CHM 106
Exam I

1. The Diels-Alder reaction is an important synthetic pathway in organic chemistry. In the prototypical reaction, ethylene reacts with butadiene to form cyclohexene:

$$C_2H_4(g) + C_4H_6(g) \rightarrow C_6H_{10}(g)$$

When kinetics experiments are performed on this reaction, a plot of ln k versus 1 / T is linear with a slope of $-1.38\times10^4\ K^{-1}$ and y-intercept of 16.12.

a) What is the activation energy for this reaction?

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$\ln k = \underbrace{\frac{-E_a}{R}}_{\text{slope}} \cdot \frac{1}{T} + \underbrace{\ln A}_{\text{y-int}}$

$\frac{-E_a}{8.314\ \frac{J}{mol\cdot K}} = -1.38\times10^4$ $\quad E_a = 8.314\,(1.38\times10^4) = \boxed{1.15\times10^5\ J/mol}$

b) What is the value of the frequency factor A?

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$\ln A = 16.12$

$A = e^{16.12} = \boxed{1.002\times10^7}$

c) What is the value of the rate constant at 200 °C?

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$\ln k = -1.38\times10^4 \left(\frac{1}{200+273}\right) + 16.12$

$\ln k = -13.056$

$k = e^{-13.056} = \boxed{2.14\times10^{-6}}$

d) The reaction is thought to proceed in a single elementary step. Write the rate law for this reaction.

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$RATE = k[C_2H_4][C_4H_6]$

2. In the gas phase, fluoromethane and water are in equilibrium with methanol and hydrogen fluoride:

$$CH_3F(g) + H_2O(g) \rightleftharpoons CH_3OH(g) + HF(g)$$

For this reaction, K = 0.85 at 100 °C.

a) What is the value of the pressure-based equilibrium constant $K_p$, when pressures are given in atmospheres and concentrations are given in molarity?

3 $K_p = K(RT)^{\Delta n} = K(RT)^0 = K = \boxed{0.85}$

b) Write an equilibrium expression for this system that relates the appropriate partial pressures to the equilibrium constant $K_p$.

3 $K_p = \dfrac{P_{CH_3OH} \cdot P_{HF}}{P_{CH_3F} \cdot P_{H_2O}}$

c) Suppose a vessel is charged with $P_{CH_3F} = P_{H_2O} = P_{CH_3OH} = P_{HF} = 1.0$ atm. Which direction does the system need to shift in order to reach equilibrium?

3 $Q = \dfrac{1 \cdot 1}{1 \cdot 1} = 1 \quad Q > K$ so SHIFT LEFT

d) What are the equilibrium concentrations of all species in this reaction?

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| | $CH_3F$ | + $H_2O$ | ⇌ $CH_3OH$ | + HF |
|---|---|---|---|---|
| INIT: | 1 | 1 | 1 | 1 |
| CHANGE: | $+x$ | $+x$ | $-x$ | $-x$ |
| EQ: | $1+x$ | $1+x$ | $1-x$ | $1-x$ |

$K_p = \dfrac{P_{CH_3OH} \cdot P_{HF}}{P_{CH_3F} \cdot P_{H_2O}}$

$0.85 = \dfrac{(1-x)^2}{(1+x)^2}$

$0.922 = \sqrt{0.85} = \dfrac{1-x}{1+x}$

$0.922 + 0.922x = 1 - x$

$1.922x = 0.078$

$x = \dfrac{0.078}{1.922} = 0.0406$

$P_{CH_3F} = P_{H_2O} = \boxed{1.04 \text{ atm}}$

$P_{CH_3OH} = P_{HF} = \boxed{0.96 \text{ atm}}$

3. One of the sources of acid rain is the production of nitric acid from nitrogen oxides in the atmosphere:

$$N_2O_5(g) + H_2O(g) \rightarrow 2\ HNO_3(g)$$

Some kinetic data were acquired for this reaction:

| | $[N_2O_5]_0$ (mol / L) | $[H_2O]_0$ (mol / L) | Initial Rate (mol / L · s ) |
|---|---|---|---|
| 1: | $1.3\times10^{-3}$ | 0.015 | $1.91\times10^{-4}$ |
| 2: | $2.6\times10^{-3}$ | 0.015 | $3.82\times10^{-4}$ |
| 3: | $2.6\times10^{-3}$ | 0.030 | $1.53\times10^{-3}$ |

a) What is the differential rate law for this reaction?

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1: $\text{RATE} = k\,[N_2O_5]^n[H_2O]^m$

$\frac{1.91\times10^{-4}}{3.82\times10^{-4}} = \frac{k\,[1.3\times10^{-3}]^n[0.015]^m}{k\,[2.6\times10^{-3}]^n[0.015]^m}$

$0.5 = 0.5^n \quad n=1$

2: $\frac{3.82\times10^{-4}}{1.53\times10^{-3}} = \frac{k\,[2.6\times10^{-3}]^n[0.015]^m}{k\,[2.6\times10^{-3}]^n[0.030]^m}$

$0.25 = 0.5^m \quad m=2$

$\text{RATE} = k\,[N_2O_5][H_2O]^2$

b) What is the value of the rate constant?

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$1.91\times10^{-4} = k\,[1.3\times10^{-3}][0.015]^2$

$k = 653\ \frac{L^2}{mol^2\cdot s}$

c) On a very humid day at 25 °C, the air contains a concentration of $[H_2O] = 0.0014$ M. The typical urban environment has a concentration of $[N_2O_5] = 2.4\times10^{-9}$ M. At what rate is nitric acid produced under these conditions?

3

$\text{RATE} = k\,[N_2O_5][H_2O]^2 = 653\,[2.4\times10^{-9}][0.0014]^2$

$= 3.07\times10^{-12}\ \frac{mol}{L\cdot s}$

d) Assuming the rate of nitric acid production in part (c) is *constant*, how long does it take to accumulate $1.0\times10^{-6}$ mol of $HNO_3$ per liter of air?

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$\frac{1.0\times10^{-6}\ mol\ HNO_3}{1\ L} \cdot \frac{L\cdot s}{3.07\times10^{-12}\ mol\ HNO_3} = 3.26\times10^5\ s$

$= 90.5$ hours

4. Explain the following phenomena:

a) While the first order reaction $C_4H_9Br(aq) + H_2O(l) \rightarrow C_4H_9OH(aq) + HBr(aq)$ can reach 90% completion (90% of the reactants are consumed) within an hour or two, it will never reach 100% completion.

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AS THE REACTION PROCEEDS AND REACTANT CONCENTRATION DROP, THE RATE DROPS. THUS, AS REACTANT CONCENTRATION APPROACH 0 (100% COMPLETION), THE RATE APPROACHES 0 AS WELL. A REACTION CAN THUS NEVER REACH 100% COMPLETION.

b) For the reaction $2\ H_2(g) + O_2(g) \rightleftharpoons 2\ H_2O(g)$, $K = 5.4\times10^{37}$ at 25 °C, but the rate of formation of $H_2O(g)$ is imperceptibly low.

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DESPITE THE FACT THAT THE PRODUCTS ARE MORE STABLE, THE REACTION DOES NOT PROCEED AT ROOM TEMPERATURE BECAUSE THE ENERGY OF ACTIVATION IS TOO HIGH AND NO MOLECULES HAVE ENOUGH ENERGY TO REACT.

c) Termolecular elementary steps in a reaction mechanism are exceedingly rare.

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IN ORDER FOR AN ELEMENTARY STEP TO BE TERMOLECULAR, THREE MOLECULES MUST COLLIDE SIMULTANEOUSLY. THIS IS STATISTICALLY UNLIKELY TO OCCUR.

5. In a reaction similar to the one we performed in the laboratory, *n*-butanol reacts with acetic acid to form *n*-butyl acetate and water under nonaqueous conditions:

$$n\text{-BuOH}(l) + \text{AcOH}(l) \rightleftharpoons n\text{-BuOAc}(l) + H_2O(l)$$

The equilibrium constant for this reaction is K = 4.24.

a) Write an equilibrium expression for this reaction that relates the appropriate concentrations to the equilibrium constant.

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$$K = \frac{[\text{BuOAc}][H_2O]}{[\text{BuOH}][\text{AcOH}]}$$

b) Suppose an empty flask is charged with initially with only $[n\text{-BuOH}]_0 = 6.00$ M and $[\text{AcOH}]_0 = 8.00$ M. What is the equilibrium concentration of the product *n*-butyl acetate?

| | *n*-BuOH | + AcOH | ⇌ *n*-BuOAc | + $H_2O$ |
|---|---|---|---|---|
| INIT: | 6.00 | 8.00 | 0 | 0 |
| CHANGE: | $-x$ | $-x$ | $+x$ | $+x$ |
| EQ: | $6-x$ | $8-x$ | $x$ | $x$ |

$$4.24 = \frac{x^2}{(6-x)(8-x)}$$

$$4.24(48 - 14x + x^2) = x^2$$

$$203.52 - 59.36x + 4.24x^2 = x^2$$

$$203.52 - 59.36x + 3.24x^2 = 0$$

$$x = \{13.754,\ 4.567\}$$

8

$$[\text{BuOAc}] = x = \boxed{4.57\text{ M}}$$

c) In many organic reactions in which water is formed, the water can be separated from the reaction mixture by distillation. Use Le Châtelier's principle to explain how such a procedure would improve the yield of the product *n*-butyl acetate.

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Removing water will push the equilibrium to the right. Since BuOAc is a product, its concentration will thus increase.

For the remaining questions, circle the letter that corresponds to the best answer.

6. Under what conditions will the following reaction proceed left to reach equilibrium?

$$4\ NH_3(g) + 7\ O_2(g) \rightleftharpoons 4\ NO_2(g) + 6\ H_2O(g)$$

(A) $K > 1$
(B) $K < 1$
(C) $Q > K$
(D) $Q < K$
(E) $Q = K$

$$Q = \frac{[NO_2]^4\,[H_2O]^6}{[NH_3]^4\,[O_2]^7}$$

7. What is the overall order of the reaction shown below?

$$Cl_2(g) + 3\ F_2(g) \rightarrow 2\ ClF_3(g)$$

(A) First order
(B) Second Order
(C) Third Order
(D) Fourth Order
(E) The order cannot be determined from the information given.

8. In aqueous solution, iron (II) reacts dipyridyl to form the tris(dipyridyl)iron (II) complex, as shown below. If $[Fe^{2+}]$ is held constant while [dipy] is doubled, the initial rate will:

$$Fe^{2+}(aq) + 3\ dipy(aq) \rightarrow Fe(dipy)_3^{2+}(aq) \qquad rate = k[Fe^{2+}][dipy]^3$$

(A) double
(B) triple
(C) increase by a factor of 6
(D) increase by a factor of 8
(E) increase by a factor of 9

$$\text{RATE} \propto [dipy]^3$$

$$2^3 = 8$$

9. In 6 M HCl, the complex ion $Ru(NH_3)_6^{3+}$ decomposes into a variety of products. The reaction is first order with respect to $Ru(NH_3)_6^{3+}$ and has a half-life of 14 hours at 25 °C. Under these conditions, how long will it take for $[Ru(NH_3)_6^{3+}]$ to decrease to 12.5% of its initial value?

(A) 2.7 hours
(B) 14 hours
(C) 28 hours
(D) 35 hours
(E) 42 hours

$$100\% \xrightarrow{14h} 50\% \xrightarrow{14h} 25\% \xrightarrow{14h} 12.5\%$$

10. When the concentration of substance B in the reaction below is doubled, all other factors being held constant, it is found that the rate of the reaction remains unchanged. The most probable explanation for this observation is:

$$2\ A(aq) + B(aq) \rightleftharpoons 2\ C(aq)$$

(A) The order of the reaction with respect to B is 1.
(B) Substance B is not involved in any of the steps in the mechanism of this reaction.
(C) Substance B is not involved in the rate determining step of the mechanism, but is involved in other steps.
(D) Substance B is probably a catalyst, and as such its effect on the rate of reaction does not depend on concentration.
(E) The reactant with the smallest coefficient in the balanced equation generally has little or no effect on the rate of the reaction.

For problems 11-14, consider the following disturbances to systems at equilibrium and predict the nature of the shift in the equilibrium position.

11. $(NH_4)_2CO_3(s)$ is removed from the system $(NH_4)_2CO_3(s) \rightleftharpoons 2\ NH_3(g) + CO_2(g) + H_2O(g)$

(A) The equilibrium position will shift left.
(B) The equilibrium position will shift right.
(C) The equilibrium position will not change.

12. The total pressure is increased on the system $CO(g) + 2\ H_2(g) \rightleftharpoons CH_3OH(g)$

(A) The equilibrium position will shift left.
(B) The equilibrium position will shift right.
(C) The equilibrium position will not change.

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13. The exothermic reaction $CH_4(g) + Cl_2(g) \rightleftharpoons CH_3Cl(g) + HCl(g)$ is heated

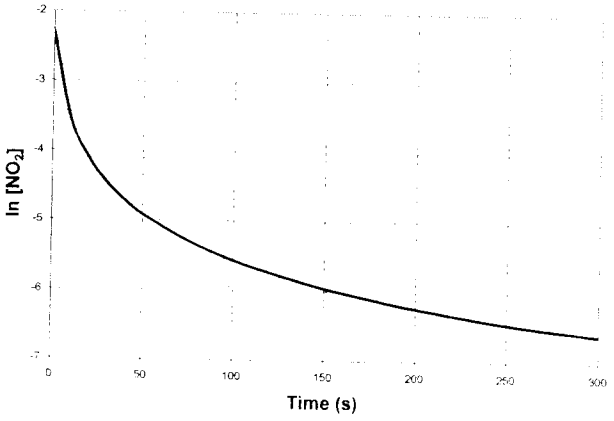
(A) The equilibrium position will shift left.
(B) The equilibrium position will shift right.
(C) The equilibrium position will not change.

14. $NaOH(aq)$ is added to $2\ H_2O(l) + 5\ ClO^-(aq) \rightleftharpoons 2\ Cl_2(aq) + ClO_3^-(aq) + 4\ OH^-(aq)$

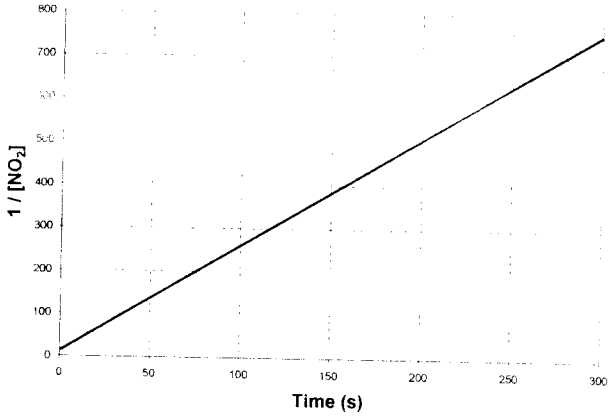
(A) The equilibrium position will shift left.
(B) The equilibrium position will shift right.
(C) The equilibrium position will not change.

15. For the reaction $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$, spectrophotometric studies were performed that monitored the concentration of the brown $NO_2$ over time:

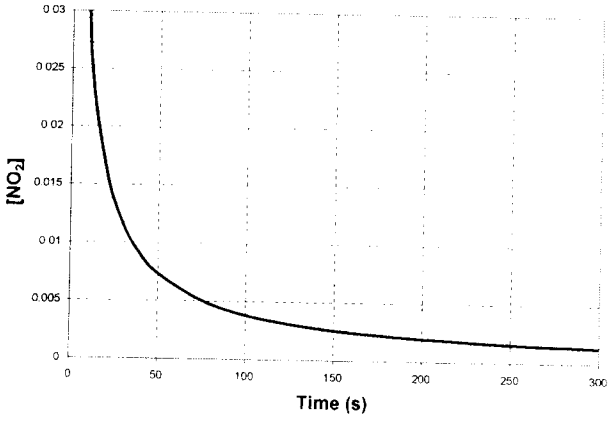
ln [$NO_2$] vs time:




1 / [$NO_2$] vs time:




[$NO_2$] vs time:




What is the order of the reaction with respect to $NO_2$?

(A) Zero order
(B) First order
(C) Second order
(D) Third order
(E) The order cannot be determined from the information given.