CH302 Worksheet 13. Typical kinetics questions you see on quizzes and exams. Before you solve, please write down the classic type of kinetics question this is.

1. Write the rate of the reaction  $2O_3 \rightarrow 3O_2$  in terms of  $\Delta[O_3]/\Delta t$ .

Question type: <u>reaction rate law</u>

$$-\frac{1}{2}\frac{\Delta[O_3]}{\Delta t}$$

2.Consider the following stoichiometric reaction:  $2A + B \rightarrow C + D$  The reaction rates are measured with the following results:

Initial rate	$[A]_0$	[B] <sub>0</sub>
1	2	1
2	4	1
1	2	2

What is the order of the reaction with respect to  $[B]_0$ ?

Question type: \_\_\_\_\_method of initial rates\_\_\_\_\_

Since we're looking at the order of [B]<sub>0</sub>, all we have to look at where [B]<sub>0</sub> changes and where [A]<sub>0</sub> stays the same. You can see that [B]<sub>0</sub> doubles from the first row to the third row. However, the rate doesn't change, therefore the rate order is 0.

3. The first-order rate constant is  $k = 3.4 \times 10^{-3}$  sec-1 for the decomposition of cyclobutane and the half-life is 204 seconds.

 $C_4H_4 \rightarrow 2 C_2H_2$ 

What fraction of a sample of cyclobutane remains after 612 seconds under the specified conditions?

 Question type:
 \_\_\_\_\_integrated rate law—half life calculation\_\_\_\_\_\_

Time	Amount left (cyclobutane = C)
0	С
204	C/2
408	C/4
612	C/8

After 612 seconds, 1/8 of the original amount of cyclobutane is left.

4. The reaction A +3B  $\rightarrow$  . C +2D has a rate constant k = 1.0 x 10<sup>-5</sup> sec<sup>-1</sup> at 27° C. If the activation energy for the reaction is 20,000 cal/mol, what is the value of the rate constant at 0°C?

Question type: \_\_\_\_\_combined Arrhenius calculation\_

Explanation: Use the combined Arrenhius equation,  $\ln \frac{k_2}{k_1} = (E_a/R) \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$ .

$$\ln \frac{k_2}{1e-5} = \left(\frac{20,000 \text{ cal/mol}}{1.987 \text{ cal/molK}}\right) \left(\frac{1}{300 \text{ K}} - \frac{1}{273 \text{ K}}\right)$$
$$k_2 = e^{\left[\left(\frac{20,000}{1.987}\right) \left(\frac{1}{300 \text{ K}} - \frac{1}{273 \text{ K}}\right) 1e-5\right]}$$
$$= 3.6 \text{ x } 10^{4}7$$

5.

The following data were collected for the following reaction at a particular temperature.

$$A + B \rightarrow C$$

Three experiments give

Trial	Initial [A] M	Initial [B] M	Initial rate $\Delta$ [C]/ $\Delta$ t M/min
1	0.1	0.1	$4.0\times10^{-4}$
2	0.2	0.2	$3.2 \times 10^{-3}$
3	0.1	0.2	$1.6 \times 10^{-3}$

What is the rate law expression for this reaction?

Question type: \_\_\_\_method of initial rates\_

 $0.4 \text{ M}^{-2} \text{min}^{-1} [A] [B]^2$ 

6. What is the rate law for the following multi-step mechanism?

$Cl_2 \rightarrow Cl + Cl$	fast
$Cl + H_2S \rightarrow HCl + HS$	fast
$HS + Cl \rightarrow HCl + S$	slow

 $Cl_2 + H_2S \rightarrow S + 2HCl$  overall

Question type: <u>reaction mechanism</u>

Identify the rate determining step. Everything that happens before this step figures into the mechanism. Everythin afterward, does not. So the third step is the rds, and we combine and cancel all reactants and products from the equations below

 $\begin{array}{ccc} Cl_2 \rightarrow Cl + Cl & fast \\ Cl + H_2S \rightarrow HCl + HS & fast \\ HS + Cl \rightarrow (we stop here at the rds) \end{array}$ 

Note that the 2Cl cancel on product and reactant side and that HS cancels on each side. So what remains is

Rate =  $[Cl_2][H_2S]/[HCl]$  so the reaction is first order in  $[Cl_2]$  and  $[H_2S]$ , negative first order in [HCl] and first order overall.

7. A first order elementary reaction,  $A \rightarrow \text{products}$ , has a rate constant of  $3.16 \times 10^8 \text{ sec}^{-1}$ . At an instant in time, a concentration of  $3.16 \times 10^{-6}$ M of species A is created. How long does it take for the concentration to fall by a factor of 4?

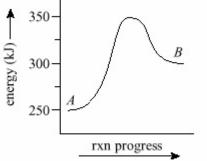
Question type: <u>integrated rate law</u>

 $ln([A_o]/[A]) = akt$ in this case, a = 1 and k = 3.16E8

Since the concentration of A is decreasing by a factor of 4,  $[A_0]/[A]$  is equal to 4.

So,  $\ln(4) = (1)^*(3.16E8)^*t$ t =  $\ln(4)/3.16E8 = 4.38E-9$  sec 8.

Consider the potential energy diagram shown below.



What is the activation energy  $E_a$  for the reaction  $A \rightarrow B$ ?

Question type: <u>activation energy diagram</u>

We need to have enough energy to 'get to the top of the hill' in order to fall down to the products. So the energy must raise from 250 kJ (where A is) up to the top of the hill at 350 kJ. 350-250 = 100 kJ