Chemistry 1B, Exam I
February 25, 2008
Professor R.J. Saykally

Name KEY

TA ______________________

1. (20) ____________

2. (20) ____________

3. (25) ____________

4. (25) ____________

5. (10) ____________

TOTAL EXAM SCORE (100) ____________

Rules:
- Work all problems to 2 significant figures
- No lecture notes or books permitted
- No word processing calculators
- Time: 50 minutes
- Show all work to get partial credit
- Periodic Table, Tables of Physical Constants, and Conversion Factors included

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1. **(10+10 points)** for the reaction

$$2\ N_2O_5(g) \rightarrow 4\ NO_2(g) + O_2(g)$$

the currently accepted mechanism is

$N_2O_5 \leftrightarrow NO_2 + NO_3$	fast, equilibrium (k_1, k_{-1})
$NO_2 + NO_3 \rightarrow NO_2 + O_2 + NO$	slow (k_2)
$NO + NO_3 \rightarrow 2\ NO_2$	fast (k_3)

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

$$\text{rate} = k_2[NO_2][NO_3]$$

$$K = k_1/k_{-1} = \frac{[NO_2][NO_3]}{[N_2O_5]} \Rightarrow [NO_3] = \frac{K[N_2O_5]}{[NO_2]}$$

Sub-in rate law:

$$\text{rate} = k_2 K[N_2O_5], \quad k' \equiv k_2 K$$

$$\therefore \text{rate} = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = k'[N_2O_5]$$

b) Suppose that the k_1, k_{-1} and k_2 reactions are all slow. Solve for the steady-state concentration of $[NO_3]$.

$$\frac{d[NO_3]}{dt} = k_1[N_2O_5] - k_{-1}[NO_2][NO_3] - k_2[NO_2][NO_3] - k_3[NO][NO_3] = 0$$

$$[NO_3] = \frac{k_1[N_2O_5]}{k_{-1}[NO_2] + k_2[NO_2] + k_3[NO]}$$

$$= \frac{k_1[N_2O_5]}{[NO_2](k_{-1}+k_2) + k_3[NO]}$$

$$= \frac{k_1}{k_3}\frac{[N_2O_5]}{[NO]}$$

if k_1 & k_2 rxns are slow $\Rightarrow k_{-1} + k_2 << k_3$

eliminate [NO]; $0 = \frac{d[NO]}{dt} = k_2[NO_2][NO_3] - k_3[NO][NO_3]$

$$[NO] = k_2/k_3\,[NO_2]$$

$$\Rightarrow [NO_3] = \frac{k_1[N_2O_5]}{[NO_2](k_{-1}+2k_2)}$$

2. (5+5+10 points) For the reaction

$$N_2O_5(g) \rightarrow 2\,NO_2(g) + \tfrac{1}{2}\,O_2(g)$$

the rate constant k at 25 °C is $3.46 \times 10^{-5}\ s^{-1}$ and at 55 °C it is $1.5 \times 10^{-3}\ s^{-1}$.

a) Calculate the activation energy, E_a (kJ/mol).

$$\ln(k_1/k_2) = -E_a/R\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{3.46\times10^{-5}\,s^{-1}}{1.5\times10^{-3}\,s^{-1}}\right) = \frac{-E_a}{8.314\ J/mol\cdot K}\left(\frac{1}{298} - \frac{1}{328}\right)$$

$$E_a = 100\ kJ/mol$$

b) Calculate the fraction of molecules that will react at 300K.

$$\sim e^{-E_a/RT} = \exp\left(-102{,}000\ J/mol \,/\, 8.31\ \tfrac{J}{mol\,K}\cdot 300K\right)$$
$$= 1.68 \times 10^{-18}$$

frac at 300K is 1.7×10^{-18}

c) Write the differential rate law that would be expected at <u>low pressure</u>.

$$rate = \frac{d[N_2O_5]}{dt} = k_1[N_2O_5]^2$$

Derivation (Lindemann); Steady-state $\frac{d[N_2O_5^*]}{dt} = 0 = k_1[N_2O_5]^2 - k_{-1}[N_2O_5^*][N_2O_5] - k_2[N_2O_5^*]$

$$\Rightarrow [N_2O_5^*] = \frac{k_1[N_2O_5]^2}{k_2 + k_{-1}[N_2O_5]}$$

$$rate = k_2[N_2O_5^*] = \frac{k_2 k_1 [N_2O_5]^2}{k_2 + k_{-1}[N_2O_5]}$$ low P $\Rightarrow k_2 \gg k_{-1}[N_2O_5]$

3. (10+10+5 points) For the reaction

$$2\,NO(g) + 2\,H_2(g) \rightarrow N_2(g) + 2\,H_2O(g)$$

these data were obtained at 1100 K:

[NO] (mol/L)	[H_2] (mol/L)	Initial Rate (mol L^{-1} s^{-1})
5.00 X 10^{-3}	2.50 X 10^{-3}	3.0 X 10^{-3}
15.0 X 10^{-3}	2.50 X 10^{-3}	9.0 X 10^{-3}
15.0 X 10^{-3}	10.0 X 10^{-3}	3.6 X 10^{-2}

a) Write the differential rate law.

$rate = k[NO]^x[H_2]^y$

NO: $\frac{rate_1}{rate_2} = \frac{5.00}{15.0} = \left(\frac{3.0}{9.0}\right)^x \Rightarrow x = 1$

H_2: $\frac{rate_2}{rate_3} = \frac{2.50}{10.0} = \left(\frac{9.0}{36}\right)^y$

or $\frac{1}{4} = \left(\frac{1}{4}\right)^y \Rightarrow y = 1$

$\therefore rate = \frac{d[N_2]}{dt} = k[NO][H_2]$

b) Calculate the rate constant.

Plug in values:

$3.0\times10^{-3}\ M/s = k\,(5.00\times10^{-3}\ M)(2.50\times10^{-3}\ M)$

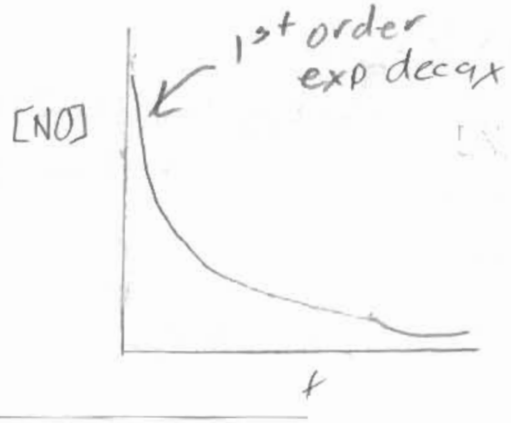
$k = 240\ L/mol\,s$

c) Graph the [NO] concentration vs. time that would be expected if H_2 were present in large excess.

If $[H_2] >> [NO]$, rxn will be pseado first order

$rate = k'[NO]$, $k' = k[H_2]$

$[NO] = [NO]_0\, e^{-k't}$



4. (5+5+10+5 points) In class, we demonstrated the disproportionation reaction of hydrogen peroxide (E_a = 76 kJ/mol):

$$2\ H_2O_2(aq) \rightarrow 2\ H_2O(\ell) + O_2(g)$$

a) We would expect this reaction to be ___activation___ controlled in the liquid.

b) What would the "encounter pair" be for this reaction?

$H_2O_2 \cdots H_2O_2$

c) Use the steady-state approximation with the general liquid state mechanism given in class to derive the steady-state concentration of the encounter pair in terms of $[H_2O_2]$.

$$H_2O_2 + H_2O_2 \underset{k_{-D}}{\overset{k_D}{\rightleftharpoons}} [H_2O_2 \cdots H_2O_2] \xrightarrow{k_2} P$$

$$\frac{d[P]}{dt} = k_2[H_2O_2 \cdots H_2O_2]$$

SS

$$k_D[H_2O_2]^2 = k_{-D}[H_2O_2 \cdots H_2O_2] + k_2[H_2O_2 \cdots H_2O_2]$$

$$[H_2O_2 \cdots H_2O_2] = \frac{k_D[H_2O_2]^2}{k_{-D} + k_2}$$

d) When MnO_2 powder is added, the reaction rate increases by a factor of 10^{10}. Estimate the corresponding reduction in the activation energy effected by the catalyst. Assume T and A are constant; T = 300K.

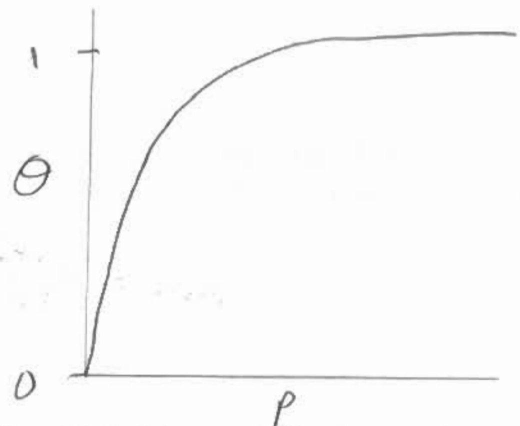
$$\ln\left(\frac{k_1}{k_2}\right) = -\frac{1}{RT}(E_a - E_a')$$

$$\ln(10^{-10}) = -\frac{1}{(8.314\ \text{J/mol K})(300\text{K})}(E_a - E_a')$$

$$\Rightarrow E_a - E_a' = 57\ \text{kJ/mol}$$

5. (5+5 points each)

a) Sketch the graph of surface coverage vs. pressure expected for non-dissociative adsorption of a gas onto a surface, if the adsorption rate constant is much larger than the desorption rate constant.



b) Sketch and label the graph for the reaction rate of an enzyme-catalyzed reaction as a function of substrate concentration.