

## VII CATALYSIS (~~Sec. 14.9~~) 8. Ed. Sec. 13.9 9. Ed.

Catalyst - substance that increases the rate of a rx. without being consumed.

Previously have seen that increasing  $T$ , or increasing concn of a reactant can speed up a rx.

Two other ways would be:-

- (i) Lower the barrier, i.e reduce  $E_a$
- (ii) Improve collision efficiency by improving orientation of molecules.

A catalyst can do this, e.g. by providing an alternative rx. path, helping to break bonds, providing a correct steric orientation, etc.

May also have a "concentrating" effect  
(i.e. inc. freq. factor)

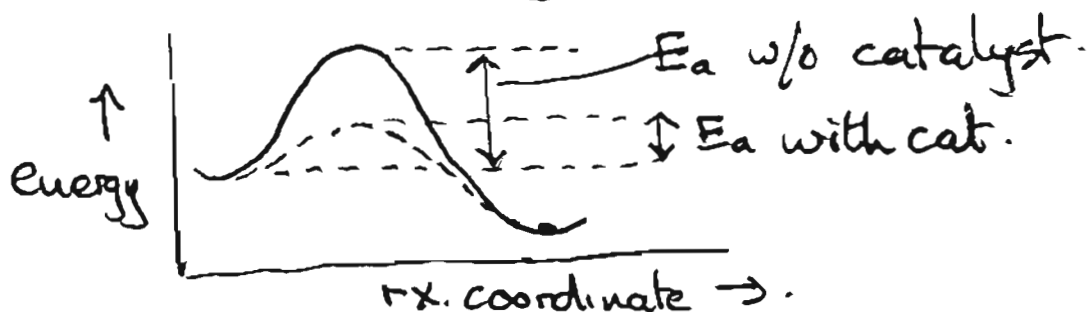
## 2 kinds of catalysts

Homogeneous:  
- same phase  
as rx. mixture

Heterogeneous  
- different phase  
from rx. mixture.

### HOMOGENEOUS CATALYSIS

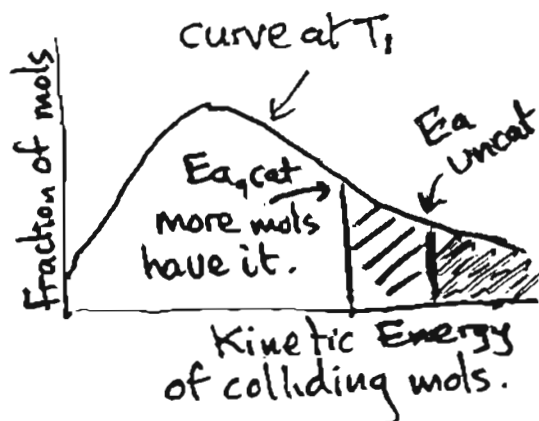
e.g.  $\text{H}_2\text{O}_2$  decomposition to  $\text{O}_2$  and  $\text{H}_2\text{O}$  is slow ( $E_a \approx 76 \text{ kJ mol}^{-1}$ ). Adding a little  $\text{I}_2$  catalyses the rx. by lowering the activation energy to  $\approx 57 \text{ kJ mol}^{-1}$ .



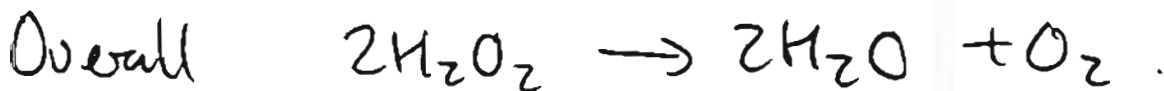
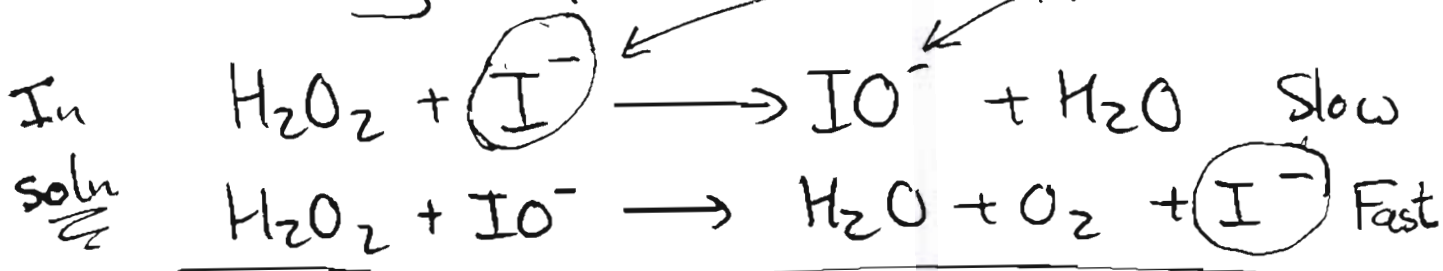
Note Barrier is lowered, so reverse rx. can also occur. Hence cat. speeds both forward & reverse rx.  $\therefore$  reach equilib. faster.

N.B. Position of equilib. }  
still the same.

(215)



Elementary steps are: <sup>catalyst</sup> <sup>intermediate</sup>



$(\text{I}^-)$  and is unchanged.  
Catalyst  $\text{I}^-$  does not appear in overall rxn

Another example

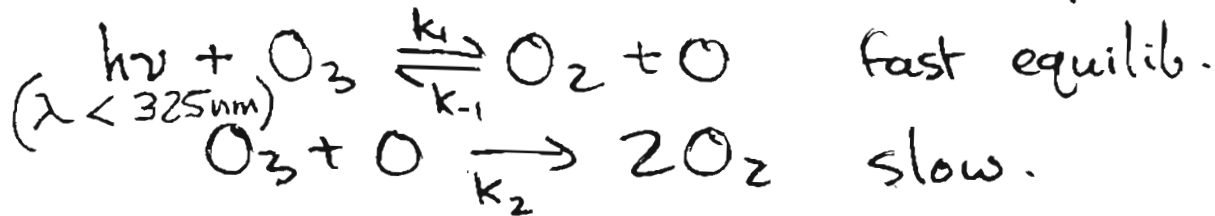


Catalysed by NO, OH, H, Br, Cl radicals (CFCs)  
(much of the Cl comes from chlorofluorocarbons,  $\wedge$ )  
e.g.  $\text{CF}_2\text{Cl}_2$ ,  $\text{CFCl}_3$ , etc

$\text{O}_3$  in the stratosphere absorbs harmful uv  $\left( \text{O}_3 \xrightarrow[240-310\text{nm}]{h\nu} \text{O}_2 + \text{O} \right)$

- spares animals, plant life, etc. from being zapped. The problem, however, is that the above radicals hasten decomposition of  $\text{O}_3$

## Non catalysed mechanism: (Chapman mech.)



$$\text{Rate} = k_2 [\text{O}_3][\text{O}] \quad \text{must get rid of intermediate O}$$

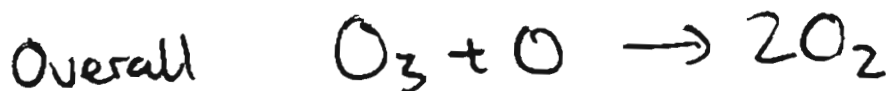
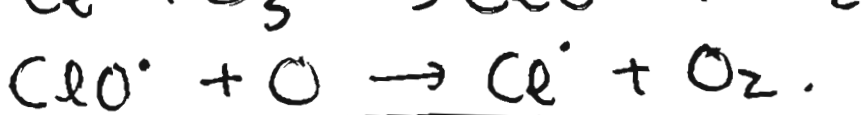
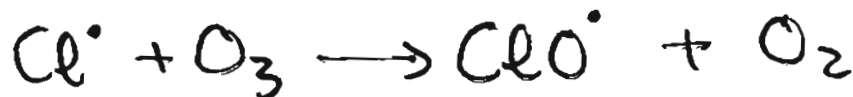
$$K = \frac{[\text{O}_2][\text{O}]}{[\text{O}_3]} \quad \text{from 1st equan.}$$

$$[\text{O}] = \frac{K[\text{O}_3]}{[\text{O}_2]}$$

$$\therefore \text{Rate} = k_2 K \frac{[\text{O}_3]^2}{[\text{O}_2]} \quad \left( \begin{array}{l} \text{observed} \\ \text{rate} = k_{\text{obs}} \frac{[\text{O}_3]^2}{[\text{O}_2]} \end{array} \right)$$

## Catalysed mech

Cl<sup>•</sup> from CFC's catalyses the 2<sup>nd</sup> step.



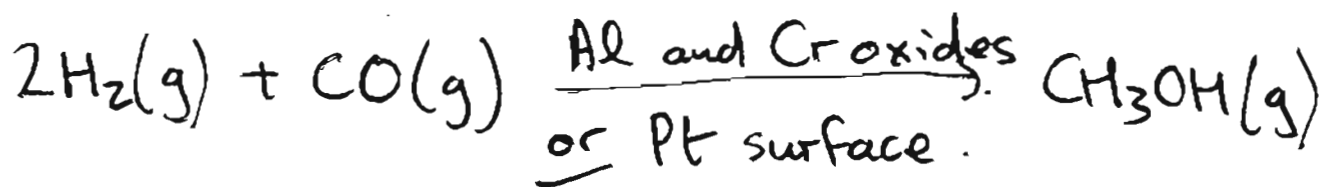
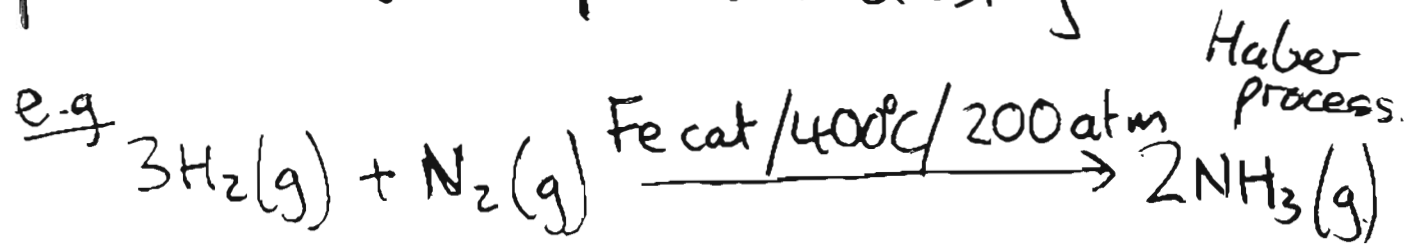
(See Fig. 14.17 for Ea's) 13.17 9. Ed.

and the naughty Cl<sup>•</sup> does it again, & again.....

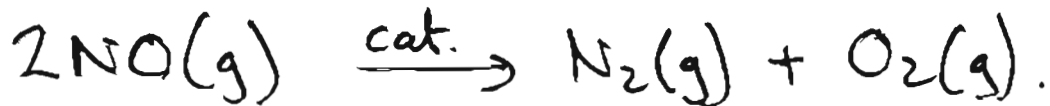
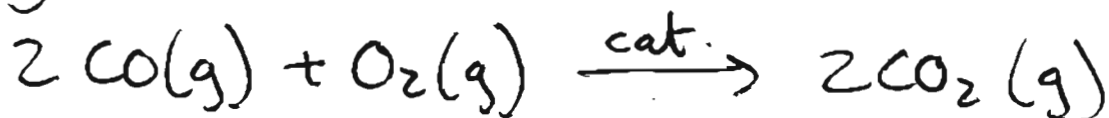
In this case the catalyst provides a different (217) mechanism. THE CATALYST emerges UNCHANGED. True in all cases.

## HETEROGENEOUS CATALYSIS

Cat. and reactants in different phases. V. imp. in industry.



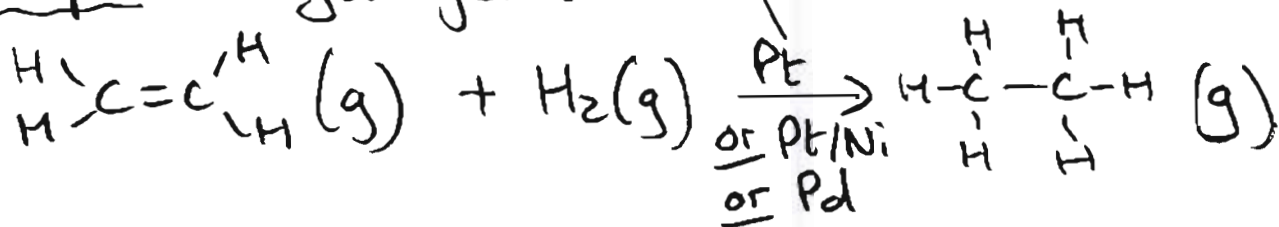
Catalytic converters



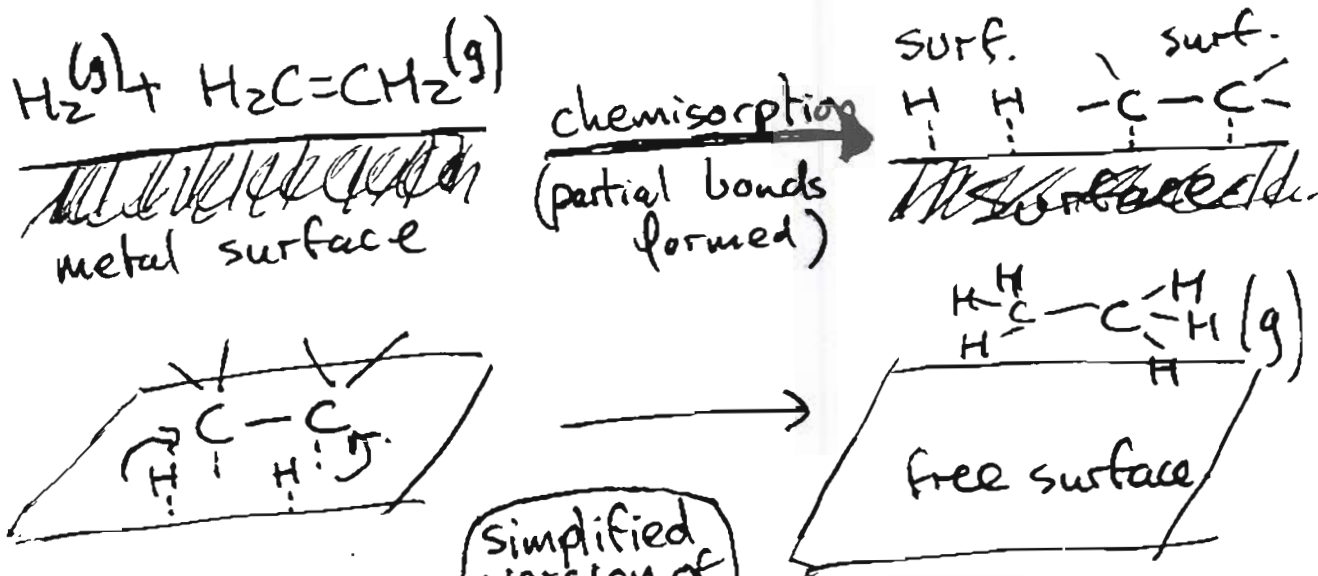
Generally a het. catalyst adsorbs a reactant onto the surface, facilitating breaking of bonds, and providing new rx. pathways and facile steric opportunities.

Mechanisms often complex, & not fully understood. Lots of interest in metal clusters, organometallic chem., surfaces/surface reactivity.

Example - hydrogenation of double bonds

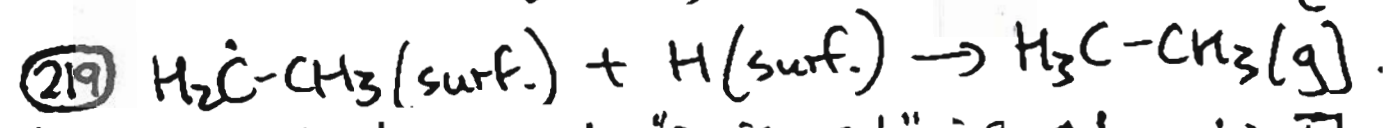
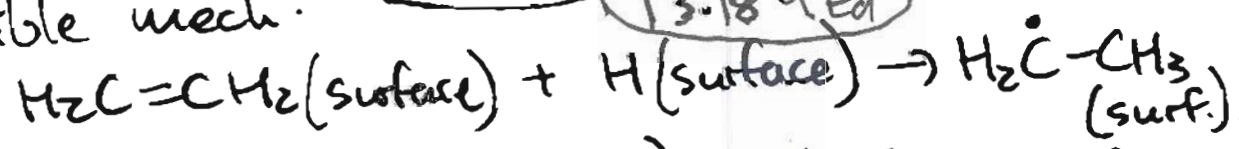


1st step is adsorption of  $\text{H}_2$  onto Pt surface - followed by dissociation of  $\text{H}_2 \rightarrow 2\text{H}$ . These can move around on surface and react with adsorbed  $\text{H}_2\text{C}=\text{CH}_2$ .



Simplified version of Fig 14.18 8. Ed. 13.18 9. Ed.

Possible mech.

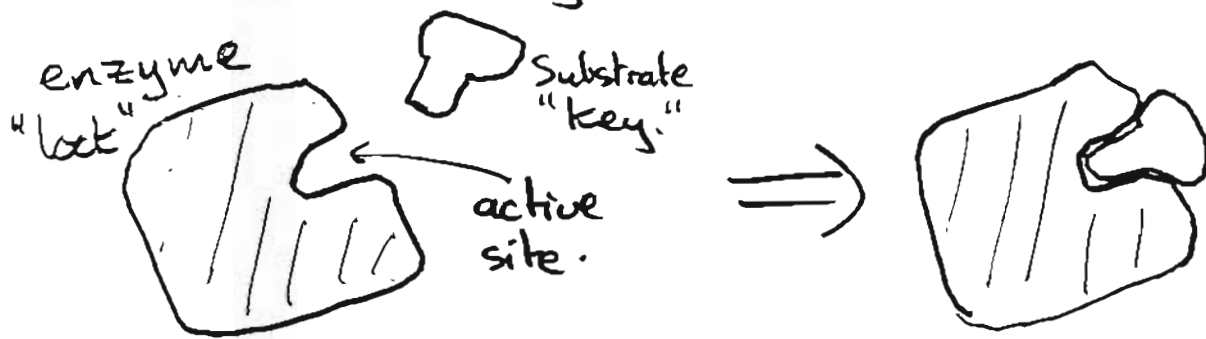


[Note: catalysts can be "poisoned" i.e. adsorption of another species inhibits intended rx. e.g. Pb in catalytic converters]

8. Ed. 9. Ed.  
ENZYMES CATALYSIS (p600) p562.

Biological catalysts - highly specific - catalyse processes in living systems. Without them many biochem. processes are too slow. Cells contain thousands of different <sup>(large proteins)</sup> enzymes - they have active sites which bind a particular reactant (substrate) and facilitates its reaction by giving a (locally) higher concn, providing better orientation for rx, and can weaken bonds in the reactant, etc. ...  $\therefore$  lowering  $E_a$ .

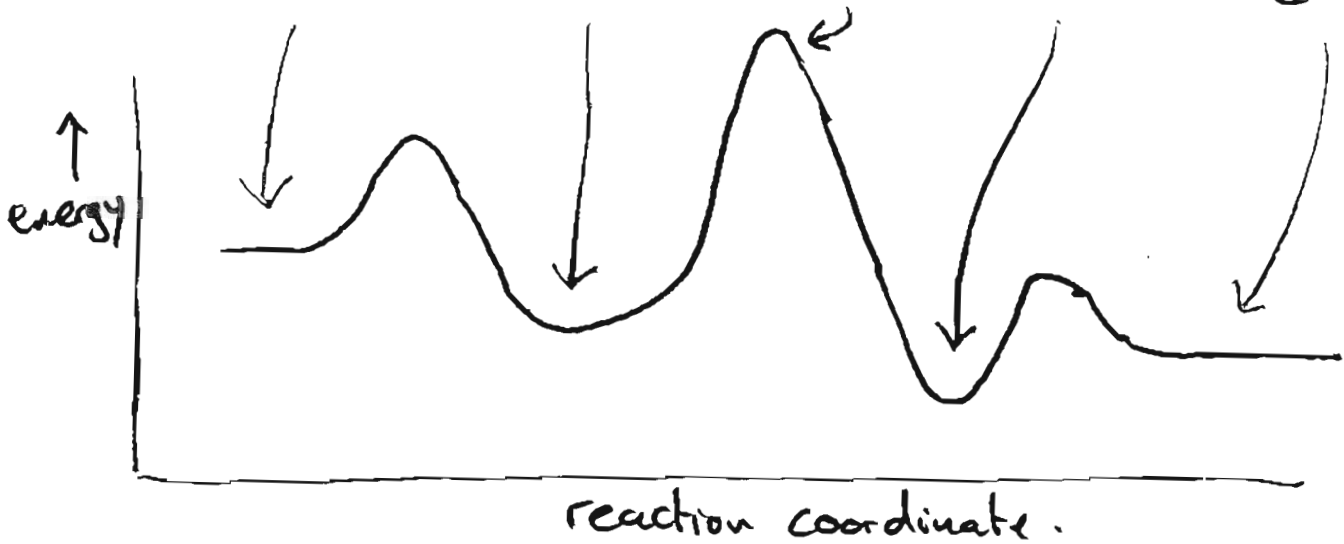
Specificity obtained by an enzyme "lock" and a substrate "key"



The protein enzyme can distort slightly as the substrate approaches. The ability to distort determines whether the "key" will fit - the induced-fit mechanism.

(220) Once in the slot the substrate reacts (e.g. by accepting a proton) and the modified substrate is released for use in the next stage ... possibly another enzyme.

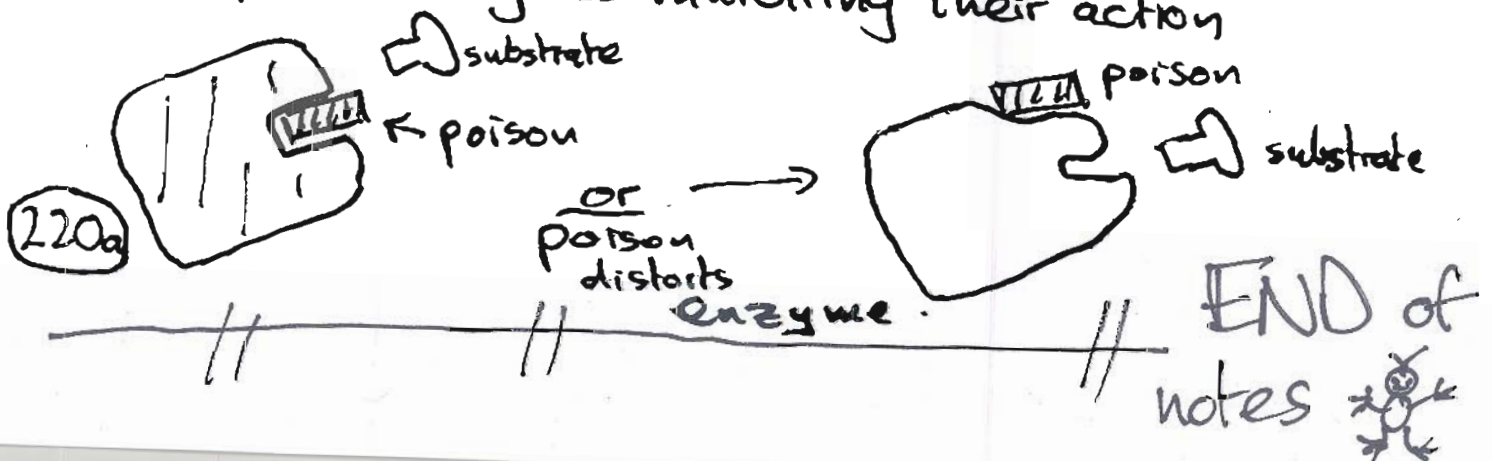
Typical, simple enzyme-catalysed rx. in which the substrate (S) is transformed into a product (P) by the enzyme (E)



Michaelis and Menten (1913) proposed a mechanism to explain the dependence of the initial rate of enzyme catalysed rxs.

Lineweaver & Burk proposed plots for studying enzyme kinetics.

Note - enzymes can be "poisoned", e.g. As V when ingested is reduced to As III which binds to -SH groups of enzymes inhibiting their action



# SUMMARY OF KINETICS

## I Rx. rates:

- units usually moles  $L^{-1} s^{-1}$
- rate of disappearance (or appearance) of each react. (or prod.) may be different 'cos of coefficients in rx.

e.g.  $2A + B \rightarrow C$ , A is used up 2x as fast as B.

- For a rx.  $aA + bB \rightarrow cC + dD$

Rate of rx is  $-\frac{1}{a} \frac{d[A]}{dt}$  etc.

Q my page 222

## II Rate law: Rate and concn.

e.g. Rate =  $-\frac{d[A]}{dt} = k [ ]^x [ ]^y \dots$  Differential form

Determined from expt.

Q my p223

## III Integrated rate laws: - relates concn & time

see page 184 summary & problems thereafter

## IV Temp. dep. of rx. rates:

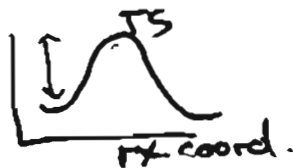
$$k = A e^{-E_a/RT} ; \ln k = \ln A - \frac{E_a}{RT}$$

For 2 temps, 2 k's ;  $\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$

Q my p224

## V Theories of rx. rates:

- concepts of collisions, steric factor,  $E_a \rightarrow$



## VI Mechanisms:

Rxs involve a series of steps - elementary processes.

Rate determining step - determines rate law (no intermeds)

see Q, my p212

see Q my p211 p213

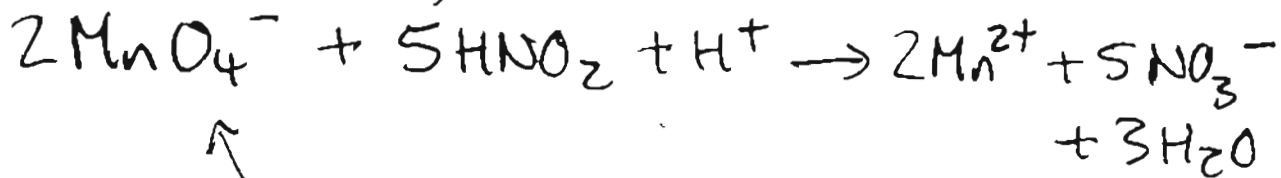
## VII Catalysis:

lowers barriers/posn of equilib. stays same/  
cat. unchanged.

(120) (homo- & het-.)  
enzyme

Q my p226

Q. For the rx;



The permanganate ion concn decreases at an instantaneous rate of  $0.012 \text{ mol L}^{-1} \text{ s}^{-1}$ . Calculate the rates at which the other concns change and the rate of rx.

$$\text{Rate of rx} = -\frac{1}{2} \frac{d[\text{MnO}_4^-]}{dt} = \frac{1}{2} \times 0.012 = 0.006 \text{ mol L}^{-1} \text{ s}^{-1}$$

$\text{HNO}_2$	disappears at	5 x	this rate	=	0.030	---
$\text{H}^+$	---	1 x	---	=	0.006	---
$\text{Mn}^{2+}$	appears at	2 x	---	=	0.012	---
$\text{NO}_3^-$	---	5 x	---	=	0.030	---
$\text{H}_2\text{O}$	---	3 x	---	=	0.018	---

Q For the rx.,  $2\text{NO} + 2\text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$ ,  
 the following initial rate data were  
 collected.

<u>Exp.</u>	<u>[NO]</u>	<u>[H<sub>2</sub>]</u>	<u>Initial rate</u> M s <sup>-1</sup>
1	0.60	0.15	0.076
2	0.60	0.30	0.15
3	0.60	0.60	0.30
4	1.20	0.60	1.21
5	0.30	0.60	0.076

- a) Find the rate law for the rx.  
 b) Calculate k

a) Rate law, Rate =  $k[\text{NO}]^2[\text{H}_2]$

b)  $0.076 = k(0.60)^2(0.15)$       $k = 1.4$

or  $0.15 = k(0.60)^2(0.30)$       $k = 1.4$

or ... etc (to check)

$\text{L}^2 \text{mol}^{-2} \text{s}^{-1}$

Q The reaction,



is first order in

each reactant and has a rate constant of  $4.88 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$  at  $18^\circ\text{C}$ . The activation energy is  $81.1 \text{ kJ mol}^{-1}$ .

a) Estimate the rate constant at  $50^\circ\text{C}$

b) Starting with  $[\text{CH}_3\text{I}] = [\text{CH}_3\text{CH}_2\text{ONa}] = 1.0 \times 10^{-1} \text{ M}$ , Dr. Nick wishes

to have at least 95% reaction in 2 hours. Calculate the minimum temperature required.

$$(a) \quad \ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right] \quad \begin{array}{l} T_1 = 291 \text{ K} \\ T_2 = 323 \text{ K} \end{array}$$

$$\ln \frac{k_2}{k_1} = \frac{81.1 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left[ \frac{323 - 291}{291 \times 323} \right] = 3.32$$

(224)

$$\frac{k_2}{k_1} = e^{3.32} = 27.7$$

$$k_2 = 27.7 \times 4.88 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$$

$$= \underline{\underline{1.35 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}}}$$

Part (b) — need to calculate the rate constant required to give 95% rx. in 2 hours.

Once we have that, then calc.  $T$  from the Arrhenius equation.

Minimum rate const. required

$$k = \frac{1}{t} \left[ \frac{1}{[A]} - \frac{1}{[A]_0} \right] = \frac{1}{7200} \left( \frac{1}{5 \times 10^{-3}} - \frac{1}{1.0 \times 10^{-1}} \right)$$

$$= 2.64 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$$

use in  $\frac{E_a}{R} \left( \frac{T_2 - T_1}{T_2 T_1} \right)$ .

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]; \quad \frac{1}{T_2} = \frac{1}{T_1} - \frac{R}{E_a} \ln\left(\frac{k_2}{k_1}\right)$$

$$\therefore \frac{1}{T_2} = \frac{1}{291} - \frac{8.314}{81.1 \times 10^3} \ln \frac{2.64 \times 10^{-2}}{4.88 \times 10^{-4}}$$

$$\underline{\underline{T_2 = 330 \text{ K} (57^\circ \text{C})}}$$

Q A rx. has an  $E_a$  of  $48 \text{ kJ mol}^{-1}$  at  $25^\circ\text{C}$ . A catalyst increases the rate of rx by a factor of 1000. What is the  $E_a$  in the presence of the catalyst, assuming the Arrhenius A-factor is unchanged?

$$k = A e^{-\frac{E_a}{RT}}$$

$$(2) \quad \ln k_2 = \ln A - \frac{E_a(\text{cat.})}{RT}$$

$$(1) \quad \ln k_1 = \ln A - \frac{E_a(\text{uncat.})}{RT}$$

$$(2) - (1) \Rightarrow \ln \frac{k_2}{k_1} = \ln 1000 = -\frac{1}{RT} (E_a - E_a)_{\text{cat. uncat.}}$$

$$\ln 1000 = -\frac{1}{8.314 \times 298} (E_a_{\text{cat}} - 48000)$$

$$E_{a(\text{cat})} = \underline{\underline{31 \text{ kJ}}}$$

# ROADMAP OF SUMMARIES

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"What can we do with -- $\Delta H_f^\circ$ $\Delta G_f^\circ$ $S^\circ$ ."	(88)
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Summary of eqns.	(89a)
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Electrochem, 1 <sup>st</sup> part	(141)
Electrochem, 2 <sup>nd</sup> part	(164)
Summary, diff'l. & integ. rate laws	(184)
Kinetics $\rightarrow$ end	(221)

