AP Chem Rate of Reaction Review!

1. For the Reaction: $2A_{(g)} + BC_{2(g)}$ -------> $A_2B_{(g)} + 2\ C_{(g)}$

← in terms of A_2B!

Trial #	Initial concentration of A(M)	Initial Concentration of ~~B~~ BC_2 (M)	Initial rate of formation of A_2B (M/s)
1	0.050	0.050 ×2	0.00016 ×4
2	0.050	0.100	0.00064
3	×2 0.10	×2 0.200	×8 0.00512

a. Find the rate law and the value of k, including units.

b. In trial 1, what was the initial rate of formation of C?

c. Predict the rate of disappearance of $A_{(g)}$ if both reactant starting concentrations are 0.030 M.

d. Calculate the intial rate of reaction (in terms of A_2B) if the initial concentrations of A and BC_2 are 0.15 M and 0.25 M, respectively.

(b) $\left(.00016\ \frac{M}{s}\ A_2B\right)\left(\frac{2\text{ mole }C}{1\text{ mole }A_2B}\right) = \boxed{.00032\ \frac{M}{s}}$

a) • In trials 1 and 2, A is constant. When BC_2 doubles, the rate increases by a factor of four. so the rxn is 2nd order with respect to BC_2

• In trials 2/3, BC_2 and A both increase by a factor of 2, and the rate increases by a factor of 8. When $[BC_2]$ doubles, this alone should cause the rate to increase by a factor of 4. so the remaining factor of 2 increase in rate must be caused by [A] doubling, so rxn is first order w.r.t. A.

so $\boxed{r = K[A]^1[BC_2]^2}$

$.00016\ \frac{M}{s} = k[.050M](.050M)^2$

$k = 1.28\ M^{-2}s^{-1} \rightarrow \boxed{1.3\ M^{-2}s^{-1}}$ k

c) $r = K[A][BC_2]^2 = 1.2(8)\ M^{-2}s^{-1}\ (.030\ M)(.030\ M)^2 = .00003456\ \frac{M}{s}$

but the rate const/experiment was in terms of formation of A_2B, and this Q asks about $A_{(g)}$

$\left(.00003456\ \frac{M}{s}\text{ of }A_2B\right)\left(\frac{2\text{ moles }A}{1\text{ mole }A_2B}\right) = \boxed{0.000069\ \frac{M}{s}}$ or $\boxed{6.9 \times 10^{-5}\ \frac{M}{s}}$

d) $r = (1.2(8)\ M^{-2}s^{-1})(.15\ M)(.0.25\ M)^2 = \boxed{0.012\ M/s}$

2. $Cu_{(s)} + 4\ HNO_{3\,(aq)}$ -------> $Cu(NO_3)_{2(aq)} + 2\ NO_{2(g)} + 2\ H_2O_{(l)}$ + heat

(colorless solution) (blue solution) (brown gas)

Suppose the above reaction is done by pouring 100.0 mL of 0.80 Molar nitric acid at 20.0°C onto 50. grams of copper in the form 1.0 cm³ cubes. How would the rate of reaction change if you changed the following things? (Increase? Decrease? Or no change?)

decrease a. Change the concentration of nitric acid to 0.60 M. .60 < .80 M

increase b. Use 50. g of copper powder, instead of the cubes. more surface area

decrease c. Add 50.0 mL of water to the 100.0 mL of 0.80 M nitric acid, and then add this solution to the 1.0 cm³ copper cubes, instead of the original solution. (still at 20.°C) this will decrease molarity to below 0.80 M

increase d. Change the temperature of the acid to 30.0°C

30°C > 20°C so rate increases.

3. $2\ C_5H_6$ ------> $C_{10}H_{12}$
(cyclopentadiene) (dicyclopentadiene)

	Initial Concentration of C_5H_6(M/s)		Initial rate of formation of $C_{10}H_{12}$ (M/s)	
Experiment 1	0.040		0.000267	
Experiment 2	0.060	$\times 3$	0.000601	$\times 8.99$
Experiment 3	0.120		0.00240	

a. Determine the rate law and the value of the rate constant. $\boxed{r = k[C_5H_6]^2}$, $\boxed{k = 0.17\ M^{-1}s^{-1}}$

b. How will the reaction rate be affected if the temp increases?
Explain your answer mathematically
Explain your answer in terms of what the molecules are doing

c. How will the reaction rate be affected if a catalyst is added?
Explain your answer mathematically
Explain in terms of what the molecules are doing

d. How is the reaction rate affected when the concentration of cyclopentadiene is increased?
Explain in terms of what the molecules are doing

e. If you start with a C_5H_6 molarity of 0.120 Molar, what concentration of C_5H_6 will remain after 2.00 minutes?

(a) when $[C_5H_6]$ triples from .040 to 0.120, the rate increases by a factor of 8.99, or approximately a factor of 9. $3^2 = 9$, so it is 2nd order wrt C_5H_6.

$r = k[C_5H_6]^2$ $\quad .000267\ \frac{M}{s} = k(.040M)^2$ $\quad k = 0.1669 \rightarrow 0.17\ M^{-1}s^{-1}$

(b) as temp increases, the rate of rxn will increase

<u>math</u>: $k = Ae^{-Ea/RT}$ as temp increases, e will be raised to a less negative exponent (the exponent will still be negative, but with a lower magnitude.) so $e^{-Ea/RT}$ will increase (and A will increase very slightly.. or you could say it is constant), so k increases. when the rate constant increases, the rate itself will also increase.

<u>Concepts/Molecules</u>: as temp increases, a large fraction of molecules will have kinetic energy that is greater than or equal to the activation energy, so a larger fraction of collisions will be successful in breaking bonds, so more molecules can react per unit time.

(the <u>number</u> of collisions per unit time will also increase slightly.. but this effect will be minor compared to the above; that's why we assume that "A" is constant)

(c) see next page

3. $2\ C_5H_6$ ------> $C_{10}H_{12}$ Cont'd

(cylopentadiene) (dicyclopentadiene)

	Initial Concentration of C_5H_6(M/s)	Initital rate of formation of $C_{10}H_{12}$ (M/s)
Experiment 1	0.040	0.000267
Experiment 2	0.060	0.000601
Experiment 3	0.120	0.00240

a. Determine the rate law and the value of the rate constant.

b. How will the reaction rate be affected if the temp increases?
Explain your answer mathematically
Explain your answer in terms of what the molecules are doing

c. How will the reaction rate be affected if a catalyst is added?
Explain your answer mathematically
Explain in terms of what the molecules are doing

d. How is the reaction rate affected when the concentration of cyclopentadiene is increased?
Explain in terms of what the molecules are doing

e. If you start with a C_5H_6 molarity of 0.120 Molar, what concentration of C_5H_6 will remain after 2.00 minutes?

(c) if you add a catalyst, the rate will increase.

math: a catalyst lowers the activation energy (Ea).

$k = Ae^{-Ea/RT}$ so e will be raised to a "less negative" exponent, so k will come out to a larger number. Larger k (rate constant) corresponds to a faster rxn.

concepts: a catalyst lowers the activation energy, so a larger fraction of collisions will be energetic enough to break bonds; a larger fraction of ~~collisions~~ collisions will have KE > Ea. so more of the reactant collisions will be "successful" in forming products, so the rate increases.

(d) if you increase $[C_5H_6]$, there will be more frequent collisions between reactant (C_5H_6) molecules. More frequent collisions will result in a faster rate of reaction.

(e) $[C_5H_6]_0 = 0.120\ M$

$k = 0.16(69)\ \frac{M^{-1}}{s}$ (from part (a))

$t = (2.00\ min)\left(\frac{60s}{1min}\right) = 120.$ seconds

2nd order: $\frac{1}{[C_5H_6]} = \frac{1}{[C_5H_6]_0} + kt = \frac{1}{0.120\ M} + (.1669\ M^{-1}s^{-1})(120s)$

$\boxed{[C_5H_6] = 0.035\ M}$

4. Consider the following 2-step reaction mechanism involving ozone (O_3) depletion:

Elementary Step #1 $O_{3(g)} + NO_{(g)} \text{ ----> } NO_{2(g)} + O_{2(g)}$ (slow)
Elementary Step #2 $O_{(g)} + NO_{2(g)} \text{ -----> } NO_{(g)} + O_{2(g)}$ (fast)

a. Determine the overall reaction. $O_3 + O \longrightarrow 2\ O_2$

b. Identify any catalyst(s) and intermediate(s)

NO = catalyst NO_2 = intermediate

c. Was the catalyst in this reaction a homogeneous or heterogeneous catalyst?

homogeneous (it is gas phase; same phase as everything else)

d. Determine the rate law for the reaction.

$r = k[O_3][NO]$ (based on the slow step)

e. Determine the "molecularity" of each elementary step
(classify each elementary step as bimolecular, unimolecular, or termolecular)

step 1 and step 2 are each bimolecular.

f. What is the difference between an elementary step and an overall reaction, in terms of collisions?

The elementary step shows the collisions of reactant molecules; step one occurs when O_3 collides with NO. The overall rxn may or may not show which collisions occur; In this case it doesnt; the rxn doesnt occur by O_3 colliding with O (not significantly anyway)

g. Suggest a heterogeneous catalyst for the reaction. Pt

(Pt is a common catalyst) →

5. Reaction: $2\ NO + O_2 \text{ -----> } 2\ NO_2$

A mechanism for the above reaction is shown below.

a. Show that the mechanism is consistent with the overall stoichiometry of the reaction.

b. Identify any catalysts or intermediates. N_2O_2 = intermediate

c. Which elementary step would you expect to have a higher activation energy?

Step 2, since it is "slow" acc to the mechanism.

d. Determine the rate law for the reaction. $r = k[NO]^2[O_2]$ (see logic, below)

e. What is the overall order of the reaction?

3rd order overall.

f. Based on the rate law, one might propose that the reaction occurred in a single elementary step. Why is this unlikely?

If it occurred in a single step, 3 molecules would have to simultaneously collide at the correct orientation. "Termolecular" collisions are rare!

Step 1 (fast eqm) $NO + NO \underset{k_r}{\overset{k_f}{\longleftrightarrow}} N_2O_2$
Step 2 (slow) $N_2O_2 + O_2 \xrightarrow[k_2]{} 2\ NO_2$

$2NO + O_2 \longrightarrow 2NO_2$

(a) it adds up to the overall rxn, so, yes, it is "consistent with the overall stoichiometry."

$\boxed{\text{Logic for the rate Law:}}$

Based on the slow step,

$r = k_2[N_2O_2][O_2]$

but N_2O_2 is an intermediate...

Based on step 1, the "fast equilibrium",

$k_f[NO]^2 = k_r[N_2O_2]$

So $[N_2O_2] = \frac{k_f}{k_r}[NO]^2$ ← substitute into above equation

So $\boxed{r = k_2\frac{k_f}{k_r}[NO]^2[O_2]}$

6. Y -----> Z

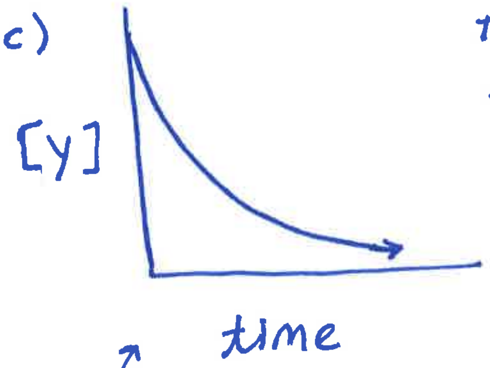
The concentration of Y vs time was determined at 25°C.
At 25°C, A plot of ln[Y] vs time was not linear.
A plot of 1/[Y] vs time was linear, with a slope of 0.080 L/mol-s.

a. Determine the rate law and the value of k. (Assume 25°C unless otherwise noted)
b. Will this reaction have a constant half-life? If so, calculate the half-life.
c. Make a graph showing the concentration of Y vs time.
Explain how the rate of reaction changes over time, why this happens, and how this relates to your graph.
d. If you start with a [Y] of 0.200 M, what will be the initial rate of reaction?
e. If you start with a [Y] of 0.200 M, what will be the concentration of Y after 40 seconds?
f. If you start with a [Y] of 0.200 M, what will be the rate of reaction after 40 seconds?
g. If the reaction has an activation energy of 42 kJ/mol, what is the value of the Arrhenius parameter A?
h. Find the rate constant at 55°C.

(a) Since $\frac{1}{[y]}$ vs time is linear, the rxn is $\underline{2^{nd}}$ order wrt [y],
so $\boxed{r = k[y]^2}$, and $\boxed{k = 0.080 \frac{l}{mol\cdot s} \text{ or } 0.080\ M^{-1}s^{-1}}$

(b) No! 2nd order rxns do not ~~half~~ have a constant half-life.
only first order rxns have constant half life.

(c)



the rate of the rxn is fastest at t=0, since the rate is proportional to the concentration of y squared, and [y] is highest at t=0; [y] decreases over time since it is a reactant.
(as [y] decreases, the collisions between y molecules occur less frequently, so the rate decreases)

the slope of the graph is equal to $\frac{\Delta[y]}{\Delta t}$. the slope is most negative at the beginning, when means that [y] is decreasing at the highest rate at the beginning.
as time passes, the rate decreases; the $\frac{\Delta[y]}{\Delta t}$ becomes less negative,
so [y] is decreasing at a lower/slower rate, and [z] is increasing at a lower/slower rate

⑥ $Y \dashrightarrow Z$ (Cont'd)

The concentration of Y vs time was determined at 25°C.
At 25°C, A plot of ln[Y] vs time was not linear.
A plot of 1/[Y] vs time was linear, with a slope of 0.080 L/mol-s.

a. Determine the rate law and the value of k. (Assume 25°C unless otherwise noted)
b. Will this reaction have a constant half-life? If so, calculate the half-life.
c. Make a graph showing the concentration of Y vs time.
Explain how the rate of reaction changes over time, why this happens, and how this relates to your graph.
d. If you start with a [Y] of 0.200 M, what will be the initial rate of reaction?
e. If you start with a [Y] of 0.200 M, what will be the concentration of Y after 40. seconds?
f. If you start with a [Y] of 0.200 M, what will be the rate of reaction after 40. seconds?
g. If the reaction has an activation energy of 42 kJ/mol, what is the value of the Arrhenius parameter A?
h. Find the rate constant at 55°C.

ⓓ $r = k[y]^2 = (.080\ M^{-1}s^{-1})(0.200\ M)^2 = \boxed{0.0032\ M/s}$ (d)

ⓔ $\frac{1}{[y]} = \frac{1}{[y]_0} + kt$ (2nd order)

$\frac{1}{[y]} = \frac{1}{0.200\ M} + (.080\ M^{-1}s^{-1})(40.s) = 5.00\ M^{-1} + 3.2\ M^{-1} = 8.2\ M^{-1}$

$[y] = \frac{1}{8.2\ M^{-1}} = 0.12195 \rightarrow \boxed{0.12\ M}$ (e)

ⓕ $r = k[y]^2 = (0.080\ M^{-1}s^{-1})(.12195\ M)^2 = 0.00119$

(f) $\boxed{0.0012\ M/s}$

ⓖ $k = Ae^{-Ea/RT}$

$0.080\ M^{-1}s^{-1} = Ae^{\frac{-42000\ J/mole}{(8.314\frac{J}{mol\cdot K})(298K)}} = Ae^{-16.952}$

$A = 1.84198\times10^6$

$\boxed{A = 1.8\times10^6\ M^{-1}s^{-1}}$

h) $k = Ae^{-Ea/RT} = 1.8(42)\times10^6\ M^{-1}s^{-1}\ e^{\frac{-42000\ J/mole}{8.314\frac{J}{mol.K}\cdot 328K}}$

$k = 0.3771 \rightarrow \boxed{0.38\ M^{-1}s^{-1}\ @\ 55°C}$

7. $W \longrightarrow 2Z$ at 25°C, $k = 0.000059\ s^{-1}$

Note: The rate constant for this reaction was calculated in terms of the rate of disappearance of **W**.

a. Based on the units of k, what is the overall order of the reaction?

b. Which of these plots would be linear?

ln[W] vs (1/time) [✓ ln[W] vs time] [W] vs time 1/[W] vs time

c. If you start with a [W] of 0.200 Molar, what will be the molarity after 4.00 hours, if the reaction occurs at 25°C?

$$(4.00\ hr)\left(\frac{3600\ s}{hr}\right) = 14400\ \text{seconds (use below)}$$

d. Does this reaction have a constant half life at 25°C? If so, what is the value?

e. What is the initial rate of formation of Z, if W has a starting concentration of 0.200 M? (25°C)

(a) It must be $\boxed{\text{first}}$ order, since k has units of $(\text{time})^{-1}$

$$\underset{\frac{M}{s}}{r} = \underset{s^{-1}}{k}\,\underset{M}{[W]}^1$$

ⓑ therefore, $\boxed{\ln[W] \text{ vs time}}$ will be linear. (with a slope of $-k$)

ⓒ 1st order, so $[W] = [W]_0 e^{-kt}$

$$[W] = 0.200\,M\,e^{-(.000059\,s^{-1})(14400\,s)} =$$

$$= 0.200\,M\,e^{-0.8496}$$

$$= 0.085517 \rightarrow \boxed{0.086\ M}$$

ⓓ why, yes, it does!

1st order rxns have a constant half-life.

$$kt_{1/2} = \ln 2$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{.000059\,s^{-1}} = 11748\ \text{seconds}$$

$$\approx \boxed{12000\ \text{seconds}}$$

$$\approx \boxed{3.3\ \text{hours.}}$$

ⓔ $r = k[W]^1$

$$= (.000059\,s^{-1})(0.200\,M)$$

$$= 0.0000118\ M/s$$ (rate of dissappearance of W, acc to note @ top)

$$\left(.0000118\,\frac{\text{mole W}}{L\cdot s}\right)\left(\frac{2\ \text{moles Z}}{1\ \text{mole W}}\right) = 0.0000236\,\frac{M}{s} \text{ or } \boxed{2.4\times10^{-5}\ M/s}$$

8. N_2O_4 + heat <----> 2 NO_2

Suppose that N_2O_4 and NO_2 are at equilibrium in a sealed container with a fixed volume.

a. How will the following things be affected if the temperature is increased?

Keq_ Increase

Forward rate of rxn _increase

Reverse Rate of Rxn_increase

Activation energy _no change

) rxn is endo, so k_f will increase more than k_r when temp ↑ and Keq will increase.

b. How will the following things be affected if a catalyst is added?

Keq_ no change

Forward rate of rxn _increase

Reverse Rate of Rxn_increase

Activation energy _lower/decrease

) k_f and k_r increase by the same factor when a catalyst is added.

9. 2 NO_2 <-----> N_2O_4 + heat

Suppose that N_2O_4 and NO_2 are at equilibrium in a sealed container with a fixed volume.

a. How will the following things be affected if the temperature is increased?

Keq_ decrease

Forward rate of rxn _increase

Reverse Rate of Rxn_increase

Activation energy _no change

) exo, so k_r increases more than k_f and Keq decr.

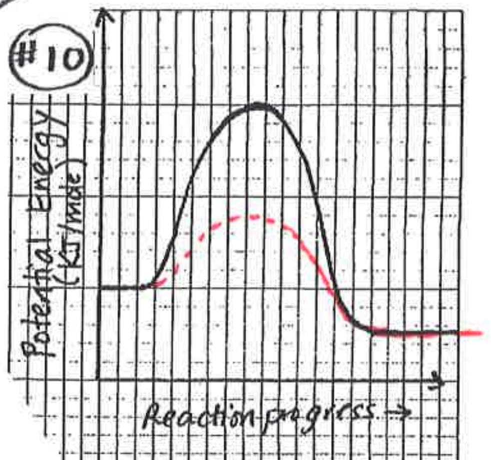
b. How will the following things be affected if a catalyst is added?

Keq_ no change

Forward rate of rxn _increase

Reverse Rate of Rxn_ increase

Activation energy _lowered /decrease



10. Reaction for the decomposition of N_2O_5:

$2\,N_2O_{5\,(g)}$ -------> $4\,NO_{2\,(g)} + O_{2(g)}$ +23 kJ

The energy diagram for this reaction is shown to the right.

a. Is this reaction exothermic or endothermic?_exo

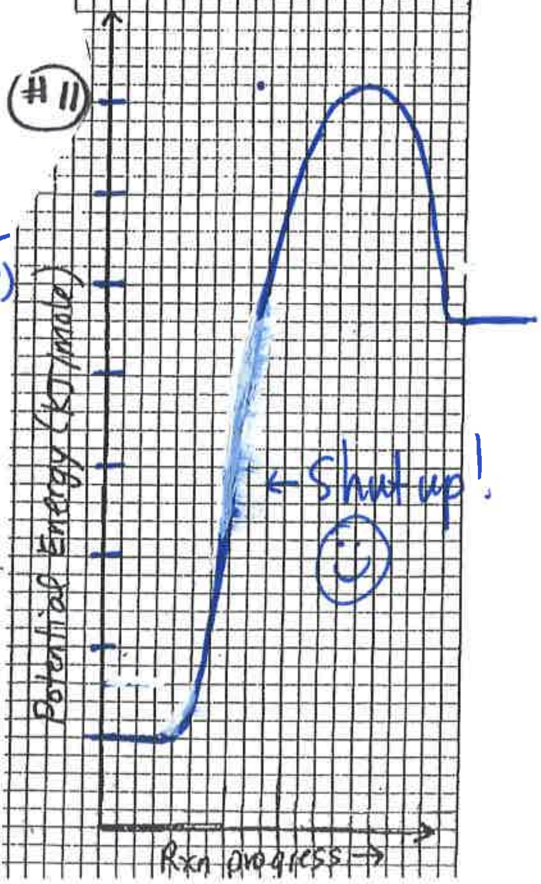
b. What is the value of ΔHrxn?_-23 kJ (-20 to -25)

c. Write the heat term into the equation on the correct side.

d. What is the value for Ea (Activation energy?)_100 kJ (or a bit less?)

e. Sketch the energy diagram (on the same graph) if a catalyst is added. - - - - -

(for 10 and 11, 1 square = 10 kJ/mol)



(11) Rxn: 230 kJ + $CO_{2\,(g)} + NO_{(g)}$ ------> $CO_{(g)} + NO_{2\,(g)}$

This reaction has an Ea = 360 kJ and a ΔHrxn of 230 kJ.

a. Is this reaction exothermic or endothermic? endo

b. Write the heat term into the equation on the correct side.

c. Sketch the energy diagram for this reaction.

go up 36 squares from start, end 23 squares above the start

d) ΔHrev = -230 kJ

e) Ea reverse = 130 kJ