OH)_2$ (s) + 2 NH_4Cl (s) → $BaCl_2$ (s) + 2 H_2O (l) + NH_3 (g)

If ammonia gas (NH_3) is produced at the rate of 0.72 mol/s, what is the corresponding rate of consumption of ammonium chloride?

- NH_4Cl is consumed at a rate of 1.4 mol/s, twice as quickly as NH_3 is produced

6. Use the following experimental data to determine the rate law and calculate the value of the rate law constant, k, (including units for k), for the reaction:

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

Trial	**[NO]**	**[O_2]**	**Rate of Formation of NO_2 (mol/L·s)**
1	0.0018	0.0036	1.28
2	0.0054	0.0036	3.84
3	0.0054	0.0144	61.44

Trials 1 and 2:

- **[O_2] is constant**
- **when [NO] is tripled, the rate of reaction also triples. The relationship is 3^1**
- **the reaction is first order with respect to [NO]**

Trials 2 and 3:

- **[NO] is constant**
- **when [O_2] is quadrupled, the rate of reaction increases by 16X. The relationship is 4^2**
- **the reaction is second order with respect to [O_2]**

The rate law is: rate = k [NO] [O_2]^2

Substituting in data from any trial, we get: rate = 5.5 x 10^7 L^2 / (mol^2 · s) **[NO] [O_2]^2**
(because this reaction is third order overall, the units for k are L^2 / (mol^2 · s)

7. The rate law for the reaction S (s) + O_2 (g) → SO_2 (g) is: rate = $k[S]^0[O_2]^2$.

a) What is the order of the reaction with regard to sulfur? **zero**

What does this mean?

A zero reaction order means that the reaction rate is completely unaffected by the concentration of this reactant, which indicates that this reactant is not involved in the rate determining step

b) What is the order of the reaction with regard to oxygen? **second order**

What does this mean?

A second order relationship means that as the concentration of the reactant doubles, the rate of the reaction will increase by 2^2 or 4X, which indicates that two particles of this reactant must collide as part of the rate determining step

c) What is the order of the reaction overall? **second order**

d) What will the units for k be? The units of k for a 2nd order reaction are: **L / (mol·s) or L (mol·s)$^{-1}$**

e) According to the rate law, what are the reactants for the rate determining step? **O_2(g) + O_2(g)**

f) What will happen to reaction rate if concentration of O_2 is doubled? **↑ 4x (2^2)** tripled? **↑ 9x (3^2)**

g) What will happen to the reaction rate if the concentration of S (s) is doubled? **no change in rate**

8. A hypothetical reaction has the rate law: rate = k [A]^2[B]^3 , how will the rate change if:

a) [A] is doubled? **↑ 4x (2^2)**

b) [A] is tripled? **↑ 9x (3^2)**

c) [B] is doubled? **↑ 8x (2^3)**

d) [B] is tripled? **↑ 27x (3^3)**

e) [A] is doubled and [B] is tripled? **↑ 108x (2^2) x (3^3)**

f) [A] is tripled and [B] is doubled? **↑ 72x (3^2) x (2^3)**

g) [A] is doubled and [B] is doubled? **↑ 32x (2^2) x (2^3)**

h) [A] is tripled and [B] is tripled? **↑ 243x (3^2) x (3^3)**

9. A reaction has the following reaction mechanism:

Step 1:	$2\ NO\ (g) \rightarrow 2\ N_2O_2\ (g)$	(slow)
Step 2:	$2\ N_2O_2\ (g) + H_2\ (g) \rightarrow N_2O\ (g) + H_2O\ (g)$	(fast)
Step 3:	$N_2O\ (g) + H_2\ (g) \rightarrow N_2\ (g) + H_2O\ (g)$	(fast)

a) Write the balanced chemical eq'n for the overall reaction: **$2\ NO\ (g) + 2\ H_2\ (g) \rightarrow N_2\ (g) + 2\ H_2O\ (g)$**

b) Identify any reaction intermediates: **$2\ N_2O_2$ (g) and N_2O (g)**

c) Which step is the rate-determining step? Why? **Step 1, it is the slowest step**

d) Based on the rate-determining step, suggest a possible rate law for this reaction: **rate = k [NO]^2**

e) If the partial pressure (concentration) of H_2 (g) is doubled, what effect does this have on the overall reaction rate? Why?

- Because H_2 is not part of the RDS, changing its concentration will have no effect on the overall reaction rate.

f) If the partial pressure (concentration) of NO (g) is doubled, what effect does this have on the overall reaction rate? Why?

- If the reaction mechanism suggested in part "d" is correct, then as the concentration of NO (g) is doubled, the reaction rate should quadruple. As the concentration of NO (g) is doubled, the number of collisions will increase 4X. Because this is the rate determining step, this should increase the rate of the overall reaction by 4X.

10. The graph to the right shows the enthalpy change for the reaction:

ΔH fwd = 40 kJ

$NH_4Cl\ (aq)$ + **heat** $\rightarrow$ $NH_3\ (g)$ + $HCl\ (aq)$

a) Label the activated complex (AC)

b) Calculate and label ΔH forward: **+ 40 kJ**

c) Calculate and label ΔH reverse: **- 40 kJ**

d) Calculate and label E_a forward: **+ 160 kJ**

e) Calculate and label E_a reverse: **+ 120 kJ**

f) Add the term "heat" to the chemical reaction

g) Is the forward reaction likely fast or slow? Why? **slow, it has a higher Ea**

h) The tendency to minimum enthalpy favours the **reverse** reaction.

i) The tendency to maximum entropy favours the **forward** reaction?

j) Is this an equilibrium reaction? Why?
Yes. The driving forces are acting in oppos directions so the reaction is reversible.

Enthalpy Changes During a Chemical