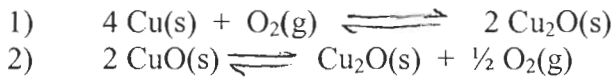


(14 points, 2 each) Circle the one best answer.

(a) Which of the following correctly describes the equilibrium constant expression for the reaction between gaseous H_2 and O_2 to form gaseous H_2O ?

- a) $K_c = [H_2O] / [H_2] [O_2]$ b) $K_c = [H_2O]^2 / [H_2] [O_2]$
 c) $K_c = [H_2O] / [H_2] [O_2]^{1/2}$ d) $K_c = [H_2] [O_2] / [H_2O]$
 e) $K_c = [H_2O]$ f) I don't know. Please give me a half point.

(b) Given the following equilibria :



$K_1 = \frac{1}{[O_2]}$
 $K_2 = [O_2]^{1/2}$

$K = \frac{1}{[O_2]}$

$(K_1)^{1/2} = \left(\frac{1}{[O_2]}\right)^{1/2}$
 $\frac{1}{K_2} = \left(\frac{1}{[O_2]^{1/2}}\right)$

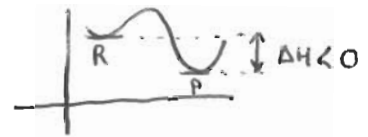
What is K , in terms of K_1 and K_2 , for the equilibrium: $2 Cu(s) + O_2(g) \rightleftharpoons 2 CuO(s)$?

- a) $K_1 \times K_2$ b) $(K_1)^{1/2} \times K_2$ c) $(K_1)^{1/2} / K_2$
 d) $(K_2)^{1/2} / K_1$ e) $K_1 \times (K_2)^{1/2}$ f) I don't know. Please give me a half point.

$K = \frac{1}{[O_2]^{1/2}} \cdot \frac{1}{[O_2]^{1/2}}$
 $= \frac{1}{[O_2]}$

(c) If $K > 1$ for an equilibrium reaction, this indicates that

- a. reactants are more stable than products.
 b. $\Delta H = 0$.
 c. forward rate of reaction is faster than the reverse rate of reaction.
 d. the forward rate constant is equal to the reverse rate constant.
 e. the products are more stable than reactants.
 f. I don't know. Please give me a half point.



(d) Choose the incorrect statement.

- a. A reaction intermediate is produced and used up during a reaction.
 b. The transition state and a reaction intermediate are the same.
 c. An activated complex has partially formed bonds.
 d. A reaction intermediate has fully formed bonds.
 e. The reactants have lower energy compared to that of the activated complex.
 f. I don't know. Please give me a half point.

(e) If a catalyst is added to a reaction

- I) the value of k is increased
 II) the value of k is decreased
 III) the rate is increased
 IV) the rate is decreased
 V) neither rate nor constant is changed, only order

- a. I and IV
 b. II and IV
 c. II and III
 d. I and III
 e. V only
 f. I don't know. Please give me a half point.

$rate = k [A]^n$

A reactant R is being consumed in a first order reaction. What fraction of the initial concentration of R is consumed in 3 half-lives?

- a. 0.963
- b. 0.875
- c. 0.333
- d. 0.003
- e. I don't know. Please give me a half point.

$$1 \xrightarrow{\frac{1}{2}} .5 \xrightarrow{\frac{1}{2}} .25 \xrightarrow{\frac{1}{2}} .125 \text{ remains, } 0.875 \text{ consumed}$$

$$\text{or } (0.5)^3 = 0.125 \text{ remains, } 1 - 0.125 = 0.875 \text{ consumed}$$

(g) For a reaction with the rate law: $\text{rate} = k[A][B]^2$, what factor will NOT affect the rate?

- a. lowering temperature
- b. adding a catalyst
- c. decreasing [A]
- d. increasing [B]
- e. none of these
- f. I don't know. Please give me a half point.

2 (10 points) A commonly stated "rule of thumb" is that the rate of reaction doubles for a temperature increase of 10 °C. (This rule is very often wrong.)

a) Consider a reaction at room temperature (25 °C). Apply the rule above and calculate the activation energy (E_a) for this reaction.

For the same rxn run at different temperatures (within a limit) the rate law is similar, not the same since k will be different at different temps.

$$2 \times \text{rate}_{25^\circ\text{C}} = \text{rate}_{35^\circ\text{C}}$$

$$2 \times k_{25^\circ\text{C}} [A]^n = k_{35^\circ\text{C}} [A]^n$$

$$k_{35^\circ\text{C}} = \frac{2 \times k_{25^\circ\text{C}} [A]^n}{[A]^n}$$

$$k_{35^\circ\text{C}} = 2 k_{25^\circ\text{C}}$$

$$\ln \left(\frac{2 k_{35^\circ\text{C}}}{k_{25^\circ\text{C}}} \right) = \frac{E_a}{R} \left(\frac{1}{298} - \frac{1}{308} \right)$$

$$\ln 2 = \frac{E_a}{(8.31 \times 10^{-3} \frac{\text{kJ}}{\text{mol} \cdot \text{K}})} \left(\frac{1}{298\text{K}} - \frac{1}{308\text{K}} \right)$$

$$E_a = 52.9 \frac{\text{kJ}}{\text{mol}}$$

b) Using no more than two brief sentences define activation energy.

+3 The activation energy of a reaction is the minimum energy above the mean kinetic energy of a set of molecules in order for molecular collisions to result in a chemical reaction.

(10 points) In the decomposition reaction $A \rightarrow \text{products}$ the following data were obtained.

Time (min)	[A] (M)
0	1.00
5	0.63
10	0.46
15	0.36
25	0.25

a) The decomposition is either zeroth, first, or second order. Determine the order of the reaction. Clearly demonstrate your method and give evidence against the other possibilities.

Not 1st order: 1st half life (1.00 M \rightarrow 0.46 M), 10 min } half-life is not constant
 2nd half life (0.46 M \rightarrow 0.25 M), 15 min }

Not 0th order: $-\frac{\Delta[A]}{\Delta t}$ is not constant, $-\frac{(0.63-1.00)M}{(5-0)\text{min}} = 0.074 M$ \neq $-\frac{(0.25-0.46)M}{(25-10)\text{min}} = 0.014 M$

By elimination, the decomposition must be second order. So, apply 2nd order integrated rate law, and solve for k.

$$\frac{1}{[A_t]} - \frac{1}{[A_0]} = kt \quad \left| \quad k = \frac{\frac{1}{[A_t]} - \frac{1}{[A_0]}}{t} = \frac{\left(\frac{1}{0.63} - \frac{1}{1.00}\right) \frac{1}{M}}{5 \text{ min}} = 0.117 M^{-1} \text{ min}^{-1} \quad \checkmark$$

b) Calculate k (an average k is not required).

$$= \frac{\left(\frac{1}{0.36} - \frac{1}{1.00}\right) \frac{1}{M}}{15 \text{ min}} = 0.119 M^{-1} \text{ min}^{-1} \quad \checkmark$$

$$\boxed{k = 0.11 M^{-1} \cdot \text{min}^{-1}} \quad +2$$

c) Calculate the half-life.

$$\frac{1}{[A_{1/2}]} - \frac{1}{[A_0]} = kt_{1/2}$$

$$\frac{2}{[A_0]} - \frac{1}{[A_0]} = kt_{1/2}$$

$$\frac{1}{[A_0]} = kt_{1/2} \Rightarrow t_{1/2} = \frac{1}{k[A_0]}$$

$$t_{1/2} = \frac{1}{(0.11 M^{-1} \cdot \text{min}^{-1})(1.00 M)}$$

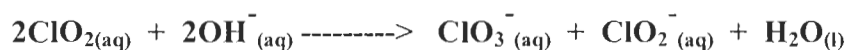
$$\boxed{t_{1/2} = 9.1 \text{ min}} \quad +2$$

d) Determine the value of the reaction rate when $[A] = 0.10 M$

$$\text{rate} = k[A]^2 = (0.11 M^{-1} \cdot \text{min}^{-1})(0.10 M)^2$$

$$= \boxed{0.0011 \frac{M}{\text{min}}} \quad +2$$

4) (15 points) The reaction below was studied and the following initial rate data were obtained.



	$[\text{ClO}_2]_0$ (mol/L)	$[\text{OH}^-]_0$ (mol/L)	Initial Rate (mol/L·s)
1	0.0500	0.100	5.76×10^{-2}
2	0.100	0.100	2.31×10^{-1}
3	0.100	0.050	1.15×10^{-1}

a) Determine the rate law for this reaction.

Compare 2 to 1 $[\text{ClO}_2]$ is doubled, rate quadruples ($[\text{OH}^-]$ constant)
 Compare 2 to 3 $[\text{OH}^-]$ is doubled, rate doubles ($[\text{ClO}_2]$ constant)
 $+8$ $\frac{\text{rate}}{\text{rate}'} = \frac{k[\text{ClO}_2]^2[\text{OH}^-]^1}{k[\text{ClO}_2]^2[\text{OH}^-]^1}$ $\text{rate} = k[\text{ClO}_2]^2[\text{OH}^-]$

b) What is the order of $[\text{ClO}_2]$, $[\text{OH}^-]$, and the overall reaction? 2 1 3
 $+3$ $[\text{ClO}_2]$ $[\text{OH}^-]$ RXN

c) What are the units of the rate constant?

$+2$ $\text{rate} = k[\text{ClO}_2]^2[\text{OH}^-] \Rightarrow \frac{\text{M}}{\text{s}} = k[\text{M}]^2[\text{M}]$

d) Which plot would indicate the order of $[\text{ClO}_2]$ determined in part b?

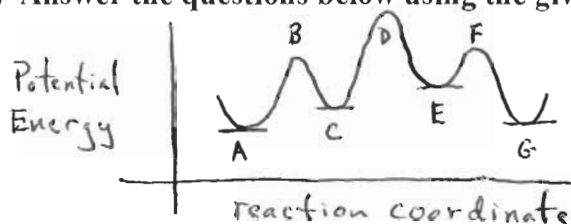
- 1) $\ln[\text{ClO}_2]$ vs. time 3) $-(\Delta[\text{ClO}_2]/\Delta t)$ vs. time
 2) $1/[\text{ClO}_2]$ vs. time 4) $[\text{ClO}_2]$ vs. time

$$k = \text{M}^{-2} \cdot \text{s}^{-1}$$

$+2$

PLOT # 2

5) (6 points) Answer the questions below using the given reaction coordinate.

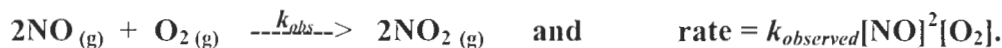


a) Identify, using a letter, the intermediate(s). C, E $+2$

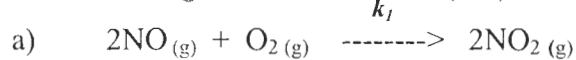
b) Identify, using a letter, the activated complex(es). B, D, F $+3$

c) Identify the rate determining step (as in $X \longrightarrow Z$). C \rightarrow E $+1$

.) (20 points) The reaction and experimental rate law for the gas phase reaction of nitrous oxide and oxygen to produce nitric oxide are:



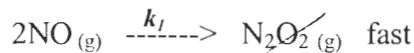
The following four mechanisms (a-d) have been proposed:



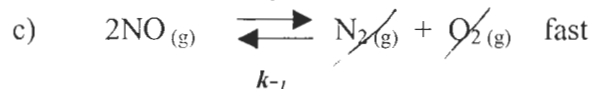
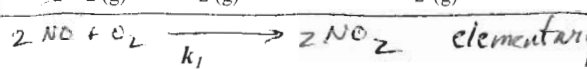
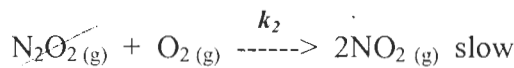
same as overall stoichiometry ✓

$$\text{rate} = k_1 [\text{NO}]^2 [\text{O}_2]$$

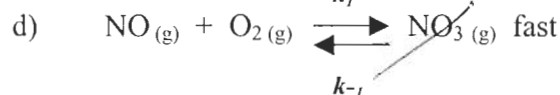
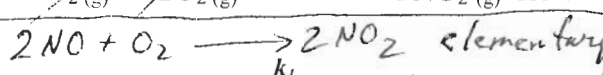
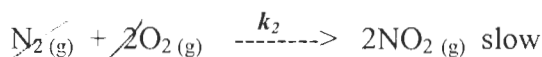
+12
(1, stoich)
(2, law) b)



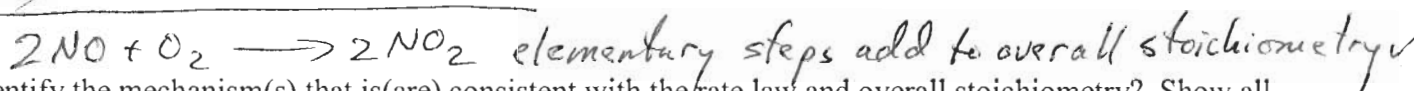
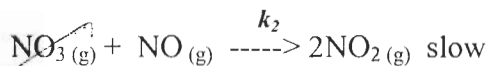
$$\text{rate} = k_2 [\text{N}_2\text{O}_2] [\text{O}_2]$$



$$\text{rate} = k_2 [\text{N}_2] [\text{O}_2]^2$$



$$\text{rate} = k_2 [\text{NO}_3] [\text{NO}]$$



i) Identify the mechanism(s) that is(are) consistent with the rate law and overall stoichiometry? Show all work to justify your answer.

a, c, d

a) satisfies rate law + stoichiometry

b) satisfies stoichiometry but not rate law, no substitution of N_2O_2 intermediate possible

c) satisfies stoichiometry and rate law

+3 $\text{rate} = k_2 [\text{N}_2] [\text{O}_2]^2$

$[\text{N}_2] = \frac{k_1 [\text{NO}]^2}{k_{-1} [\text{O}_2]}$

$k_1 [\text{NO}]^2 = k_{-1} [\text{N}_2] [\text{O}_2]$

$\text{rate} = \frac{k_2 k_1 [\text{NO}]^2 [\text{O}_2]^2}{k_{-1} [\text{O}_2]} = k' [\text{NO}]^2 [\text{O}_2]$

+3 d) satisfies stoichiometry

$\text{rate} = k_2 [\text{NO}_3] [\text{NO}]$

$k_1 [\text{NO}] [\text{O}_2] = k_{-1} [\text{NO}_3]$

$[\text{NO}_3] = \frac{k_1 [\text{NO}] [\text{O}_2]}{k_{-1}}$

$\text{rate} = \frac{k_2 k_1 [\text{NO}] [\text{NO}] [\text{O}_2]}{k_{-1}}$

$\text{rate} = k' [\text{NO}]^2 [\text{O}_2]$

ii) For each consistent mechanism consider its molecularity and briefly discuss its reasonableness.

+2 a) This is a termolecular rxn, unlikely

c) This is a bimolecular rxn followed by a termolecular rxn, unlikely

Extra Credit (3 points), please put on back of exam.

d) This is a set of bimolecular steps, likely

A reaction between A and B has the following stoichiometry: $3\text{A} + \text{B} \rightarrow \text{Products}$.

The initial rate of reaction is $1.00 \times 10^{-1} \text{ M/s}$ with $[\text{A}]_0 = 5.0 \text{ M}$ and $[\text{B}]_0 = 2.0 \text{ M}$. After 10.0s what is the concentration of A? $\text{rate of rxn} = 1.00 \times 10^{-1} \frac{\text{M}}{\text{s}} = -\frac{1}{3} \frac{\Delta[\text{A}]}{\Delta t} = -\frac{\Delta[\text{B}]}{\Delta t}$

after 10s: $1.00 \times 10^{-1} \frac{\text{M}}{\text{s}} \times 10.0\text{s} = 1.00 \text{ M}$

+2 Since A is lost $3 \times$ as fast as B: $[\text{A}]_{10.0\text{s}} = 5.0 \text{ M} - (3 \times 1.00 \text{ M}) = 2.0 \text{ M}$

rate law satisfies observed rate law