Dr. Zellmer
Time: 40 min

Chemistry 1220
Summer Semester 2017
Quiz II

Thursday
June 22, 2017

Name KEY Rec. Instr. ______________________

1. (8 pts) The rate law for the decomposition of AB_2 ($AB_2 \rightarrow AB + \frac{1}{2} B_2$) is

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

a) (5 pts) If the initial concentration of AB_2 is 3.00 M what will the **<u>concentration</u>** 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

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

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

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

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

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

b) (3 pts) What is the **<u>half-life</u>** (in min) for the reaction based on an initial concentration of 0.0100 M?

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

For a 2^{nd} order reaction: $t_{1/2} = 1/(k\ [A]_0)$ (dependent of the initial conc)

$t_{1/2} = 1/\{(0.630\ M^{-1}s^{-1})(0.0100\ M)\} = 15\underline{\mathbf{8}}.6\ s = 2.65\ min$ (takes 2.65 min for conc to dec. by ½)

1^{st} order: $t_{1/2} = 0.693/k$ 0 order: $t_{1/2} = [A]_0/(2k)$

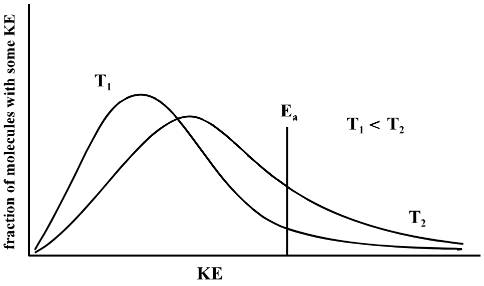
Both 0 (zero) and 2^{nd} order half-lives depend on the initial conc of reactant, while 1^{st} order does not.

2. (3 pts) Explain how **raising** the **temperature** **increases** the **rate** by using the **Arrhenius Equation**. (**Show this equation and use it in your explanation!**)

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

Inc. T inc KE (KE $\propto$ T). At a higher temp there are more molecules w. KE > Ea so rxn is faster (get to the top of the "hill" faster to form transition state). We can see this using the above eqn

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

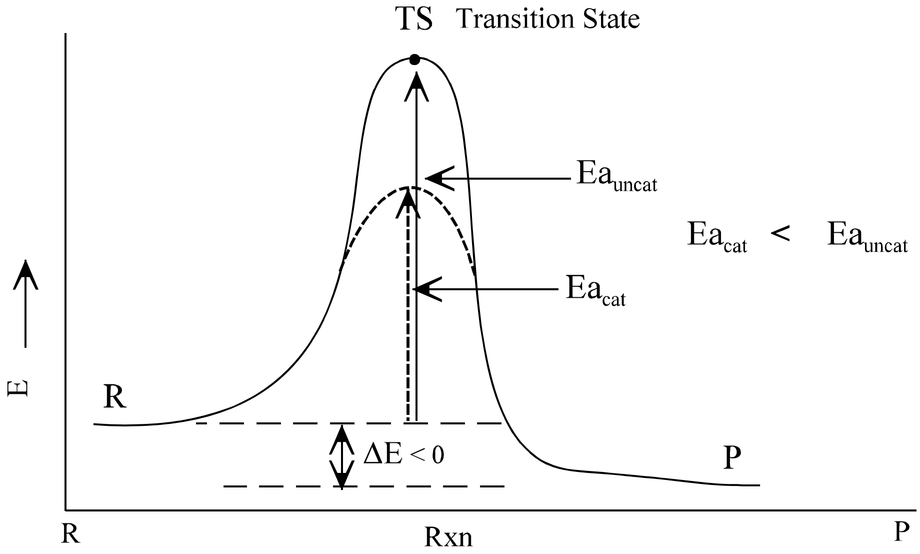


$\therefore$ T inc => k inc => rate inc and T dec => k dec => rate dec

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

3. ***** see next page *****

4. (3 pts) Draw a "reaction coordinate diagram" (energy profile or potential energy diagram) for an exothermic reaction. **Label** the **axes**, **activation energy**, $\mathbf{E_a}$, and the **transition state** (activated complex) and **ΔE** on the diagram. **Also**, **show** the **effect** of a **catalyst** on this graph (i.e. what is the main way in which a catalyst speeds up a reaction).



This is a "reaction coordinate diagram" (energy profile or potential energy diagram are other common names given to this diagram). The transition state (activated complex) is at the top of the hill (barrier to reaction). I've labeled the activation energy, E_a, for both the uncatalyzed and catalyzed reaction. This reaction is exothermic since the products are lower in energy than the reactants ($\Delta E < 0$). The ΔE for a reaction is related to the Ea_{for} and Ea_{rev}. To get the proper sign of ΔE for both exothermic and endothermic reactions you would find, $\Delta E = Ea_{for} - Ea_{rev}$.

A catalyst speeds up a reaction. It's conc. CAN appear in a rate law so that is one way it could speed up a reaction. However, it's conc. isn't always in a rate law. The main way the catalyst speeds up a reaction is to **lower** the activation energy, $\mathbf{E_a}$, the "hill" or reaction barrier. In general, the lower the E_a the faster the reaction.

3. (9 pts) The following mechanism has been proposed for the gas-phase reaction of bromoform, $CHBr_3$, and bromine.

$$Br_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2\,Br(g) \qquad \text{(fast, equilibrium)}$$

$$Br(g) + CHBr_3(g) \rightarrow HBr(g) + CBr_3(g) \qquad \text{(slow)}$$

$$Br(g) + CBr_3(g) \rightarrow CBr_4(g) \qquad \text{(fast)}$$

$$Br_2(g) + 2Br(g) + CHBr_3(g) + CBr_3(g) \rightarrow 2\,Br(g) + HBr(g) + CBr_3(g) + CBr_4(g)$$

(a) What is the overall reaction?

$Br_2(g) + CHBr_3(g) \rightarrow HBr(g) + CBr_4(g)$

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

$Br(g)$ & $CBr_3(g)$ 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 molecules)	(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?

$r = k_2\,[Br]\,[CHBr_3]$ based on reactants in step 2 (slowest, rate-determining step)

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

For step 1

$rate_{forward\ 1} = rate_{reverse\ 1}$

Write rate law for each rate

$k_1\,[Br_2] = k_{-1}\,[Br]^2$

solve for [Br]

$[Br] = \{ (k_1/k_{-1})\,[Br_2] \}^{1/2}$

Substitute this into rate eqn base on step 2

$r = k_2\,[Br]\,[CHBr_3]$

$r = k_2\,\{ (k_1/k_{-1})\,[Br_2] \}^{1/2}\,[CHBr_3]$

$r = k_2\,(k_1/k_{-1})^{1/2}\,[Br_2]^{1/2}\,[CHBr_3]$

$r = k\,[Br_2]^{1/2}\,[CHBr_3]$

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

5. (3 pts) You are given the general rate law $r = k[A]^n$, and concentration and rate data. Convert this to a linear equation and explain how you graphically obtain k and n (i.e. what do you plot as x and y and how do you obtain **n** and **k** from the graph)?

$r = k\ [A]^n$ k = rate constant n = order

Convert this to a linear equation.

Take the log of both sides, use the rules of logarithms and rearrange to make it look like an equation for a straight line. You can use either log or ln.

$$\log(r) = \log\{k[A]^n\} = \log(k) + \log\{[A]^n\} = \log(k) + n \log[A]$$

$$\log(r) = n*\log[A] + \log(k) \quad \text{or} \quad \ln(r) = n*\ln[A] + \ln(k)$$

$$y = m*x + b$$

Using the equation from (a) how do you graphically obtain k and n (i.e. what do you plot as x and y and what are n and k related to on the graph)?

The data you have is concentration, [A], and the corresponding rate. You take the log of each and plot log(r) vs log[A] (i.e. log(r) is on the y axis and log[A] is on the x axis) or ln(r) and ln[A].

if using log: log(k) = y-intercept $k = 10^{(\text{y-int})}$

if using ln: ln(k) = y-intercept $k = e^{(\text{y-int})}$

n = slope (The slope can be either positive or negative depending on the order.)

6. (6 pts) For the following reaction $K_P = 48.5$ at 480.0 °C

$$6\ HCl\ (g) \ + \ 3/2\ O_2\ (g) \ \rightleftarrows \ 3\ Cl_2\ (g) \ + \ 3\ H_2O\ (g) \qquad \textbf{Rxn 1}$$

a) (3 pts) What is the value of K_P for the following reaction? **Show all work or explain.**

$$2\ Cl_2\ (g) \ + \ 2\ H_2O\ (g) \ \rightleftarrows \ 4\ HCl\ (g) \ + \ O_2\ (g) \qquad \text{(rxn 2)}$$

When multiply a rxn by some factor the K for the new rxn is equal to original K raised to the factor the rxn was multiplied by. Remember if you multiply a reaction by a -1 that's the same as reversing it since you need to flip the action around to get rid of the negative coefficients you would get by multiplying by -1. (multiplying by -1 reverses the rxn)

Based on this K_{rev} for rev. rx is $1/K_{for}$ ($K_{for}{}^{-1}$, the reciprocal of K_{for} for the forward rx)

To get reaction (2) you need to reverse the original reaction (rxn 1) and multiply it by 2/3. This is the same as multiplying reaction (1) by −2/3 .

$$K_2 \ = \ K_1{}^{-2/3} \ = \ 1/(K_1{}^{2/3}) \ = \ (48.5)^{-2/3} \ = \ 0.075\underline{1}92 \ = \ 0.0752 \qquad \text{(3 s.f.)}$$

b) (3 pts) What is the value of K_C for reaction 1 at 480.0 °C? **Show all work or explain.**

$$K_P \ = \ K_C\ (RT)^{\Delta n}$$

Δn = change in moles of gas   Do **NOT** include pure **solids** or **liquids** when calculating Δn.

= (moles of gaseous products) − (moles of gaseous reactants)

R = 0.08206 L•atm/mol•K   **NOT** 8.314 J/mol•K

$T \ = \ 480.0°C \ + \ 273.15 \ = \ 753.\underline{1}5\ K$ (**must** be in **kelvin**)

$$K_P \ = \ 48.5$$

$$\Delta n \ = \ 6 \ - \ 7.5 \ = \ - \ 1.5$$

Do **NOT** include **solids** or **liquids**

$$K_C \ = \ K_p\ (RT)^{-\Delta n}$$

$$K_C \ = \ 48.5\{(0.08206)(753.\underline{1}5\ K)\}^{-\ (-\ 1.5)}$$

$$K_C \ = \ 2.3\underline{5}64 \times 10^4$$

$$K_C \ = \ 2.36 \times 10^4$$

7. (8 pts) For the following reaction K_C equals 7.10×10^{-4}, at 25 °C.

$$CaCrO_4\,(s) \rightleftarrows Ca^{2+}\,(aq) + CrO_4^{2-}\,(aq)$$

a) (5 pts) What are the **<u>equilibrium</u>** concentrations of Ca^{2+} and CrO_4^{2-} if solid $CaCrO_4$ is placed in water to form a saturated solution at 25 °C? (**Show the ICE table. When appropriate, state any assumptions made and check your percent error.**)

<u>Use ICE (equil.) table</u> (in Molarity when dealing w. K_C)

	$CaCrO_4$ (s)	$\rightleftarrows$	Ca^{2+} (aq)	+	CrO_4^{2-} (aq)
initial	C		0 M		0 M
change	-x		+ x		+ x
equil	constant		+ x		+ x

$$K_C = [Ca^{2+}] \bullet [CrO_4^{2-}] = 7.10 \times 10^{-4}$$

$CaCrO_4$ (s) doesn't appear in K (pure solids and liquids do not appear in K)

$$x^2 = 7.10 \times 10^{-4}$$

$$x = (7.10 \times 10^{-4})^{1/2} = 2.6\underline{\mathbf{6}}45 \times 10^{-2}\ M$$

$$[Ca^{2+}] = [CrO_4^{2-}] = 2.66 \times 10^{-2}\ M \quad \text{(3 s.f.)}$$

b) (1 pt) For the system at equilibrium, what happens when $CaCl_2$(s), a soluble compound, is added?? (i.e. does the equilibrium shift and if so in what direction? If no shift then why not.) **EXPLAIN!**

$CaCl_2$(s) dissolves to give Ca^{2+} and 2 Cl^- ions. The Cl^- does nothing since it's not part of the equilibrium. The Ca^{2+} is an aqueous product. **Adding** a **product** shifts the reaction to the **LEFT**.

Shift: **AWAY** from **ADDED** **TOWARD** what's **REMOVED**

This means the $CaCrO_4$ (s) will be less soluble in the presence of Ca^{2+}.

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c) (1 pts) Assume the above reaction is endothermic. For the system at equilibrium, what happens to the reaction when the temperature increases? (i.e. does the equilibrium shift and if so in what direction? If no shift then why not.) **EXPLAIN!**

$$\mathrm{CaCrO_4\,(s)} \;+\; \text{Heat} \;\rightleftarrows\; \mathrm{Ca^{2+}\,(aq)} \;+\; \mathrm{CrO_4^{2-}\,(aq)}$$

For temperature changes you treat heat as a reactant or product. Also, changes in temperature are the only changes that cause a numerical change in the equilibrium constant, K.

Since the rxn. is endothermic **heat** is a **reactant**. You inc. temp by adding heat. Move **AWAY from ADDED**. That means the reaction **shifts** to the **right** (forward direction). As it does, the conc. of products increases and conc. of reactants decreases. These changes cause the numerical value of the **equilibrium constant**, **K**, to **increase**.

<u>Remember</u>:

$\Delta H < 0$ (−); **<u>exo</u>**thermic; **heat** is a **<u>product</u>**
- inc T (add heat, a product), shift left (K dec)
- dec T (remove heat, a product), shift right (K inc)

$\Delta H > 0$ (+); **<u>endo</u>**thermic; **heat** is a **<u>reactant</u>**
- inc T (add heat, a reactant), shift right (K inc)
- dec T (remove heat, a reactant), shift left (K dec)

$\Delta H < 0$	$\Delta H > 0$
T ↑, ←, K ↓	T ↑, →, K ↑
T ↓, →, K ↑	T ↓, ←, K ↓
T & K move in opposite direction	T & K move in same direction
<u>Product</u> favored by **<u>LOW</u> T**	**<u>Product</u>** favored by **<u>HIGH</u> T**

d) (1 pt) For the system at equilibrium, what happens when part of the $\mathrm{CaCrO_4}$ is **removed**? (i.e. does the equilibrium shift and if so in what direction? If no shift then why not.) **EXPLAIN!**

No shift. Normally if you remove something the equil. would shift toward what's removed. However, this is a solid. The **conc**. of a **solid** is **<u>constant</u>** so adding some or removing part of it does not change it's conc. so it has **<u>no</u> <u>affect</u>** on the equil. The solid does not appear in Q or K so it has no affect on the equilibrium if some more is added or some is removed (as long as some is present). The amount (mass) of the solid changes but it's conc. doesn't so the reaction doesn't shift.