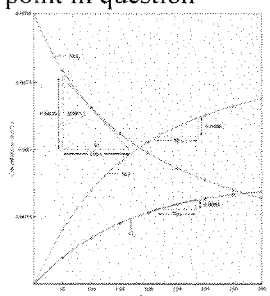
Kinetics Cheat Sheet	
Relationships	
Differential Rate Law (concentration vs. rate data): Rate = $k\,[A]^x[B]^y$	
Be able to explain with algebraic equations or words how an order is determined. It is important to state which concentration(s) is/are held constant and which concentration is varied as well the effect that has on the rate of the reaction if you choose not to justify with algebraic equations.	Mechanisms – must agree with the stoichiometry of the reaction and the "summary rate law" must agree with the slow step; identify intermediates and catalysts and clearly state that the correct mechanism "agrees with the experimentally determined rate law".
Discuss number of *effective collisions* in relation to increasing or decreasing rates	E_a predicts speed but the relationship is an inverse one; high = slow rate; low = fast rate
"rate in terms of" is code for "relative rates" – use stoichiometry ratios on rate value $2\ N_2O_5(g) \rightarrow 4\ NO_2(g) + O_2(g)$ $\text{rate} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$	Instantaneous rate = slope of the line tangent to the time point in question 
Catalyst – lowers Activation Energy and provides an alternate pathway/mechanism	Distinguish between catalyst and intermediate – especially in the steps of a mechanism!
Temperature increases of approx.. 10°C	
Connections	
Stoichiometry – "using up" one component of the system might indicate a limiting reactant in effect	Electrochemistry – if reaction is redox in nature, rate problems could come into play
Thermochemistry – E_a and ΔH°_{rxn} and reaction diagrams	
Potential Pitfalls	
Units on k ! Make sure you can solve for units for k	

NMSI SUPER PROBLEM

$$X(g) + 2Y(g) \rightarrow Z(g)$$

The reaction represented above was studied at 25°C. The data collected are shown in the table below.

Experiment	[X]	[Y]	Initial rate of formation of Z (mol L^{-1} sec^{-1})
1	0.200	0.200	1.20×10^{-5}
2	0.200	0.400	2.40×10^{-5}
3	0.100	0.200	6.00×10^{-6}

(a) Calculate the initial rate of disappearance of substance Y in Experiment 1.

Since 2 mol Y is reacted for every 1 mol of Z formed the rate of disappearance of Y must be TWICE the rate of formation of Z 2.4×10^{-4} mol L^{-1} s^{-1} or $\text{rate} = -\frac{1}{2}\frac{\Delta[Y]}{\Delta t} = \frac{\Delta[Z]}{\Delta t}$ $-\frac{\Delta[Y]}{\Delta t} = 2\frac{\Delta[Z]}{\Delta t}$ $-\frac{\Delta[Y]}{\Delta t} = 2(1.2\times10^{-5}) = 2.4\times10^{-5}$	**1 point** is earned for the correct value of the rate of disappearance of substance Y.

(b) Determine the order of the reaction with respect to each reactant. Show your work.

i. X

$\left(\frac{0.200}{0.100}\right)^x\left(\frac{0.200}{0.200}\right)^y = \left(\frac{1.20\times10^{-5}}{6.00\times10^{-6}}\right)$ $2^x = 2$ $x = 1$ FIRST order with respect to X Alternatively, in experiments 1 and 3, [Y] was held constant while [X] was doubled which doubled the rate. Thus the reaction is FIRST order in [X].	**1 point** is earned for the correct order with work or justification

ii. Y

$\left(\frac{0.200}{0.200}\right)^x\left(\frac{0.400}{0.200}\right)^y = \left(\frac{2.40x10^{-5}}{1.20x10^{-5}}\right)$ $2^y = 2$ $y = 1$ 1st order with respect to Y Alternatively when experiment 2 is compared to 1, [X] remains constant while [Y] doubles. This caused the reaction rate to to double, thus that the reaction is 1st order in [Y]	**1 point** is earned for the correct order with work or justification

(c) Write the rate law for the reaction consistent with part B.

Rate = k[X][Y]	**1 point** is earned for the correct rate law consistent with part (a)

(d) Calculate the value of the rate constant, *k*. Be sure to include proper units.

$rate = k[\text{X}][\text{Y}]$ $\frac{rate}{[\text{X}][\text{Y}]} = k = \frac{6.00\times10^{-6}}{[0.100][0.200]} = 3.00\times10^{-4}\text{ L mol}^{-1}\text{sec}^{-1}$	**1 point** is earned for the correct value of *k* **1 point** is earned for the correct units for *k*

(e) In a closed 2.50 L reaction vessel at 22°C, 0.0254 mole of substance X was reacted with 0.0495 mol Y

i. Determine the limiting reactant. Justify your answer mathematically.

$\text{X}(g) + 2\text{Y}(g) \rightarrow \text{Z}(g)$ 0.0254 mol 0.0495 mol $0.0248\text{ mol} = \left(\frac{1}{2}\right)(0.0495\text{ mol Y})$ Therefore X is in excess by 0.0006 mol and Y is limiting	**1 point** is earned for the correct limiting reactant with justification

ii. Calculate the number of moles of Z formed.

Since Y is limiting: $\text{X}(g) + 2\text{Y}(g) \rightarrow \text{Z}(g)$ 0.0254 mol 0.0495 mol $(0.0495\text{ mol Y})\left(\frac{1\text{ mol Z}}{2\text{ mol Y}}\right) = 0.0248\text{ mol Z}$	**1 point** is earned for the correct number of moles of Z consistent with the answer in part (e) i.

iii. Calculate the total pressure in the flask at the completion of the reaction.

Since Y is limiting: $X(g) + 2Y(g) \rightarrow Z(g)$ 0.0254 mol 0.0495 mol 0 mol –0.0248 mol –0.0495 mol +0.0248 mol At completion of the reaction: 0.0006 mol X and 0.0248 mol Z present $P_{Total}V = n_{Total}RT$ $P = \frac{n_{Total}RT}{V} = \frac{(0.0006+0.0248)(0.0821)(295)}{(2.50)} = 0.246\ atm$	**1 point** is earned for the total mol of gas present consistent with the answers given in part (e) i and ii. **1 point** is earned for the total pressure consistent with the answers given in part (e) i and ii

(f) Three possible mechanisms for this reaction are shown below.

Mechanism 1	Mechanism 2	Mechanism 3
Y + Y □D (fast) $X + D \rightarrow Z$ (slow)	$X \rightarrow D$ (slow) $D + Y \rightarrow G$ (fast) $G + Y \rightarrow Z$ (fast)	$X + Y \rightarrow D$ (slow) $Y + D \rightarrow Z$ (fast)

i. Select the one most consistent with the experimental data. Justify your choice by writing a rate law for each of the three mechanisms.

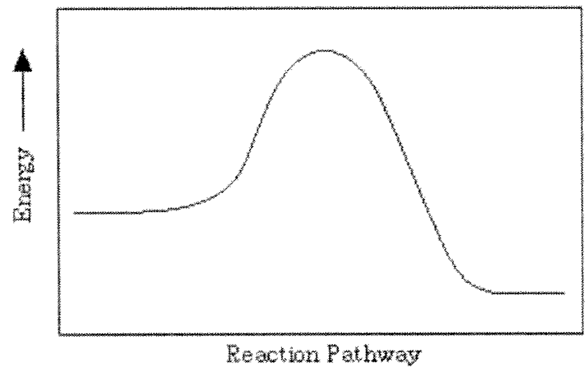
Mechanism 3 is most consistent with the experimental data. Its rate law is the same as that determined from the experimental data, rate = k [X][Y] The rate law for Mechanism 1 would be rate = k [X][D] which would be rate = k [X][Y]^2 solving for the intermediate D which is not consistent with the experimental data. The rate law for Mechanism 2 would be rate = k [X] which is not consistent with the experimental data.	**1 point** is earned for the correct mechanism. **1 point** is earned for justification, with the rate laws, for each mechanism.

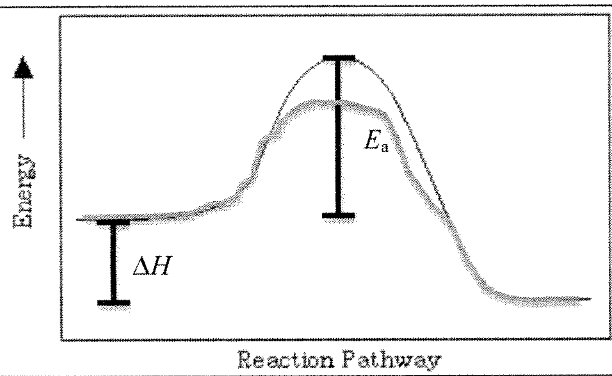
ii. Identify substance D in the mechanisms shown above as an intermediate or a catalyst. Justify your answer.

Substance D is an intermediate because it is a product of one step of the reaction that is used as a reactant in a later step.	**1 point** is earned for identifying and justifying D as an intermediate.

(g) The following diagram shows the energy of the reaction as the reaction progresses.

i. Clearly label the activation energy for the forward reaction.
ii. Clearly label the enthalpy change for the reaction.
iii. On the diagram draw a second energy curve showing the effect of a catalyst on the reaction.



	**1 point** is earned for correctly labeling the activation energy, E_a **1 point** is earned for correctly labeling the enthalpy change, ΔH. **1 point** is earned for sketching the plot of the catalyzed reaction – must start and end at the same energy level and exhibit a lower activation energy, E_a

(h) The collision between X and Y occur with enough energy to overcome the activation energy barrier, E_a, however no products are formed. Identify and explain one other factor that affects whether the collision will result in a reaction.

For a collision to be successful, the molecules must have the correct orientation. Only collisions with the correct orientation will be able to begin to form and begin to break the bonds as the transition state is approached. In other words the molecules must contact each other at very specific locations on their surfaces for the transition state to be possible.	**1 point** is earned for the identifying that the correct orientation for the collision is required. **1 point** is earned for the explanation that refers to specific locations of the molecules must collide.

Question 3
(9 points)

$$8\ H^+(aq) + 4\ Cl^-(aq) + MnO_4^-(aq) \rightarrow 2\ Cl_2(g) + Mn^{3+}(aq) + 4\ H_2O(l)$$

$Cl_2(g)$ can be generated in the laboratory by reacting potassium permanganate with an acidified solution of sodium chloride. The net-ionic equation for the reaction is given above.

(a) A 25.00 mL sample of 0.250 M NaCl reacts completely with excess $KMnO_4(aq)$. The $Cl_2(g)$ produced is dried and stored in a sealed container. At 22°C the pressure of the $Cl_2(g)$ in the container is 0.950 atm.

(i) Calculate the number of moles of $Cl^-(aq)$ present before any reaction occurs.

mol Cl^- = (0.02500 L)(0.250 M) = 6.25×10^{-3} mol	One point is earned for the correct numerical value.

(ii) Calculate the volume, in L, of the $Cl_2(g)$ in the sealed container.

mol Cl_2 = $\frac{\text{mol } Cl^-}{2} = \frac{6.25 \times 10^{-3}\ \text{mol}}{2} = 3.125 \times 10^{-3}$ mol Cl_2	One point is earned for the correct number of moles of Cl_2 based on stoichiometry.
$V = \frac{nRT}{P} = \frac{(3.125 \times 10^{-3}\ \text{mol } Cl_2)(0.0821\ \text{L atm mol}^{-1}\ \text{K}^{-1})(295\ \text{K})}{0.950\ \text{atm}}$ = 0.0797 L Cl_2	One point is earned for substitution into ideal gas law and correct numerical result.

An initial-rate study was performed on the reaction system. Data for the experiment are given in the table below.

Trial	$[Cl^-]$	$[MnO_4^-]$	$[H^+]$	Rate of Disappearance of MnO_4^- in $M\ s^{-1}$
1	0.0104	0.00400	3.00	2.25×10^{-8}
2	0.0312	0.00400	3.00	2.03×10^{-7}
3	0.0312	0.00200	3.00	1.02×10^{-7}

Question 3 (continued)

(b) Using the information in the table, determine the order of the reaction with respect to each of the following. Justify your answers.

(i) Cl^-

The reaction is second order. Tripling $[Cl^-]$ between trials 1 and 2 with no change in $[MnO_4^-]$ results in a nine-fold increase in the rate: $$\left(\frac{0.0312\ M}{0.0104\ M}\right)^x = \frac{2.03\times10^{-7}}{2.25\times10^{-8}}$$ $$3^x = 9$$ $$x = 2$$ Thus the order of the reaction must be 2 with respect to Cl^-.	One point is earned for the correct order of reaction with justification.

(ii) MnO_4^-

The reaction is first order. Doubling $[MnO_4^-]$ between trials 3 and 2 with no change in $[Cl^-]$ results in a doubling of the rate: $$\left(\frac{0.00400\ M}{0.00200\ M}\right)^y = \frac{2.03\times10^{-7}}{1.02\times10^{-7}}$$ $$2^y = 2$$ $$y = 1$$ Thus the order of the reaction must be 1 with respect to MnO_4^-.	One point is earned for the correct order of reaction with justification.

(c) The reaction is known to be third order with respect to H^+. Using this information and your answers to part (b) above, complete both of the following:

(i) Write the rate law for the reaction.

rate = $k[Cl^-]^2[MnO_4^-][H^+]^3$	One point is earned for the correct rate law.

Question 3 (continued)

(ii) Calculate the value of the rate constant, k, for the reaction, including appropriate units.

Using data from trial 1: $2.25 \times 10^{-8}\ M\,s^{-1} = k(0.0104\ M)^2(0.00400\ M)(3.00\ M)^3$ $k = 1.93 \times 10^{-3}\ M^{-5}s^{-1}$	One point is earned for the correct numerical result. One point is earned for the correct units.

(d) Is it likely that the reaction occurs in a single elementary step? Justify your answer.

It is not likely that the reaction occurs in a single step because the orders of the reaction with respect to the reactants do not correspond to the coefficients in the balanced equation ***OR*** It is not likely that the reaction occurs in a single step because the reaction requires the collision of many (13) reactant particles and the frequency of a 13-particle collision is negligible.	One point is earned for the correct answer with justification.

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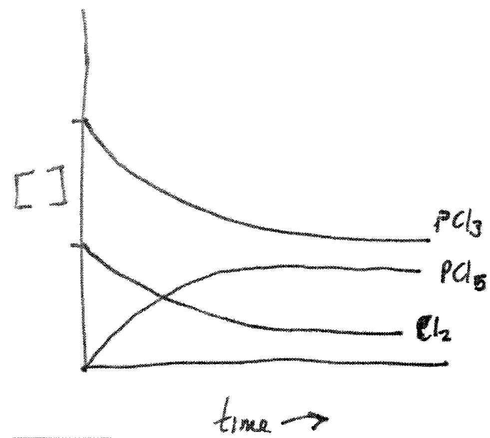
(4 points)

ADAPTED for a Short Free Response

In the equation below, the forward reaction is first order in both PCl_3 and Cl_2 and the reverse reaction is first order in PCl_5.

$$PCl_3\,(g) + Cl_2\,(g) \rightleftharpoons PCl_5\,(g)$$

(a) Suppose that 2 moles of PCl_3 and 1 mole of Cl_2 are mixed in a closed container at constant temperature. Draw a graph that shows how the concentrations of PCl_3, Cl_2, and PCl_5 change with time until after equilibrium has been firmly established.

	**1 point** is earned for • the correct initial amounts of all three species. • lines that show reactants decreasing and product increasing. **1 point** is earned for • lines that are curved initially and flat after equilibrium.

(b) Provide a molecular explanation for the dependence of the rate of the forward reaction on

i. the concentrations of the reactants.

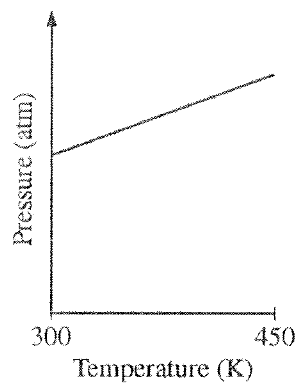
Reaction requires effective collisions between molecules of PCl_3 and Cl_2 As concentrations of these molecules increase, the number of effective collisions increases so the rate of reaction increases.	**1 point** is earned for the correct response.

ii. the temperature.

The fraction of effectively colliding molecules with the required activation energy increases as the temperature increases.	**1 point** is earned for the correct response.

Question 5
(8 points)

A sample of $C_2H_4(g)$ is placed in a previously evacuated, rigid 2.0 L container and heated from 300 K to 450 K. The pressure of the sample is measured and plotted in the graph below.



(a) Describe TWO reasons why the pressure changes as the temperature of the $C_2H_4(g)$ increases. Your descriptions must be in terms of what occurs at the molecular level.

Two reasons are: (1) As the temperature increases, the average speed of the molecules increases, and the molecules collide more frequently with the container walls. (2) As the temperature increases, the average kinetic energy of the molecules increases, and the molecules strike the walls of the container with greater force.	1 point is earned for each correct reason.

$C_2H_4(g)$ reacts readily with $HCl(g)$ to produce $C_2H_5Cl(g)$, as represented by the following equation.

$$C_2H_4(g) + HCl(g) \rightarrow C_2H_5Cl(g) \qquad \Delta H° = -72.6 \text{ kJ/mol}_{rxn}$$

(b) When $HCl(g)$ is injected into the container of $C_2H_4(g)$ at 450 K, the total pressure increases. Then, as the reaction proceeds at 450 K, the total pressure decreases. Explain this decrease in total pressure in terms of what occurs at the molecular level.

The decrease in pressure after the initial increase is a consequence of the reaction that produces fewer gas molecules than it consumes. When fewer gas molecules are present, there are fewer collisions with the container walls, resulting in a decrease in pressure.	1 point is earned for the correct reason.

Question 5 (continued)

It is proposed that the formation of $C_2H_5Cl(g)$ proceeds via the following two-step reaction mechanism.

Step 1: $C_2H_4(g) + HCl(g) \rightarrow C_2H_5^+(g) + Cl^-(g)$ rate-determining step

Step 2: $C_2H_5^+(g) + Cl^-(g) \rightarrow C_2H_5Cl(g)$ fast step

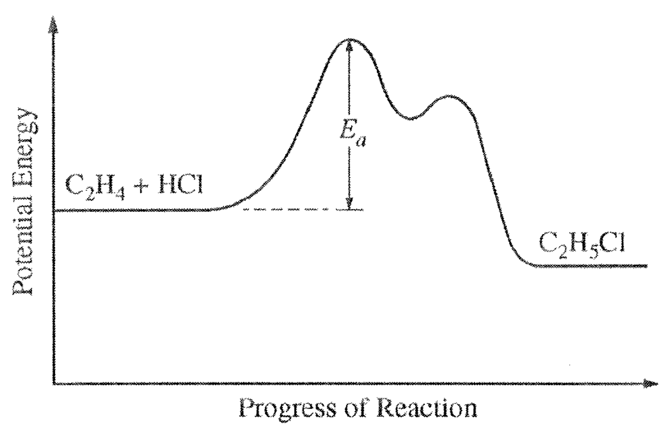
(c) Write the rate law for the reaction that is consistent with the reaction mechanism above.

rate $= k[C_2H_4][HCl]$	1 point is earned for the correct rate law.

(d) Identify an intermediate in the reaction mechanism above.

$C_2H_5^+(g)$ or $Cl^-(g)$	1 point is earned for identification of either species.

(e) Using the axes provided below, draw a curve that shows the energy changes that occur during the progress of the reaction. The curve should illustrate both the proposed two-step mechanism and the enthalpy change of the reaction.



See drawing above.	1 point is earned for the potential energy of the product being lower than the potential energy of the reactants (exothermic reaction). 1 point is earned for a reaction-energy curve that reflects a two-step process.

(f) On the diagram above, clearly indicate the activation energy, E_a, for the rate-determining step in the reaction.

See drawing above.	1 point is earned for the correct identification of E_a in Step 1.

Question 4
(*9 points*)

(a) $\frac{1.3\times10^{-3}}{4.3\times10^{-4}} = \frac{k(0.75)^x(0.75)^y}{k(0.25)^x(0.75)^y} \Rightarrow 3 = (3)^x \Rightarrow x = 1 \Rightarrow$ First order in A — *1 point*

$\frac{5.3\times10^{-3}}{1.3\times10^{-4}} = \frac{k(1.50)(1.50)^y}{k(0.75)(0.75)^y} \Rightarrow 4 = 2(2)^y \Rightarrow y = 1 \Rightarrow$ First order in B — *2 points*

Notes: Verbal descriptions accepted, but no point earned for just "if A doubles, the rate doubles".
If A given as second order, 2 points can be earned for showing that B must be zero order.

(b) rate = k[A][B] (equation must be consistent with part (a)) — *1 point*

$k = \frac{4.3\times10^{-4}\ M\cdot\text{min}^{-1}}{(0.25\ M)(0.75\ M)} = 2.3\times10^{-3}\ M^{-1}\cdot\text{min}^{-1}$ — *1 point*

Note: Units must be correct to earn second point.
If no part (a) shown, 1 point can be earned for a reasonable (first or second order) rate law.

(c) $\frac{\Delta[A]}{\Delta t} = -2\,(5.3\times10^{-3}\ M^{-1}\cdot\text{min}^{-1}) = -1.06\times10^{-2}\ M^{-1}\cdot\text{min}^{-1}$ — *1 point*

Note: Units ignored; no penalty for (–) sign.

(d) $8.0\times10^{-3}\ M^{-1}\cdot\text{min}^{-1} = (2.3\times10^{-2}\ M^{-1}\cdot\text{min}^{-1})(1.75\ M)[B]$ — *1 point*

$[B] = 2.0\ M$

Note: No penalty if answer is consistent with wrong part (b).

(e) Mechanism 2 is consistent — *1 point*

rate $\propto$ [M][A] and [M] $\propto$ [B] $\Rightarrow$ rate $\propto$ [A][B] — *1 point*

Notes: Verbal discussion accepted for second point.
Mechanism must be consistent with rate law in part (b).
Showing that mechanisms 1 and 3 are inconsistent is not required.

- CHEMISTRY -

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

5. For the exothermic reaction represented above, carried out at 298 K, the rate law is as follows.

$$\text{Rate} = k[H_2][I_2]$$

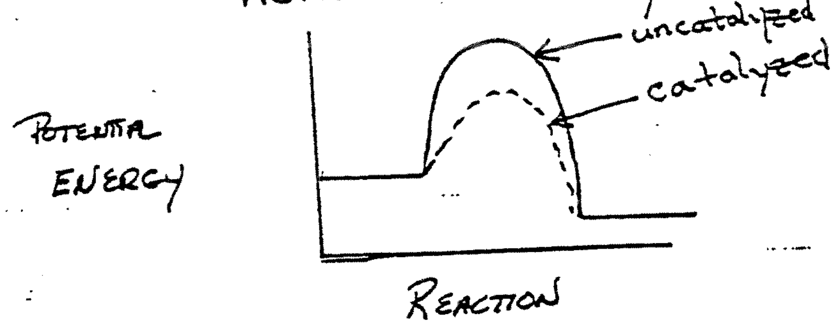
Predict the effect of each of the following changes on the initial rate of the reaction and explain your prediction.

(a) Addition of hydrogen gas at constant temperature and volume
(b) Increase in volume of the reaction vessel at constant temperature
(c) Addition of a catalyst. In your explanation, include a diagram of potential energy *versus* reaction coordinate.
(d) Increase in temperature. In your explanation, include a diagram showing the number of molecules as a function of energy.

a) EFFECT - INITIAL RATE WILL INCREASE (1)
EXPLANATION - RELATE INCREASE IN CONCENTRATION OF HYDROGEN TO AN INCREASE IN COLLISION RATE OR TO THE RATE LAW. (1)

b) EFFECT - INITAL RATE WILL DECREASE
EXPLANATION - DECREASE IN THE CONCENTRATION OF REACTANTS (1)

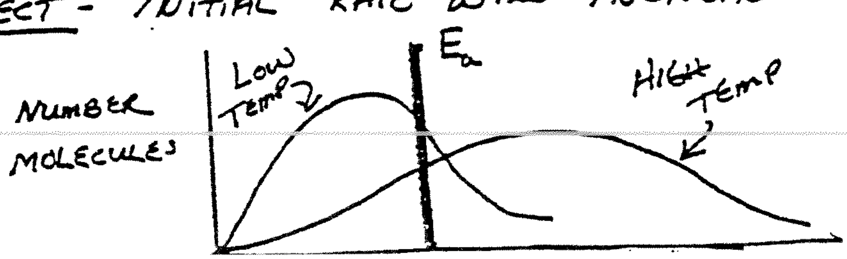
c) EFFECT - INITIAL RATE WILL INCREASE (1)
EXPLANATION -
ACTIVATION ENERGY IS LOWERED (1)



(1)

(d) EFFECT - INITIAL RATE WILL INCREASE (1)

EXPLANATION -



(1)

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