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Chemistry 142 Practice Exam #1

Question 1. For H_2A, $K_{a1} = 2.0\times10^{-3}$ and $K_{a2} = 3.3\times10^{-8}$. For a 1.00*M* solution of H_2A calculate: $[H_2A]$, $[H^+]$, $[HA^-]$, and $[A^{2-}]$.

$K_{a_1} = \frac{x^2}{1.00-x} = 2.0\times10^{-3}$

$x = 0.0447$

H_2A	$+ H_2O \rightleftharpoons$	HA^-	$+ H_3O^+$
1.00		0	0
$-x$		$+x$	$+x$
$1.00-x$		x	x

$K_{a_2} = \frac{x(0.0447+x)}{0.0447-x} = 3.3\times10^{-8}$

HA^-	$+ H_2O \rightleftharpoons$	A^{2-}	$+ H_3O^+$
0.0447		0	0.0447
$-x$		$+x$	$+x$
$0.0447-x$		x	$0.0447+x$

$[H_2A] = 1.00 - 0.0447$

$[HA^-] = 0.0447 - 3.3\times10^{-8}$

$[H^+] = 0.0447 + 3.3\times10^{-8}$

$[A^{2-}] = 3.3\times10^{-8}$

Question 2. A two step mechanism has been suggested for the reaction of nitric oxide, NO, and bromine, Br_2.

(1) $NO(g) + Br_2(g) \rightarrow NOBr_2(g)$

(2) $NOBr_2(g) + NO(g) \rightarrow 2\ NOBr(g)$

a) What is the overall reaction?

$2NO + Br_2 \rightarrow 2NOBr$

b) What is the role of $NOBr_2$ in this reaction

NOBr is an intermediate

c) What is the predicted rate law if the first step is much slower than the ~~first~~ 2nd step?

rate = k[NO][Br₂]

d) The experimentally determined rate law is $R = k[NO]^2[Br_2]$. What can you conclude about this mechanism and the rate-determining step?

This mechanism is probably incorrect.

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Question 3. The following reaction has been studied at 540 K.

$$CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g).$$

The initial rates and initial concentrations are given in the table.

	[CO] mol/L	$[NO_2]$ mol/L	Initial Rate mol/Lhour
1	5.1×10^{-4}	0.35×10^{-4}	3.4×10^{-8}
2	5.1×10^{-4}	0.70×10^{-4}	6.8×10^{-8}
3	5.1×10^{-4}	0.18×10^{-4}	1.7×10^{-8}
4	1.0×10^{-3}	0.35×10^{-4}	6.8×10^{-8}
5	1.5×10^{-3}	0.35×10^{-4}	10.2×10^{-8}

Use the information to:

- Write out the rate expression
- Determine the order with respect to each reactant
- Calculate the value(including the units) of the rate constant and
- Write out the complete differential rate law.

$$\frac{\text{Rate } 2}{\text{Rate } 1} = \frac{6.8\times10^{-8}}{3.4\times10^{-8}} = \frac{k_2\,[CO]^x[NO_2]^y}{k_1\,[CO]^x[NO_2]^y} = \frac{k_2\,(5.1\times10^{-4})^x\,(0.70\times10^{-4})^y}{k_1\,(5.1\times10^{-4})^x\,(0.35\times10^{-4})^y}$$

$$\frac{\text{Rate } 2}{\text{Rate } 1} = \frac{6.8\times10^{-8}}{3.4\times10^{-8}} = 2 = \left(\frac{0.70\times10^{-4}}{0.35\times10^{-4}}\right)^y;\ y=1$$

$$\frac{\text{Rate}_4}{\text{Rate}_1} = \frac{6.8\times10^{-8}}{3.4\times10^{-8}} = 2 = \frac{k_4\,(1.0\times10^{-3})^x\,(0.35\times10^{-4})^1}{k_1\,(5.1\times10^{-4})^x\,(0.35\times10^{-4})^1} = 2 = 2^x;\ x=1$$

Rate law:

$$\text{Rate} = k\,[CO][NO_2]$$

$$k = \frac{3.4\times10^{-8}\ \text{mol/L hr}}{(5.1\times10^{-4})(0.35\times10^{-4})} = 1.90\ \text{L/mol hr}$$

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Question 4. The decomposition of SO_2Cl_2 is first order in SO_2Cl_2. The half life for the reaction is 4.1 hours at a certain temperature. If the initial amount of SO_2Cl_2 is 1.6×10^{-3} moles of SO_2Cl_2 in a flask, how many hours elapse until 2.00×10^{-4} moles remain? [Remember – the volume of the flask will not change.]

$$SO_2Cl_2(g) \rightarrow SO_2(g) + CO_2(g)$$

$t_{1/2} = \frac{\ln 2}{k} = 4.1\text{ hrs}$; $k = \frac{\ln 2}{4.1} = 0.1691$ ← use the half-life to determine "k".

$\ln[SO_2Cl_2]_t = -kt + \ln[SO_2Cl_2]_0$

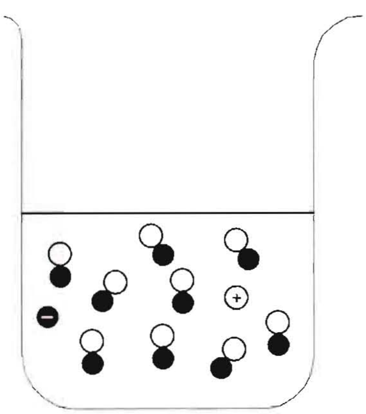
$\ln(2.00\times10^{-4}) = -0.1691t + \ln(1.6\times10^{-3})$

$-8.517 = -0.1691t + (-6.645)$

$-1.872 = -0.1691t$

$t = 12.3$ hrs.

Question 5. What is the K_a of the monoprotic acid indicated by the diagram below?



$K_a = \frac{[\ominus][\oplus]}{[8]} = \frac{1^2}{9}$

$K_a = 0.11$

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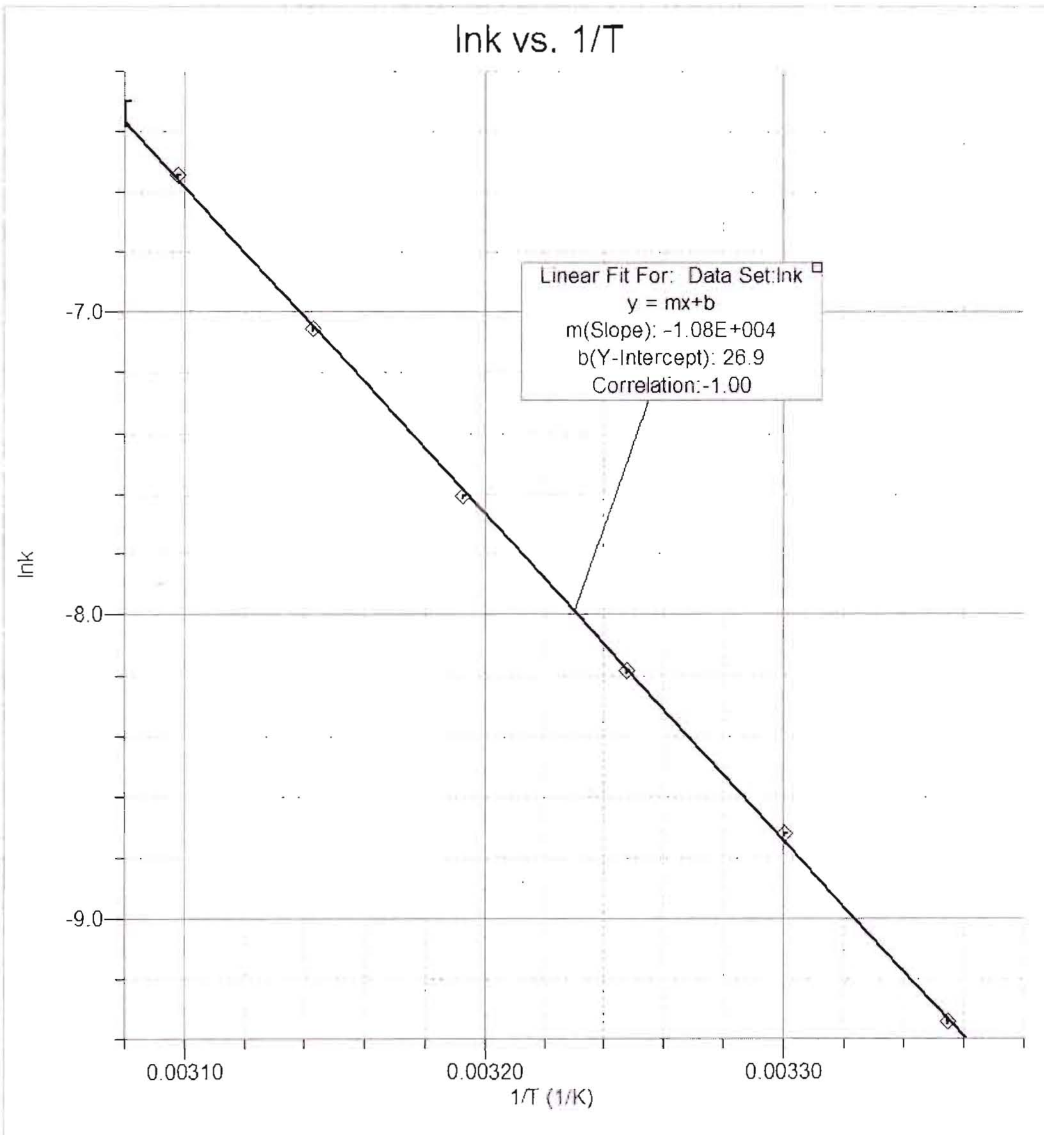
Question 6. The reaction shown in the equation is second order overall. The value of *k*, the specific rate constant, was measured at several temperatures. Determine the activation energy for this reaction by plotting your data. Estimate the linear fit with a ruler.

$$C_2H_5Br(aq) + OH^-(aq) \rightarrow C_2H_5OH(aq) + Br^-(aq)$$

°C	k, L mol^{-1}s^{-1}
25.1	8.76×10^{-5}
30.0	1.63×10^{-4}
34.9	2.80×10^{-4}
40.2	4.97×10^{-4}
45.2	8.63×10^{-4}
49.8	1.44×10^{-3}

Slope $= \frac{-Ea}{R} = -1.08 \times 10^4$

Ea = 89791 J/mol



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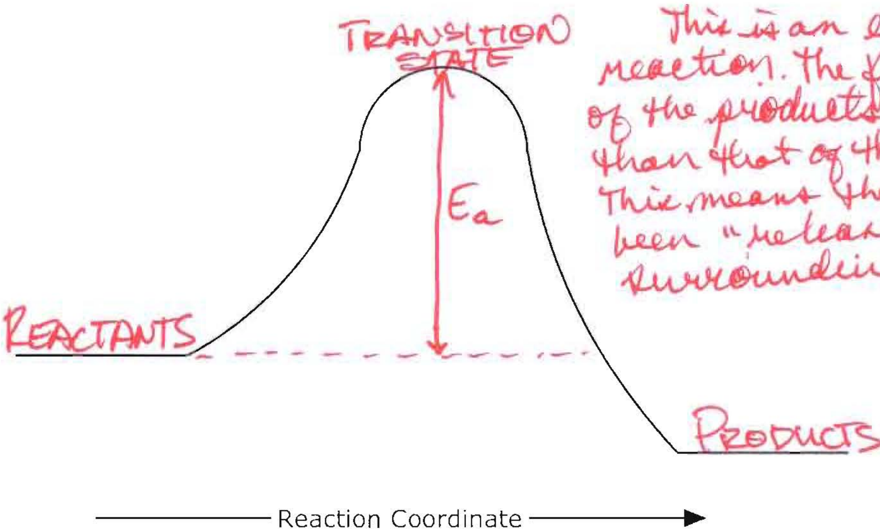
Question 7. Label the diagram below. Show reactants, products, transition state, and illustrate graphically, the activation energy. In this reaction an exothermic or endothermic reaction? Explain your reasoning.



This is an exothermic reaction. The free energy of the products is lower than that of the reactants. This means that energy has been "released" to the surroundings.

Question 8. While spending the entire day in Room 3252, Erica began wondering what the pH of a 0.300*M* solution of oxalic acid is. Help her out and calculate the molarity of all species as well as the pH for a 0.300*M* solution of $H_2C_2O_4$. $K_{a1} = 5.9\times10^{-2}$, $K_{a2} = 6.4\times10^{-5}$.

$$K_{a_1} = \frac{[HC_2O_4^-][H_3O^+]}{[H_2C_2O_4]} = \frac{x^2}{0.300-x} = 5.9\times10^{-2}$$

$H_2C_2O_4$	$+ H_2O \rightleftharpoons$	$HC_2O_4^-$	$+ H_3O^+$
0.300		0	0
$-x$		$+x$	$+x$
$0.300-x$		x	x

~~$K_{a_1} = 5.9\times10^{-2} = \frac{x^2}{0.300}$~~

$x = 0.13304$ ← Doesn't pass 5% test

$5.9\times10^{-2} = \frac{x^2}{0.300-0.133}$; $x = 0.09925$

$5.9\times10^{-2} = \frac{x^2}{0.300-0.0992}$; $x = 0.1088$

$5.9\times10^{-2} = \frac{x^2}{0.300-0.1088}$; $x = 0.1062$

$5.9\times10^{-2} = \frac{x^2}{0.300-0.1062}$; $x = 0.1069$ ← ok to stop here.

$HC_2O_4^-$	$+ H_2O \rightleftharpoons$	$C_2O_4^{2-}$	$+ H_3O^+$
0.1069		0	0.1069
$-x$		$+x$	$+x$
$0.1069-x$		x	$0.1069+x$

$$K_{a_2} = \frac{x(0.1069+x)}{0.1069-x} = 6.4\times10^{-5}$$

$$x = 6.4\times10^{-5}$$

$[H_3O^+] = 0.1069 + 6.4\times10^{-5}$; $pH = 0.97$

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$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

Question 9. Acetone is a useful solvent and is used in a variety of industrial processes. It decomposes via a first-order process to form methane and ketene. At 600 °C the rate constants is 8.7 x $10^{-3}s^{-1}$.

a) What is the half-life of the reaction?

$$t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{8.7\times10^{-3}} = 79.7\,s$$

b) How much time is required for 34% of a sample to decompose?

$$\ln\frac{[A]_t}{[A]_0} = -kt \qquad [A]_t = 0.66[A]_0$$

$$\ln\frac{0.66[A]_0}{[A]_0} = 8.7\times10^{-3}$$

$$t = 48\,s$$

Question 10. What is the expected pH of a 0.200 *M* NH_4NO_3 solution? K_b for ammonia is 1.8 × 10^{-5}.

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

	NH_4^+	NH_3	H_3O^+
	0.200	0	0
	$-x$	$+x$	$+x$
	$0.200-x$	x	x

NO_3^- is the conj. base for a strong acid. Therefore it has no acidic or basic props.

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]};\quad K_a = \frac{K_w}{K_b} = \frac{1.0\times10^{-14}}{1.8\times10^{-5}} = 5.56\times10^{-10}$$

$$5.56\times10^{-10} = \frac{x^2}{0.200-x};\quad x = 1.05\times10^{-5} = [H_3O^+]$$

$$pH = 4.98$$

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Question 11. A 1.00×10^{-3} *M* solution of quinine, a malaria drug, has a pH of 9.75. What is the value of K_b for quinine?

$B + H_2O \rightleftharpoons BH^+ + OH^-$

$pOH = 4.25$

$[OH^-] = 10^{-4.25}$

$[OH^-] = [BH^+]$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

$$K_b = \frac{(10^{-4.25})^2}{(1.0\times10^{-3} - 10^{-4.25})} = \frac{3.162\times10^{-9}}{9.44\times10^{-4}}$$

$$K_b = 3.35\times10^{-6}$$

Question 12. Will the following salts alter the pH a of distilled water solution? If so, will they be acidic, basic or neutral? Be sure to offer an explanation for each.

a) $NaNO_3$

This would yield a neutral solution because Na^+ is the cation of a strong base, and has no acidic properties. Also, NO_3^- is the conjugate base of a strong acid and has virtually no affinity for protons.

b) Na_3PO_4

This would yield a basic solution. See Na^+ discussion above in "a". PO_4^{3-} is the conjugate base of the weak acid, HPO_4^{2-} and has an affinity for protons.

c) $NH_4C_2H_3O_2$

In this case the cation is acidic and the anion is basic. one must look at the K_a of the acid and K_b of the base.

K_a for NH_4^+ is $\frac{K_w}{K_b \text{ for } NH_3}$ and K_b for $C_2H_3O_2^-$ is $\frac{K_w}{K_a \text{ for } HC_2H_3O_2}$.

Since K_a for $HC_2H_3O_2$ is 1.8×10^{-5} and K_b for NH_3 is 1.8×10^{-5}, the K_a for NH_4^+ is equal to K_b for $C_2H_3O_2^-$. This condition predicts a neutral pH!