Dr. Zellmer
Time: 7 PM Sun.
30 min

Chemistry 1220
Spring Semester 2023
Quiz III

All Sections
February 5, 2023

Name KEY Rec. TA/time

1. (6 pts) The rate law for the decomposition of AB_2 ($AB_2 \rightarrow A + 2B$) at 200°C is

$$r = (0.630\ M^{-1} \bullet s^{-1})\ [AB_2]^2 \qquad 2^{nd} \text{ order in } AB_2;\ \ k = 0.630\ M^{-1} \bullet s^{-1}$$

a) (4 pts) If the initial concentration of AB_2 is 3.00 M what will the **concentration** of AB_2 be (in M) after 1.00 minute?

Want $[AB_2]$ after 1.00 min (60.0 seconds) given $[AB_2]_0 = 3.00$ M

- use the **integrated rate equation** for a 2^{nd} order reaction

Need to know the order of reaction; look at the rate law above - it is 2^{nd} order in AB_2

$$1/[A]_t = kt + 1/[A]_0$$

$$1/[AB_2]_t = kt + 1/[AB_2]_0$$

$$1/[AB_2]_{50.0\ s} = (0.630\ M^{-1}s^{-1})\ (60.0\ s) + 1/3.00M$$

$$1/[AB_2]_{50.0\ s} = 38.13 = 38.1\ M^{-1}$$

$$[AB_2]_{50.0\ s} = 2.6\underline{\mathbf{2}}2 \times 10^{-2}\ M = 2.62 \times 10^{-2}\ M\ \ (3\ s.f.)$$

b) (2 pts) What is the rate after 1.00 minute? Not asked for on the Carmen quiz.

Asked for the rate you need to use the rate law, not an integrated rate eqn. This problem asks for the rate after 1.00 minute. This means you need to use the integrated rate eqn. to get the conc. at 1.00 min and then use this conc. to get the rate.

After 1.00 min, $[AB_2] = 2.622 \times 10^{-2}$ M

$$r = (0.630\ M^{-1} \bullet s^{-1})\ [AB_2]^2 = (0.630\ M^{-1} \bullet s^{-1})\ [2.62 \times 10^{-2}\ M]^2$$

$$r = 4.3\underline{\mathbf{3}}2 \times 10^{-4}\ M \bullet s^{-1} = 4.33 \times 10^{-4}\ M \bullet s^{-1}$$

Compare this to the rate at the very start of the reaction when $[AB_2] = 3.00$ M.

$$r = (0.630\ M^{-1} \bullet s^{-1})\ [AB_2]^2 = (0.630\ M^{-1} \bullet s^{-1})\ [3.00\ M]^2$$

$$r = 5.67\ M \bullet s^{-1}$$

2. (4 pts) The decomposition of AB (AB → A + B) is zero order in AB with a rate constant of 1.10×10^{-3} $\mathbf{M{\bullet}s^{-1}}$. If the initial concentration is 0.100 M at the very start of the reaction what is the second half-life (in minutes)?

half-life, $t_{1/2}$, is the time it takes for conc. to dec. to ½ of the previous conc.

For a zero-order reaction: $t_{1/2} = [A]_0/(2k)$ (dependent on the initial conc)

$t_{1/2} = 0.100\text{M}/\{2(1.10 \times 10^{-3}\ \text{M}^{\bullet}\text{s}^{-1})\} = 45.\underline{\mathbf{4}}5\ \text{s} = 0.75\underline{7}5\ \text{min}$ (takes 0.758 min for conc to dec. by ½)

This is the first half-life.

For zero-order reactions <u>successive</u> <u>half-lifes</u> **<u>decrease</u>** (each is **half** of previous)

(takes less time for conc. to dec. by ½ each period)

So the 2nd half-life would be $0.75\underline{7}5/2$ min = $0.37\underline{\mathbf{8}}7$ min = **0.379 min**

Half-lives (similar to #50 on Ch 14 extra practice problems handout)

1st order: $t_{1/2} = 0.693/k$ 2nd order: $t_{1/2} = 1/(k\,[A]_0)$

Both 0 (zero) and 2nd order half-lives depend on the initial conc of reactant, while 1st order does not.

* Note* The half-life for a 1st order rxn is independent of the conc. (i.e. the half-life for a particular rxn will be the same no matter what is the initial conc. and successive half-lives will be the same). This is not true for other orders, for which successive half-lives change.

Zero-order	1st-order	2nd-order
$t_{1/2} = \dfrac{[A]_o}{2\,k}$	$t_{1/2} = \dfrac{0.693}{k}$	$t_{1/2} = \dfrac{1}{k\,[A]_o}$
DECREASES as rx. proceeds (successive ½-lifes get smaller - ½ previous e.g. $t_{1/2,1} = 40$ s $t_{1/2,2} = 20$ s $t_{1/2,3} = 10$ s)	CONSTANT as rx. proceeds (successive ½-lifes are same e.g. $t_{1/2,1} = 40$ s $t_{1/2,2} = 40$ s $t_{1/2,3} = 40$ s)	INCREASES as rx. proceeds (successive ½-lifes get larger - doubles e.g. $t_{1/2,1} = 10$ s $t_{1/2,2} = 20$ s $t_{1/2,3} = 40$ s)

3. (8 pts) The rate law for the decomposition of N_2O_5 ($N_2O_5 \rightarrow 2\ NO_2 + ½\ O_2$) at 70°C is

$$r = (6.82 \times 10^{-3}\ s^{-1})\ [N_2O_5]$$

a) (5 pts) If the initial concentration of N_2O_5 is 1.50 M, how **long** (in minutes) will it take for the reaction to reach 90% completion?

Want time it takes for the reaction to be 90 % complete. This means the time it takes for 90 % of the N_2O_5 to react. This means only 10 % of it remains. This is the same as asking for the time it takes the $[N_2O_5]$ to decrease to 10.0 % of its initial conc., $\mathbf{[N_2O_5]_t = 0.100\ [N_2O_5]_0}$

- use the **integrated rate equation** for a 1st order reaction

Need to know the order of reaction; look at the rate law above - it is 1st order in N_2O_5

$$ln([A]_t / [A]_0) = -k\,t \quad \text{or} \quad [A]_t = [A]_0\, e^{-kt} \quad \text{or} \quad ln[A]_t = -kt + ln[A]_0$$

$$ln([N_2O_5]_t / [N_2O_5]_0) = -k\,t \qquad ln(0.10[N_2O_5]_0 / [N_2O_5]_0) = -k\,t$$

Note: for a 1st order integrate rate law you don't need the actual initial concentration (this means you can do the problem by picking any conc. you want for the initial N_2O_5 conc. and you will get the same answer).

$$ln(0.100) = -k\,t \quad t = -\,ln(0.100)/k = -\,ln(0.100)/(6.82 \times 10^{-3}\ s^{-1})$$

$$t = 33\underline{7}.622\ s = 5.6\underline{2}70\ min = 5.63\ min \text{ (3 s.f.)}$$

b) (3 pts) What is the **half-life** (in min) for the reaction based on the initial concentration of 1.50 M?

half-life, $t_{1/2}$, is the time it takes for conc. to dec. to ½ of the previous conc.

For a 1st order reaction: $t_{1/2} = 0.693/k$ (independent of the initial conc)

$t_{1/2} = 0.693/(6.82 \times 10^{-3}\ s^{-1}) = 10\underline{1}.6129\ s = \mathbf{1.69}\ min$ (takes 1.69 min for conc to dec. by ½)

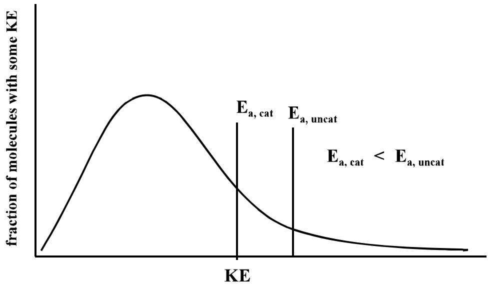
2nd order: $t_{1/2} = 1/(k\,[A]_0)$ 0 order: $t_{1/2} = [A]_0/(2k)$

Both 0 (zero) and 2nd order half-lives depend on the initial conc of reactant

4. (3 pts) Explain the main way a catalyst **increases** rate by using the **Arrhenius Equation**. (**Show this equation and use it in your explanation!**)

No question like this on the Carmen quiz.

Arrhenius eqn: $k = A\,e^{-(Ea/RT)} = A/(e^{(Ea/RT)})$



A catalyst lowers the E_a for a reaction. A lower E_a (regardless of T) means more molecules will have enough KE to react (get to the top of the "hill" faster to form transition state). A catalyst speeds rxns a lot by lowering E_a. We can see this using the above eqn.

Smaller E_a => smaller E_a/RT => $e^{(\text{smaller }\#)}$ => smaller # =>
1/(smaller #) => BIGGER # => **larger k**

$\therefore$ E_a dec => k inc => rate inc and E_a inc => k dec => rate dec

(r $\propto$ k; the rate is directly proportional to the rate constant, k; if k doubles rate doubles, etc.)

5. (5 pts) The rate constant for a reaction at 40.0°C is exactly three times that at 20.0°C. Calculate the Arrhenius **energy of activation**, **E_a**, (in kJ/mol) for the reaction.

Use Arrhenius equation in its two point form.

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

T in KELVIN, R = 8.314 J/mol•K

k_1 $T_1 = 20.0°C = 293.15\ K$
$k_2 = 3\ k_1$ $T_2 = 40.0°C = 313.15\ K$

$E_a = ?$

$$\ln\left(\frac{3\ k_1}{k_1}\right) = \frac{E_a}{8.314\ J/mol\bullet K}\left(\frac{1}{293.15\ K} - \frac{1}{313.15\ K}\right)$$

$\ln(3) = (2.620 \times 10^{-5}\ J^{-1}\bullet mol)\ E_a$

$E_a = 4.1924 \times 10^{4}\ J/mol = 41.9\ kJ/mol$

6. (3 pts) Which of the following statements is (are) **TRUE**?

1) reaction rates depend on temperature, reactant structure, concentration of reactants and the presence of catalysts

2) catalysts shift reaction equilibria toward the side of the products

3) enzymes are catalysts in living organisms and increase rate by lowering the activation energy, E_a.

4) activation energy is required for both exothermic and endothermic reactions

5) a catalyst never has its concentration appear in the rate law

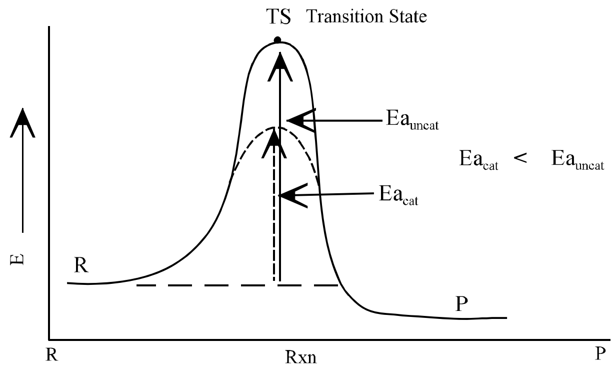
Statements 1, 3, 4 are true.

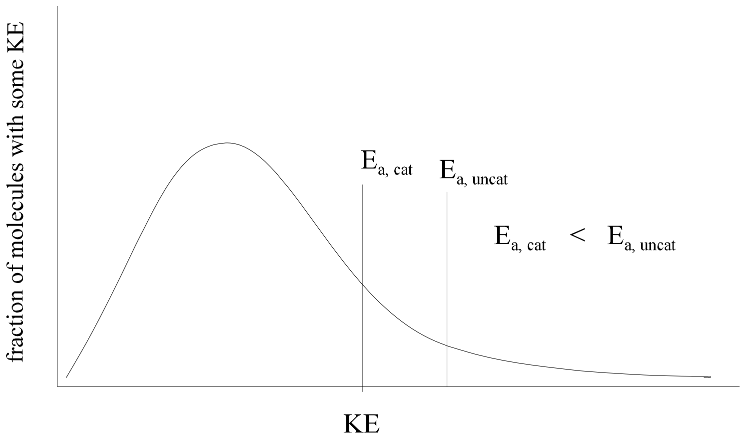
1) T: The factors effecting the rate of a reaction are: concentration of reactants (and maybe products), structure of reacting molecules, temperature and the presence of catalysts.

2) F: Catalysts do **not** shift the equilibrium toward products. **Catalysts speed** up the **rate** at which equilibrium is reached but do **not effect** the **position** of **equilibrium** (i.e. Amounts of reactant and product at equilibrium). **Catalyst inc** rxn **rate** by **lowering Ea** so that at the same temp more molecules have KE > Ea. A catalyst lowers the "hill" (rxn barrier) so it takes less energy to get over (through the transition state, TS). Can use the Arrhenius eqn to see this.

$k = A\, e^{-(Ea/RT)}$ Arrhenius eqn.

As $\mathbf{E_a}$ **inc**., E_a/RT inc, $e^{-(Ea/RT)}$ dec., **k dec**., **rate dec** ($r \propto k$)
$\mathbf{E_a}$ **dec**., E_a/RT dec, $e^{-(Ea/RT)}$ inc., **k inc**., **rate inc** ($r \propto k$)





3) T: Enzymes are catalysts in living organisms. They speed up the reactions in organisms.

4) T: Activation energy is required for both exothermic and endothermic reactions.

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6. (Cont.)

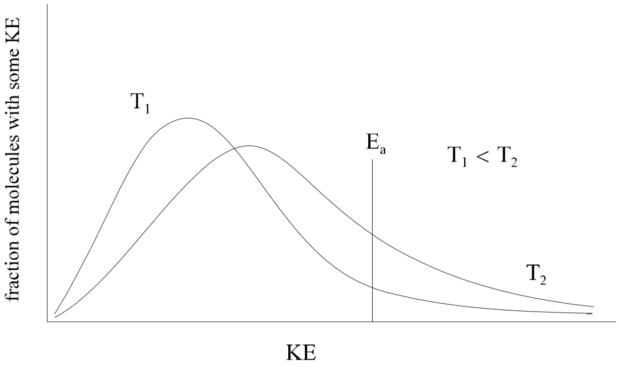
5) F: The concentration of a catalyst (gaseous or in solution) can appear in a rate law. It gets it's biggest effect by lowering the E_a but it's concentration can affect the rate by appearing in the rate law.

Aside: You can see how Temp effects rate by looking at the Arrhenius eqn.

$k = A e^{-(Ea/RT)}$ Arrhenius eqn.

As **T** **inc**., E_a/RT dec, $e^{-(Ea/RT)}$ inc., **k** **inc**., **rate** **inc** ($r \propto k$)
T **dec**., E_a/RT inc, $e^{-(Ea/RT)}$ dec., **k** **dec**., **rate** **dec** ($r \propto k$)

An inc. in T causes an inc. in K.E. so more molecules have KE > Ea and may therefore react



7. (3 pts) Given the following mechanism, identify which species which may be classified as **intermediate(s)** and which as **catalyst(s)** in the formation of XO_2 from X and O_2 ($X + O_2 \rightarrow XO_2$)?

$X + O_2 \rightarrow XO_2$ (balanced equation)

Mechanism below:

$X + YO_2 \rightarrow XO + YO$
$XO + YO \rightarrow XO_2 + Y$
$Y + O_2 + Z \rightarrow YO + ZO$
$YO + ZO \rightarrow YO_2 + Z$

intermediates: XO, YO, Y, ZO

Appear for the **first** **time** as a **product** and **used** in **subsequent** **step** as a **reactant**.

catalysts: YO_2, Z

Appear for the **first** **time** as **reactant** and **reproduced** in **subsequent** **step** as a **product**.

8. (9 pts) The following mechanism has been proposed for the gas phase reaction between H_2 and CO.

$$H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2\,H \qquad \text{(fast, equilibrium)}$$

$$H + CO \xrightarrow{k_2} HCO \qquad \text{(slow)}$$

$$H + HCO \rightarrow H_2CO \qquad \text{(fast)}$$

$$H_2(g) + 2\,H(g) + CO(g) + HCO(g) \rightarrow 2\,H(g) + HCO(g) + H_2CO(g)$$

(a) What is the overall reaction? (cancel things that appear on both sides)

$$H_2(g) + CO(g) \rightarrow H_2CO(g)$$

(b) What are the **intermediates** in the mechanism?

H(g) & HCO(g) Things that don't appear in overall eqn., but appear in mechanism are either intermediates or catalysts. Intermediates appear for the first time as a product and used in following step(s) as a reactant.

(c) What is the **molecularity** of each elementary step? **# reactant molecules** in a step

Step 1	Step 2
unimolecular	**bi**molecular
(1 reactant molecule)	(2 reactant molecules)

(d) What is the **rate-determining step** (explain why)?

Step **2** - **slowest step** **rate** for entire rxn can **NOT** be **faster** than **SLOWEST step** in mech.

(e) What is the **rate law** predicted by this mechanism?

$r = k_2\,[H]\,[CO]$ based on reactants in step 2 (slowest, rate-determining step)

Can't have intermediate, H, in the rate law - use step 1 (fast equilibrium step) to find [H]

For step 1

$\text{rate}_{\text{forward 1}} = \text{rate}_{\text{reverse 1}}$

Write rate law for each rate

$k_1\,[H_2] = k_{-1}\,[H]^2$

solve for [H]

$[H] = \{\, (k_1/k_{-1})\,[H_2] \,\}^{1/2}$

Substitute this into rate eqn base on step 2

$r = k_2\,[H]\,[CO]$

$r = k_2\,\{\, (k_1/k_{-1})\,[H_2] \,\}^{1/2}\,[CO]$

$r = k_2\,(k_1/k_{-1})^{1/2}\,[H_2]^{1/2}\,[CO]$

$r = k\,[H_2]^{1/2}\,[CO]$

where, $k = k_2\,(k_1/k_{-1})^{1/2}$

9. Consider the following hypothetical reaction and the established rate law. Select an acceptable mechanism.

$A_2 + B_2 \rightarrow X + Y$ rate = $k [A_2] [B_2]/[Y]$ (experimentally determined rate law)

The rate law is written based on the slow (rate determining) step

a) 2nd step is the slow step

$A_2 \rightleftarrows 2 A$ (fast)

$B_2 + A \rightarrow C$ (slow)

$C + A \rightarrow X + Y$ (fast)

$r = k_2 [B_2] [A]$ A is an intermediate - try to replace it using conc. of reactants &/or product

Use 1st fast equilibrium step to determine [A]

$r_{forward,1} = r_{reverse,1}$

$k_1 [A_2] = k_{-1} [A]^2$

$[A] = (\frac{k_1}{k_{-1}})^{1/2} \bullet [A_2]^{1/2}$ substitute this expression for [A] into r from step 2

$r = k_2 [B_2] [A]$

$r = k_2 [B_2] \{ (\frac{k_1}{k_{-1}})^{1/2} \bullet [A_2]^{1/2} \}$

$r = k_2 (\frac{k_1}{k_{-1}})^{1/2} [B_2] [A_2]^{1/2} = k [B_2] [A_2]^{1/2}$

This does not agree w. exp. rate law given - NOT the proper mechanism

b) 2nd step is the slow step

$A_2 + B_2 \rightleftarrows C$ (fast)

$C \rightarrow X + Y$ (slow)

$r = k_2 [C]$ C is an intermediate - try to replace it using conc. of reactants &/or product

Use 1st fast equilibrium step to determine [C]

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9. (Cont.)

$r_1 = r_{-1}$

$k_1 [A_2] [B_2] = k_{-1} [C]$

$[C] = (\frac{k_1}{k_{-1}}) [A_2] [B_2]$ substitute this expression for [A] into r from step 2

$r = k_2 [C]$

$r = k_2\{ (\frac{k_1}{k_{-1}}) [A_2] [B_2] \} = (\frac{k_2 k_1}{k_{-1}}) [A_2] [B_2] = k [A_2] [B_2]$

This does not agree w. exp. rate law given - NOT the proper mechanism

c) 2nd step is the slow step

$A_2 \rightleftarrows C + Y$ (fast)

$B_2 + C \rightarrow X$ (slow)

$r = k_2 [B_2] [C]$ C is an intermediate - try to replace it using conc. of reactants &/or product

Use 1st fast equilibrium step to determine [C]

$r_1 = r_{-1}$

$k_1 [A_2] = k_{-1} [C] [Y]$

$[C] = \frac{k_1}{k_{-1}} \bullet \frac{[A_2]}{[Y]}$ substitute this expression for [C] into r from step 2

$r = k_2 [B_2] [C]$ - rate law from above

$r = k_2 [B_2] \{\frac{k_1}{k_{-1}} \bullet \frac{[A_2]}{[Y]} \}$

$r = \{\frac{k_2 k_1}{k_{-1}} \} \bullet \frac{[B_2] [A_2]}{[Y]}$

$r = k \frac{[B_2] [A_2]}{[Y]}$

This agrees w. exp. rate law given - It **IS** the proper mechanism

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9. (Cont.)

d) 1st step is the slow step

$B_2 \rightarrow 2\,B$ (slow)

$B + A_2 \rightarrow C$ (fast)

$C + B \rightarrow X + Y$ (fast)

$r = k_1\,[B_2]$ This does not agree w. exp. rate law given - NOT the proper mechanism

e) 2nd step is the slow step

$B_2 \rightleftarrows 2\,B$ (fast)

$B \rightarrow C + Y$ (slow)

$A_2 + C + B \rightarrow X$ (fast)

$r = k_2\,[B]$ B is an intermediate - try to replace it using conc. of reactants &/or product

Use 1st fast equilibrium step to determine [B]

$r_1 = r_{-1}$

$k_1\,[B_2] = k_{-1}\,[B]^2$

$[B] = \left(\frac{k_1}{k_{-1}}\right)^{1/2} \bullet [B_2]^{1/2}$ substitute this expression for [B] into r from step 2

$r = k_2\,[B]$

$r = k_2 \left\{ \left(\frac{k_1}{k_{-1}}\right)^{1/2} \bullet [B_2]^{1/2} \right\}$

$r = k_2 \left(\frac{k_1}{k_{-1}}\right)^{1/2} [B_2]^{1/2} = k\,[B_2]^{1/2}$

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9. (Cont.)

<u>Note</u>: Anything that appears in the rate law must appear as a **<u>reactant</u>** in the **<u>slow</u> step** or as a **<u>reactant</u>** and/or **<u>product</u>** in the **fast <u>equilibrium</u> steps** which **<u>precede</u>** the **<u>slow</u> step**.

The fast steps which follow the slow step have no effect on the rate law. They are only there to make sure all steps add up to the balanced equation.

This brings up a good point that makes this type of problem easier to approach.

First look at mech. w. slow step 1 - easy to determine these rate laws (only the reactants in this step will appear in the rate law).

Then look at remaining mech.

To get a rate law with a ½ power (e.g. $[A_2]^{1/2}$) there would need to be the following type of elementary step as a fast step preceding the slow step.

$A_2 \rightleftarrows 2\,A$ (fast)

$r_{\text{forward},1} = r_{\text{reverse},1}$

$k_1\,[A_2] = k_{-1}\,[A]^2$

$$[A] = \left(\frac{k_1}{k_{-1}}\right)^{1/2} \bullet [A_2]^{1/2}$$

Also, look at the following mechanism: Get C in the rate law based on step 2. Then if you look at step 1 you will get something for [C] involving A and X (a product). X will appear in the denominator in the rate law. You really shouldn't have to go through the math to see you will wind up with X in the rate law. In order to get a product in the rate law the first step can't be the rate determining step.

$A \rightleftarrows C + X$ (fast)

$B + C \rightarrow Y$ (slow)