30/30

CHEMISTRY 12 – Chemical Principles **Spring 2008**

Quiz IV

Monday, April 28, 2008

Name Emma Fink Section # & time 4, Anupam Bonny 2pm

Each question carries 10 points. For each question, you have to show ALL steps you take to arrive at your answer. Points are awarded for each step required.

1. In acid solution, the mechanism for the reaction $\mathbf{NH_4^+ + HNO_2 \longrightarrow N_2 + 2H_2O + H^+}$ is:

Assume: water, fast eq for 1+2

intermediates: NO^+, NH_3, NH_3NO^+

$$HNO_2 + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O + NO^+$$ fast equil (1)

$$NH_4^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} NH_3 + H^+$$ fast equil (2)

$$NO^+ + NH_3 \xrightarrow{k_3} NH_3NO^+ \quad \text{(slow)}$$ (3)

$$NH_3NO^+ \xrightarrow{k_4} H_2O + H^+ + N_2 \quad \text{(fast)}$$ (4)

Derive the rate law.

10

$$Rate = k_3[NO^+][NH_3] \checkmark$$

in solution so $[H_2O]$ about constant

Not necessary:

$$\frac{d[NO^+]}{dt} = k_1[HNO_2][H^+] - k_{-1}[NO^+] - k_3[NO^+][NH_3] = 0$$

$$[NO^+] = \frac{k_1[HNO_3][H^+]}{k_{-1} + k_3[NH_3]}$$

Since fast equilibrium for 1st two steps

$$[NO^+] = \frac{k_1[HNO_2][H^+]}{k_{-1}}$$

From (2): $k_2[NH_4^+] = k_{-2}[NH_3][H^+] \checkmark$

$$\frac{k_2}{k_{-2}}\frac{[NH_4^+]}{[NH_3]} = [H^+]$$

From (1): $[HNO_2][H^+]k_1 = k_{-1}[NO^+]$

$$[NO^+] = \frac{k_1k_2}{k_{-1}k_{-2}}[HNO_2]\frac{[NH_4^+]}{[NH_3]}$$

$$Rate = \frac{k_1k_2k_3}{k_{-1}k_{-2}}[NH_3][HNO_2]\frac{[NH_4^+]}{[NH_3]}$$

$$Rate = \frac{k_1k_2k_3[HNO_2][NH_4^+]}{k_{-1}k_{-2}} \checkmark$$

2. Kinetic studies of the reaction $\mathbf{A_2 + B_2 \rightarrow 2AB}$ suggested the mechanism as follows,

$$A_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2A \qquad \text{(fast)}$$

$$A + B_2 \xrightarrow{k_2} AB + B \qquad \text{(slow)}$$

$$B + A_2 \xrightarrow{k_3} AB + A \qquad \text{(fast)}$$

What is the order of the reaction with respect to [A_2]?

general $\text{Rate} = k[A_2]^m [B_2]^n$

$\text{Rate} = k_2[A][B_2]$ ✓

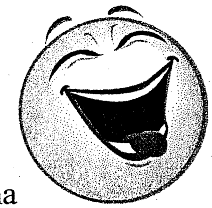
Since the first reaction is fast and reversible, it will go to equilibrium so

$k_1[A_2] = k_{-1}[A]^2$ (10)

solving for [A] $[A] = \sqrt{\frac{k_1}{k_{-1}}[A_2]}$ ✓

$\text{Rate} = k_2 \sqrt{\frac{k_1}{k_{-1}}[A_2]}\,[B_2]$ $\text{Rate} = k[A_2]^{1/2}[B_2]$

Thus the reaction is half order with respect to [A_2].



3. Ha ha ha ha ha
Haaaaa ha ha ha ha
Ha ha ha ha ha ha ha

Excuse me – this one is extremely funny.

Laughing gas, N_2O, can be prepared (ha, ha ha ha!) from H_2 and NO, according to the reaction:

Rate = $[H_2]^m [NO]^n$

$$H_{2(g)} + 2NO_{(g)} \qquad\qquad N_2O_{(g)} + H_2O_{(g)}$$

A study of initial concentration (ha, ha!) versus initial rate at a certain temperature yields the following data for this reaction (ha, ha!):

$[H_2]$, M	[NO], M	initial rate, M s^{-1}
0.1000	0.5000	2.560×10^{-6}
0.2000	0.3000	1.843×10^{-6}
0.1000	0.3000	9.216×10^{-7}
0.2000	0.6000	7.373×10^{-6}

double $[H_2]$ at constant [NO], rate doubles, m=1

double [NO] at constant $[H_2]$, rate quadruples, n=2

(a) Determine the order of each reactant and write the differential rate law for this reaction. Rate = $k[H_2][NO]^2$ = $-\frac{d[H_2]}{dt}$

(b) Calculate the value of the rate constant, k, for this reaction. Be sure to include the appropriate units for the rate constant! (work on back)

1.024×10^{-4} $M^{-2} sec^{-1}$ = k

(c) What is the overall order for this reaction?

This reaction is 3rd order overall. Overall order = m+n = 1+2 = 3.

(d) Describe what would happen to the rate of this reaction if we tripled the concentration of H_2 and doubled the concentration of NO.

On its own, tripling the concentration of H_2 would cause the rate to triple. Doubling [NO] on its own would cause the rate to quadruple. Together, the rate would be multiplied by 12. (increased by 12 times), since 3x4 = 12.

Example:
Rate = kAB^2
$3A(2B)^2k = 3 \cdot 4AB^2k = 12AB^2k$
12x, initial rate