Chemistry 1B SU'12, Exam I Name KEY

Multiple Choice Section. Answer each of the following questions and list your answers on page 2 in the space provided. Each multiple-choice question is worth 3 points.

Consider the elementary reaction $A + A \rightarrow D$ where the rate constant of the forward reaction is $k_f = 0.685$ and the rate constant for the reverse reaction is $k_r = 0.00462$.

1. What should the appropriate units of k_r be in this reaction? Rate = k[D]

M/S = (M)(S^{-1})

E (A) $M^{-1}s^{-1}$ (B) $M^{-2}s^{-2}$ (C) $M^{-2}s^{-1}$ (D) M [✓ (E) s^{-1}]

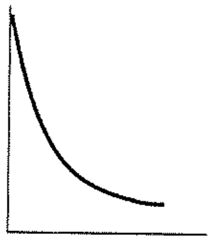
2. What should the appropriate units of k_f be in this reaction? M/S = (M^2)(M^{-1}S^{-1})

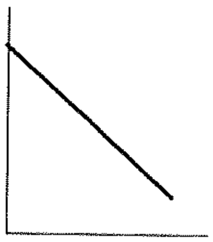
A [✓ (A) $M^{-1}s^{-1}$] (B) $M^{-2}s^{-2}$ (C) $M^{-2}s^{-1}$ (D) M (E) s^{-1}

3. What is the equilibrium constant for this reaction? $K = \frac{k_f}{k_R} = \frac{.685}{.00462}$

B (A) 3.16×10^{-3} [✓ (B) 148] (C) 6.74×10^{-3} (D) 297

Consider the elementary reaction $SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$, along with the following graphs:


A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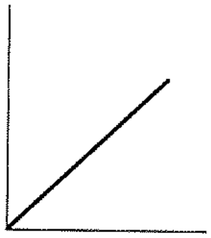
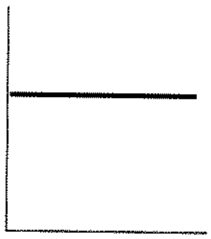
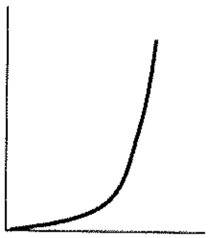

C


D


E

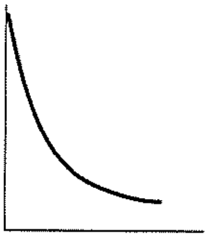
A 4. Which plot best represents the relationship between $[SO_2Cl_2]$ versus time?

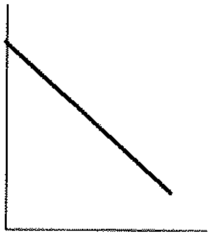
5. Looking at plot B, which of the following would need to be plotted on the y-axis to obtain this type of plot if time is on the x-axis?

A (A) $ln[SO_2Cl_2]$ (B) $[SO_2Cl_2]^{-1}$ (C) $[SO_2Cl_2]$ (D) $[SO_2Cl_2]^2$

D 6. Which plot best represents the dependence of $[SO_2Cl_2]^{-1}$ on $t_{1/2}$ for this reaction?

Consider the elementary reaction $HO_2(g) + HO_2(g) \rightarrow H_2O_2(g) + O_2$. And the following graphs:


A


B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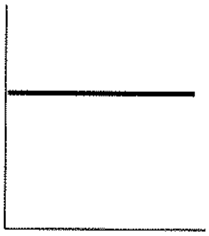
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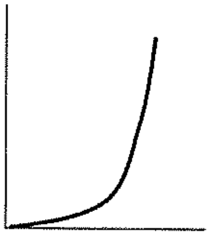

E

A **7.** Which plot best represents the relationship between $[HO_2]$ versus time?

A **8.** Which plot best represents the relationship between $ln[HO_2]$ versus time?

C **9.** Which plot best represents the relationship between $t_{1/2}$ for this reaction versus $[HO_2]^{-1}$

C **10.** Which plot best represents the relationship between $[HO_2]^{-1}$ versus time?

Calculations Section. Please show ALL work to receive partial credit. Place your final answers in a circle or box for clarity.

11. (15 points) The following kinetic data were obtained for the reaction $X + Y \rightarrow Z$.

	Initial concentration (mol·L^{-1})		
Experiment	**$[X]_0$ (M)**	**$[Y]_0$ (M)**	**Initial rate (mol·L^{-1}·s^{-1})**
1	1.5	1.5	$3.7\text{x}10^{-4}$
2	3.0	1.5	$3.7\text{x}10^{-4}$
3	3.0	4.5	$1.0\text{x}10^{-2}$
4	4.7	2.7	?

(a) Write the differential rate law for the reaction.

$$\text{Rate} = k_{obs}[X]^0[Y]^3$$

(b) From the data, determine the value of the rate constant (with proper units).

$$3.7\times10^{-4}\ \text{M/s} = k(1.5\ \text{M})^3$$

$$3.7\times10^{-4}\ \text{M/s} = (3.375\ \text{M}^3)k$$

$$\boxed{k = 1.10\times10^{-4}\ \text{M}^{-2}\text{s}^{-1}}$$

(c) Use the data to predict the reaction rate for Experiment 4.

$$\text{Rate} = (1.10\times10^{-4}\ \text{M}^{-2}\text{s}^{-1})(4.7\ \text{M})^0(2.7\ \text{M})^3$$

$$\boxed{\text{Rate} = 2.17\times10^{-3}\ \text{M/s}}$$

12. (25 points) The mechanism of the reaction of hydrogen and bromine involve the five following elementary steps.

$$Br_2 \xrightarrow{k_1} 2Br$$
$$(Br + H_2 \xrightarrow{k_2} HBr + H) \times 2$$
$$H + Br_2 \xrightarrow{k_3} HBr + Br$$
$$H + HBr \xrightarrow{k_4} H_2 + Br$$
$$Br + Br \xrightarrow{k_5} Br_2$$

in equilibrium

(a) Write down the balanced overall equation for this chain reaction.

$$H_2 + Br_2 \rightarrow 2HBr$$

(c) Assume all steps in the reaction are slow and use the steady state approximation to determine the rate of formation of HBr in terms of [HBr], [H$_2$] and [Br$_2$].

$$\frac{d[HBr]}{dt} = k_2\underline{\underline{[Br]}}[H_2] + k_3\underline{\underline{[H]}}[Br_2] - k_4\underline{\underline{[H]}}[HBr]$$

step1 + step5 are equilibrium ∴

$$k_5[Br]^2 = k_1[Br_2]$$
$$[Br] = \sqrt{\frac{k_1}{k_5}[Br_2]}$$

SSA: [H]

$$\frac{d[H]}{dt} = 0 = k_2[Br][H_2] - k_3[H][Br_2] - k_4[H][HBr]$$
$$k_2[Br][H_2] = (k_3[Br_2] + k_4[HBr])[H]$$
$$[H] = \frac{k_2[Br][H_2]}{k_3[Br_2] + k_4[HBr]}$$
$$[H] = \frac{k_2 k_1^{1/2} k_5^{-1/2}[Br_2]^{1/2}[H_2]}{k_3[Br_2] + k_4[HBr]}$$

$$\frac{d[HBr]}{dt} = \frac{k_2 k_1^{1/2}}{k_5^{1/2}}[Br_2]^{1/2}[H_2] + (k_3[Br_2] + k_4[HBr])\left(\frac{k_2 k_1^{1/2}[Br_2]^{1/2}[H_2]}{k_5^{1/2}(k_3[Br_2] + k_4[HBr])}\right)$$

Can simplify to: $\frac{2k_2(k_1/k_5)^{1/2}[Br_2]^{3/2}[H_2]}{[Br] + k_4/k [HBr]}$

13. (20 points) In class we studied the reaction of the decomposition of hydrogen peroxide as written below.

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

We performed this reaction twice, once with KI *(aq)* and once with MnO_2 *(s)* as a catalyst.

(a) If the activation energy of this reaction is 76 kJ/mol we should expect this liquid state reaction to have Activation controlled kinetics. Explain what this limit represents in terms of collisions and energy of molecules to complete the reaction.

Energy must accumulate in $(H_2O_2 \cdots H_2O_2)$ encounter pair from collisions w/ solvent until $E(H_2O_2 \cdots H_2O_2) > E_a$

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

$$H_2O_2 + H_2O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [H_2O_2 \cdots H_2O_2] \xrightarrow{k_2} P$$

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

SSA: $k_1[H_2O_2]^2 = k_{-1}[H_2O_2 \cdots H_2O_2] + k_2[H_2O_2 \cdots H_2O_2]$

$$\boxed{[H_2O_2 \cdots H_2O_2] = \frac{k_1[H_2O_2]^2}{k_{-1} + k_2}}$$

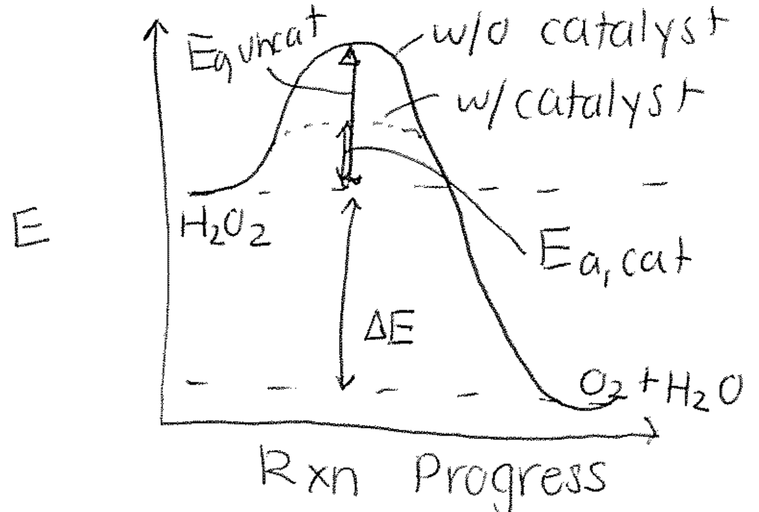
(c) When a catalyst is added the reaction rate increases by a factor of 10^{14}. Estimate the reduction in activation energy associated with adding the catalyst. Assume T (T=298 K) and A are constant.

$$\ln(k_1/k_2) = -\frac{1}{RT}(\Delta E_a)$$

$$\ln(10^{-14}) = -\frac{1}{8.314\,J/K\cdot mol \cdot 298\,K}(\Delta E_a)$$

$$\boxed{\Delta E_a = 80\ KJ/mol}$$

(d) Draw a reaction coordinate, or potential energy, diagram showing the reaction progress with and without the catalyst. Label reactants (H_2O_2), products (O_2, H_2O), activation energy without catalyst, activation energy with catalyst, and overall energy released by the reaction.



14. (10 points) The decomposition of HI is a second order reaction.

$$2HI(g) \rightarrow I_2(g) + H_2(g)$$

The following data were collected to try to describe the rate as a function of temperature. Assume the starting concentrations of reactants were the same in each trial.

Experiment	**Temperature** (°C)	**Rate Constant** ($\mathrm{mol \cdot L^{-1} \cdot s^{-1}}$)
1	300	6.5×10^{-6}
2	400	7.1×10^{-4}
3	500	1.4×10^{-3}

(a) Determine the activation energy for the decomposition of HI.

$$\ln\left(\frac{6.5\times10^{-6}\,M/s}{7.1\times10^{-4}\,M/s}\right) = \frac{E_a}{8.314\,J/Kmol}\left(\frac{1}{\underset{673K}{400+273}} - \frac{1}{\underset{573K}{300+273}}\right)$$

$$\boxed{E_a \doteq 150\ kJ/mol}$$

(b) What fraction of HI gas molecules have the correct energy to produce a successful reaction at 500 °C?

$$\sim e^{-E_a/RT}$$

$$\sim e^{-\left(150{,}000\,J/mol / 8.314\,J/Kmol \cdot 773K\right)}$$

$$\boxed{\sim 7.30\times10^{-11}\ \text{molecules}}$$

15. (10 points) An enzyme, ribonuclease, catalyzes the reaction to degrade RNA into smaller components. It was shown to have a $K_m = 7.9 \times 10^{-3}$ M and a $k_{cat} = 7.9 \times 10^{2}$ s^{-1}.

(a) What is the maximum rate this enzyme can degrade RNA if the concentration of ribonuclease is 3.4×10^{-4} M.

$$V_{max} = k_2 [ES]$$
$$= 7.9 \times 10^{2}\, s^{-1} \cdot 3.4 \times 10^{-4} M$$
$$= \boxed{0.269\ M/s}$$

(b) At what the substrate concentration would the rate be a quarter of that calculated in part (a)?

$$Rate = \frac{V_{max} [S]}{K_m + [S]}$$
$$0.0672\, M/s = \frac{(0.269\, M/s)\, [S]}{7.9 \times 10^{-3} M + [S]}$$
$$\boxed{[S] = 1.98 \times 10^{-3}\ M}$$

16. (4 points each) True/False. Confirm whether each statement below is true or false. Explain your reasoning for each question in full sentences for full credit. Diagrams and/or figures are also valid and sometimes very useful for full explanations, but not required.

(a) Rate laws can only be determined experimentally.

True

(b) When you increase the temperature of a reaction the rate increases due solely to the increase in the number of collisions in the sample.

False. b/c Maxwell-Boltzmann.

↑ T ↑ fraction of molecules w/ $E \geq E_a$

(c) If you compare the rate of the same reaction in gas versus in pure liquid state at the same temperature. The reaction in liquid state is faster.

True

Liquid = Higher # density + ↓ mean free path

(d) A catalyst is not present in the overall reaction and therefore can not appear in the rate law.

False.

Catalyst can be in rate law

(e) The rate of a reaction always slows down over time, assuming the reaction vessel maintains a constant temperature.

True

17. (4 points each) Short Answer. Use complete sentences in your explanations for full credit.

(a) Given the overall reaction $A + B \rightarrow C$ and the experimentally determined rate law, $rate = k_{obs}[A]^2$. Does this reaction happen in one step? Explain your reasoning.

No, elementary step must be a collision between 2 A molecules according to rate law. Rate law & equation do not match

(b) Describe three ways to increase the rate of a reaction as discussed in class.

(1) ↑ reactant concentration

(2) Temp.

(3) catalyst

(c) Why do many reactions that occur in aqueous solution have rate laws that are determined to be pseudo first order?

Rate law depends on solvent, but solvent concentration is so high as reaction proceeds the change in concentration is so small it is not observed.