South Pasadena • AP Chemistry

Name _____
Period ___ Date ___/___/___

15 • Chemical Kinetics

STUDY QUESTIONS

1. In the following reaction, what is the relationship between the rate at which the nitrous oxide is used up, the rate at which the oxygen is used, and the rate at which the nitrogen dioxide is produced?

$$2N_2O(g) + 3O_2(g) \rightarrow 4NO_2(g)$$

2. Ammonia can be oxidized by oxygen to produce nitrogen dioxide according to the equation:

$$4NH_3(g) + 7O_2(g) \rightarrow 4NO_2(g) + 6H_2O(g)$$

If, in this reaction, water is formed at a rate of 36 mol L^{-1} min^{-1},

a. at what rate is the ammonia used?
b. at what rate is the oxygen used?
c. at what rate is the nitrogen dioxide formed?

3. If a reactant is used up according to a first order rate equation, and the initial concentration of the reactant is 3.2 mol L^{-1}, what is the concentration of the reactant after two half-lives have passed, and after six half-lives have passed?

4. For each of the following rate equations, describe what would happen to the rate if the concentration of reactant A was tripled and the concentration of reactant B is halved.

a. Rate = $k[A][B]$
b. Rate = $k[A]^2[B]$
c. Rate = $k[A]^2[B]^2$
d. Rate = $k[A][B]^3$

5. The reaction of ^{t}butyl-bromide $(CH_3)_3CBr$ with water is represented by the equation:

$$(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + HBr$$

The following data were obtained from three experiments using the method of initial rates:

	Initial $[(CH_3)_3CBr]$ mol L^{-1}	Initial $[H_2O]$ mol L^{-1}	Initial rate mol $L^{-1}min^{-1}$
Experiment 1	5.0×10^{-2}	2.0×10^{-2}	2.0×10^{-6}
Experiment 2	5.0×10^{-2}	4.0×10^{-2}	2.0×10^{-6}
Experiment 3	1.0×10^{-1}	4.0×10^{-2}	4.0×10^{-6}

a. What is the order with respect to $(CH_3)_3CBr$?
b. What is the order with respect to H_2O?
c. What is the overall order of the reaction?
d. Write the rate equation.
e. Calculate the rate constant k for the reaction.

6. At 150°C the decomposition of acetaldehyde CH_3CHO to methane is a first order reaction. If the rate constant for the reaction at 150°C is 0.029 min^{-1}, how long does it take a concentration of 0.050 mol L^{-1} of acetaldehyde to reduce to a concentration of 0.040 mol L^{-1}?

7. The decomposition of hydrogen iodide into hydrogen and iodine is a second order reaction. The rate constant k = 0.080 L $mol^{-1}s^{-1}$. How long does it take an initial concentration of 0.050 M to decrease to half this concentration?

8. Describe some industrial uses of catalysts.

9. The gold-198 isotope has a half-life of 2.7 days. If you start with 10 mg at the beginning of the week, how much remains at the end of the week, seven days later?

10. If the rate of a reaction increases by a factor of 10 when the temperature is increased by 35°C from 300K to 335K, what is the activation energy E_a for the reaction?

11. The decomposition of ozone in the upper atmosphere to dioxygen occurs by a two-step mechanism. The first step is a fast reversible step and the second is a slow reaction between an oxygen atom and an ozone molecule:

Step 1:	$O_3(g) \rightleftharpoons O_2(g) + O(g)$	Fast, reversible, reaction
Step 2:	$O_3(g) + O(g) \rightarrow 2O_2(g)$	Slow

a. Which is the rate determining step?
b. Write the rate equation for the rate-determining step.
c. Write the rate equation for the overall reaction.

12. The rate equation for the reaction of nitrogen dioxide and carbon monoxide in the gas state to form carbon dioxide and nitric oxide is represented by the equation:

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

The following data were collected at 125°C:

	Initial $[NO_2]$ mol L^{-1}	Initial [CO] mol L^{-1}	Initial rate mol $L^{-1}min^{-1}$
Experiment 1	5.0×10^{-4}	1.6×10^{-2}	1.7×10^{-7}
Experiment 2	5.0×10^{-4}	3.2×10^{-2}	1.7×10^{-7}
Experiment 3	1.5×10^{-3}	3.2×10^{-2}	1.5×10^{-6}

a. What is the order with respect to NO_2?
b. What is the order with respect to CO?
c. What is the overall order of the reaction?
d. Write the rate equation.
e. How do you know this is not a single step reaction?

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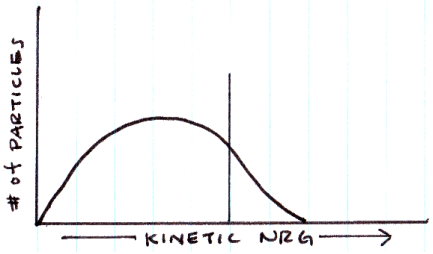
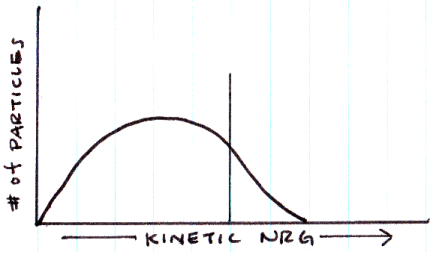
Station 1 – KINETIC ENERGY DIAGRAMS

Draw how the KE diagram would change if:

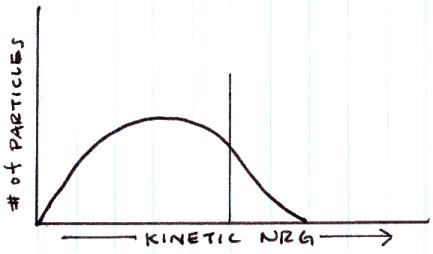
the temperature of the sample is increased.



a catalyst is added to the reaction mixture.



more chemical is added at the same temperature.



What is the name of the vertical line intersecting the graph? _____ _____

Why do particles need kinetic energy to react?

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Station 2 – POTENTIAL ENERGY DIAGRAMS

The energy of the **reactants** is 30 kJ/mol.

ΔH = -20 kJ/mol

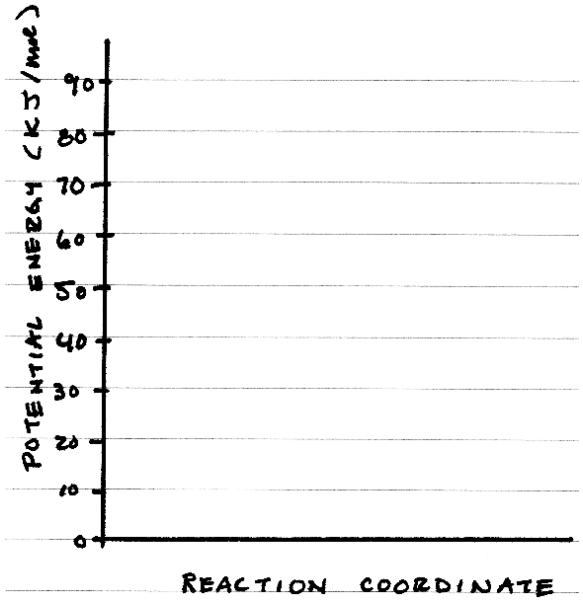
Ea = +40 kJ/mol

Draw the PE curve.

The energy of the **products** is _____

The **activation energy** for the **reverse** reaction is _____

Draw the same curve with a catalyst included. (- - - - - - -)



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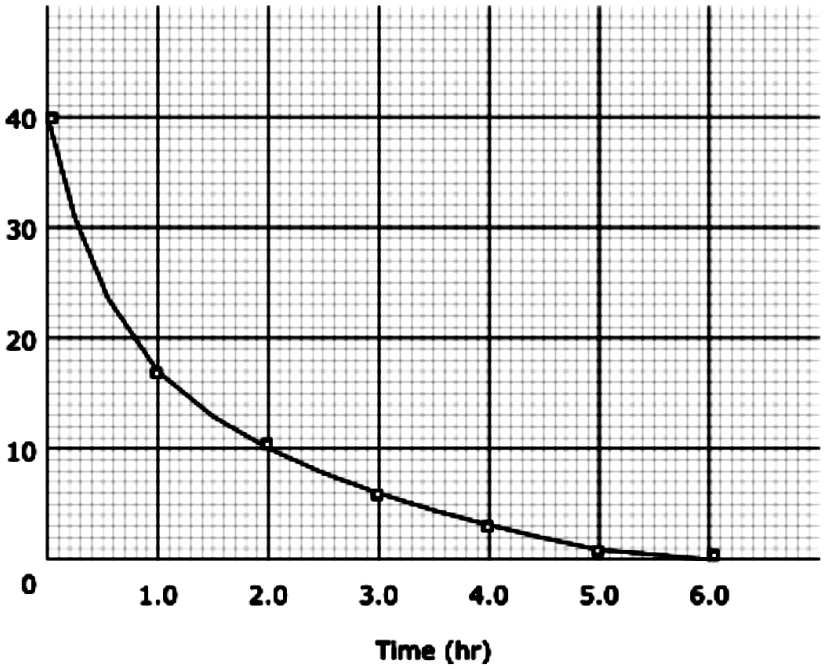
Station 3 – RATE FROM GRAPHS

The vertical axis is [R] in $mol \cdot L^{-1}$



Show your work for these two problems.

The **average** rate of the reaction for the first 2.0 hours is _____.

The **instantaneous** rate of the reaction at 2.0 hours is _____.

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Station 4 – CALCULATING RATES OF REACTION

Consider the combustion of propane, $C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(g)$

The rate of disappearance of $O_2(g)$ is 6.4 $mol \cdot L^{-1} \cdot s^{-1}$

What is the rate of disappearance of $C_3H_8(g)$?

What is the rate of appearance of $CO_2(g)$?

What is the rate of appearance of $H_2O(g)$?

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Station 5 – RATE LAWS – THE METHOD OF INITIAL RATES

Here is some initial rate data for the reaction, $A + B \rightarrow 2C$.

[A]	[B]	Rate ($mol \cdot L^{-1} \cdot s^{1}$)
0.40	0.10	3.5×10^{3}
0.20	0.10	1.8×10^{3}
0.20	0.50	4.5×10^{4}

a) Determine the **orders** of reactants A _____ and B _____

b) Write the **rate law** for this reaction: _____

c) Calculate the value of the **rate constant, k**, with **units**. _____

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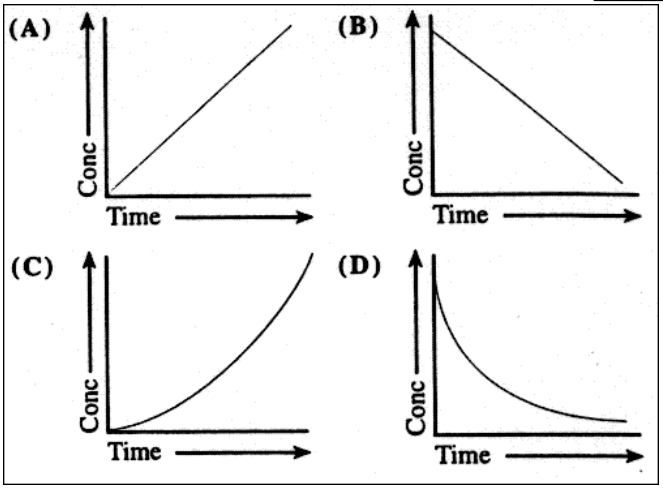
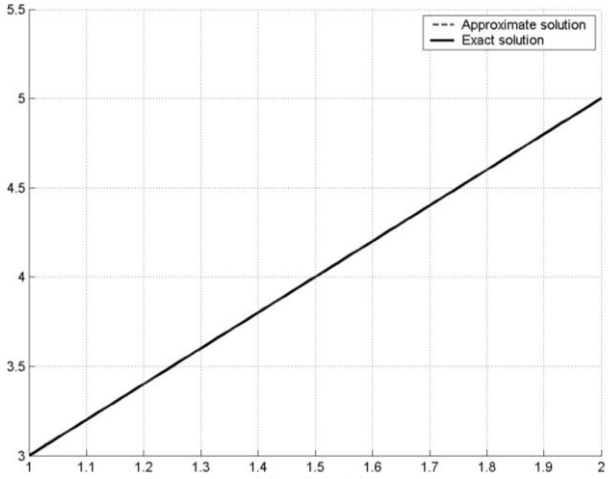
Station 6 – ORDERS OF REACTIONS – GRAPHICAL METHODS

Which graph corresponds to the change in concentration of a reactant that is first order? _____



This graph is a chemical that is second order. The horizontal axis is time. What is the vertical axis? ____



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Station 7 – REACTION MECHANISMS

Consider this reaction mechanism:

$$HCOOH + H_2SO_4 \rightarrow HCOOH_2^+ + HSO_4^-$$
$$HCOOH_2^+ \rightarrow COH^+ + H_2O$$
$$COH^+ + HSO_4^- \rightarrow CO + H_2SO_4$$

a) What is the overall reaction? _____

b) List any "intermediates." _____

c) List any catalysts. _____

d) If the first step is the slow step, what is the rate law? _____

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Station 8 – HALF LIFE PROBLEMS

a) A first-order chemical has a half-life of 8.00 minutes.
How long will it take for 93.75% of this chemical to decay?

b) The reaction X → Y follows first-order kinetics with a half-life of 4.00 minutes. What is the value of k?
If the initial concentration of X is 3.6 M, what is the concentration after 15.0 minutes?

Formula:

$$\ln[A]_t - \ln[A]_0 = -kt$$

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Station 9 – THE ARRHENIUS EQUATION

Calculate the activation energy, E_a, for $N_2O_5(g) \rightarrow 2\ NO_2(g) + ½\ O_2(g)$
given k (at 25°C) = $3.46 \times 10^{-5}\ s^{-1}$ and k (at 50°C) = $1.10 \times 10^{-3}\ s^{-1}$.

Formula:

$$\ln k = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

$$R = 8.31\ \text{J mol}^{-1}\ \text{K}^{-1}$$

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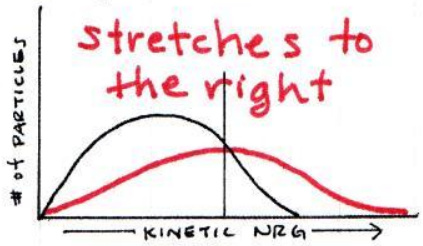
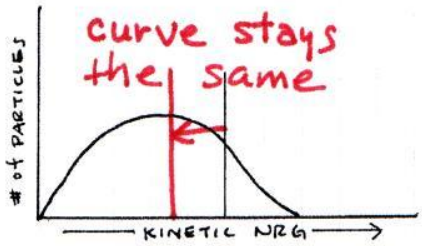
Station 1 – KINETIC ENERGY DIAGRAMS

Draw how the KE diagram would change if:

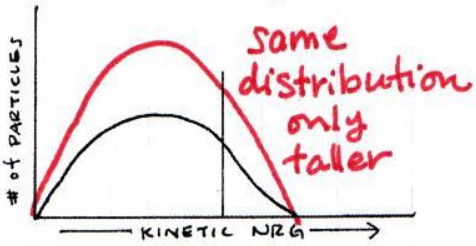
the temperature of the sample is increased.



a catalyst is added to the reaction mixture.



more chemical is added at the same temperature.



What is the name of the vertical line intersecting the graph? threshold energy

Why do particles need kinetic energy to react?

The particles need to collide hard enough to form the higher potential energy activated complex.

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Station 2 – POTENTIAL ENERGY DIAGRAMS

The energy of the **reactants** is 30 kJ/mol.

ΔH = -20 kJ/mol exothermic; downhill

Ea = +40 kJ/mol

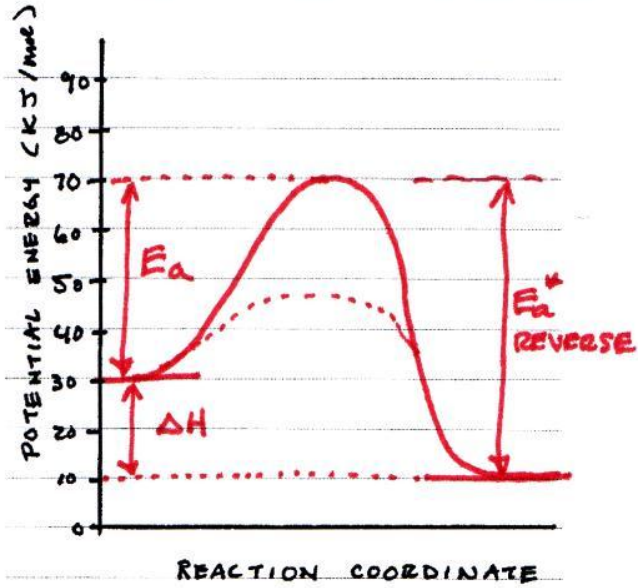
Draw the PE curve.

The energy of the **products** is 10 kJ/mol

The **activation energy** for the **reverse** reaction is 60 kJ/mole

Draw the same curve with a catalyst included. (- - - - - - -)

Any lower energy line is OK.



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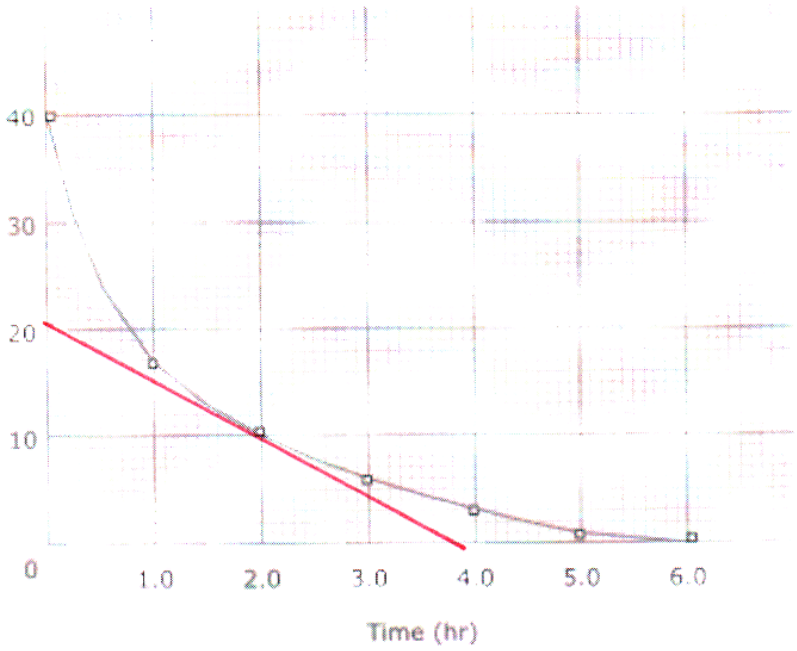
Station 3 – RATE FROM GRAPHS

The vertical axis is [R] in $mol \cdot L^{-1}$



Show your work for these two problems.

The **average** rate of the reaction for the first 2.0 hours is _____.

$\frac{\Delta \text{Reactant}}{\Delta \text{time}}$ $\frac{40-10}{2.0\,hr} = \frac{30}{2.0}$

$= 15\ mol \cdot L^{-1} \cdot hr^{-1}$

The **instantaneous** rate of the reaction at 2.0 hours is _____.

SLOPE OF A TANGENT LINE at 2.0.

$\frac{\text{RISE}}{\text{RUN}} = \frac{20\ mol \cdot L^{-1}}{3.8\ hr} =$

$= 5.26\ mol \cdot L^{-1} \cdot hr^{-1}$

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Station 4 – CALCULATING RATES OF REACTION

Consider the combustion of propane, $C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(g)$

The rate of disappearance of $O_2(g)$ is $6.4\ mol \cdot L^{-1} \cdot s^{-1}$

What is the rate of disappearance of $C_3H_8(g)$? $\text{Rate}_{C_3H_8} = \frac{1}{5}\ 6.4\ mol \cdot L^{-1} \cdot s^{-1} = 1.28\ mol \cdot L^{-1} \cdot s^{-1}$

What is the rate of appearance of $CO_2(g)$? $\frac{1}{5}(6.4) = \frac{1}{3}\text{Rate}_{CO_2} = 3.84\ mol \cdot L^{-1} \cdot s^{-1}$

What is the rate of appearance of $H_2O(g)$? $\frac{1}{5}(6.4) = \frac{1}{4}\text{Rate}_{H_2O} = 5.12\ mol \cdot L^{-1} \cdot s^{-1}$

NOTE: Signs are not necessary because the words "disappearance" and "appearance" are used.

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Station 5 – RATE LAWS – THE METHOD OF INITIAL RATES

Here is some initial rate data for the reaction, A + B → 2C.

[A]	[B]	Rate ($mol \cdot L^{-1} \cdot s^{1}$)
0.40	0.10	3.5×10^{3}
0.20	0.10	1.8×10^{3}
0.20	0.50	4.5×10^{4}

×2 ( ) ~2
×5 [ ] 25

a) Determine the **orders** of reactants A 1 and B 2

b) Write the **rate law** for this reaction: $Rate = k[A][B]^2$

c) Calculate the value of the **rate constant, k**, with **units**. _____

$k = \frac{Rate}{[A][B]^2} = 8.75 \times 10^{5}\ L^2 \cdot mol^{-2} \cdot s^{-1}$

$\frac{mol \cdot L^{-1} \cdot s^{-1}}{mol^3 \cdot L^{-3}} = mol^{-2} \cdot L^2 \cdot s^{-1}$

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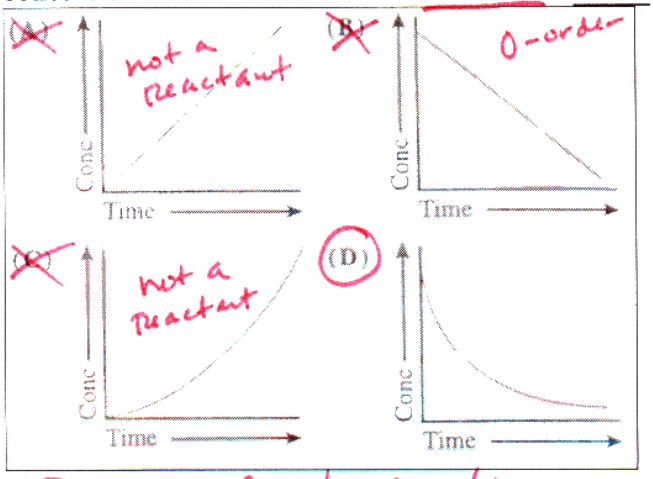
Station 6 – ORDERS OF REACTIONS – GRAPHICAL METHODS

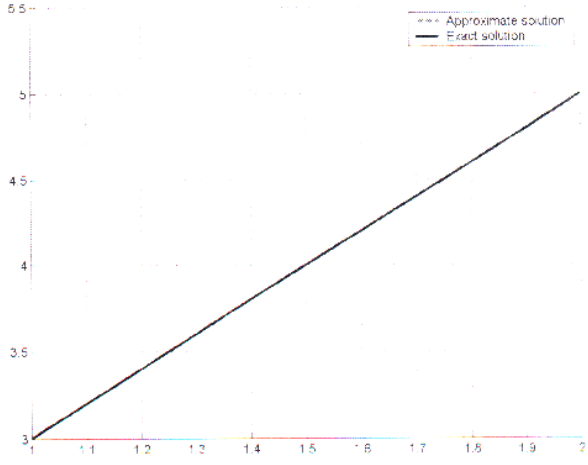
Which graph corresponds to the change in concentration of a reactant that is first order? _____



Process of elimination. You can't really tell if this is 1st or 2nd order.

This graph is a chemical that is second order. The horizontal axis is time. What is the vertical axis? $\frac{1}{[R]}$

$\frac{1}{[R]}$



time

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Station 7 – REACTION MECHANISMS

Consider this reaction mechanism:

$$HCOOH + H_2SO_4 \rightarrow HCOOH_2^+ + HSO_4^-$$
$$HCOOH_2^+ \rightarrow COH^+ + H_2O$$
$$COH^+ + HSO_4^- \rightarrow CO + H_2SO_4$$

} FROM THE FILM

a) What is the overall reaction? $HCOOH \rightarrow CO + H_2O$

b) List any "intermediates." $HCOOH_2^+$, HSO_4^-, COH^+

c) List any catalysts. H_2SO_4

d) If the first step is the slow step, what is the rate law? $Rate = k[HCOOH]$

NOTE: H_2SO_4 is not a reactant.

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Station 8 – HALF LIFE PROBLEMS

a) A first-order chemical has a half-life of 8.00 minutes. How long will it take for 93.75% of this chemical to decay?

100 − 93.75% = 6.25% LEFT!

100 → 50 → 25 → 12.5 → 6.25

4 × 8 min = **32.0 min**

b) The reaction X → Y follows first-order kinetics with a half-life of 4.00 minutes ($t_{1/2}$). What is the value of k? If the initial concentration of X is 3.6 M, what is the concentration after 15.0 minutes?

$\ln 2 = k t_{1/2}$

$k = \frac{.693}{4.00\ min} = 0.17325\ min^{-1}$

$k = 0.173\ min^{-1}$

$\ln(x) - \ln(3.6) = -(0.173\ min^{-1})(15.0\ min)$

$\ln x - 1.28 = -2.595$

$+1.28 \quad +1.28$

$\ln x = -1.315$

$x = e^{-1.315} = 0.268\ M$

Formula:

$$\ln[A]_t - \ln[A]_0 = -kt$$

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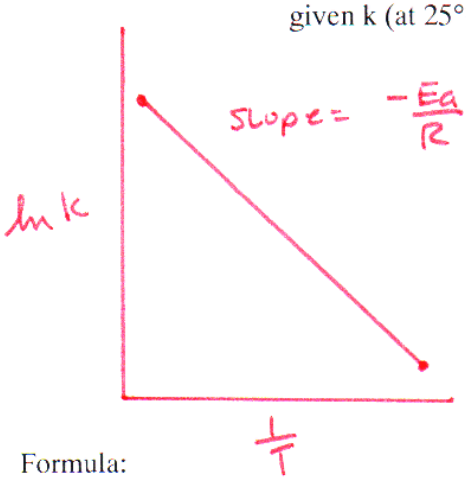
Station 9 – THE ARRHENIUS EQUATION

Calculate the activation energy, E_a, for $N_2O_5(g) \rightarrow 2\ NO_2(g) + \frac{1}{2}\ O_2(g)$

given k (at 25°C) = $3.46 \times 10^{-5}\ s^{-1}$ and k (at 50°C) = $1.10 \times 10^{-3}\ s^{-1}$.



Formula:

$$\ln k = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

$R = 8.31\ J\ mol^{-1}\ K^{-1}$

$\frac{1}{298K} = .0033557$ $\quad \ln(3.46 \times 10^{-5}) = -10.27$

$\frac{1}{323K} = .00309597$ $\quad \ln(1.10 \times 10^{-3}) = -6.812$

$\frac{RISE}{RUN} = \frac{(-6.812)-(-10.27)}{.0033557-.00309597} = \frac{-3.458}{.00025973}$

$= 13,313.8 = \frac{-Ea}{R}$

$Ea = +(13,313.8)\ 8.31\ \frac{J}{mol \cdot K}$

$= +110,637\ J/mol$

$= \boxed{+111\ kJ/mol}$

* I HAVE THIS REVERSED

$(-10.27) - (-6.812)$