

TJ

1. The reaction $X + Y + Z \rightarrow P$ is known to follow the rate law: $d[P]/dt = k [X]^1 [Y]^2 [Z]^3 [P]^{-1}$. Shown below are concentration data and initial rate for one experiment. Fill in the expected initial rate data for the four experiments where it is left blank. (conc in M) in the four empty boxes below:

	[X]	[Y]	[Z]	[P]	initial rate M/s
$2^1 = \frac{x}{32000}$	0.2	0.2	0.2	0.2	32,000
$2^2 = \frac{y}{32000} = 4$	0.4	0.2	0.2	0.2	64,000
$2^3 = \frac{z}{32000} = 8$	0.2	0.4	0.2	0.2	128,000
$2^{-1} = \frac{p}{32000} = \frac{1}{2} = \frac{1}{2} \cdot 0.2$	0.2	0.2	0.4	0.2	256,000
	0.2	0.2	0.2	0.4	16,000

2. Suppose that a catalyst lowers the activation barrier of a reaction from 125 kJ/mol to 75 kJ/mol. By what factor would you expect the rate constant to increase by at 25 °C (assume that the frequency factors for the catalyzed and uncatalyzed reactions are the identical).

$$\frac{125}{75} = \frac{5}{3}$$

2. $\frac{3}{5}$

-6
 60×10^8

3. The half life for decay of carbon-14 is 5730 years. An object contains 0.250 grams carbon-14. The limit of detection of carbon-14 is 2×10^{-10} grams, how long will it take until there is no detectable amount of carbon-14 in the object.

$$k = \frac{.693}{t_{1/2}} = \frac{.693}{5730 \text{ yr}} = .000120942 \text{ yr}^{-1}$$

$$\ln\left(\frac{.25 \text{ g}}{2 \times 10^{-10} \text{ g}}\right) = kt$$

$$t = \frac{\ln(125 \times 10^9)}{k} = \frac{20.94641}{.000120942 \text{ yr}^{-1}} = 173193.8$$

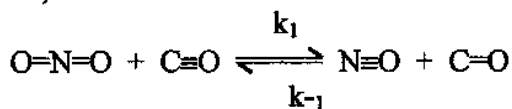
3.
173,193.8
years

$$k_1 = 640 \text{ s}^{-1} \quad T_1 = 298 \text{ K}$$

$$k_{-1} = 1370 \text{ s}^{-1} \quad T_2 = 298 \text{ K}$$

$$E_{\text{forward}} = +23200 \text{ J/mol} \quad \Delta E = +7600 \text{ J/mol}$$

4. The reaction shown below has a forward rate constant k_1 at 298 K of 640 s^{-1} ; a reverse rate constant k_{-1} at 298 K of 1370 s^{-1} . The activation energy for the forward reaction is +23,200 J/mol and a value of $\Delta E^\circ \approx \Delta H^\circ$ for the reaction is +7,600 J/mole.



a. Calculate the activation energy for the reverse reaction (E_a for k_{-1}) at 298 K.

$$\Delta E_a = E_{\text{forward}} - E_{\text{reverse}}$$

$$7600 \text{ J/mol} = 23200 \text{ J/mol} - E_{\text{reverse}}$$

$$-(7600 - 23200) \text{ J/mol} = E_{\text{reverse}}$$

3a. Sign, units.

$$E_a^{k_{-1}} = 15,400 \text{ J/mol}$$

b. Calculate the value the forward rate constant k_1 will have at 398 K.

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

$$\ln\left(\frac{640 \text{ s}^{-1}}{k}\right) = \frac{-23200 \text{ J/mol}}{8.314 \text{ J/mol}\cdot\text{K}} \left(\frac{1}{298} - \frac{1}{398}\right)$$

$$\ln\left(\frac{640}{k}\right) = (-2795.18 \text{ K}) \left(\frac{138 - 298 \text{ K}}{118604 \text{ K}^2}\right)$$

$$\ln\left(\frac{640}{k}\right) = -2.3567$$

$$\frac{640 \text{ s}^{-1}}{k} = e^{-2.3567}$$

$$\frac{640 \text{ s}^{-1}}{k} = .094729167$$

$$\frac{640 \text{ s}^{-1}}{.094729167} = k$$

3b. Sign, units.

$$6756.1 \text{ s}^{-1}$$

c. Calculate the equilibrium constant K_{eq} for the reaction at 298 K.

$$K_{\text{eq}} = \frac{k_{\text{for}}}{k_{\text{rev}}} = \frac{640 \text{ s}^{-1}}{1370 \text{ s}^{-1}} = .467$$

3c. Sign, units.

$$.467$$

d. Calculate the values of ΔG° and ΔS° for the reaction at 298 K.

$$\Delta G^\circ = -RT \ln(K_{\text{eq}})$$

$$= (-8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})(\ln(.467))$$

$$= (8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})(.761097842)$$

$$= 1882.5 \text{ J/mol}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$1882.5 \text{ J/mol} = 7600 \text{ J/mol} - (298 \text{ K})\Delta S^\circ$$

$$5717.5 \text{ J/mol} = (298 \text{ K})\Delta S^\circ$$

$$19.1862 \text{ J/mol}\cdot\text{K} = \Delta S^\circ$$

3d. Sign, units.

$$\Delta G^\circ = 1882.5 \text{ J/mol}$$

$$\Delta S^\circ = 19.19 \text{ J/mol}\cdot\text{K}$$

5. The half-life for decay of a certain radioisotope is 8 seconds and it obeys first order kinetics independent of temperature or environment. A person accidentally breathes in 8×10^{20} atoms of this isotope.

a. What is the first order rate constant for decay of this isotope?

$$t_{1/2} = \frac{.693}{k}$$

$$k = \frac{.693}{t_{1/2}} = \frac{.693}{8s} = .0866s^{-1}$$

5a. Include sign, units

$$.0866s^{-1}$$

b. How many atoms of the isotope will be present 400 seconds after initial ingestion of the 8×10^{20} atoms?

$$\ln\left(\frac{\text{original}}{\text{current}}\right) = kt$$

$$\frac{\text{original}}{\text{current}} = e^{kt}$$

$$\text{current} = \frac{\text{original}}{e^{kt}} = \frac{8 \times 10^{20} \text{ atoms}}{e^{(.0866s^{-1})(400s)}} = \frac{8 \times 10^{20} \text{ atoms}}{e^{34.65}} = \frac{8 \times 10^{20} \text{ atoms}}{1.1176 \times 10^{15}} = 715819.6135$$

5b. Include sign, units

$$715819.6 \text{ atoms}$$

$$E_a = 60,000 \text{ J/mol}$$

$$k_1 = 20s^{-1}$$

$$T_1 = 300K$$

$$k_2 = 1.6s^{-1}$$

$$T_2 = ?$$

6. The activation energy for release of O_2 from the Hemoglobin- $Fe-O_2$ complex is 60 kJ/mol and its rate constant at 300 K is $20s^{-1}$. at what temperature will its rate constant for isomerization be $1.6s^{-1}$.

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

$$\ln\left(\frac{1.6s^{-1}}{20s^{-1}}\right) = \frac{-60,000 \text{ J/mol}}{8.314 \text{ J/mol}\cdot\text{K}} \left(\frac{1}{T_2} - \frac{1}{300K}\right)$$

$$.000349392 k = \frac{1}{T_2} - \frac{1}{300K} = \frac{300K - T_2}{(300K)T_2}$$

$$T_2 (1.104817739K) = 300K - T_2$$

$$T_2 (1.104817739K) = 300K$$

$$T_2 = 271.538$$

6. Include sign and units.

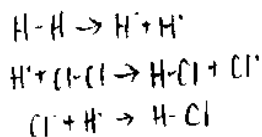
$$271.54 K$$

7. For a third order reaction occurring in solution the rate constant will have what units (M = concentration = molarity = moles/liter) (circle one answer only)

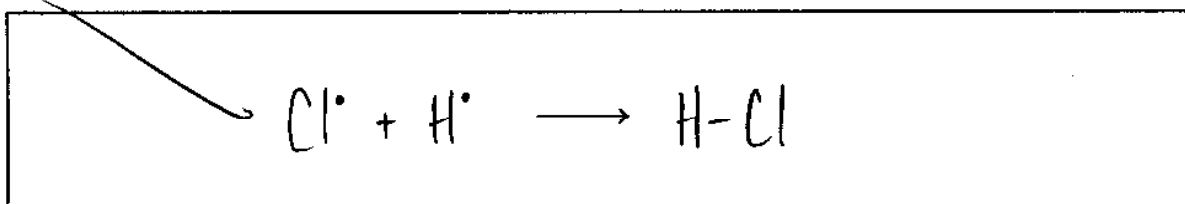
s^{-1}	$M^1 s^{-1}$	$M^2 s^{-1}$	$M^3 s^{-1}$	$M^4 s^{-1}$	$M^5 s^{-1}$
	$M^1 s^{-1}$	$M^{-2} s^{-1}$	$M^3 s^{-1}$	$M^4 s^{-1}$	$M^5 s^{-1}$
s^{-1}	$M^1 s^{-1}$	$M^2 s^{-1}$	$M^3 s^{-1}$	$M^4 s^{-1}$	$M^5 s^{-1}$
	$M^1 s^{-1}$	$M^2 s^{-1}$	$M^3 s^{-1}$	$M^4 s^{-1}$	$M^5 s^{-1}$

$$\frac{m}{s} = k m^3$$

$$k = s^{-1} m^{-2}$$



8. Reaction of H_2 and Cl_2 occurs by a radical chain reaction. In the space below write a balanced chemical reaction for a termination step in this reaction.



9. What is the principal difference between a homogeneous and a heterogeneous catalyst?

homogeneous \rightarrow

heterogeneous \rightarrow



10. For an elementary reaction step a plot of $1/[\text{A}]$ versus time gives a straight line. What is the reaction order in $[\text{A}]$: (circle one answer only)

-4 -3 ~~-2~~ ~~-1~~ 0 1 **2** 3 4

11. For an elementary reaction step a plot of $[\text{A}]$ versus time gives a straight line. What is the reaction order in $[\text{A}]$: (circle one answer only)

-4 -3 ~~-2~~ ~~-1~~ **0** ~~1~~ ~~2~~ ~~3~~ 4

12. For an elementary reaction step a plot of $\ln [\text{A}]$ versus time gives a straight line. What is the reaction order in $[\text{A}]$: (circle one answer only)

-4 -3 -2 ~~0~~ **1** ~~2~~ ~~3~~ 4

NOTE: *There are two bonus questions this week, but you may answer only one of them so choose between this one and the one on the next page—after finishing exam.*

Bonus Question: (this is worth only 3 points and it is bonus credit. Do not work on it until you have finished and checked your work on the rest of the exam).

In the text on page 593 the reaction between $K(g)$ and $Br_2(g)$ is discussed. It is stated that for most reactions the orientation factor has a maximum value of 1 but that for this reaction the orientation factor is $p = 4.8$. It explains this in terms of what is called the “harpoon” mechanism. In the space below describe what that is, how it works, and how it allows $K(g)$ and $Br_2(g)$ to apparently react as quoted by the book: “In other words, there are more reactions than collisions—the reactants do not have to collide to react”.

Bonus Question Answer

Bonus Question: (this is worth only 3 points and it is bonus credit. Do not work on it until you have finished and checked your work on the rest of the exam).

In class we discussed Zeno's paradox about Achilles catching a rabbit (actually according to Wikipedia it is a turtle). The assumption was made that both Achilles and the rabbit were points. Like many assumptions this is useful in some cases but must be abandoned in others. One point was that to never forget the assumptions made in solving a problem. In the space below give an example of any other scientific theory in which assumptions are made which are useful under some conditions but which lead to wrong conclusions under other conditions.

Bonus Question Answer

It is generally assumed that when two molecules combine that they will (assuming things like position on the activity series are in order) react with each other. However, this is not always true. If the molecules were not oriented properly at the time of collision they may not react as expected (or at all). Also, a reaction may not occur if the energy of the molecules and the collision was not enough to overcome the energy of activation needed for the reaction to proceed.

NOT REALLY A VALID ANSWER.

0/3

DO YOU MEAN COLLIDE?
NO ONE ASSUMES A REACTION AT EVERY COLLISION.

$$\frac{1}{A} = kt + \frac{1}{A_0} \quad \text{or} \quad t \cdot 1/2 = \frac{1}{k + A_0}$$

C1124 SOA T3

1. Iodine atoms combine to form I_2 with a second order rate constant of $1.5 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$. If the initial concentration of I atoms is 0.02 M calculate the time needed for that concentration to be reduced to a value of 0.00005 M .

$$\frac{1}{0.00005 \text{ M}} = (1.5 \times 10^{10} \text{ M}^{-1}\text{s}^{-1})t + \frac{1}{0.02 \text{ M}}$$

$$19950 = 1.5 \times 10^{10} \text{ M}^{-1}\text{s}^{-1} t$$

1. units

$$1.33 \times 10^{-6} \text{ s}$$

$$t = 1.33 \times 10^{-6} \text{ s}$$

2. Dissociation of carbon monoxide from hemoglobin $\text{Hb-CO} \rightarrow \text{Hb} + \text{CO}$ is a first order process. At 298 K , $k = 4 \times 10^{-3} \text{ s}^{-1}$ but at 328 K , $k = 8 \text{ s}^{-1}$. The energy change for the reaction ΔE° is $+40 \text{ kJ/mol}$. The rate constant of the reverse reaction $\text{Hb} + \text{CO} \rightarrow \text{Hb-CO}$ is unknown, but the equilibrium constant for $\text{Hb-CO} \rightleftharpoons \text{Hb} + \text{CO}$ is 9.2×10^{-6} at 298 K .

$$A = A_0 e^{-kt}$$

T = 298

a. A person has an initial $[\text{Hb-CO}]$ of 0.01 M . Calculate the time required for $[\text{Hb-CO}]$ to reach $1 \times 10^{-8} \text{ M}$.

$$A_0 = 0.01 \text{ M}$$

$$A = 1 \times 10^{-8} \text{ M}$$

$$1 \times 10^{-8} \text{ M} = 0.01 \text{ M} \cdot e^{-(4 \times 10^{-3})t}$$

$$\ln 1 \times 10^{-8} = \ln 0.01 \text{ M} - (4 \times 10^{-3})t$$

$$-13.81551056 = -4 \times 10^{-3}t$$

2a. t =

$$3453.9 \text{ sec}$$

$$t = 3453.9 \text{ sec}$$

b. Calculate the activation energy for the reaction $\text{Hb-CO} \rightarrow \text{Hb} + \text{CO}$:

$$\ln\left(\frac{8 \text{ s}^{-1}}{4 \times 10^{-3} \text{ s}^{-1}}\right) = \frac{E_a}{8.3} \left(\frac{1}{298} - \frac{1}{328}\right)$$

$$7.60090246 = \left(\frac{E_a}{8.3}\right)(0.000306924)$$

$$E_a = 205547.6$$

2b. sign, units

$$205547.6 \text{ J/mol}$$

* c. Calculate the rate constant for the reaction $\text{Hb} + \text{CO} \rightarrow \text{Hb-CO}$ at 298 K .

$$K_{eq} = \frac{k_1}{k_{-1}} \quad 9.2 \times 10^{-6} = \frac{4 \times 10^{-3} \text{ s}^{-1}}{x}$$

$$x = 434.78$$

2c. sign, units

$$434.78 \text{ s}^{-1}$$

* d. Calculate the activation energy for the reaction $\text{Hb} + \text{CO} \rightarrow \text{Hb-CO}$

$$\ln\left(\frac{434.78}{4 \times 10^{-3}}\right) = \frac{E_a}{8.3} \left(\frac{1}{298} - \frac{1}{298}\right)$$

$$E_a = -96.25 \text{ J/mol}$$

2d. sign, units

$$96.25 \text{ J/mol}$$

$$\Delta E = E_{a \text{ For}} - E_{a \text{ Rev}}$$

-5

$$k_1 = 3 \times 10^{-3} \text{ s}^{-1}$$

$$k_2 = 500 \text{ s}^{-1}$$

$$T = 2000 \text{ K}$$

$$T = ?$$

$$E_a = 440 \text{ kJ}$$

3. The activation energy for dissociation of H_2 to two H atoms is + 440 kJ/mol. The rate constant at 2000 K is found to be $3 \times 10^{-3} \text{ s}^{-1}$. Calculate the temperature at which the rate of dissociation will be 500 s^{-1} .

$$\ln\left(\frac{500 \text{ s}^{-1}}{3 \times 10^{-3} \text{ s}^{-1}}\right) = \frac{440,000 \text{ J/mol}}{8.3 \text{ J/mol}\cdot\text{K}} \left(\frac{1}{2000} - \frac{1}{x}\right)$$

$$0.000226812 = \frac{1}{2000} - \frac{1}{x}$$

$$-0.000273188 = -\frac{1}{x}$$

$$x = 3660.48 \text{ K}$$

3. sign, units

$$3660.48 \text{ K}$$

4. Data for the reaction below is collected in the table (conc in M):



[A]	[B]	[C]	[P]	initial rate M/s
0.2	0.2	0.2	0.2	0.502
0.4	0.2	0.2	0.2	0.995
0.2	0.4	0.2	0.2	0.126
0.2	0.2	0.4	0.2	2.003
0.2	0.2	0.2	0.4	0.499

Determine the individual reaction orders and overall reaction order (ORO):

$$2x = 2$$

$$x = 1$$

$$2x = \frac{1}{4}$$

$$x = -2$$

$$x = -2$$

$$2x = 4$$

$$x = 2$$

$$2x = 1$$

$$x = 0$$

4. Reaction order in:

$$1 \text{ [A]}$$

$$-2 \text{ [B]}$$

$$2 \text{ [C]}$$

$$0 \text{ [P]}$$

$$1 \text{ (ORO)}$$

5. Fourth order reactions are unknown. If one were discovered, what would be the units of the rate constant for it:

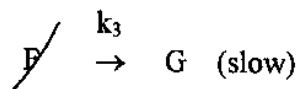
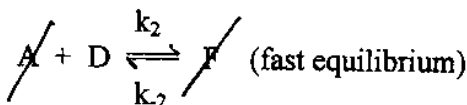
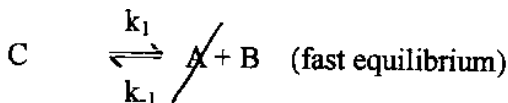
$$\text{rate} = k[\text{A}]^4$$

$$\frac{\text{M}}{\text{S}} = k \cdot \text{M}^4 \quad \frac{\text{M}}{\text{S}} = \frac{\text{M}^4}{\text{S} \cdot \text{M}^3}$$

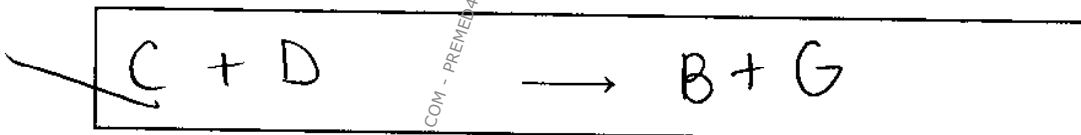
5. Units =

$$\text{M}^{-3} \text{ S}^{-1}$$

6. A chemical reaction follows the following series of elementary steps:



a. Write the balanced chemical equation for this reaction:



b. Derive the rate law for the reaction (must show work for credit)

$$\text{rate} = k_3 [F] \Rightarrow \frac{k_2 [A][D]}{k_{-2}} = [F] \Rightarrow [F] = \frac{k_2 [A][D]}{k_{-2}}$$

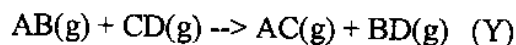
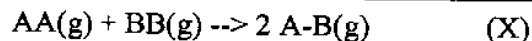
$$= k_3 \cdot \frac{k_2 [A][D]}{k_{-2}} \Rightarrow \frac{k_1 [A][B]}{k_{-1}} = [C] \Rightarrow [A] = \frac{k_{-1} [C]}{k_1 [B]}$$

$$\text{rate law} = k_3 \cdot \frac{k_2 k_1 [C][D]}{k_{-2} k_{-1} [B]}$$

b. rate law:

$$\frac{(k_3)(k_2)k_1 [C][D]}{(k_{-2})(k_{-1}) [B]}$$

7. Consider the two gas phase reactions shown below. If the two reactions have identical activation barriers and are run under the same conditions would reaction X occur at a faster, slower or the same rate as reaction Y. Circle one answer and explain.



15

7. Circle one only and explain: Compared to (Y) reaction (X) is: faster slower same

Explanation: In reaction Y all reactants and products have a coefficient of 1. Reaction X has a product of 2A-B indicating rate = $k[A]^2$ meaning it's a second order. Second order reactions are much slower than first order reactions.

8. Give clear definitions, or correct answers or examples to the following:

a. Termolecular reaction.

A type of reaction in which has three reactants that form and collide to become products

b. Transition state.

A high energy intermediate state between reactants and products

c. The book discusses a zero order reaction-use either that example or give a different clear example of a reaction that follows zero order kinetics:

$$\text{rate} = k[A]^0 = k[I] = k$$



NOT AN EXAMPLE

d. In the space below write the equation that relates half life and rate constant for a first order chemical reaction:

$$t_{1/2} = \frac{0.693}{k}$$

e. The text says that in the Arrhenius equation the A factor can be broken down to be the product of two other factors, p and z which both influence the net rate of reaction. In the space below describe what each of these separate factors correspond to:

p = collision frequency

z = steric factor

C112H S10 T3

$$t_{1/2} = \frac{.693}{k} \quad A = A_0 e^{-kt}$$

1. The half-life for decay of a certain radioisotope is 4 days and it obeys first order kinetics independent of temperature or environment. A person accidentally breathes in 6×10^{23} atoms of this isotope.

a. What is the first order rate constant for decay of this isotope?

$$k = \frac{.693}{4} = .17325$$

premed411
.COM

a. Include sign, units

(+) .17325 s^{-1}

b. How many atoms of the isotope will be present after 144 days after initial ingestion of the 6×10^{23} atoms? $A_0 = 6 \times 10^{23}$ $A = ?$ $t = 144$

$$A = 6 \times 10^{23} e^{-.17325(144)}$$

$$A = 6 \times 10^{23} (1.4629 \times 10^{-11})$$

$$A = 8.778 \times 10^{12}$$

$$A = 6 \times 10^{23} e^{-.17325(144)}$$

b. Include sign, units

(+) 8.778×10^{12} atoms

c. How long will it take until only 6 atoms are present in the person?

$$A = 6$$

$$6 = 6 \times 10^{23} e^{-.17325(t)}$$

$$1.792 = 54.75 - .17325t$$

$$-52.958 = -.17325t$$

$$t = 305.674 \text{ DAYS}$$

$$6 = 6 \times 10^{23} e^{-.17325(t)}$$

$$1.792 = 54.75 - .17325t$$

$$-52.959 = -.17325t$$

$$t = 305$$

c. Include sign, units

(+) 305.674 DAYS

2. A certain reaction has an activation energy in the forward direction of 87 kJ/mol and an activation energy in the reverse direction of 108 kJ/mol. In the presence of a catalyst the activation energy in the forward direction is 32 kJ/mol.

$$E_{af} = 87 \frac{\text{kJ}}{\text{mol}}$$

$$E_{ar} = 108 \frac{\text{kJ}}{\text{mol}}$$

$$E_{afc} = 32 \frac{\text{kJ}}{\text{mol}}$$

a. Calculate $\Delta E^\circ \approx \Delta H^\circ$ for the reaction

$$\Delta E = E_{af} - E_{ar}$$

$$\Delta E = 87 - 108$$

$$\Delta E = -21 \frac{\text{kJ}}{\text{mol}}$$

a. Include sign, units

(-) 21 $\frac{\text{kJ}}{\text{mol}}$

b. Calculate the activation energy in the presence of a catalyst for the reverse reaction. E_{arc}

$$-21 = 32 - x$$

$$-53 = -x$$

$$x = 53 \frac{\text{kJ}}{\text{mol}}$$

b. Include sign, units

(+) 53 $\frac{\text{kJ}}{\text{mol}}$

3. The activation energy for a reaction is 58.6 kJ/mol and the frequency factor is 1.5×10^{11} /s. Calculate the rate constant for the reaction at 25 °C.

$E_a = 58.6 \text{ kJ/mol}$ $k = A e^{-E_a/RT}$

$$k = (1.5 \times 10^{11}) e^{-\frac{58600}{8.3(298)}}$$

$$k = (1.5 \times 10^{11}) (5.1364 \times 10^{-11})$$

$$k = 7.7045$$

3. Include sign, units

7.7045 s^{-1}

4. Dissociation of oxygen from a hemoglobin like molecule is a first order process with a rate constant of 32 s^{-1} at 298 K and 98 s^{-1} at 308 K.

① $k = 32 \text{ s}^{-1}$ @ 298 K $t_{1/2} = \frac{0.693}{k}$
 ② $k = 98 \text{ s}^{-1}$ @ 308 K

a. Calculate the rate of dissociation of oxygen at 298 K when the concentration of the hemoglobin oxygen complex is 0.024 M.

$$\begin{aligned} \text{RATE} &= k[A]^1 \quad 32 \text{ s}^{-1} \\ &= 32 \text{ s}^{-1} (0.024) \\ &= 0.768 \text{ mol/s} \end{aligned}$$

4a. Include sign, units

0.768 s^{-1}

b. Calculate the activation energy for dissociation of oxygen from the hemoglobin oxygen complex.

$$\begin{aligned} \ln\left[\frac{98}{32}\right] &= \frac{E_a}{8.3} \left(\frac{1}{298} - \frac{1}{308}\right) \\ 1.119 &= \frac{E_a}{8.3} (0.000108951) \\ 9.2896 &= E_a (0.000108951) \\ E_a &= 85263.66 \end{aligned}$$

4b. Include sign, units

85263.66 J/mol

c. Calculate the temperature at which the dissociation of oxygen will have a rate constant of 0.04 s^{-1} .

$$\begin{aligned} \ln\left[\frac{0.04}{32}\right] &= \frac{85263.66}{8.3} \left(\frac{1}{298} - \frac{1}{T}\right) \\ -6.695 &= 10272.73 \left(\frac{1}{298} - \frac{1}{T}\right) \\ -0.0006507 &= \frac{1}{298} - \frac{1}{T} \end{aligned}$$

4c. Include sign, units

249.597 K

5. The reaction $X + Y + Z \rightarrow P$ is known to follow the rate law: $d[P]/dt = k [X]^0 [Y]^3 [Z]^{-1} [P]^2$. Shown below are concentration data and initial rate for one experiment. Fill in the expected initial rate data for the four experiments where it is left blank. (conc in M) in the four empty boxes below and calculate the numerical value of the rate constant k in the fifth box:

	[X]	[Y]	[Z]	[P]	initial rate M/s
$2^0 = 1$	0.2	0.2	0.2	0.2	32,000
$2^3 = 8$	0.4	0.2	0.2	0.2	32,000
$2^{-1} = 1/2$	0.2	0.4	0.2	0.2	256,000
$2^2 = 4$	0.2	0.2	0.4	0.2	16,000
	0.2	0.2	0.2	0.4	128,000

$$32,000 = k (0.2)^0 (0.2)^3 (0.2)^{-1} (0.2)^2$$

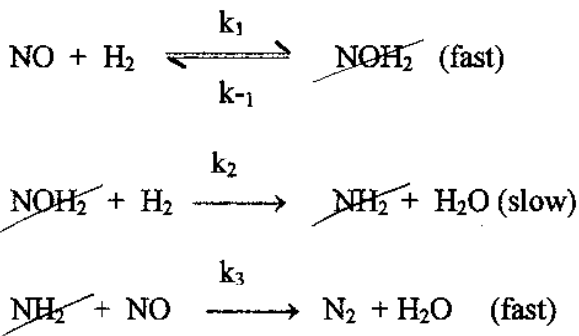
$$= k (1)(0.008)(5)(.04)$$

$$32,000 = k \cdot 0.016 \quad k = 2 \times 10^7 \text{ M}^{-3} \text{ s}^{-1}$$

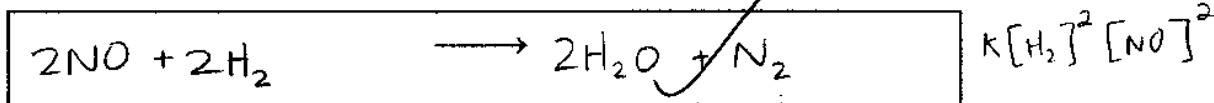
Value of rate constant-include units:

$$k = 2 \times 10^7 \text{ M}^{-3} \text{ s}^{-1}$$

6. Shown below is a possible reaction mechanism composed of the elementary steps shown:



a. Write the net reaction occurring--write a balanced equation for the overall reaction:



b. Derive the rate law for the reaction in terms of the rate constant k , $[\text{NO}]$, $[\text{H}_2]$, $[\text{N}_2]$.

$$K_2 = \frac{[\text{NOH}_2]}{[\text{H}_2][\text{NO}]}$$

$$\frac{k_1}{k_{-1}} [\text{H}_2][\text{NO}] = [\text{NOH}_2]$$

$$\frac{k_2 k_1 k_3}{k_{-1}} [\text{H}_2]^2 [\text{NO}]^2$$

rate =

$$k [\text{H}_2]^2 [\text{NO}]^2$$

$$K_2 k_1 [\text{NO}] [\text{H}_2]^2$$

$$M^{-2} s^{-1} = M^{-1} s^{-1}$$

7. For a second order reaction occurring in solution the rate constant will have what units (M = concentration = molarity = moles/liter) (circle one answer only)

- | | | | | | |
|---------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|
| s^{-1} | $M^1 s^{-1}$ | $M^2 s^{-1}$ | $M^3 s^{-1}$ | $M^4 s^{-1}$ | $M^5 s^{-1}$ |
| s^{-1} | <u>$M^{-1} s^{-1}$</u> | $M^2 s^{-1}$ | $M^3 s^{-1}$ | $M^4 s^{-1}$ | $M^5 s^{-1}$ |
| s^{-1} | $M^1 s^{-1}$ | $M^2 s^{-1}$ | $M^3 s^{-1}$ | $M^4 s^{-1}$ | $M^5 s^{-1}$ |
| $M^{-1} s^{-1}$ | $M^1 s^{-1}$ | $M^2 s^{-1}$ | $M^3 s^{-1}$ | $M^4 s^{-1}$ | $M^5 s^{-1}$ |

8. The text defines the A factor that $A = pz$. In the space below indicate what p and z are named and what their physical meaning is:

Name	Physical meaning
$p =$ STERIC FACTOR	The correct way the molecules must collide in order for a reaction to occur.
$z =$ COLLISION FREQUENCY	The amount of times the molecules bump into each other. The more collision, the better chance of reacting.

9. Zero order reactions are rare-give an example of a zero order reaction and explain briefly why it is zero order.

Example $2HI \rightarrow H_2 + I_2$

Reason SURFACE AREA. BECAUSE THE REACTANTS AND PRODUCTS ARE THE SAME.

~~X~~ NO FREE 5

10. Define "Elementary step" in chemical kinetics:

AN ELEMENTARY STEP IS A RXN THAT OCCURS IN ONLY ONE STEP. USUALLY A REACTION IS MADE UP OF MULTIPLE ELEMENTARY STEPS.

11. For a second order of reaction $A + A \rightarrow B$, plotted against time which of the following will be a straight line: (circle one answer only)

- ~~ln A~~ $e^{A/RT}$ $e^{-A/RT}$ A^1 A^2 A^3 A^{-1} A^{-2} A^{-3}

NOTE: There are two bonus questions this week, but you may answer only one of them so choose between this one and the one on the next page—after finishing exam.

Bonus Question: (this is worth only 3 points and it is bonus credit. Do not work on it until you have finished and checked your work on the rest of the exam).

Some enzymatic processes are shut down by the product they produce. For example if a bacteria produced too much ammonia it might poison itself, and so after a certain level of ammonia is produced, ammonia inhibits the process. Using conversion of dinitrogen to ammonia as an example, explain how production of ammonia will be slowed down and stopped by ammonia itself. Make your answer clear and show with drawings of the active site of the enzyme how this might work.

Bonus Question Answer

Ammonia will act as an inhibitor and will bind to the enzyme, not allowing it to go forward with the reaction.

C.K.
3/2