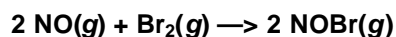


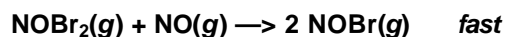
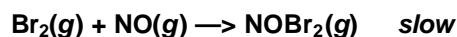
Note: I skipped all the NORMAL ones. When I say normal, I mean the ones dealing with only rate laws, orders, value of K, rate of appearance/disappearance, mechanisms, etc. Those are the ones we all know how to do, or are SUPPOSED to know how to do. Most of the questions here will be the strange ones. I think that between 1999 and 1980, I can cover a wide variety of the tricks that these pathetic test makers have created.



A rate study of the reaction represented above was conducted at 25°C. The data that were obtained are shown in the table below.

Experiment	Initial [NO] (mol L ⁻¹)	Initial [Br ₂] (mol L ⁻¹)	Initial Rate of Appearance of NOBr (mol L ⁻¹ s ⁻¹)
1	0.0160	0.0120	3.24 X 10 ⁻⁴
2	0.0160	0.0240	6.38 X 10 ⁻⁴
3	0.0320	0.0060	6.42 X 10 ⁻⁴

- Calculate the initial rate of disappearance of Br₂(g) in experiment 1.
- Determine the order of the reaction with respect to each reactant, Br₂(g) and NO(g). In each case, explain your reasoning.
- For the reaction,
 - write the rate law that is consistent with the data, and
 - calculate the value of the specific rate constant, *k*, and specify units.
- The following mechanism was proposed for the reaction:



Is this mechanism consistent with the given experimental observations? Justify your answer.

Notes: This problem is from 1999, so I'm not sure if he has it yet. However, we know everyone on here...

ANSWER:

9 points:

One point deduction for mathematical error (maximum once per question)

One point deduction for error in significant figures* (maximum once per question)

*number of significant figures must be correct within +/- one digit.

- 1 point

Rate of Br₂(g) loss occurs at 1/2 the rate of NOBr(g) formation.

$$\text{Rate of Br}_2(g) \text{ loss} = \frac{3.24 \times 10^{-4} \text{ M}}{2 \text{ sec}} = 1.62 \times 10^{-4} \text{ M sec}^{-1} \text{ (or mol L}^{-1} \text{ sec}^{-1}\text{)}$$

Note: No penalty for missing units; ignore + or - signs

b. **1 point**

Comparing experiments 1 and 2, [NO] remains constant, [Br₂] doubles, and rate doubles; therefore, rate is directly proportional to [Br₂]¹ --> reaction is first-order with respect to [Br₂].

2 points

$$\frac{6.38 \times 10^{-4}}{6.42 \times 10^{-4}} \text{ is about equal to } 1 = \frac{k[\text{NO}]^x[\text{Br}_2] \quad k[0.0160]^x[0.0240]}{k[\text{NO}]^x[\text{Br}_2] \quad k[0.0320]^x[0.0060]} = (1/2)^x 4 = 1 \text{ --}$$

>

1/4 = (1/2)^x --> x = 2 --> reaction is second-order with respect to [NO]

Note: One point earned for a proper set-up, comparing experiments 2 and 3 (as is shown here) or experiments 1 and 3. Second point earned for solving the ratios correctly and determining that the exponent = 2. Also, credit can be earned for a non-mathematical approach (e.g., one point for describing the change in [Br₂] and subsequent effect on rate, another point for describing the change in [NO] and subsequent effect on rate).

c.

i. **1 point**

$$\text{Rate} = k[\text{NO}]^2[\text{Br}_2]$$

Note: Point earned for an expression that is **not inconsistent** with the answer in part (b)

ii. **2 points**

$$k = \frac{\text{Rate}}{[\text{NO}]^2[\text{Br}_2]} = \frac{3.24 \times 10^{-4} \text{ M sec}^{-1}}{(0.0160)^2(0.0120) \text{ M}^3} = 105 \text{ M}^{-2} \text{ sec}^{-1} \text{ (or } 105 \text{ L}^2 \text{ mol}^{-2} \text{ sec}^{-1} \text{)}$$

iii. (Using rate of Br₂(g) loss = 1.62 x 10⁻⁴ M sec⁻¹ --> k = 52.7 M⁻² sec⁻¹ is also correct.)

iv. **Note:** One point for solving for the value of the rate constant **consistent** with the rate-law expression found in part (b) or stated in part (c); one point for the correct units **consistent** with the rate-law expression found in part (b) or stated in part (c).

d. **1 point**

No, it is not consistent with the given experimental observations.

1 point

This mechanism gives a reaction that is first-order in [NO], and first-order in [Br₂], as those are the two reactants in the rate-determining step. Kinetic data show the reaction is second-order in [NO] (and first-order in [Br₂]), so this cannot be the mechanism.

Note: One point earned for "No" [or for "Yes" if rate = k[NO][Br₂] in part (b)]. One point earned for justifying why this mechanism is inconsistent with the observed rate-law [or consistent with rate law stated earlier in response].

2. Answer the following questions regarding the kinetics of chemical reactions.

(a) The diagram below at right shows the energy pathway for the reaction O₃ + NO --> NO₂ + O₂.

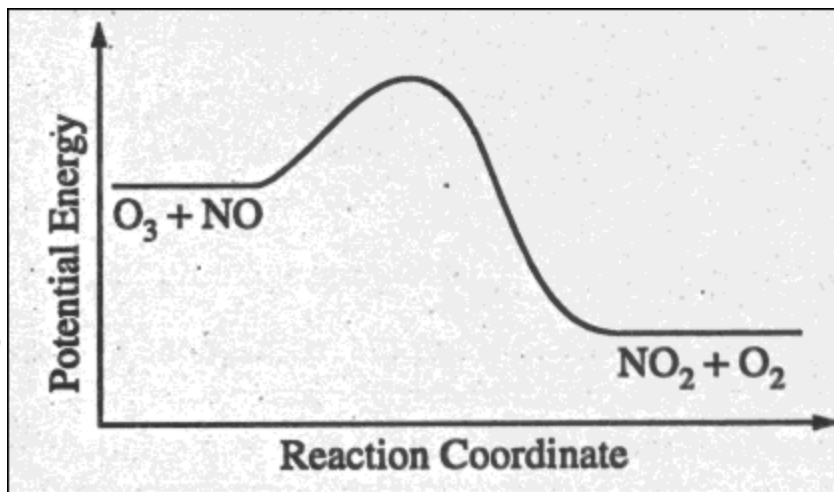
Clearly label the following directly on the diagram.

(i) The activation energy (E_a) for the forward reaction

(ii) The enthalpy change (ΔH) for the reaction

(b) The reaction 2 order with respect

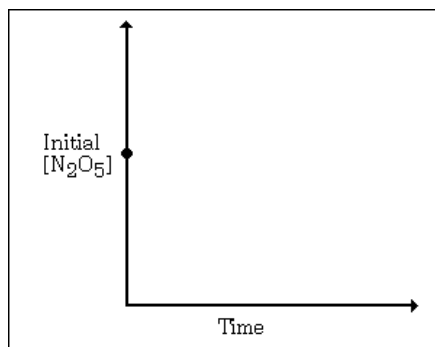
(i) Using complete represents over time proceeds. graph in (i) find the given time, (iii) law and describe rate be



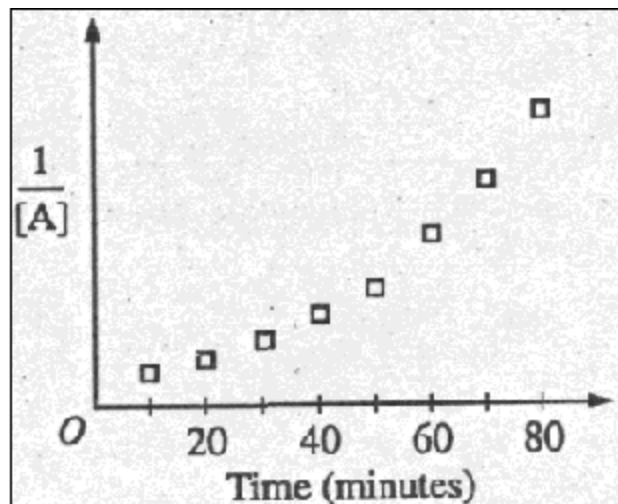
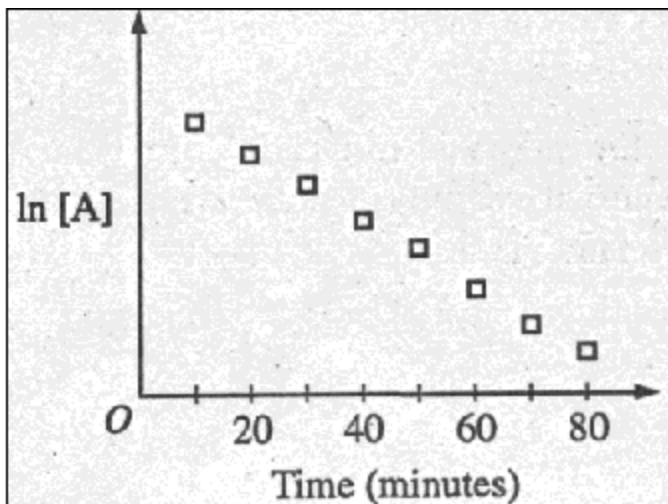
$N_2O_5 \rightarrow 4 NO_2 + O_2$ is first to N_2O_5 .

the axes at right, the graph that the change in $[N_2O_5]$ as the reaction (ii) Describe how the could be used to reaction rate at a t. Considering the rate the graph in (i), how the value of the constant, k, could determined.

(iv) If more N_2O_5 were added to the reaction mixture at constant temperature, what would be the effect on the rate constant, k? Explain.



(c) Data for the chemical reaction $2A \rightarrow B + C$ were collected by measuring the concentration of A at 10-minute intervals for 80 minutes. The following graphs were generated from analysis of data.



Use the

information in the graphs above to answer the following.

(i) Write the rate-law expression for the reaction. Justify your answer.

(ii) Describe how to determine the value of the rate constant for the reaction.

ANSWER:

6)

(a) Response must clearly indicate (and distinguish between) E_{act} and H_{rxn} on graph

Each earns one point

(b) i. Response shows a softly curving line that approaches the time axis and whose slope changes continually.

No penalty if curve crosses time axis or levels out above time axis.

Curve must drop initially and continually. No credit earned if $[\text{N}_2\text{O}_5]$ increases

ii. Reaction rate is the **slope** of the line **tangent** to any point on the curve. (one point)

Rate must be tied somehow to slope of the graph

Answer may be indicated directly on the graph

Instantaneous rate must be indicated rather than the average rate

iii. Since "rate = slope = $k[\text{N}_2\text{O}_5]$ ", the value of k can be determined algebraically from the slope at a known value of $[\text{N}_2\text{O}_5]$. (one point)

No penalty for "rate = $2k [\text{N}_2\text{O}_5]$ " as a reaction stoichiometry could suggest this answer.

Point can be earned for rate constant = slope of graph if $\ln[\text{N}_2\text{O}_5]$ vs. time since reaction is first order.

Use half-life or integrated rate law to solve for k can be accepted.

iv. The value of the rate constant is independent of the reactant concentrations, so adding more reactant will not affect the value of k . (one point)

no point earned for simply stating that value of k will not change.

Response must distinguish between rate and rate constant.

(c) i. Rate = $k[A]$ or $\ln([A]/[A]_0) = kt$. Since graph of $\ln[A]$ vs. time is linear, it must be a first-order reaction. (one point)

Either form of the rate law is acceptable, and both the equation and the brief justification are required to earn the point.

No point earned if response indicates first order because the first graph is not linear.

ii. Determine the slope of the second graph and set " $k = -\text{slope}$." (one point)

Response must indicate both the negative sign and the slope.

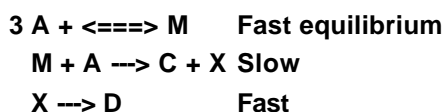
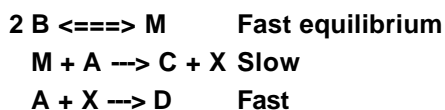
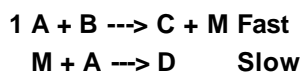
3. $2A + B \rightarrow C + D$

The following results were obtained when the reaction represented above was studied at 25 °C

Experiment	Initial [A]	Initial [B]	Initial Rate of Formation of C ($\text{mol L}^{-1} \text{min}^{-1}$)
1	0.25	0.75	4.3×10^{-4}
2	0.75	0.75	1.3×10^{-3}

3	1.50	1.50	5.3×10^{-3}
4	1.75	??	8.0×10^{-3}

- a) Determine the order of the reaction with respect to A and B. Justify your answer.
- b) Write the rate law for the reaction. Calculate the value of the rate constant, specifying units.
- c) Determine the initial rate of change of [A] in Experiment 3.
- d) Determine the initial value of [B] in Experiment 4.
- e) Identify which of the reaction mechanisms represented below is consistent with the rate law developed in part (b). Justify your choice.



ANSWER:

(a) three points

$$1.3 \times 10^{-3} / 4.3 \times 10^{-4} = k (0.75)^x (0.75)^y / k (0.25)^x (0.75)^y \text{ leads to } 3 = (3)^x \text{ leads to } x = 1, \text{ first order in A}$$

$$5.3 \times 10^{-3} / 1.3 \times 10^{-4} = k(1.50)(1.50)^y / k(0.75)(0.75)^y \Rightarrow 4 = 2(2)^y \Rightarrow y=1 \Rightarrow \text{First order in B}$$

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) two points

rate = $k[A][B]$ (equation must be consistent with part (a))

$$k = 4.3 \times 10^{-4} \text{ M min}^{-1} / (0.25\text{M})(0.75\text{M}) = 2.3 \times 10^{-3} \text{ M}^{-1} \text{ min}^{-1}$$

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) one point

$$? [A] / ? t = -2 (5.3 \times 10^{-3} \text{ M}^{-1} \text{ min}^{-1}) = -1.06 \times 10^{-2} \text{ M}^{-1} \text{ min}^{-1}$$

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

(d) one point

$$8.0 \times 10^{-3} \text{ M}^{-1} \text{ min}^{-1} = (2.3 \times 10^{-2} \text{ M}^{-1} \text{ min}^{-1}) (1.75 \text{ M}) [B]$$

$$[B] = 2.0 \text{ M}$$

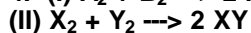
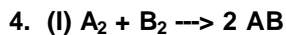
Note; No penalty if answer is consistent with wrong part (b).

(e) two points

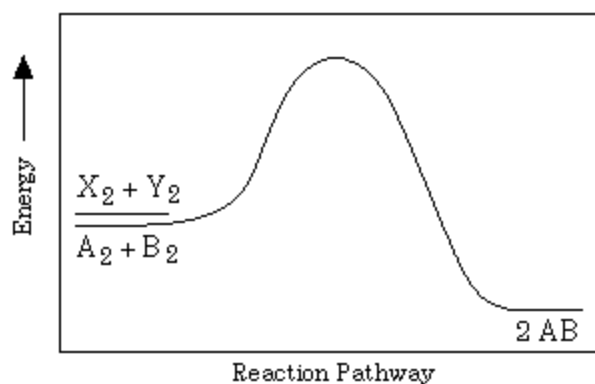
Mechanism 2 is consistent

rate proportional to $[M][A]$ and $[M]$ proportional to $[B] \Rightarrow$ rate proportional to $[A][B]$

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.



Two reactions are represented above. The potential-energy diagram for reaction I is shown below. The potential energy of the reactants in reaction II is also indicated on the diagram. Reaction II is endothermic, and the activation energy of reaction I is greater than that of reaction II.



(a) Complete the potential-energy diagram for reaction II on the graph above.

(b) For reaction I, predict how each of the following is affected as the temperature is increased by 20°C . Explain the basis for each prediction.

- (i) Rate of reaction
- (ii) Heat of reaction

(c) For reaction II, the form of the rate law is $\text{rate} = k[X_2]^m[Y_2]^n$. Briefly describe an experiment that can be conducted in order to determine the values of m and n in the rate law for the reaction.

(d) From the information given, determine which reaction initially proceeds at the faster rate under the same conditions of concentration and temperature. Justify your answer.

ANSWER:

a) two points

Sketch must show start at $X_2 + Y_2$, rise to E_a that is less than that for reaction I, then drop to $2 XY$, which must be at a higher PE than $X_2 + Y_2$ to show an endothermic process.

b) two points

The rate increases because more molecules have energy greater than E_a at higher temperature and/or the higher speed of the molecules generates a greater collision frequency.

$[\Delta]H$ for the reaction is changed only slightly, or not at all with small changes in temperature.

c) two points

Hold one reactant concentration constant, vary the other, and measure initial rate of reactant disappearance or product formation. Take ratios of rates equal to $([]_1 / []_2)^n$; repeat for the other reactant.

OR

Follow concentrations of both reactants as functions of time, plot and test for order of each (1st, 2nd, etc.) or do integral law calculations.

OR

Add large concentrations of one reactant, follow the concentration of the other as a function of time; repeat for the other reactant.

Note: 1 point awarded for less complete description

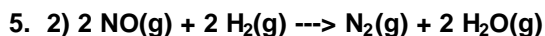
d) two points

Reaction II proceeds faster.

The reaction with the lower E_a , under the same conditions of concentration and temperature, will have a faster rate.

OR

It is not possible to determine which reaction has the faster rate without knowledge of other (preexponential) factors. It cannot be assumed these factors will be the same for X_2 , Y_2 , as for A_2 , B_2 , or that a similar mechanism is involved.



Experiments conducted to study the rate of the reaction represented by the equation above. Initial concentrations and rates of reaction are given in the table below.

Experiment	Initial Concentration (mol/L)		Initial Rate of Formation of N_2 (mol/L min)
	[NO]	[H ₂]	
1	0.0060	0.0010	1.8×10^{-4}
2	0.0060	0.0020	3.6×10^{-4}
3	0.0010	0.0060	0.30×10^{-4}
4	0.0020	0.0060	1.2×10^{-4}

(a)

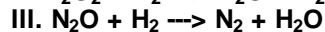
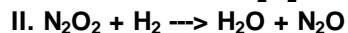
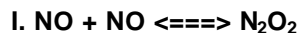
(i) Determine the order for each of the reactants, NO and H₂, from the data given and show your reasoning.

(ii) Write the overall rate law for the reaction.

(b) Calculate the value of the rate constant, k , for the reaction. Include units.

(c) For experiment 2, calculate the concentration of NO remaining when exactly one-half of the original amount of H_2 has been consumed.

(d) The following sequence of elementary steps is a proposed mechanism for the reaction.



Based on the data present, which of the above is the rate-determining step? Show that the mechanism is consistent with:

(i) the observed rate law for the reaction, and

(ii) the overall stoichiometry of the reaction.

ANSWER:

a) three points (point for each order must include justification)

From exps. 1 and 2: doubling $[H_2]$ while keeping $[NO]$ constant doubles the rate, therefore the reaction is first order in $[H_2]$.

From exps. 3 and 4; doubling $[NO]$ while keeping $[H_2]$ constant quadruples the rate, therefore the reaction is second order in $[NO]$.

$$\text{Rate} = k [H_2] [NO]^2$$

Note: full credit is earned for the rate expression as long as it is consistent with orders described by student.

b) two points (one for value and one for units)

$$k = \text{Rate} / ([H_2] [NO]^2)$$

$$\text{From exp. 1: } k = 1.8 \times 10^{-4} \text{ M/min} / [(1.0 \times 10^{-3} \text{ M}) (6.0 \times 10^{-3} \text{ M})^2]$$

$$= 5.0 \times 10^3 \text{ M}^{-2} \text{ min}^{-1}$$

Note: the unit is often written as $L^2 \text{ mol}^{-2} \text{ min}^{-1}$

c) one point

Stoichiometry: NO : H_2 is 1:1

When 0.0010 mole of H_2 had reacted, it must have reacted with 0.0010 mole NO; thus $[NO]$ remaining = $0.0060 - 0.0010$
= 0.0050 M

d) three points

(i)

$$\text{For I : } K_{\text{eq}} = [\text{N}_2\text{O}_2] / [\text{NO}]^2$$

$$\text{For II: Rate} = k[\text{H}_2][\text{N}_2\text{O}_2]$$

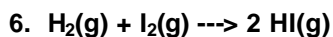
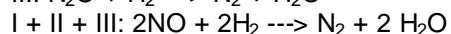
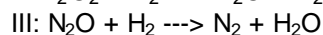
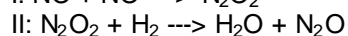
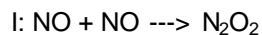
$$[\text{N}_2\text{O}_2] = K_{\text{eq}} [\text{NO}]^2$$

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

Note: there must be some clear algebraic manipulation showing that $[\text{N}_2\text{O}_2]$ is proportional (NOT equal) to $[\text{NO}]^2$.

Step II is the rate determining step.

(ii)



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

$$\text{Rate} = k [\text{H}_2] [\text{I}_2]$$

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.

ANSWER:

a) two points

EFFECT: addition of H_2 would increase the rate.

EXPLANATION: Since the reaction is first-order in H_2 , doubling the concentration would double the rate. The inclusion of H_2 in the rate law indicates it participates in the rate-determining step.

OR

Relate the increase in concentration of hydrogen to an increase in collision rate.

b) one point

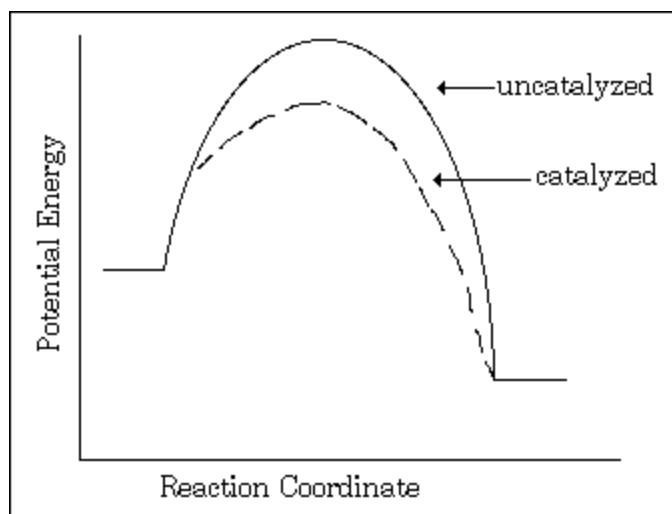
EFFECT: The initial rate would decrease.

EXPLANATION: Increasing the volume would decrease the concentration of both H_2 and I_2 . At the lower concentration there would be a lesser number of overall collisions (due to greater distance between individual molecules), leading to a lesser number of effective collisions.

c) three points

EFFECT: addition of a catalyst will increase the rate of both forward and reverse reactions.

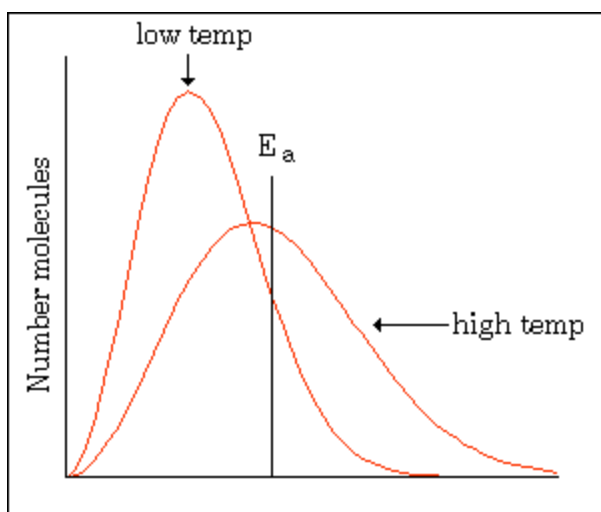
EXPLANATION:



d) two points

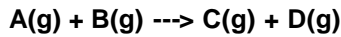
EFFECT: The initial rate of reaction will increase.

EXPLANATION:



If E_a is missing from explanation, this gets one point.

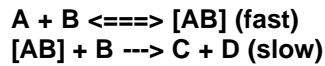
7) Consider the following general equation for a chemical reaction.



(a) Describe the two factors that determine whether a collision between molecules of A and B results in a reaction.

(b) How would a decrease in temperature affect the rate of the reaction shown above? Explain your answer.

(c) Write the rate law expression that would result if the reaction proceeded by the mechanism shown below.



(d) Explain why a catalyst increases the rate of a reaction but does not change the value of the equilibrium constant for that reaction.

ANSWER:

a) two points

1. the kinetic energy of the molecules
(A certain minimum energy is required for a reaction to occur (activation energy))
 2. The orientation of the molecules relative to one another. Even very energetic collisions may not lead to a reaction if the molecules are not oriented properly.
-

b) two points

1. A decrease in temperature would decrease the rate.
 2. Fewer molecules would have the energy necessary to react. (Fewer effective collisions)
-

c) two points

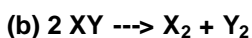
$$\text{Rate} = [A][B]^2$$

d) two points

1. Catalyst increases the rate by providing an alternate pathway which has a lower activation energy.
 2. The value of the equilibrium constant does not change as a catalyst does not affect the energies (or concentrations) of the reactants and products.
-

8. The overall order of a reaction may not be predictable from the stoichiometry of the reaction.

(a) Explain how this statement can be true.



1. For the hypothetical reaction above, give a rate law that shows that the reaction is first order in the reactant XY.
2. Give the units for the specific rate constant for this rate law.
3. Propose a mechanism that is consistent with both the rate law and the stoichiometry.

ANSWER:

6) Average score = 3.24

a) two points

order of reaction determined by the slowest step in the mechanism

OR

order of reaction determined by exponents in the rate law

OR

providing a counterexample where the coefficients in equation and exponents in rate law are different

b) six points

1. Rate = $k[XY]$ or equivalent

2. $k = 1/\text{time}$ or units consistent with student's rate equation

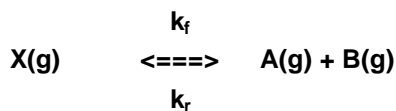
3. Mechanism proposed should show:

a) steps adding up to the overall reaction

b) one step starting with XY

c) rate-determining step involving XY

9. The decomposition of compound X is an elementary process that proceeds as follows:



? H° for the above reaction = +15 kilocalories

The forward reaction is slow at room temperature but becomes rapid when a catalyst is added.

(a) Draw a diagram of potential energy versus reaction coordinate for the uncatalyzed reaction. On this diagram label

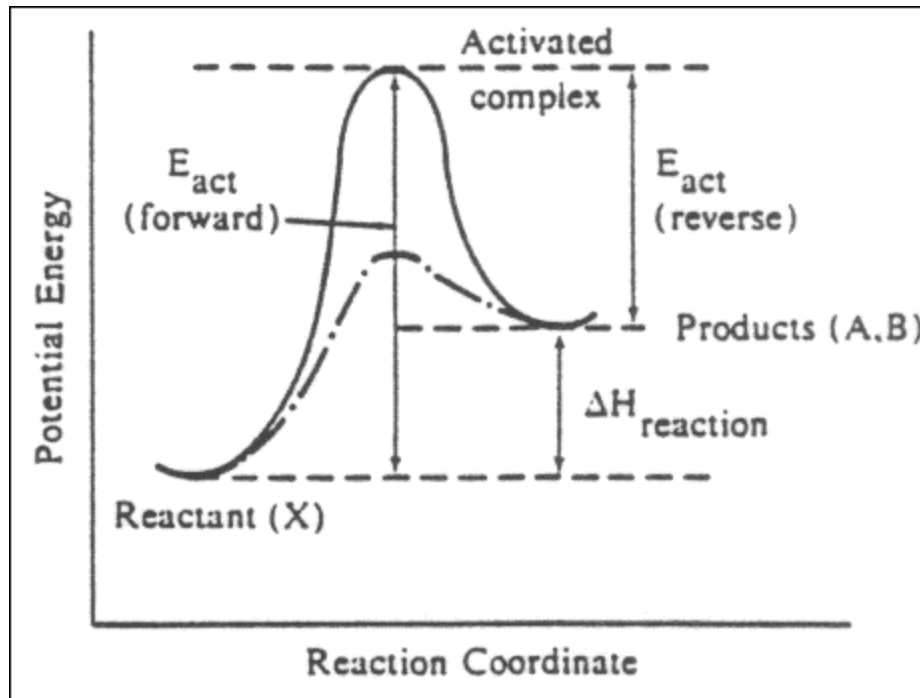
- (1) the axes
- (2) the energies of the reactants and the products
- (3) the energy of the activated complex
- (4) all significant energy differences

(b) On the same diagram indicate the change or changes that result from the addition of the catalyst. Explain the role of the catalyst in changing the rate of the reaction.

(c) If the temperature is increased, will the ratio k_f / k_r increase, remain the same, or decrease? Justify your answer with a one- or two-sentence explanation. (k_f and k_r are the specific rate constants for the forward and the reverse reactions, respectively.)

ANSWER:

a) 4 points



At 1/2 point each: Curve shape, labeled axes, reactant energy, product energy, energy of activated complex, enthalpy change, activation energy (forward), and activation energy (reverse).

b) 2 points

Catalyzed path (dotted line on diagram)

Catalyst role: changes mechanism, or increases fraction of molecules with sufficient energy to react.

c) 2 points

The ratio, k_f / k_r increases with temperature, because...

$k_f / k_r = K$ and LeChatelier shift

or

Boltzmann distribution graph

or

$T[\Delta]S$ changes for net reaction influencing $[\Delta]G$

or

k_f increased more than k_r for endothermic reaction.

10. 2) For a hypothetical chemical reaction that has the stoichiometry $2 X + Y \rightarrow Z$, the following initial rate data were obtained. All the measurements were made at the same temperature.

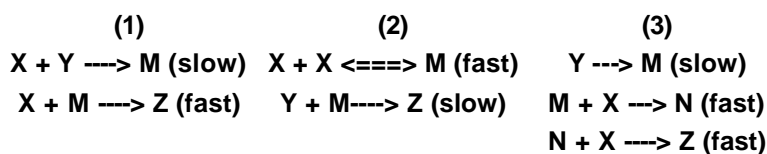
Initial Rate of Formation of Z, mol L ⁻¹ sec ⁻¹	Initial [X] ₀ , mol L ⁻¹	Initial [Y] ₀ , mol L ⁻¹
7.0 x 10 ⁻⁴	0.20	0.10
1.4 x 10 ⁻³	0.40	0.20
2.8 x 10 ⁻³	0.40	0.40
4.2 x 10 ⁻³	0.60	0.60

(a) Give the rate law for this reaction from the data above

(b) Calculate the specific rate constant for this reaction and specify its units.

(c) How long must the reaction proceed to produce a concentration of Z equal to 0.20 molar, if the initial reaction concentrations are [X]₀ = 0.80 molar, [Y]₀ = 0.60 molar, and [Z]₀ = 0 molar?

(d) Select from the mechanisms below the one most consistent with the observed data, and explain your choice. In these mechanisms M and N are reaction intermediates. (NB - the words fast and slow are placed above the reaction arrow on the original test.)



ANSWER:

Average score 4.81

a) three points; one point for correct form of law and two points for correct methodology without an error; one point for correct methodology with an error

$$\text{Rate} = k[Y]$$

b) two points

$$7.0 \times 10^{-4} \text{ mole / L sec} = k (0.10 \text{ mole / L})$$

$$k = 7.0 \times 10^{-3} \text{ sec}^{-1}$$

c) two points

$$2.3 \log c_0 / c = k t$$

$$2.3 \log 0.60 / 0.40 = (7.0 \times 10^{-3}) (t)$$

$$t = 58 \text{ s}$$

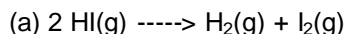
d) two point

Mechanism 3 is correct.

The rate law shows that the slow reaction must involve one Y, consistent with mechanism 3.

Mechanisms 1 and 2 would involve both [X] and [Y] in the rate law, not consistent with the rate law.

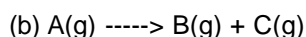
11. 4) Graphical methods are frequently used to analyze data and obtain desired quantities.



The following data give the value of the rate constant at various temperatures for the gas phase reaction above.

T(k)	647	666	683	700	716
k (liter/mole sec)	8.58×10^{-5}	2.19×10^{-4}	5.11×10^{-4}	1.17×10^{-3}	2.50×10^{-3}

Describe, without doing calculations, how a graphical method can be used to obtain the activation energy for this reaction.



The following data give the partial pressure of A as a function of time and were obtained at 100 °C for the reaction above.

P_A (mm Hg)	348	247	185	105	58
t(sec)	0	600	1,200	2,400	3,600

Describe, without doing calculations, how graphs can be used to determine whether this reaction is first or second order in A and how these graphs are used to determine the rate constant.

ANSWER:

a) three points

Plot $\ln k$ or $\log k$ vs $1/T$

Slope = $-R$ (slope) or $-2,303 R$ (slope)

For partial credit, if the 2-point equation is given for the activation energy, the student may receive a point. A student may also receive a point if it is stated that k is plotted vs $1/T$ or if $\ln k$ or $\log k$ is plotted vs T .

b) five points

Plot $\ln P_A$ or $\log P_A$ vs time.

Plot $1/P_A$ vs time.

If $\ln P_A$ vs time is linear, the reaction is first order. If $1/P_A$ vs time is linear, the reaction is second order.

If first order, slope = $-k_1$ or $-k_1 / 2.303$.

If second order, slope = k_2 .

Questions

How can you describe if mechanisms are accurate w/o the "substitution idea"?

How can you find the mechanism in 8b?