2nd

Reaction Mechanisms and Reaction Profiles Practice

1. A. How many elementary steps are in the reaction mechanism shown below?

   B. On the energy profile below, indicate

   a. the position of the reactants and products

   b. the activation energy for the overall reaction

   c. ΔE for the reaction

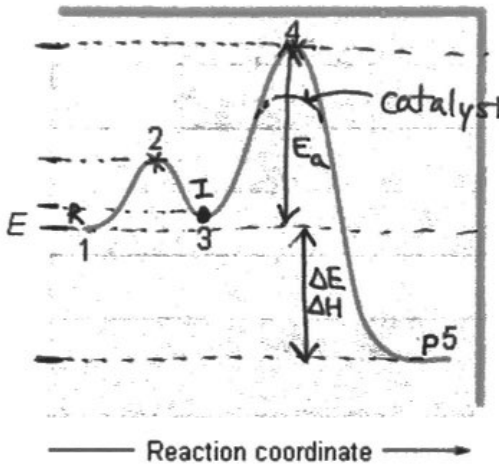
   d. the point on the plot that represents the energy of the intermediate 3

   e. the transition state (activated complex) 2 + 4

   f. the rate-determing step step 2

   g. how a catalyst would affect the reaction ↓ E_a of step 2

   C. Is the overall reaction endothermic or exothermic?



2 step mechanism
2 elementary steps

$E_R > E_P$ exothermic

(2.) Consider the following 3-step mechanism for an exothermic reaction.

Step 1: $Cl_2(g) \leftrightarrow 2Cl(g)$ *fast, k_1 forward, k_{-1} reverse*

Step 2: $Cl(g) + CHCl_3(g) \rightarrow HCl(g) + CCl_3(g)$ *slow, k_2*

Step 3: $Cl(g) + CCl_3(g) \rightarrow CCl_4(g)$ *fast, k_3*

(A.) What is the overall reaction?

$$Cl_2 + CHCl_3 \rightarrow HCl + CCl_4$$

(B.) What are the reaction intermediates? Cl, CCl_3

* C. Write the rate law that is consistent with this mechanism, showing how you derive it.

Rate = $k[Cl][CHCl_3]$

* Rate = $k[Cl_2]^{\frac{1}{2}}[CHCl_3]$

$Cl_2 \leftrightarrow 2Cl$

$\frac{1}{2}Cl_2 \leftrightarrow Cl$

Discussion of k

Step 1: Rate of Forward Reaction = Rate of Reverse Reaction

$$k_1[Cl_2] = k_{-1}[Cl]^2$$

$$\frac{k_1[Cl_2]}{k_{-1}} = [Cl]^2$$

$$\sqrt{\frac{k_1}{k_{-1}}}[Cl_2]^{1/2} = [Cl]$$

$$\text{Rate} = k_2[Cl][CH_3Cl]$$

$$= k_2\sqrt{\frac{k_1}{k_{-1}}}[Cl_2]^{1/2}[CH_3Cl]$$

$k_2\sqrt{\frac{k_1}{k_{-1}}}$ → overall k

3. A. How many elementary steps are in the reaction mechanism shown below? 2

B. On the energy profile below, indicate

a. the position of the reactants and products

b. the activation energy for the overall reaction 10 kJ

c. ΔE for the reaction − 15 kJ

d. the point on the plot that represents the energy of the intermediate

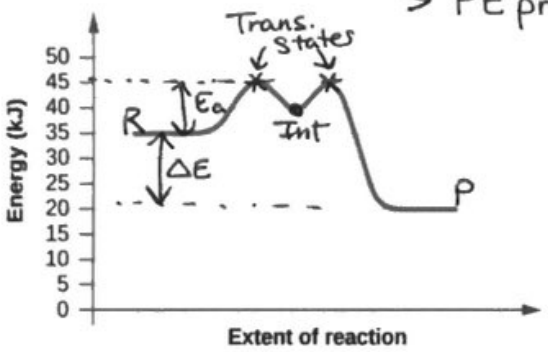
e. the transition state (activated complex)

f. the rate-determing step Step 1 → highest E_a

g. how a catalyst would affect the reaction → lower E_a of Step 1

C. Is the overall reaction endothermic or exothermic?

→ PE prod < PE react



4. A. How many elementary steps are in the reaction mechanism shown below? 3

B. On the energy profile below, indicate

a. the position of the reactants and products

b. the activation energy for the overall reaction E_a = 43 kJ

c. ΔE for the reaction ΔE = +8 kJ

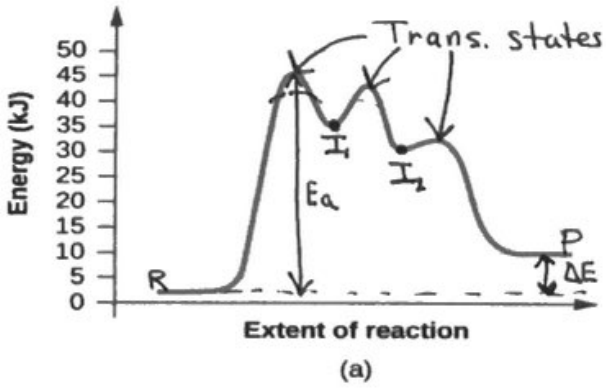
d. the point on the plot that represents the energy of the intermediate

e. the transition state (activated complex)

f. the rate-determing step step 1 → highest E_a

g. how a catalyst would affect the reaction → lower the E_a of Step 1

C. Is the overall reaction endothermic or exothermic?



(a)

3 steps

PE prod > PE react

5. Consider the following 3-step mechanism for an exothermic reaction.

Step 1: $I_2(g) \leftrightarrow 2I(g)$ *fast, k_1 forward, k_{-1} reverse*

Step 2: $I(g) + H_2(g) \leftrightarrow H_2I(g)$ *fast, k_2 forward, k_{-2} reverse*

Step 3: $H_2I(g) + I(g) \rightarrow 2HI(g)$ slow, k_3

A. What is the overall reaction?

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

B. What are the reaction intermediates? I, H_2I

* C. Write the rate law that is consistent with this mechanism, showing how you derive it.

$$\text{Rate} = k[H_2I][I]$$

$$= k[I][H_2][I_2]^{1/2}$$

$$= k[I_2]^{1/2}[H_2][I_2]^{1/2}$$

$$= k[I_2][H_2]$$

$I_2 \leftrightarrow 2I$

$\frac{1}{2}I_2 \leftrightarrow I$

6. A. How many elementary steps are in the reaction mechanism shown below?

B. On the energy profile below, indicate

a. the position of the reactants and products

b. the activation energy for the overall reaction 3

c. ΔE for the reaction 6

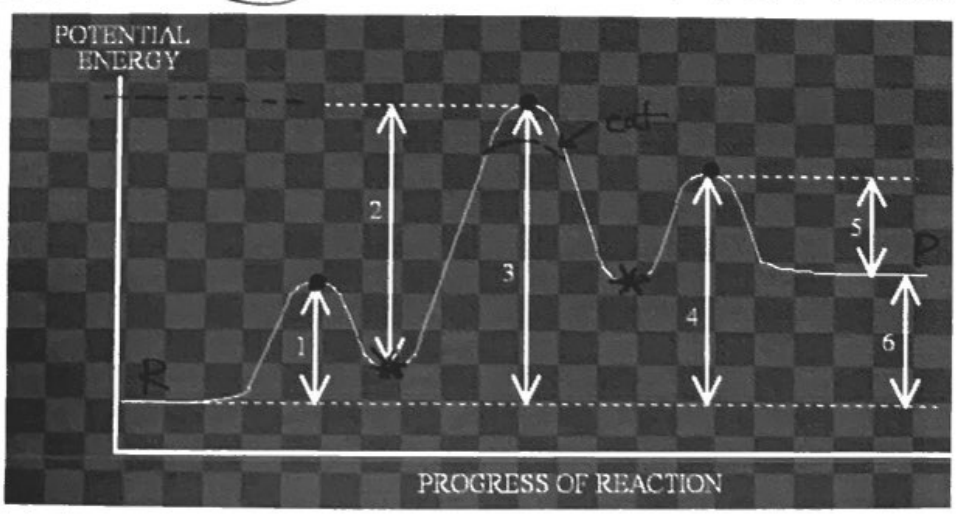
d. the point on the plot that represents the energy of the intermediate ✱

e. the transition state (activated complex) •

f. the rate-determing step 2

g. how a catalyst would affect the reaction

C. Is the overall reaction endothermic or exothermic? $PE_{prod} > PE_{react}$



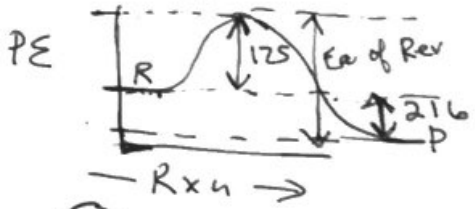
3 steps

make a sketch

7. The activation energy for the reaction

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ → exothermic → $PE_{prod} < PE_{react}$

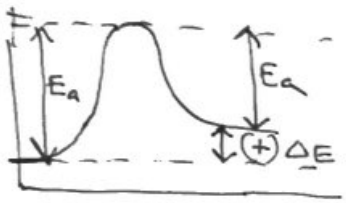
is 125 kJ/mole, and ΔE for the reaction is -216 kJ/mole. What is the activation energy for the reverse reaction [$NO(g) + CO_2(g) \rightarrow NO_2(g) + CO(g)$]?



125 + 216 = 341 kJ

make a sketch

8. For a certain reaction, the activation energy is greater for the forward reaction than the reverse reaction. Does the reaction have a positive or negative value for ΔE?



endothermic
+ ΔE

9. The following mechanism has been proposed for the reaction of methane gas with chlorine gas. All species are in the gas phase.

Step 1:	$Cl_2 \leftrightarrow 2Cl$	*fast equilibrium*
Step 2:	$CH_4 + Cl \rightarrow CH_3 + HCl$	*slow*
Step 3:	$CH_3 + Cl_2 \rightarrow CH_3Cl + Cl$	*fast*
Step 4:	$CH_3Cl + Cl \rightarrow CH_2Cl_2 + H$	*fast*
Step 5:	$H + Cl \rightarrow HCl$	*fast*

$2Cl_2 + CH_4 \rightarrow HCl + CH_2Cl_2$

A. In the mechanism, is CH_3Cl a catalyst, or is it an intermediate? Justify your answer.

Rate law?

* B. Identify the order of the reaction with respect to each of the following according to the mechanism. In each case, justify your answer.

(i) CH_4 1st order

(ii) Cl_2 ½ order

Rate = $k[CH_4][Cl]$

Rate = $k[CH_4][Cl_2]^{1/2}$ ← $\begin{cases} Cl_2 \leftrightarrow 2Cl \\ \frac{1}{2}Cl_2 \leftrightarrow Cl \end{cases}$

10. The rate law for a reaction is found to be Rate = $k[A]^2[B]$. Which of the following mechanism gives this rate law?

I. $A + B \leftrightarrow E$ (fast)
$E + B \rightarrow C + D$ (slow)
Rate = $k[E][B]$
$= k[A][B][B]$
$= k[A][B]^2$

II. $A + A \rightarrow E$ (fast) — not reversible
$E + B \rightarrow C + D$ (slow)
Rate = $k[E][B]$

III. $A + B \leftrightarrow E$ (fast)
$E + A \rightarrow C$ (slow)
Rate = $k[E][A]$
$= k[A][B][A]$
$= k[A]^2[B]$

Please study! **

11. The following mechanism has been proposed for the decomposition of ozone into oxygen gas. All species are in the gas phase.

so sorry about mistakes

$O_3 \leftrightarrow O_2 + O$ *fast, reversible* (k_1 *forward,* k_{-1} *reverse*)
$O_3 + O \rightarrow 2O_2$ *slow* (k_2)

A. What is the overall reaction?

$2O_3 \rightarrow 3O_2$

B. What are the reaction intermediates? O

C. Write the rate law that is consistent with this mechanism, showing how you derive it.

Rate = $k_2[O_3][O]$
$= k_2 \frac{k_1}{k_{-1}}[O_3][O_3][O_2]^{-1}$
$= k[O_3]^2[O_2]^{-1}$
↓ overall k

$O_3 \leftrightarrow O_2 + O$
Rate For = Rate Rev
$k_1[O_3] = k_{-1}[O_2][O]$
$\frac{k_1[O_3]}{k_{-1}[O_2]} = [O]$
$\frac{k_1}{k_{-1}}[O_3][O_2]^{-1} = [O]$

Replace O with all of this!

The rate is inversely proportional to $[O_2]$, so as $[O_2]$ in atmosphere increases, the rate of O_3 decomposition decreases.

over

Similar to #11 on worksheet. Try it!

112. p.619 of text

step 1 $(CH_3)_3AuPH_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (CH_3)_3Au + PH_3$ fast

step 2 $(CH_3)_3Au \xrightarrow{k_2} C_2H_6 + (CH_3)Au$ slow

step 3 $(CH_3)Au + PH_3 \xrightarrow{k_3} (CH_3)AuPH_3$ fast

A) overall $(CH_3)_3AuPH_3 \rightarrow C_2H_6 + (CH_3)AuPH_3$

B) Intermediates: $(CH_3)_3Au$, PH_3, $(CH_3)Au$

C) 1 → unimolecular
2 → unimolecular
3 → bimolecular

D) Rxn 2 (slow step)

E) Rate = $k_2[(CH_3)_3Au]$

$$\text{Rate} = \frac{k_2 k_1 [(CH_3)_3AuPH_3]}{k_{-1}[PH_3]}$$

$$\text{Rate} = k[(CH_3)_3AuPH_3][PH_3]^{-1}$$

For Step 1:
Rate F = Rate R

$$k_1[(CH_3)_3AuPH_3] = k_{-1}[(CH_3)_3Au][PH_3]$$

$$\frac{k_1[(CH_3)_3AuPH_3]}{k_{-1}[PH_3]} = [(CH_3)_3Au]$$

F) The rate is inversely proportional to $[PH_3]$, so adding PH_3 to the $(CH_3)_3AuPH_3$ solution would decrease the rate of the reaction.