VI) Reaction Mechanisms

Detailed sequence of steps that occur in producing the observed overall rx.

- what happens on a molecular level

For a rx. to occur the reacting molec. must collide

True for,

Elementary Reactions

A) Single-Step Mechamism

$$A + B \longrightarrow \text{Products}$$

A & B must collide

Double # of A or B molec. (in a given vol.) leads to twice as many A, B collisions

$\Rightarrow$ doubles rate

$$\text{rate} = k[A][B]$$

$$2A \longrightarrow \text{products}$$

$$\text{rate} = k[A][A] = k[A]^2$$

General Rule

The same numbers & kinds of molec. involved in the coll. appear in the rate eqn.

We CAN predict the rate law for elementary steps or rx's.

The rate law tells something about the species colliding

- Mechanism

1) Mechanism Must:

a) Include a process that involves the number & kind of molecules present in rate law

b) Result in an overall chem. change corresponding to the balanced chem. eqn.

2) Ex.

$$2\,HI \rightarrow H_2 + I_2$$

experimentally find:

$$\text{rate} = k\,[HI]^2$$

exponent agrees w. coeff. in eqn.

Could mean:

- 2 molec. of HI collide for rx. to occur
- Results in overall chem. rx.
- One-step mechanism
  - overall chem. eqn. represents elementary process

B) Multistep Mechanisms

Elementary steps must always add to give the chem. eqn. of the overall process.

Example

$$2\,NO + 2\,H_2 \longrightarrow N_2 + 2\,H_2O$$

rate $= k[H_2][NO]^2$ (exp.)

exponents in rate law are diff. from coef. in chemical eqn.

- rx. occurs in steps

1) First Possible Mechanism

$$NO + NO + H_2 \longrightarrow N_2 + H_2O_2 \qquad (1)$$

$$H_2O_2 + H_2 \longrightarrow 2H_2O \qquad (2)$$

$$2NO + 2H_2 \longrightarrow N_2 + 2H_2O$$

H_2O_2 does not appear in overall chem. eqn.

- Intermediate

Step (1) : includes no. & kinds of molec. appearing in rate eqn.

Rate law for overall rx. is rate law for slowest step

- products can not form faster than slowest step

2) Molecularity

no. molecules of reactant in an elementary rx.

Step (1) of previous ex. is termolecular

- 3 body rx. (collision)
- possible but NOT very probable & rarely encountered.

Unimolecular (single molecule) and bimolecular (two molec.) elementary steps are much more probable.

3) Second Possible Mechanism

All bimolecular steps:

$$2\,NO \longrightarrow N_2O_2 \qquad (1)$$
$$N_2O_2 + H_2 \longrightarrow N_2O + H_2O \qquad (2)$$
$$N_2O + H_2 \longrightarrow N_2 + H_2O \qquad (3)$$

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what is the rate-determining step (slowest step)?

step (1) is NOT rate determining step - would give

$$\text{rate} = k_1[NO]^2$$

Assume step (2) is rate det.

rate $= k_2 [N_2O_2][H_2]$

NOT allowed
- intermediate in rate eqn. that does not appear in exp. rate law

Express $[N_2O_2]$ in terms of reactants + products

a) Steady State Equilibrium Approx.

Solve for conc. of the intermediate by assuming that an equilibrium is established in the fast step which precedes the slowest step

$$2\,NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2 \qquad \text{(fast)}$$

rate of N_2O_2 formation = rate of N_2O_2 decomposition

$$k_1[NO]^2 = k_{-1}[N_2O_2]$$

Solve for $[N_2O_2]$

$$[N_2O_2] = \frac{k_1}{k_{-1}}[NO]^2$$

Substitute into rate law based on step (2):

$$\text{rate} = k_2\left(\frac{k_1}{k_{-1}}[NO]^2\right)[H_2]$$

$$= k\,[NO]^2[H_2]$$

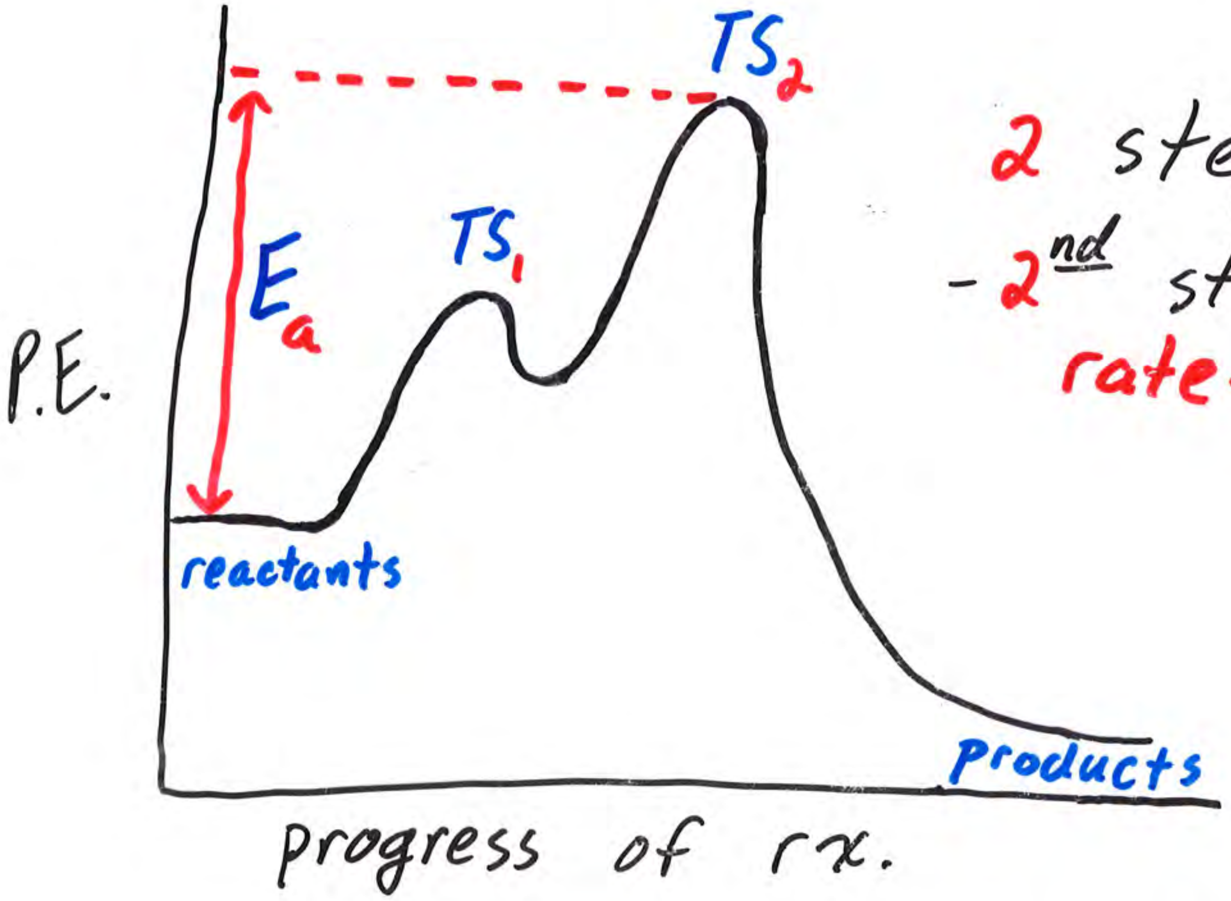
(observed rate law)

Rate law depends only on steps up to & including slowest step

Subsequent steps (fast) result in overall change corresponding to balanced chemical eqn.

3) E_a for Multistep Mechanism

Measured E_a is difference between P.E. of T.S. of the rate-det. step & P.E. of reactants



2 step mech.
- 2nd step is rate-det.

P.E. of TS$_2$ is the highest during course of rx - slowest step

VII) Catalysis

Catalyst : substance that inc. rate of rx. w/o being consumed.

A) Common Characteristics

1) Catalyst is unchanged chemically at the end of rx.

Amount is same

$$2\,KClO_3(s) \xrightarrow[\Delta]{MnO_2} 2KCl(s) + 3O_2(g)$$

Frequently changes physical form

MnO_2 may change from crystals to fine powder

2) A small amount of catalyst is often sufficient to bring about a considerable amount of rx.

- regenerated to take part again

3) A catalyst does not affect the position of equilibrium in a reversible rx.

- just inc. rate of reaching equil.

4) Catalyst can only accelerate a rx. that is already occurring

Rx. must be thermodynamically possible

$(\Delta G < 0)$

B) How a Catalyst Works

$$k = A e^{-E_a/RT}$$

A catalyst may affect rate by altering either E_a or A

Largest affect is due to lowering E_a.

A catalyst lowers the overall E_a for a chem. rx.

Catalyst usually provides a completely different pathway for rx.

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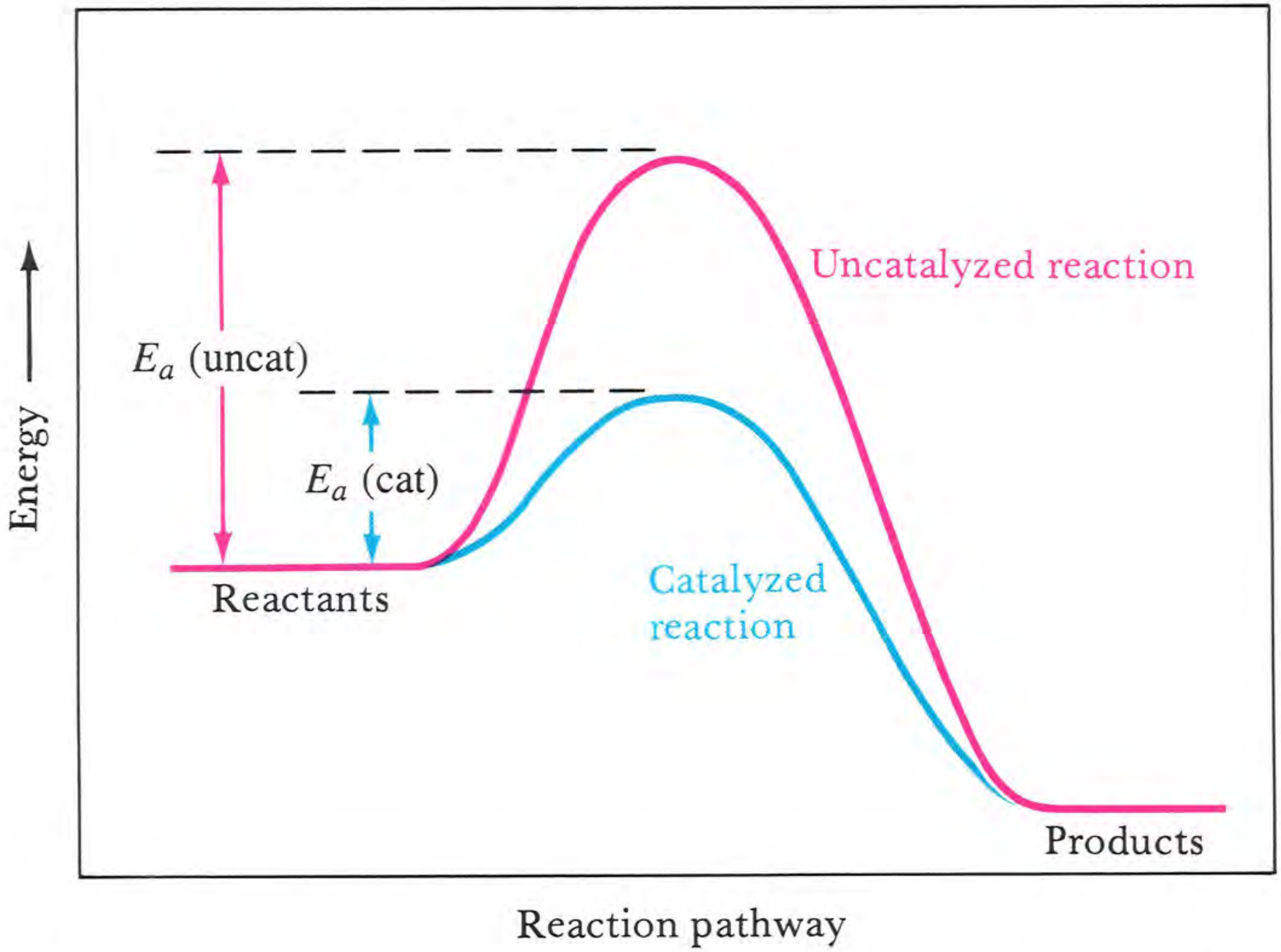
Figure 14.16 Energy profiles for a catalyzed and uncatalyzed reactions



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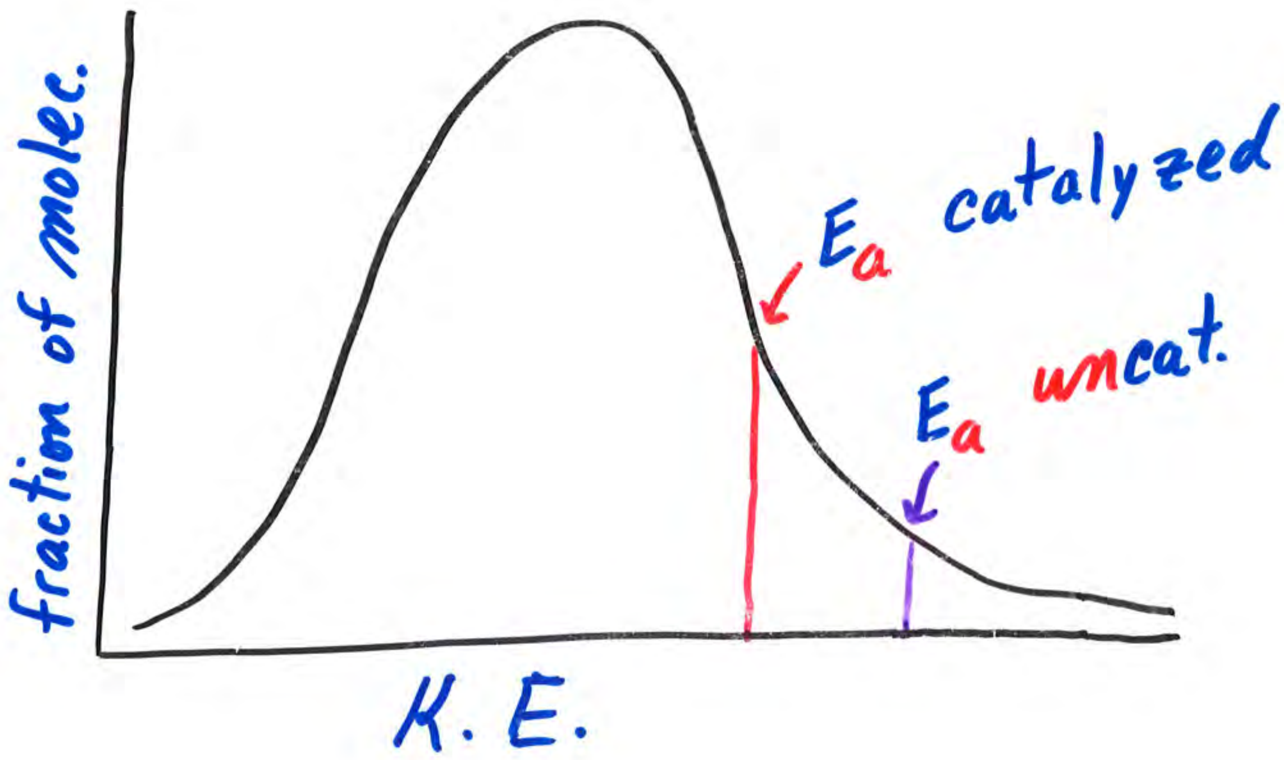
The catalyzed path will be faster because at a given temp., more molec. will have lower energy req. to form the T.S.



E_a for catalyzed rx. is often on order of 100 kJ less than uncatlyzed rx.

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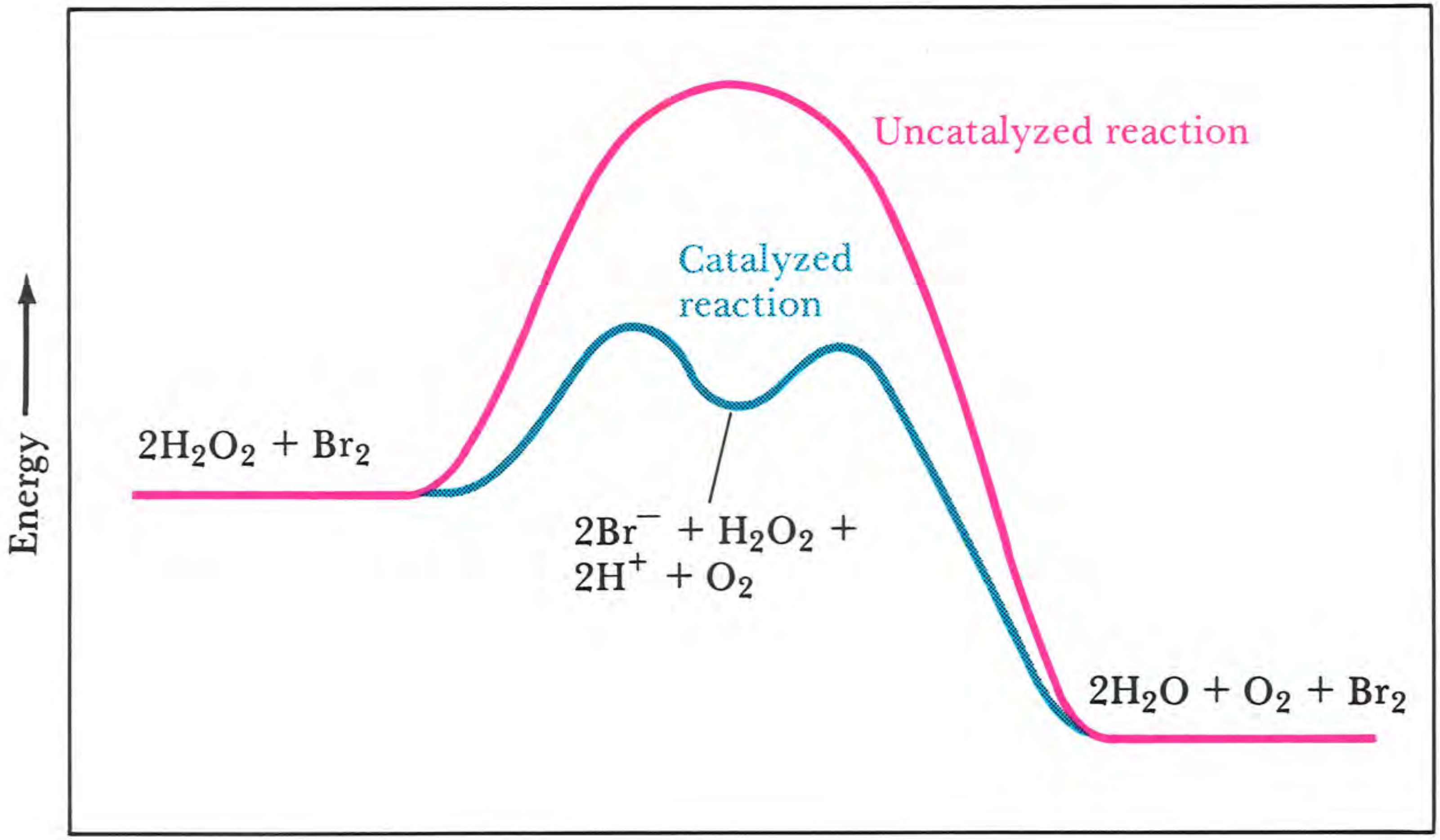
Figure 14.17 Energy profiles for catalyzed and uncatalyzed H_2O_2 decomposition



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C) Homogeneous Catalysis

Homogeneous Catalyst:

Catalyst present in same phase as the components of the rx. mixture.

1) Ex. of homogeneous gas rx.

$$2\,SO_2(g) + O_2(g) \xrightarrow{NO\,(g)} 2\;SO_3(g)$$

1 possible mech.

$$2\;NO + O_2 \rightarrow 2\;NO_2 \qquad (1)$$

$$NO_2 + SO_2 \rightarrow SO_3 + NO \qquad (2)$$

NO regenerated in step (2)

NO_2 is intermediate

D) Heterogeneous Catalysis

Heterogeneous Catalyst : exists in phase different from reactants but provides a favorable surface on which the rx. takes place.

1) Ex: gaseous reactants

$$H_2 + \frac{1}{2}O_2 \xrightarrow{Cu} H_2O$$

Mechanism

$$2\,Cu + \frac{1}{2}O_2 \longrightarrow Cu_2O$$

$$Cu_2O + H_2 \longrightarrow H_2O + 2\,Cu$$

Cu_2O : intermediate

- has been detected

Lower energy T.S. formed on surface of the solid

- Molecules are Adsorbed on the surface

Adsorption: process in which molec. adhere to surface

Physical Adsorption

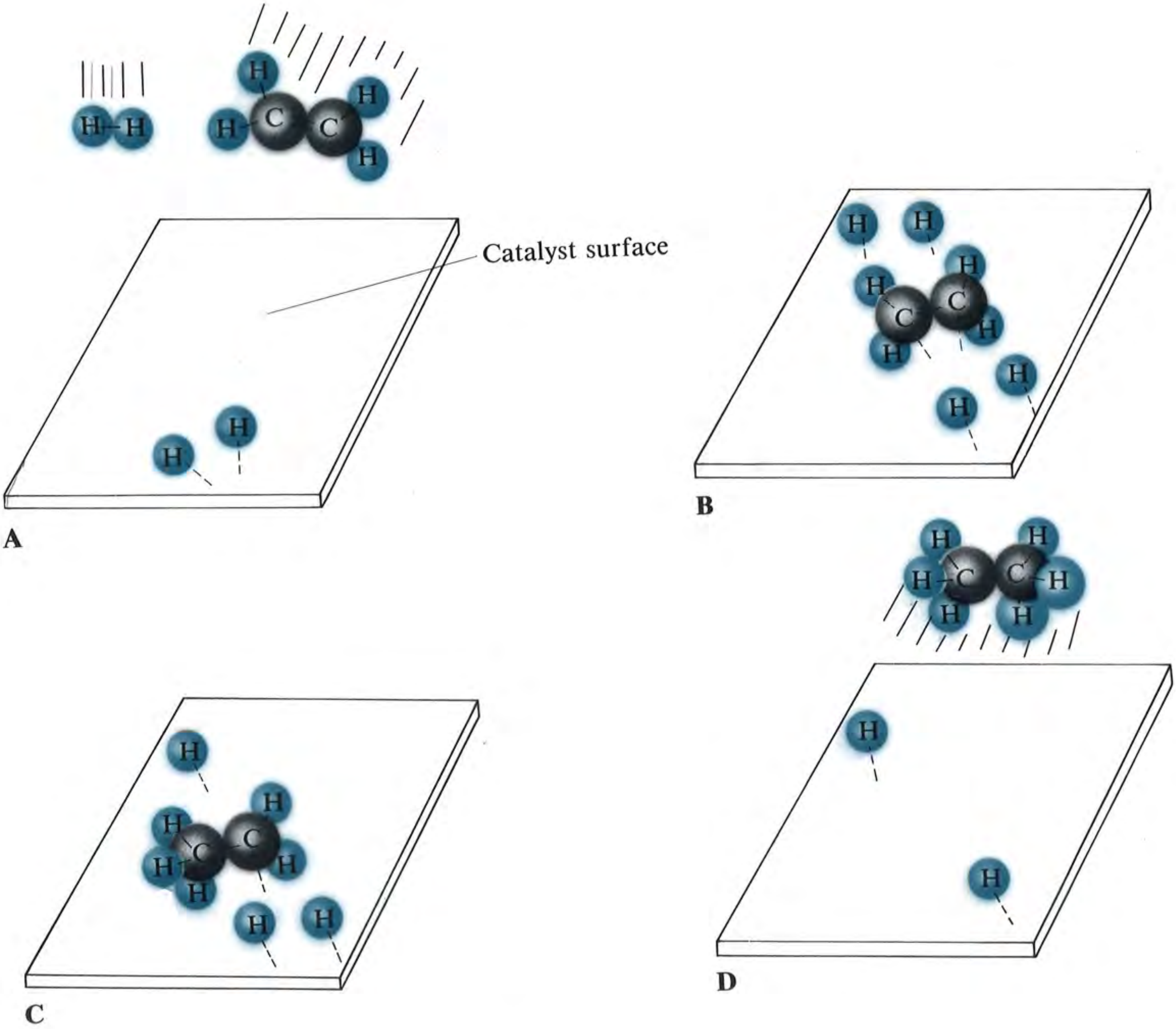
weak intermolecular forces

Chemisorption

chemical bonding forces

- relatively strong

Ebbing, GENERAL CHEMISTRY, Third Edition
Figure 14.17 Mechanism of catalytic hydrogenation of C_2H_4



Adsorption causes partial weakening of bonds in the reacting molecules.

- less energy req. to form T.S.
- results in faster rate

Anything that interferes w. adsorption will reduce effectiveness of the catalyst

- Inhibitor (Poison)

Ex: gas phase rx

$2SO_2 + O_2 \xrightarrow{Pt} 2SO_3$

Arsenic cmpds. act as inhibitors

As strongly adsorbed at active sites (places on surface where rx's take place) preventing access by reactants

For oxidation of SO_2 to SO_3

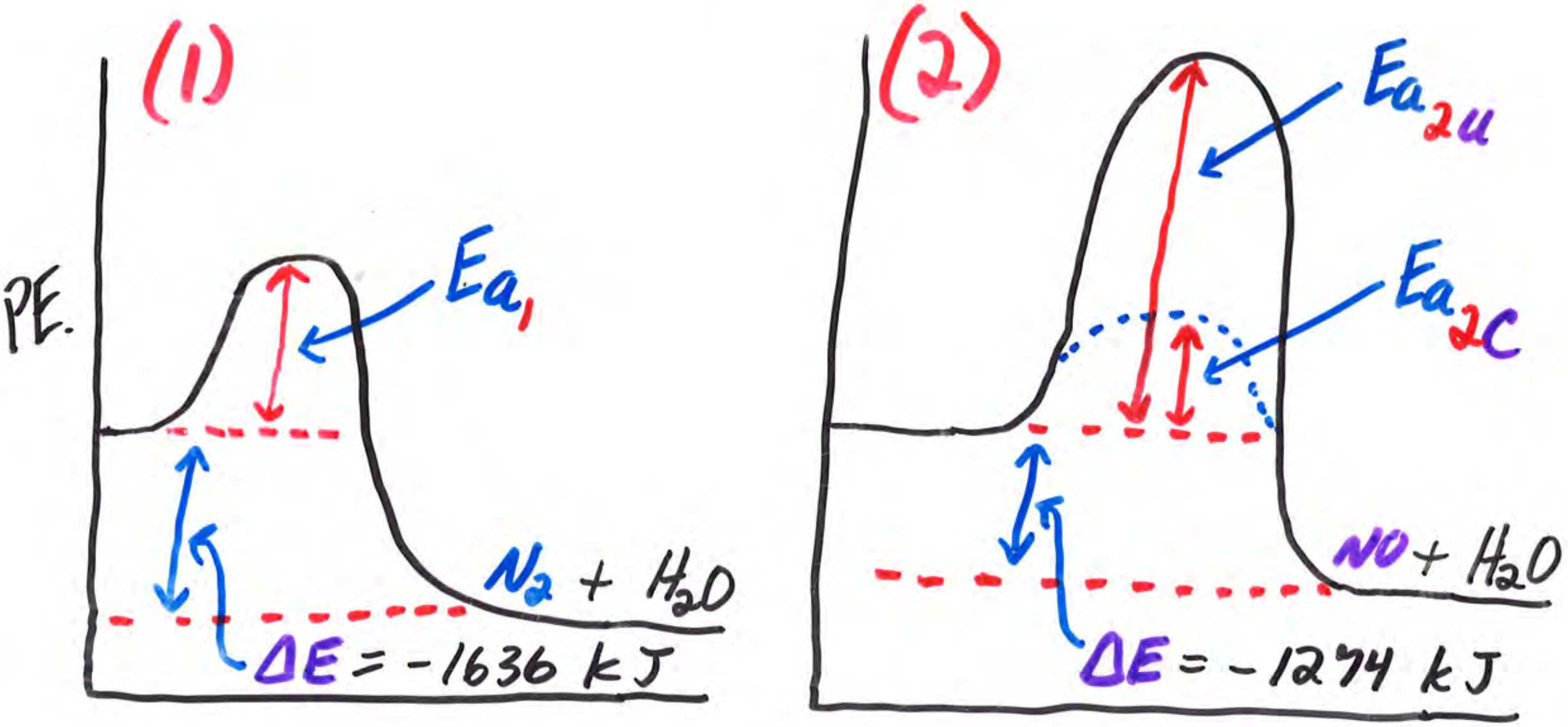
uncatal.
catal. by NO (homogeneous)
catal. by Pt (heterogeneous)

Each mech. has a diff. T.S. & a diff. E_a

E) Catalyst can "Change" Products

(1) $4\ NH_3 + 3O_2 \longrightarrow 2\ N_2 + 6\ H_2O$

(2) $4\ NH_3 + 5\ O_2 \xrightarrow[1000\,°C]{Pt} 4NO + 6\ H_2O$



$$Ea_{2c} < Ea_1 < Ea_{2u}$$

Note: Both rx's are thermodyn. possible but (2) is much slower than (1) w/o catalyst