

LECTURE 23/23

MAY-09-02

- CATALYSIS

- MODELING

CATALYSIS

CATALYST IS A SUBSTANCE THAT INCREASES THE RATE OF A REACTION AND CAN BE RECOVER CHEMICALLY UNCHANGED AT THE END OF A REACTION.

THE CATALYST PROVIDES AN ALTERNATIVE

MECHANISM THAT IS FASTER THAN A.N.

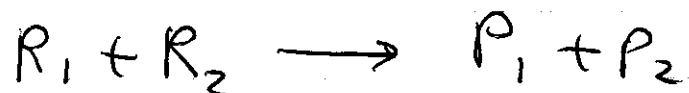
ORIGINAL MECHANISM WITHOUT A CATALYST.

IN THE ALTERNATE MECHANISM THE

CATALYST PARTICIPATES IN SOME OF THE

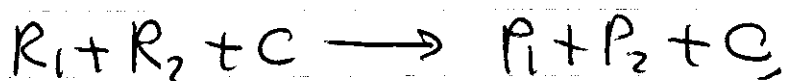
STEPS, BUT AT THE END IT HAS TO BE

REGENERATED.



THIS REACTION HAS TO BE THERMODYNAMICALLY FAVOR AND MOREOVER SPONTANEOUS THAT IS $\Delta G_{rxn}^{\circ} < 0$.

IN THE PRESENCE OF A CATALYST



WHICH MEANS THE SAME EQUILIBRIUM CONSTANT FOR BOTH MECHANISMS. IN

OTHER WORD, THE EQUILIBRIUM CONSTANT

IS INDEPENDENT OF THE CATALYZED

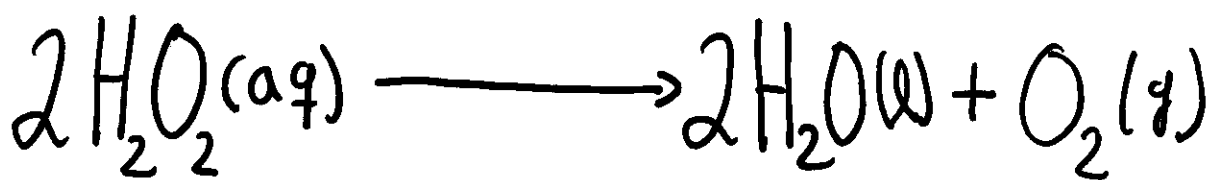
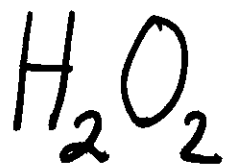
OR UNCATALYZED MECHANISM. ALSO

WE COULD SAY THAT THE CATALYST

CANNOT CHANGE THE EQUILIBRIUM POSITION,

ALSO A CATALYST FOR A FORWARD REACTION

Catalytic Decomposition



$$\Delta H_{rxn}^{\circ} = -94.66 \text{ kJ} < 0$$

$$\Delta S_{rxn}^{\circ} = 28.52 \text{ kJ} > 0$$

at 298 K

$$\Delta G_{rxn}^{\circ} = -103.15 \text{ kJ}$$

The reaction is Spontaneous
at all temperatures.

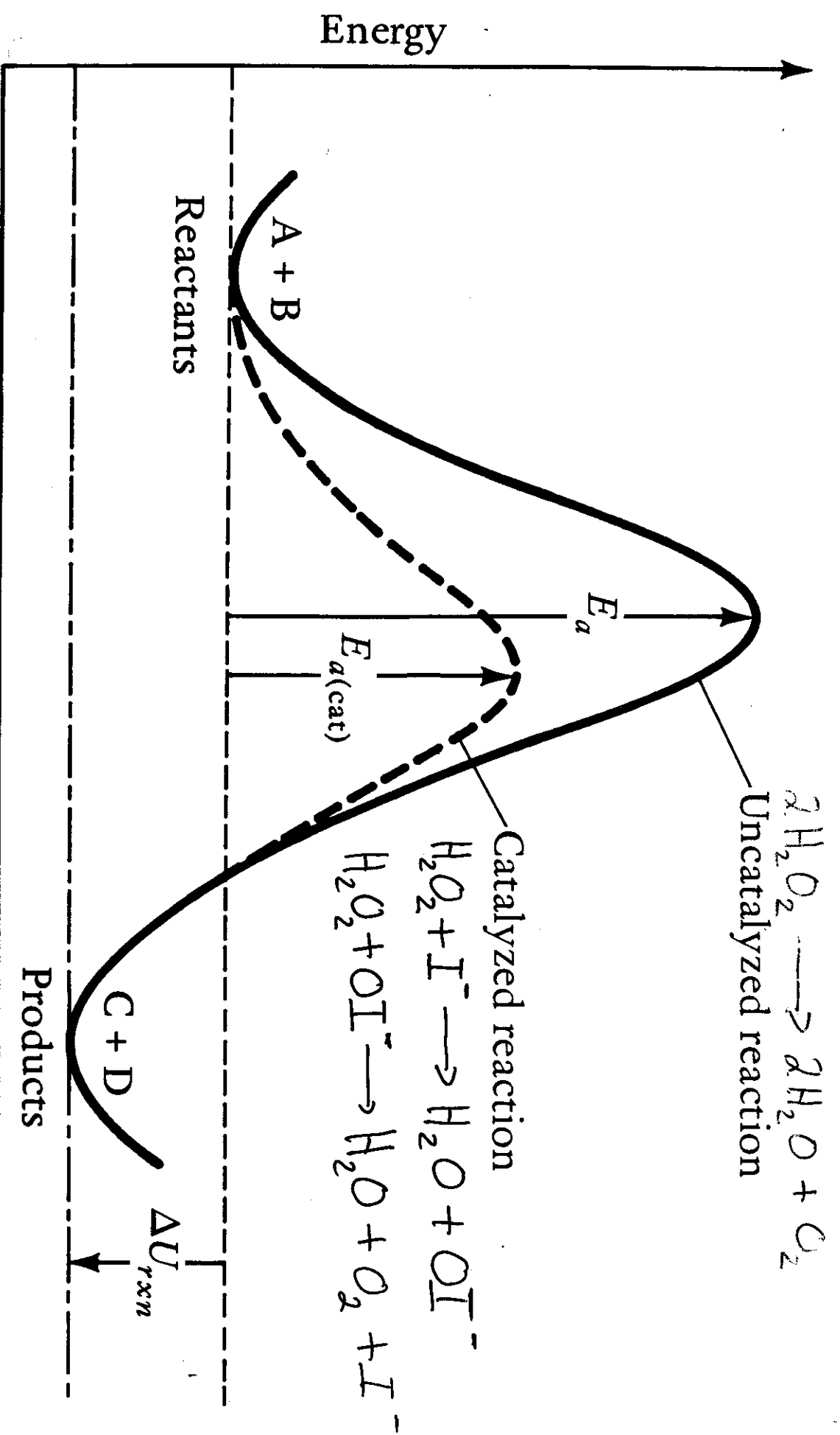


FIGURE 13-7

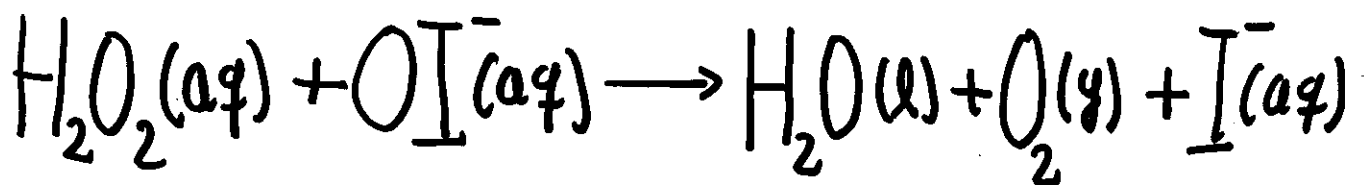
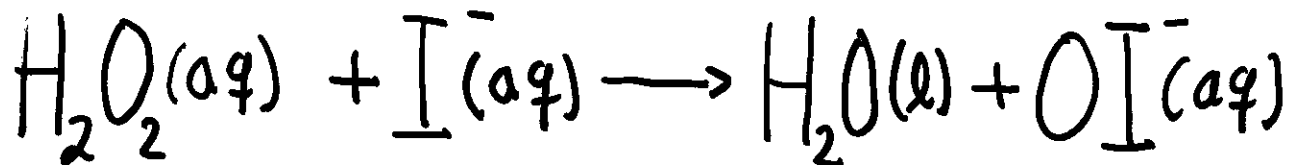
McQuarrie and Rock: GENERAL CHEMISTRY, Second Edition

© 1984, 1987 by Donald A. McQuarrie and Peter A. Rock

Activation Energy

$$E_a = 76 \text{ kJ mol}^{-1}$$

In the presence of iodide

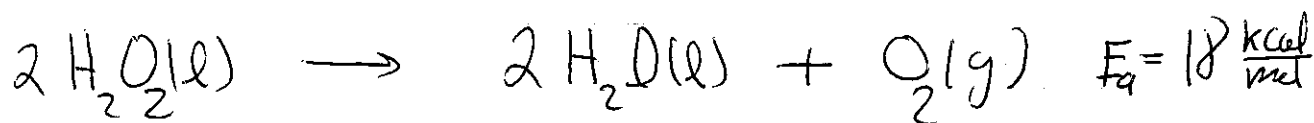


with $E'_a = 57 \text{ kJ mol}^{-1}$

$$\frac{k'}{k} = e^{\frac{E_a - E'_a}{RT}} = 2.1 \times 10^3$$

$$T = 298 \text{ K}$$

FOR THE DECOMPOSITION OF $H_2O_2(l)$



CATALYZED BY I^- $14 \frac{\text{kcal}}{\text{mol}}$

COLLOIDAL Pt PARTICLES $12 \frac{\text{kcal}}{\text{mol}}$

LIVER CATALASE

HYDROGEN

PEROXYDASE

$6 \frac{\text{kcal}}{\text{mol}}$

IF WE CONSIDER THE RATE CONSTANTS

$$\frac{k_c}{k_u} = e^{-\frac{1}{RT} [E_c - E_u]} \sim 5 \times 10^8$$

$$\Delta H_{rxn}^\circ = -94.66 \text{ kJ}$$

$$\Delta S_{rxn}^\circ = 28.52 \text{ J}$$

$$\Delta G_{rxn}^\circ = -103.15 \text{ kJ}$$

MUST BE A CATALYST FOR THE REVERSE REACTION TOO.

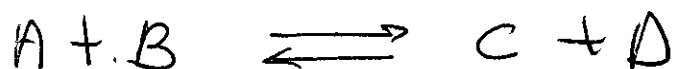
1. ENZYMES THAT CATALYZE THE HYDROLYSIS OF PROTEINS TO AMINO ACIDS MUST ALSO CATALYZE THE POLYMERIZATION OF AMINO ACIDS TO PROTEINS.

CATALYSIS IS DIVIDED IN

HOMOGENEOUS (SAME PHASE)

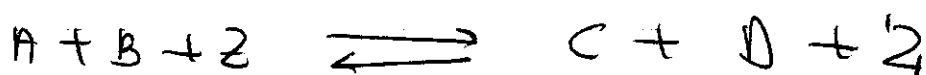
HETEROGENEOUS (DIFFERENT PHASE)

A CATALYST IS A SUBSTANCE THAT INCREASES THE RATE OF SPONTANEOUS RXN, BUT IT IS NOT CONSUMED BY THE RXN. THE CATALYST PROVIDES A DIFFERENT PATHWAY WITH A LOWER ACTIVATION ENERGY. A CATALYST DOES NOT CHANGE THE POSITION OF EQUILIBRIUM BUT SPEEDS UP BOTH THE FORWARD AND THE BACKWARD REACTION



$$K^{eq} = \frac{[C]_{eq} [D]_{eq}}{[A]_{eq} [B]_{eq}}$$

IN THE PRESENCE OF A CATALYST



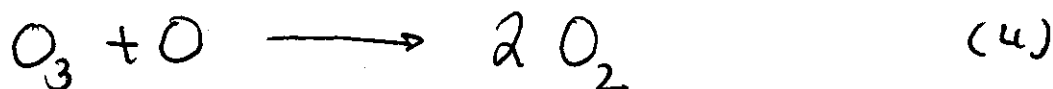
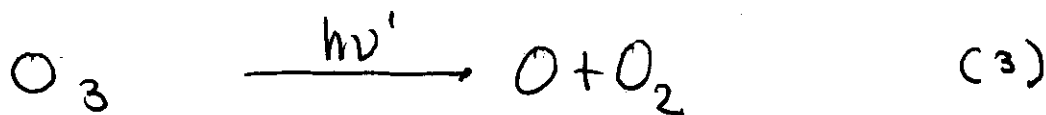
$$K^{eq} = \frac{[C]_{eq} [D]_{eq}}{[A]_{eq} [B]_{eq}}$$

SAME EQUILIBRIUM CONSTANT
 \Rightarrow SAME ΔG°_{rxn}

OTHER IMPORTANT PROCESSES ARE
AUTOCATALYSIS AND INHIBITION. IN
AUTOCATALYSIS THE PRODUCT SPEEDS
UP THE REACTION. AN INHIBITOR IS
A REAGENT THAT DECREASES THE RATE
OF THE REACTION WHEN ADDED IN
SMALL QUANTITIES.

NO_x AND ClO_x

NITROGEN OXIDES LIKE NO OR NO₂ ARE FORMED BY COMBUSTION. FOR EXAMPLE SUPERSONIC AIRPLANES (CONCORD) GENERATES NO_x WHEN FLYING IN THE STRATOSPHERE (10 - 50 km ALTITUDE). AT THIS ALTITUDE WE OBSERVE THE FOLLOWING REACTIONS

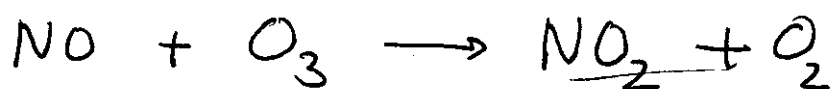


FOR THIS MECHANISM $E_{a2} = 24 \text{ kcal/mol}$,

$E_{a4} = 93 \text{ kcal/mol}$, $\lambda' \approx 290 \text{ nm}$, AND

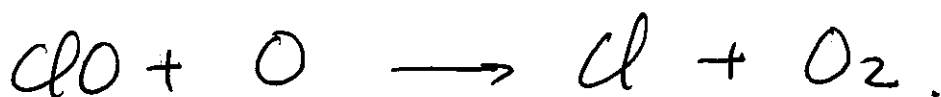
$[O_3]$ IS IN STEADY STATE.

ABOUT 100 km THE GAS PRESSURE IS ABOUT 10^{-4} torr AND DIFFUSION IS NOT AN IMPORTANT TRANSPORT PROCESS, BUT THE PRESENCE OF NO_x YIELD THE FOLLOWING RXN



THUS NO_x IS A CATALYST FOR THE DECOMPOSITION OF OZONE, WHICH IMPLIES AN INCREASE OF UV REACHING US, AND INCREASING THE INCIDENCE OF SKIN CANCER.

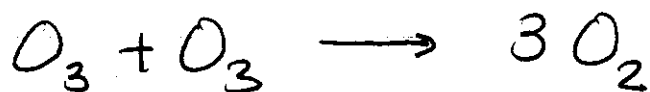
ALSO ClO_x WORK AS CATALYST



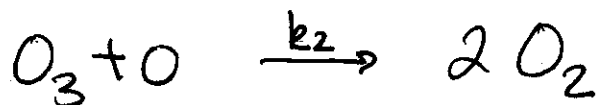
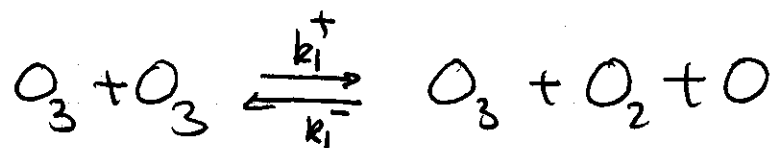
CHLOROFLUOROCARBONS (CFCl_3 AND CF_2Cl_2) ARE POTENTIAL SOURCES OF Cl , AND HAVE BEEN USED AS PROPELLANTS FOR AEROSOL SPRAYS. THIS COMPOUNDS, WHEN RELEASED, DIFFUSE TO THE STRATOSPHERE (ACCOUNTS OF CHEM.

RESEARCH 3, 9 (1970)) AND GENERATE Cl ATOMS BY ABSORBING UV LIGHT. IN 1978 CHLOROFLUOROCARBONS WERE BANNED AS AEROSOL PROPELLANTS.

OVER ALL RXN



MECHANISM



$$r = \frac{1}{3} \frac{d[O_2]}{dt} = -\frac{1}{2} \frac{d[O_3]}{dt}$$

$$\frac{d[O]}{dt} \approx 0 = k_1^+ [O_3]^2 - k_1^- [O_3][O_2][O] - k_2 [O_3][O]$$

$$[O]_{ss} = \frac{k_1^+ [O_3]}{k_2 + k_1^- [O_2]}$$

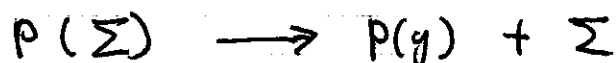
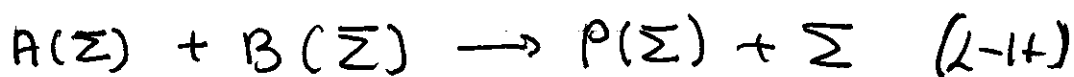
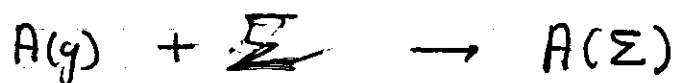
$$\begin{aligned} \frac{d[O_2]}{dt} &= k_1^+ [O_3]^2 - k_1^- [O_3][O][O_2] + 2 k_2 [O_3][O] \\ &= k_2 [O_3][O] + 2 k_2 [O_3][O] = 3 [O_3][O] k_2 \\ &= 3 k_2 [O_3][O] \end{aligned}$$

$$r = \frac{k_2 k_1^+ [O_3]^2}{k_2 + k_1^- [O_2]} = -\frac{1}{2} \frac{d[O_3]}{dt}$$

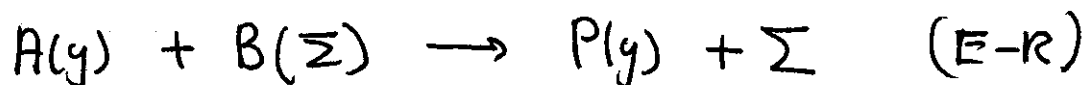
HETEROGENEOUS CATALYSIS

A SURFACE (TRANSITION METAL) HAS ACTIVE SITES WHERE REACTANTS EITHER PHYSISORBED (MOBILE) OR CHEMISORBED (STATIC).

CONSIDER THE FOLLOWING MECHANISM



OR



L-H LANGMUIR-HINSHELWOOD

E-R ELEY-RIDEAL