

1. (10 pts) Short Answer Questions

a) For the majority of reactions, reaction rate is fastest when:

 E_a high, T low E_a high, T high E_a low, T low E_a low, T high

b) In the reaction: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ ($\Delta H = 57.2 \text{ kJ/mol}$), the reactant is a colourless gas and the product is a brown gas. A flask contains a mixture of these gases at equilibrium. In the box, write the equilibrium constant and choose the best means which would lead to a decrease in the observed colour.

- remove NO_2 and add heat
 add NO_2 and decrease volume
 remove N_2O_4 and add heat
 add N_2O_4 and increase volume

$$K = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}}$$

c) For the equilibrium $\text{A}(\text{g}) \rightleftharpoons \text{B}(\text{g})$, $K_C = 10$ at 300 K. If 11 moles of A are added to a 1 L flask and it is allowed to equilibrate, at 300 K it will contain 1 mol of A and 10 mol of B.

d) For the reaction in part (c), we observe that the rate decreases as the reaction progresses and the half-life depends on the initial concentration of A. Therefore, for the reaction:

Since the rate is NOT constant, we know it CAN'T be zero order – that leaves 1st or 2nd order
 1st order half life is INDEPENDENT of $[\text{A}]_0$ – therefore, this must be 2nd order

- the graph of $1/[\text{A}]$ versus time will be a linear plot
- the half-life will INCREASE DECREASE as $[\text{A}]_0$ increases $\text{half-life} = 1/(k[\text{A}]_0)$
- if $[\text{A}]_0$ is doubled, the initial reaction rate will change by a factor of: 2 $1/2$ 4 $1/4$

e) Predict the products of the following acid-base reaction. Is $K >$ or < 1 ?



f) 100 mL of 0.100 M acetic acid and 50 mL of 0.100 M NaOH are added together. The resulting pH of the solution would be equal to (provide value) 4.74.

g) For the following three hydrofluoric acid solutions, circle the one with the highest percent ionization and underline the one with the lowest pH.

0.100 M HF

0.500 M HF

0.050 M HF

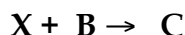
0.010 M HF

h) A buffer made from HA ($pK_a = 4.82$) and NaA has a pH of 4.25. The buffer therefore contains: $[\text{HA}] > [\text{A}^-]$ $[\text{HA}] < [\text{A}^-]$ $[\text{HA}] = [\text{A}^-]$

2. The mechanism for the gas-phase reaction described by the equation



is suggested to be:



THIS QUESTION WAS TAKEN FROM THE 2014 FINAL EXAM

a) (4 pts) Assuming that [X] is governed by steady-state conditions, derive the rate law for the production of C in terms of [A] and [B], and any appropriate k values.

$$\text{rate } \textcircled{2} = k_2[X][B]$$

SSA for X: rates of reactions that form X = rates of reactions that consume X

$$\text{rate } \textcircled{1} \text{ forward} = \text{rate } \textcircled{1} \text{ reverse} + \text{rate } \textcircled{2}$$

$$k_1[A] = k_{-1}[X] + k_2[X][B]$$

$$\therefore [X] = \frac{k_1[A]}{k_{-1} + k_2[B]}$$

$$\begin{aligned} \text{rate} &= k_2 \left(\frac{k_1[A]}{k_{-1} + k_2[B]} \right) [B] \\ &= \frac{k_1 k_2 [A][B]}{k_{-1} + k_2[B]} \end{aligned}$$

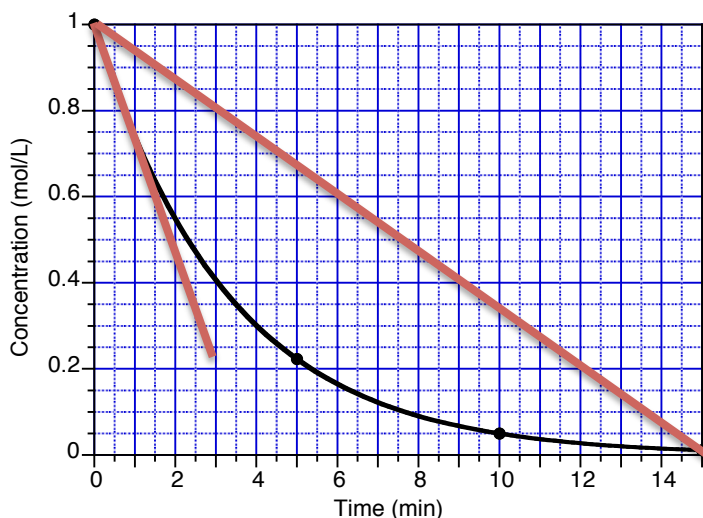
b) (1 pt) What is the expected overall order of the rate law at *very low* gas pressures?

ZERO ORDER FIRST ORDER **SECOND ORDER** THIRD ORDER

c) (1 pt) What is the expected overall order of the rate law at *very high* gas pressures?

ZERO ORDER **FIRST ORDER** SECOND ORDER THIRD ORDER

d) (4 pts) Using the graph below, calculate the initial rate *and* average rate (both in M/s) for the reaction.



Initial Rate = - slope of tangent

$$-\frac{\Delta y}{\Delta x} = -\frac{(0.65 - 1.0) \text{ M}}{(1.5 - 0) \text{ min}} \times \frac{1 \text{ min}}{60 \text{ s}} = 3.9 \times 10^{-3} \text{ M/s}$$

Average Rate = - slope of diagonal

$$-\frac{\Delta y}{\Delta x} = -\frac{(0 - 1.0) \text{ M}}{(15 - 0) \text{ min}} \times \frac{1 \text{ min}}{60 \text{ s}} = 1.1 \times 10^{-3} \text{ M/s}$$

3. Consider the following reaction: $2A(g) + B(g) \rightleftharpoons C(g)$

To a 2.50 L flask, A and B are added at initial pressures of 0.200 bar each. The mixture was allowed to equilibrate at 1000 K and the flask was found to contain 0.00289 mol of C.

THIS QUESTION IS VERY SIMILAR TO ONE ON THE 2009 MIDTERM#2

a) (4 pts) What is the value of K_P for the reaction?

$$P_C \text{ at EQM} = \frac{n_C RT}{V} = \frac{(0.00289 \text{ mol})(0.083145 \text{ L} \cdot \text{bar/mol} \cdot \text{K})(1000 \text{ K})}{2.50 \text{ L}}$$

$$= 0.0961 \text{ bar}$$

	2A(g) +	B(g) ⇌	C(g)
I	0.200	0.200	0
C	-2(0.0961)	-0.0961	+0.0961
E	0.0078	0.1039	0.0961

$$K_P = \frac{P_C}{(P_A)^2 \times P_B} = \frac{0.0961}{(0.0078)^2 (0.1039)} = 1.52 \times 10^4$$

b) (2 pts) What is the value of K_C for the reaction?

$$K_P = K_C (RT)^{\Delta n_{\text{gas}}}$$

$$K_C = \frac{K_P}{(RT)^{\Delta n_{\text{gas}}}} = \frac{1.52 \times 10^4}{(0.083145 \times 1000)^{1-3}} = 1.05 \times 10^8$$

c) (3 pts) What is the percent yield of C?

$$? \text{ theoretical } P_C \text{ from A} = 0.200 \text{ bar A} \times \frac{1 \text{ bar C}}{2 \text{ bar A}} = 0.100 \text{ bar}$$

$$? \text{ theoretical } P_C \text{ from B} = 0.200 \text{ bar B} \times \frac{1 \text{ bar C}}{1 \text{ bar B}} = 0.200 \text{ bar}$$

Therefore, A is the LIMITING REAGENT.

$$\% \text{ yield} = \frac{0.0961 \text{ bar}}{0.100 \text{ bar}} \times 100\% = 96.1\%$$

d) (1 pt) If the equilibrated gas mixture was then transferred to a container of larger volume, what would be the resulting effect on the equilibrium?

SHIFT TOWARDS REACTANTS

SHIFT TOWARDS PRODUCTS

NO EFFECT

4. Two FBI agents, Mulder and Scully, are investigating a series of strange murders. In each case, the victim was found suspended in a solution of ammonium benzoate, $\text{NH}_4\text{C}_7\text{H}_5\text{O}_2$.

THIS QUESTION IS NEARLY IDENTICAL TO A QUESTION FROM THE 2014 MIDTERM#2

a) (4 pts) Will these salt solutions be acidic, basic, or neutral? Show your reasoning to earn full points. (K_b of ammonia is 1.8×10^{-5}).

Dissolution of the salt: $\text{NH}_4\text{C}_7\text{H}_5\text{O}_2 (\text{s}) \rightarrow \text{NH}_4^+ (\text{aq}) + \text{C}_7\text{H}_5\text{O}_2^- (\text{aq})$

Both ions will hydrolyze, so which one hydrolyzes more?

$\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$	$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$
$\text{C}_7\text{H}_5\text{O}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HC}_7\text{H}_5\text{O}_2 + \text{OH}^-$	$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.3 \times 10^{-5}} = 1.59 \times 10^{-10}$

Since $K_a > K_b$, we know that the first equilibrium favours the products more. Therefore, the solution should be ACIDIC.

b) (6 pts) Agent Scully determines that the solution concentration is 0.166 M. What is the exact pH of the solution?

	NH_4^+	H_2O	\rightleftharpoons	H_3O^+	$+$	NH_3
I	0.166	-		0		0
C	-x	-		+x		+x
E	0.166 - x	-		x		x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]}$$

$$5.56 \times 10^{-10} = \frac{x^2}{0.166 - x} \approx \frac{x^2}{0.166}$$

$$\therefore x \approx 9.61 \times 10^{-6} \text{ M} = [\text{H}_3\text{O}^+]$$

$$\text{Check: } \frac{9.61 \times 10^{-6}}{0.166} \times 100\% = 0.006\% \longrightarrow \text{PASSES}$$

	$\text{C}_7\text{H}_5\text{O}_2^-$	H_2O	\rightleftharpoons	$\text{HC}_7\text{H}_5\text{O}_2$	$+$	OH^-
I	0.166	-		0		0
C	-x	-		+x		+x
E	0.166 - x	-		x		x

$$K_b = \frac{K_w}{K_a} = \frac{[\text{OH}^-][\text{HC}_7\text{H}_5\text{O}_2]}{[\text{C}_7\text{H}_5\text{O}_2^-]}$$

$$1.59 \times 10^{-10} = \frac{x^2}{0.166 - x} \approx \frac{x^2}{0.166}$$

$$\therefore x \approx 5.14 \times 10^{-6} \text{ M} = [\text{OH}^-]$$

$$\text{Check: } \frac{5.14 \times 10^{-6}}{0.166} \times 100\% = 0.003\% \longrightarrow \text{PASSES}$$

$[\text{H}_3\text{O}^+] > [\text{OH}^-]$, therefore, the excess H_3O^+ will determine the pH of the solution:

$$\text{leftover } [\text{H}_3\text{O}^+] = 9.61 \times 10^{-6} - 5.14 \times 10^{-6} = 4.47 \times 10^{-6} \text{ M}$$

$$\text{pH} = -\log(2.80 \times 10^{-6}) = 5.35$$

5. A buffer that contains 0.150 M HA and 0.640 M A⁻ has a pH of 8.17.

THIS IS A NEW QUESTION, BUT SIMILAR TO MANY EXAMPLES SEEN ALREADY

a) (4 pts) What is the pK_a of the buffer?

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

$$8.17 = \text{pK}_a + \log\left(\frac{0.640}{0.150}\right)$$

$$\text{pK}_a = 7.54$$

b) (6 pts) What is the change in pH after 0.0015 mol of Ba(OH)₂ is added to 0.500 L of this buffer solution?

$$? \frac{\text{mol OH}^-}{\text{L}} \text{ added} = \frac{0.0015 \text{ mol Ba(OH)}_2}{0.500 \text{ L}} \times \frac{2 \text{ mol OH}^-}{1 \text{ mol Ba(OH)}_2} = 0.0060 \text{ M}$$

	HA	+ OH ⁻	⇌	A ⁻	+ H ₂ O
B	0.150			0.640	-
A		0.0060			-
M	-0.0060	-0.0060		+0.0060	-
A	0.144	0		0.646	-

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right) = 7.54 + \log\left(\frac{0.646}{0.144}\right) = 8.19$$

$$\therefore \Delta\text{pH} = \text{pH}_2 - \text{pH}_1 = 8.19 - 8.17 = +0.02$$

BONUS - 2 pts

What are HA and A⁻? (Give their formulas). Show your reasoning to obtain the points.

Since pK_a = 7.54, K_a = 10^{-7.54} = 2.9 × 10⁻⁸

From the K_a table in the data sheets, we see that this corresponds to HOCl.

Therefore, HA and A⁻ are HOCl and OCl⁻, respectively.