

2nd ORDER REACTIONS



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

OR



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

INTEGRATED
RATE EXPRESSION

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

HALF LIFE

$$t_{1/2} = \frac{1}{k[A]_0}$$

EXAMPLE

THE REACTION $2A \rightarrow B$ IS 2nd ORDER WITH

$$k = 51 \text{ M}^{-1} \text{ min}^{-1} \text{ AND } [A]_0 = 0.0092 \text{ M}$$

1) GET HALFLIFE

2) HOW LONG TO GET $[A]_t = 0.0037 \text{ M}$

$$1) t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{51 \text{ M}^{-1} \text{ min}^{-1} \times 0.0092 \text{ M}} = \frac{1}{0.469 \text{ min}^{-1}} = 2.1 \text{ min}$$

2) .0037M IS MORE THAN 1 HALFLIFE BUT LESS THAN 2
ESTIMATE ABOUT 3.0 MIN

$$\frac{1}{\Delta[A]_t} = kt + \frac{1}{[A]_0}$$

$$\frac{1}{\Delta[A]_t} = \frac{1}{.0037 \text{ M}} = 270 \text{ M}^{-1}$$

$$\frac{1}{[A]_0} = \frac{1}{.0092} = 109 \text{ M}^{-1}$$

$$270 \text{ M}^{-1} = 51 \text{ M}^{-1} \text{ min}^{-1} t + 109 \text{ M}^{-1}$$

$$161 \text{ M}^{-1} = 51 \text{ M}^{-1} \text{ min}^{-1} t$$

$$\frac{161 \text{ M}^{-1}}{51 \text{ M}^{-1} \text{ min}^{-1}} = 3.2 \text{ MIN}$$

ZERO ORDER REACTIONS

RATE IS INDEPENDENT OF $[X]$

$$\text{RATE} = k[A]^0 = k$$

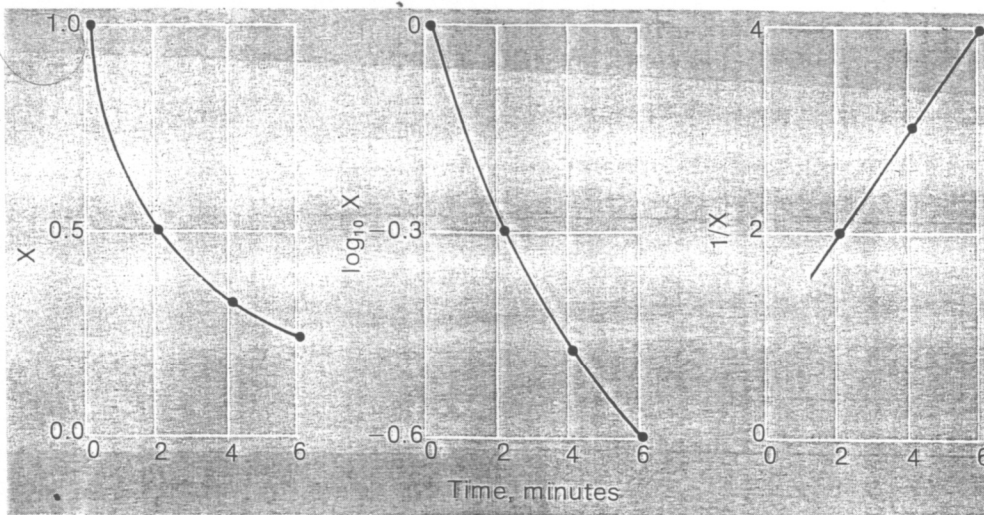
$$\text{INTEGRATED } [X]_0 - [X]_t = kt \quad t_{1/2} = \frac{[X]_0}{2k}$$

SUMMARY

ORDER	RATE LAW	CONCENTRATION-TIME EQUATION	$t_{1/2}$	LINEAR PLOT
0	RATE = k	$[X]_0 - [X]_t = kt$	$\frac{[X]_0}{2k}$	X vs t
1	RATE = $k[X]$	$\ln\left(\frac{[X]_t}{[X]_0}\right) = -kt$	$\frac{0.693}{k}$	$\ln[X]$ vs t
2	RATE = $k[X]^2$	$\frac{1}{[X]_t} = kt + \frac{1}{[X]_0}$	$\frac{1}{k[X]_0}$	$\frac{1}{[X]_t}$ vs t

DETERMINE THE ORDER OF A REACTION GRAPHICALLY
 USING THIS DATA: GET THESE PLOTS

(MIN)	time	$[X]$
	0	1.00
	2	0.50
	4	0.33
	6	0.25



t	X	$\log_{10} X$	$1/X$
0	1.00	0.00	1.0
2	0.50	-0.30	2.0
4	0.33	-0.48	3.0
6	0.25	-0.60	4.0

TEMPERATURE AND RATE

REACTIONS OFTEN GO MUCH FASTER AT HIGHER TEMP
A RULE OF THUMB IS THAT THE RATE DOUBLES FOR
A 10°C INCREASE

COLLISION THEORY

WE USE COLLISION THEORY TO EXPLAIN THE RATE
DEPENDENCE ON TEMPERATURE

FOR A REACTION TO OCCUR, ATOMS MUST COLLIDE
WITH AN ENERGY GREATER THAN SOME MINIMUM VALUE
AND WITH THE PROPER ORIENTATION.

THE REQUIRED MINIMUM ENERGY IS CALLED
ACTIVATION ENERGY E_a

COLLISION THEORY SAYS THAT THE RATE DEPENDS ON:

- ① COLLISION FREQUENCY - SLIGHTLY INCREASED AT HIGHER T
- ② PROPER ORIENTATION - UNAFFECTED BY T
- ③ ACTIVATION ENERGY - STRONGLY TEMP DEPENDENT

THE FRACTION OF COLLISIONS WITH ENOUGH ENERGY IS:

$$f = e^{-\frac{E_a}{RT}}$$

where:

f = fraction of collisions
with enough energy

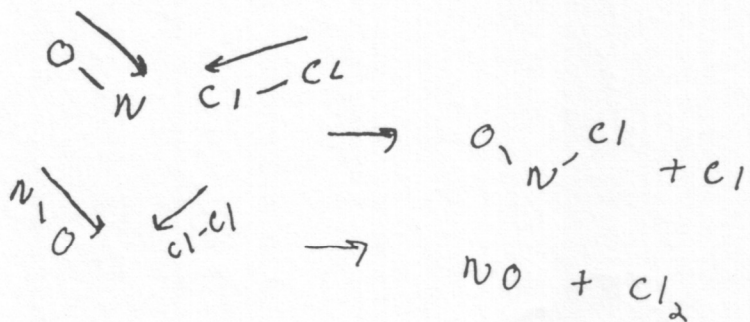
e = 2.718 BASE OF
NATURAL LOGARITHMS

E_a = ACTIVATION ENERGY

T = TEMPERATURE

R = GAS CONSTANT

ORIENTATION DEPENDENCE

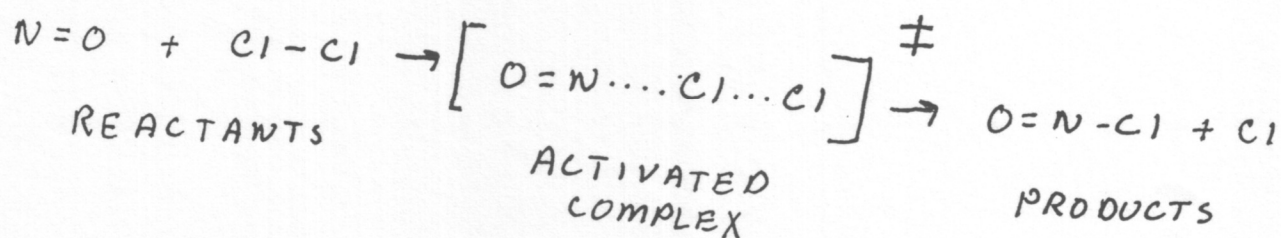


$$f = e^{-\frac{E_a}{RT}}$$

SO REACTIONS WITH LARGER E_a
GO SLOW
REACTIONS WITH SMALLER E_a
GO FAST

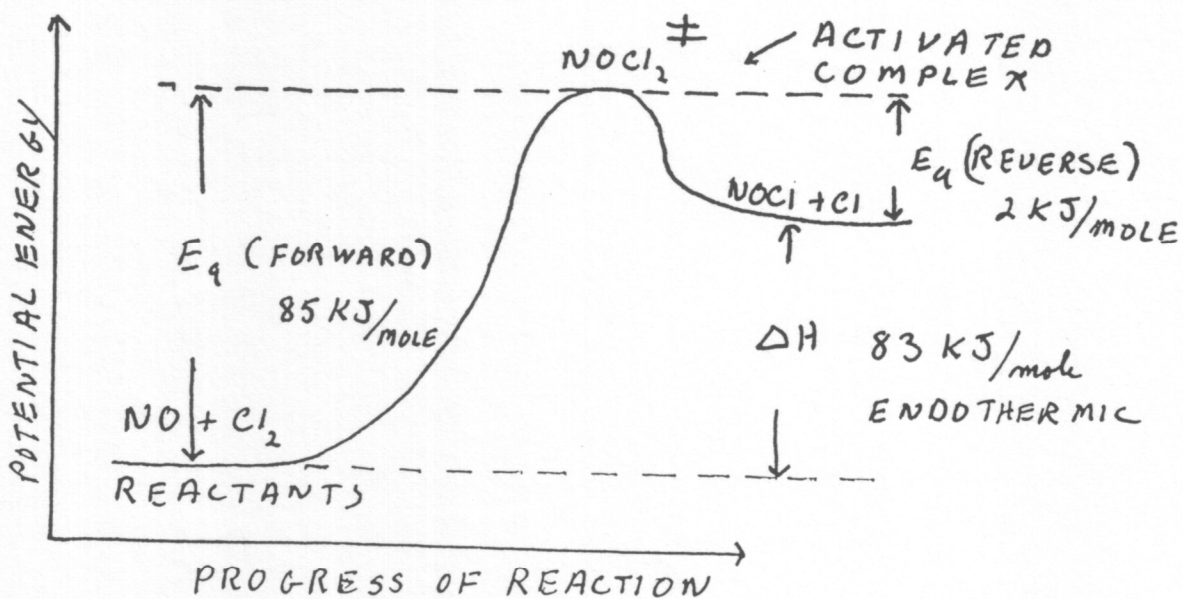
TRANSITION STATE THEORY EXPLAINS THE REACTION RESULTING FROM THE COLLISION OF TWO MOLECULES IN TERMS OF AN ACTIVATED COMPLEX

WHICH IS AN UNSTABLE GROUPING OF ATOMS THAT CAN BREAK UP TO FORM PRODUCTS.

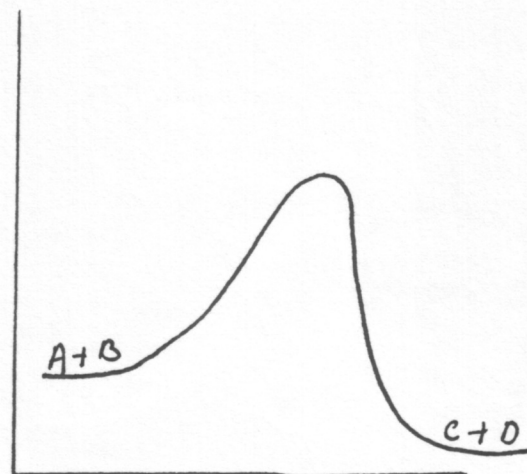
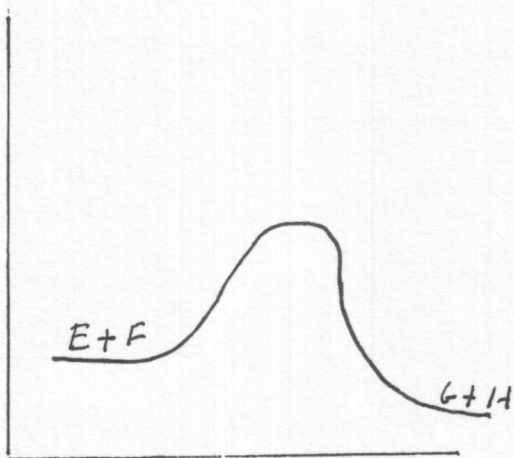
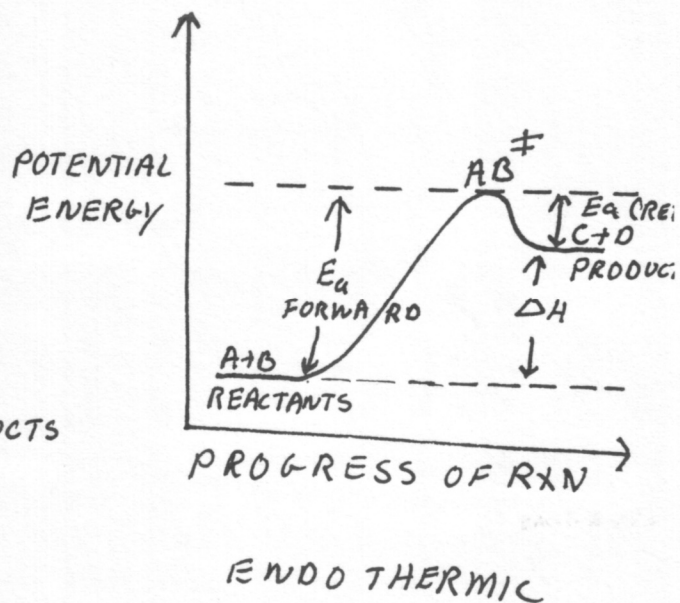
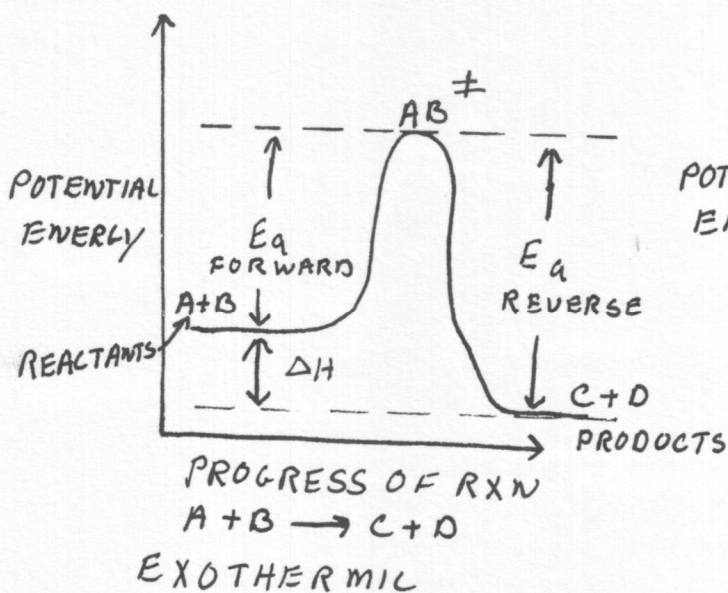


POTENTIAL ENERGY DIAGRAMS

A GRAPH OF POTENTIAL ENERGY VS PROGRESS OF REACTION



MORE POTENTIAL ENERGY DIAGRAMS



- ① WHICH REACTION HAS A HIGHER E_a FOR THE FORWARD RXN?
- ② WHICH HAS A HIGHER E_a FOR THE REVERSE RXN?
- ③ ARE THESE REACTIONS ENDOTHERMIC OR EXOTHERMIC?
- ④ WHICH REACTION WILL HAVE THE LARGER RATE CONSTANT IF ALL OTHER FACTORS (TEMP, CONC, ORIENTATION) ARE THE SAME?

TEMPERATURE AND ACTIVATION ENERGY

THE ARRHENIUS EQUATION GIVES THE DEPENDENCE OF RATE CONSTANT ON TEMPERATURE

GIVEN 2 TEMPERATURES AND 2 RATES

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{T_1 - T_2}{T_1 T_2} \right)$$

GIVEN $k_1 = 4.68 \times 10^{-2} \text{ s}^{-1}$ AT $T_1 = 298 \text{ K}$ AND $E_a = 33.1 \frac{\text{KJ}}{\text{MOL}}$

WHAT IS k_2 AT 375 K ?

SOLVING

$$\ln \frac{4.68 \times 10^{-2} \text{ s}^{-1}}{k_2} = \frac{33.1 \times 10^3 \text{ J/mol}}{8.314 \text{ J/K}\cdot\text{mol}} \left(\frac{298 \text{ K} - 375 \text{ K}}{298 \text{ K} \times 375 \text{ K}} \right)$$

$$= -2.74$$

$$\frac{4.68 \times 10^{-2} \text{ s}^{-1}}{k_2} = e^{-2.74} = 0.0646$$

$$k_2 = 0.724 \text{ s}^{-1}$$

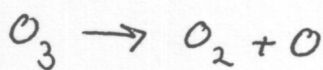
MOLECULARITY IS THE NUMBER OF MOLECULES ON THE REACTANT SIDE OF AN ELEMENTARY REACTION

UNIMOLECULAR - ONE REACTANT MOLECULE
(DECOMPOSITIONS)

BIMOLECULAR - TWO REACTANT MOLECULES
(MOST COMMON)

TERMOLECULAR - THREE REACTANT MOLECULES
(RARE)

UNIMOLECULAR: DECOMPOSITION OF OZONE



(DO PROBLEM 13.64)

BIMOLECULAR $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$

RATE EQUATIONS FOR ELEMENTARY REACTIONS

THE OVERALL RATE EQUATION MUST BE DETERMINED EXPERIMENTALLY

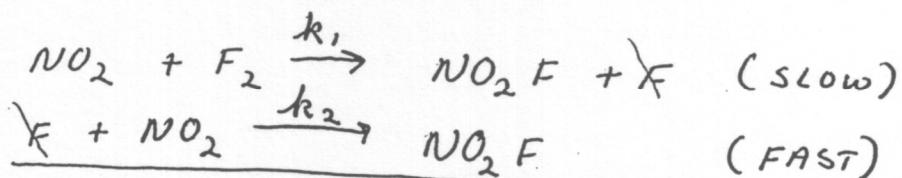
IN CONTRAST, AN ELEMENTARY REACTION GIVES A RATE EQUATION DIRECTLY. THAT IS, THE RATE OF AN ELEMENTARY REACTION IS PROPORTIONAL TO THE PRODUCT OF THE CONCENTRATIONS OF EACH REACTANT

SO, FOR THE REACTION $A \rightarrow B + C$ RATE = $k[A]$

OR, FOR THE REACTION $A + B \rightarrow C$ RATE = $k[A][B]$

ANY REACTION YOU OBSERVE IS LIKELY TO CONSIST OF SEVERAL ELEMENTARY STEPS, AND THE RATE LAW THAT YOU FIND IS THE COMBINED RESULT OF THESE STEPS. THIS IS WHY YOU CANNOT PREDICT THE RATE LAW BY LOOKING ONLY AT THE OVERALL REACTION.

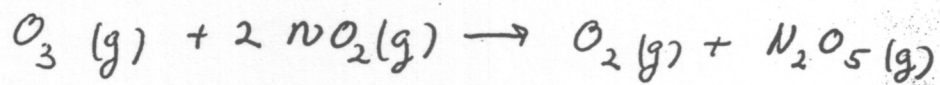
EXAMPLE OF A RATE DETERMINING STEP



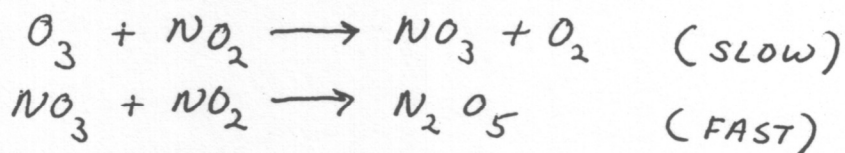
ADDING $2\text{NO}_2 + \text{F}_2 \longrightarrow 2\text{NO}_2\text{F}$ F IS AN INTERMEDIATE
THE OVERALL RATE IS DOMINATED BY k_1

(DO PROBLEM 13.69)

ANOTHER EXAMPLE

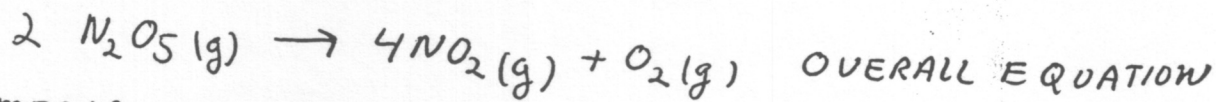


THE PROPOSED MECHANISM IS:

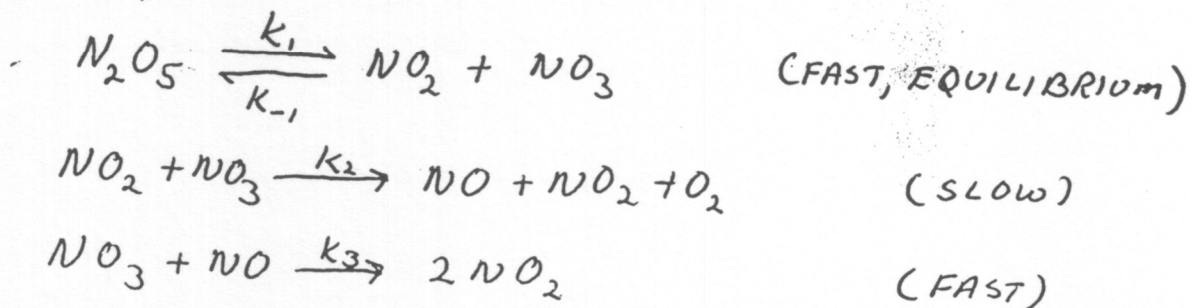


WHAT IS THE RATE LAW PREDICTED BY THIS MECHANISM?

REACTIONS WITH AN INITIAL, FAST STEP



PROPOSED MECHANISM

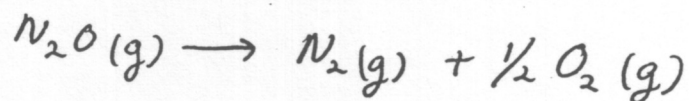


NOTE THAT NO_3 AND NO ARE INTERMEDIATES

CATALYSIS

A CATALYST IS A SUBSTANCE THAT SPEEDS UP A REACTION WITHOUT BEING CONSUMED BY IT

FOR EXAMPLE, THE REACTION OF N_2O

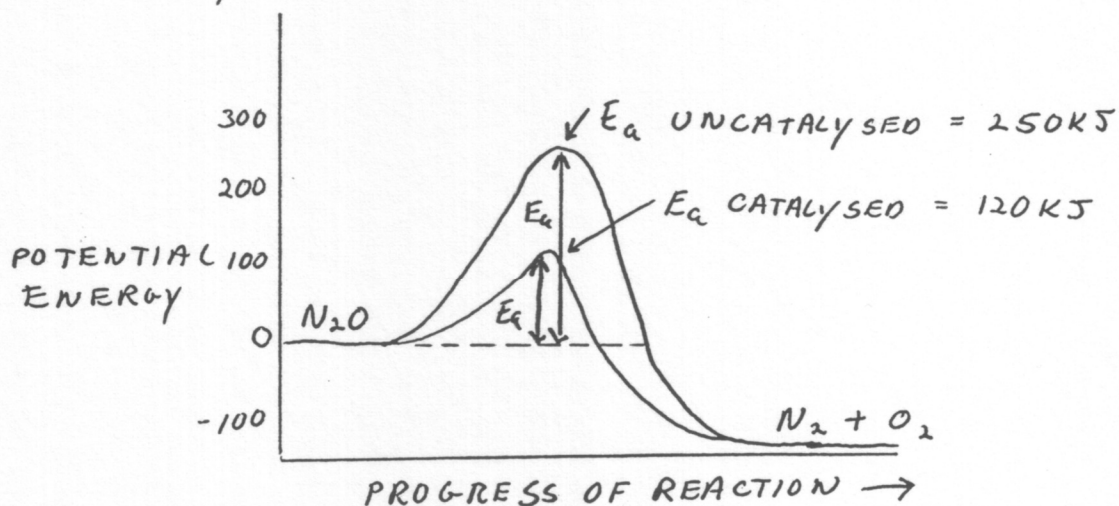


E_a FOR THE REACTION IS 250 KJ

BUT WHEN THE REACTION IS DONE ON A GOLD (Au) SURFACE

E_a FOR THE CATALYZED REACTION IS 120 KJ

THE CATALYST PROVIDES AN ALTERNATIVE PATHWAY OF LOWER ENERGY.



IN THIS REACTION, THE N_2O FORMS A BOND TO THE GOLD SURFACE THIS IS CALLED CHEMISORPTION. THIS WEAKENS THE BOND BETWEEN N AND O, MAKING IT EASIER FOR THE N_2O MOLECULE TO BREAK APART.

SOME IMPORTANT POINTS ABOUT CATALYSIS

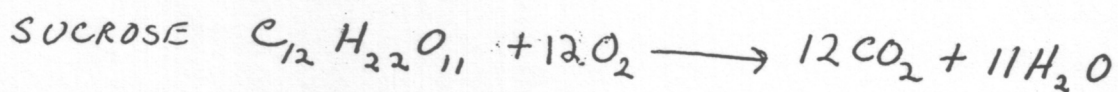
- 1) A CATALYST DOES NOT AFFECT THE RELATIVE ENERGY OF PRODUCTS AND REACTANTS
- 2) A CATALYST DOES NOT INCREASE OR DECREASE THE YIELD OF PRODUCTS
- 3) A CATALYST SIMPLY ALLOWS THE REACTION TO PROCEED FASTER

OUTSTANDING EXAMPLES OF CATALYSIS

IN PETROLEUM CHEMISTRY "CRACKING" AND "REFORMING" CATALYSTS ARE USED TO MAKE FUELS AND SYNTHESIS CHEMICALS FOR PLASTICS AND OTHER POLYMERS

ENZYME CATALYSIS

BIOLOGICAL SYSTEMS EMPLOY ENZYMES AS CATALYSTS FOR EXAMPLE

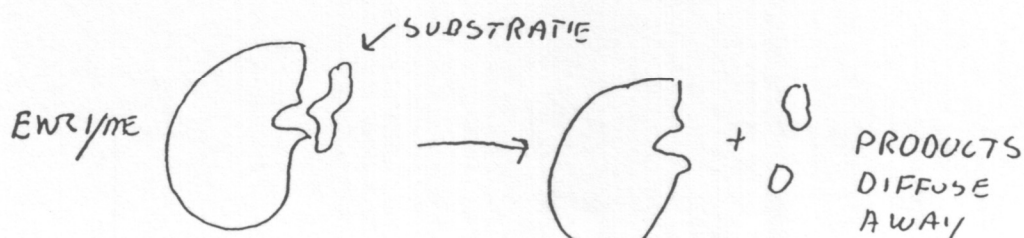


THIS REACTION DOESN'T HAPPEN DIRECTLY
INSTEAD, A SERIES OF ENZYME CATALYSED REACTIONS

ENZYMES ARE LARGE PROTEINS MW 10,000 TO 10,000,000

THEY ARE FLEXIBLE AND OFTEN CONTAIN AN ACTIVESITE TO WHICH

A SUBSTRATE CAN BIND



MANY PHARMACEUTICALS
BIND TO ACTIVESITE
AND PREVENT REACTION