Chemistry 4A F'00, Exam III
November 17, 2000
Professors Cohen/Sauer/Boering

Problems

1. (15) 15

2. (10) 10

3. (25) 17

4. (25) 9

5. (25) 14

TOTAL EXAM SCORE (100)

Rules:

- No lecture notes or books permitted
- No word processing calculators
- Time: 50 minutes
- Show all work to get partial credit

- $R = 8.3 J\ mol^{-1} K^{-1}$

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1.(5+5+5points)

The rate law for the reaction:

$$3\,VO^{2+} + HCrO_4^- + H^+ \rightarrow 3VO_2^+ + Cr^{3+} + H_2O$$

has been shown to be:

$$-\frac{d[HCrO_4^-]}{dt} = k\frac{\overset{4}{[VO^{2+}]^2}\overset{8}{[HCrO_4^-]}}{[VO_2^+]}$$

a) If the rate of disappearance of $HCrO_4^-$ is $8.3\text{x}10^{-2}$ moles liter^{-1}sec^{-1}; the rate of disappearance of VO^{2+} is?

8.3×10^{-2} moles/L $\times \frac{3 \text{ moles}}{\text{mol}} =$

0.249 moles/Ls

+5

b) If the concentrations of all the solutes present in the reaction are doubled, how does the rate of disappearance of $HCrO_4^-$ change? Circle your answer:

no change

doubled

[✓ quadrupled] unless at an early stage the ≈ 8 times

halved

+5

8 times

c) The rate law described in this problem is an example of product inhibition. Write the rate law for the initial disappearance of $HCrO_4^-$ in the absence of products.

$$\frac{-d[HCrO_4^-]}{dt} = K[VO^{2+}]^2[HCrO_4^-]$$ +5

~~K forward [VO]~~

10

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2. (10 points) For the reaction A+2B→ products, the following data were observed:

Initial Rate (mole liter^{-1}sec^{-1})	Initial Concentration (mole liter^{-1})	
	[A]	[B]
6.3×10^{-8}	2.0×10^{-3}	4.0×10^{-3}
12.6×10^{-8}	2.0×10^{-3}	8.0×10^{-3}
25.2×10^{-8}	4.0×10^{-3}	4.0×10^{-3}

The rate law for this reaction is (circle your answer)

~~rate = k~~

rate = k[A][B]

[✓ rate = k[A]^2[B]] +10

rate = k[A][B]^2

rate = k[A]$^{1/2}$[B]

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3. (10 + 10 + 5 points)

The detailed mechanism for the association reaction

$$NO_2 + NO_3 \rightarrow N_2O_5$$

consists of two elementary reactions

$$NO_2 + NO_3 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} N_2O_5^*$$

$$N_2O_5^* + M \xrightarrow{k_2} N_2O_5 + M$$

✓ a) Write a rate law for disappearance of N_2O_5 based on your mechanism.

$$\frac{d[N_2O_5]}{dt} = k_2[N_2O_5^*][M]$$ +2

use and assume steady state

$$[N_2O_5^*] = \frac{k_1[NO_2][NO_3]}{k_{-1} + k_2[M]}$$ +6

10/10

substitute in →

$$\frac{d[N_2O_5]}{dt} = \frac{k_2 k_1 [NO_2][NO_3][M]}{k_{-1} + k_2[M]}$$ +2

b) Write the rate law at low pressure and at high pressure. Sketch the dependence of the rate of appearance of N_2O_5 on pressure. (assume gaseous reaction where ↑ pressure ↑ reactants + products)

assume k_2 is slow (single arrow) ~~and pressure is doubled~~

~~at initial high reaction at the reaction~~ ~~Low pressure rate for~~

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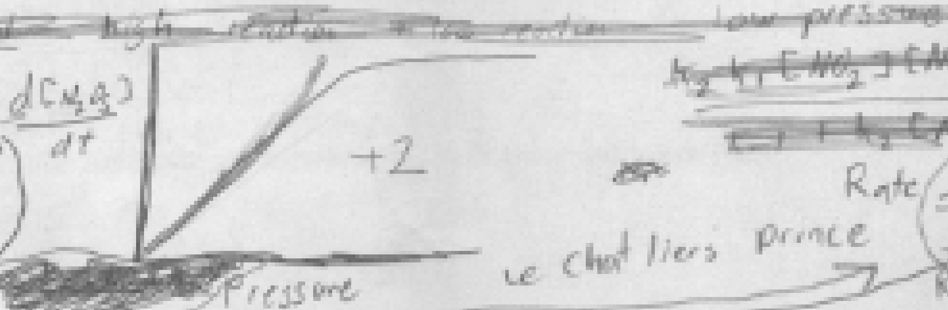
~~$\frac{k_2 k_1 [NO_2][NO_3][M]}{k_{-1} + k_2[M]}$~~

Low Pressure ↓

$k_2[M]$ shadows k_{-1}

High P

Rate = $k_1[NO_2][NO_3]$ +3



+2

le Chatliers prince

Rate $= \frac{k_2 k_1 [NO_2][NO_3][M]}{k_{-1}}$

Rate = $k_2[M][NO_2][NO_3]$ +2

Low pressure k_{-1} shadows k_2

c) ~~The overall reaction proceeds faster at low temperature.~~ Why?

~~The first process~~

The rate limiting process, the second one, is exothermic, and thus le Chatliers principle predicts a shift toward products when a product (heat) is removed ✗

0/5

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4 (10 + 9 + 6 points)

a) Write a catalytic cycle for the net reaction

$$2O_3 \rightarrow 3O_2$$

that involves ClOOCl. Label the rate determining step.

~~ClO + ClO → ClOOCl~~
~~ClOOCl + O_3 → ClO + O_2 + ClOO~~
~~ClOO + O_3 → ClO + $2O_2$~~

$2O_3 \rightarrow 3O_2$

~~ClO + ClO → ClOOCl~~
~~ClOOCl + M → 2ClO~~ ~~+ Cl + M~~
~~Cl~~
~~ClOOCl + M → 2ClO~~
~~ClO + O_3 → Cl + $2O_2$~~

~~2ClO → ClOOCl~~
~~ClOOCl → Cl + ClOO~~
~~Cl + O_3 → ClO + O_2~~
~~ClO + O_3 → ClO + $2O_2$~~
~~Cl~~

ClO + ClO + M → ClOOCl + M +1

ClOOCl ~~+ M~~ → ClO + O_2 + ClOO

Rate limit step ↗ ClOO + O_3 → ClO + $2O_2$ ~~(It may not be right, but it answers the problem)~~

1/10

b) Use your mechanism to write a rate equation for ozone disappearance that shows the rate of ozone disappearance is proportional to $[ClO]^2$. (I answered the question correctly even if the answer does not fit real life)

① $-\frac{d[O_3]}{dt} = k_2[ClOOCl][O_3] + k_3[ClOO][O_3]$

inconsistent w/ above

② steady state approx

$[ClOOCl] = \frac{k_1[ClO]^2}{k_2[O_3] + k_{-1}}$

③ and $[ClOO] = \frac{k_1[ClO]^2[O_3]}{(k_2[O_3] + k_{-1})(k_2[ClO][O_2] + k_3[O_3])}$

④ plug in and get $-\frac{d[O_3]}{dt} = \frac{k_2 k_1 [ClO]^2 [O_3]}{k_2[O_3] + k_{-1}} + \frac{k_3 k_2 k_1 [ClO]^2 [O_3]^2}{(k_2[O_3] + k_{-1})(k_2[ClO][O_2] + k_3[O_3])}$

5 factor out $[ClO]^2$ from both terms.

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c) List 2 reasons the Antarctic ozone hole forms in October and not in June.

The Antarctic ~~summer~~ spring is beginning in the October period thus this is the time after which the first light has reached the region (beginning the catalysis of O_3). Also, the reactions that produce the catalysts are encouraged by (PSC) clouds that form around 195 °K, temperatures reached only during the winter dark period... thus there is an excess of catalyst present at the beginning of the Antarctic

+3

+3

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5. (5+15+5 points)

For the reaction of $HOCl^-$ with an organic dye, assume it is first order in each reactant with a rate constant of 10^{-2}liter-mole^{-1}s^{-1}. The dye concentration is 10^{-1}mole-liter^{-1}.

a) What is the lifetime of the bleach? (circle your answer)

$\frac{1}{K}$ ~~t lifetime = $\frac{1}{k}$~~

10,000sec

[✓ 1000sec]

~~100sec~~

10sec

1sec

0

✓ b) The reaction rate doubles when the temperature is raised from 280K to 320K. Estimate the activation energy for this reaction.

assume 1st order reaction

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{R}\left(\frac{1}{320} - \frac{1}{280}\right)$$

$$\left(\frac{1}{320}-\frac{1}{280}\right)^{-1} R \ln 2 = E_a$$

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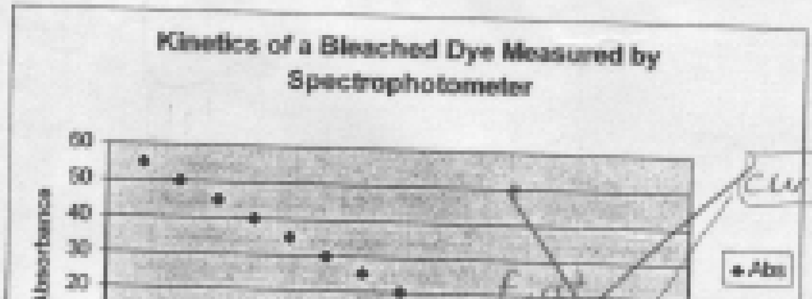
$E_a \approx 12909$ kJ/mol

SIG FIGS

-1

c) The following observations of transmission vs. time were made after mixing bleach and dye:



0

curve here

dye is not Zeroth order, even at pseudo 1st order for dye.

NO!!!...

Mark the first and last data point you would include in an analysis to determine the reaction rate constant.