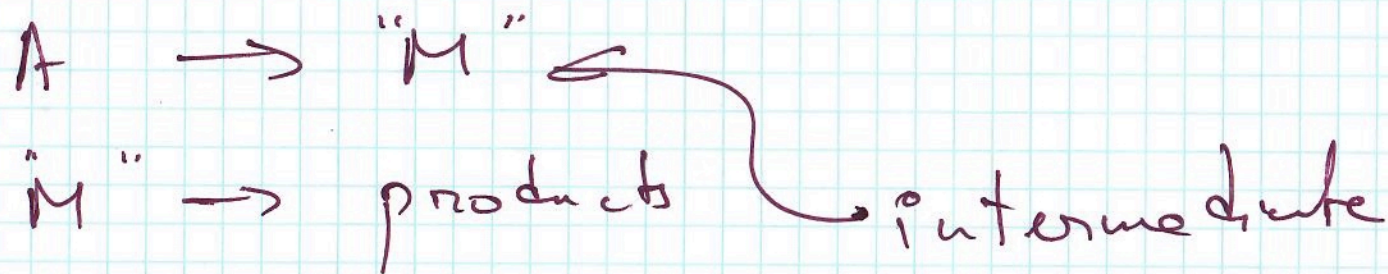
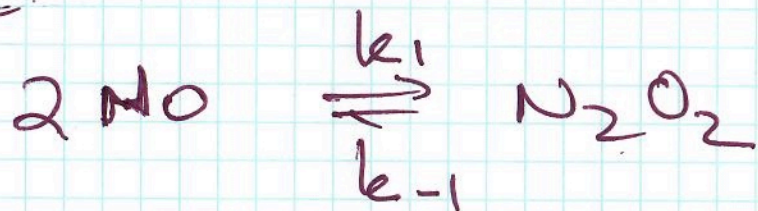
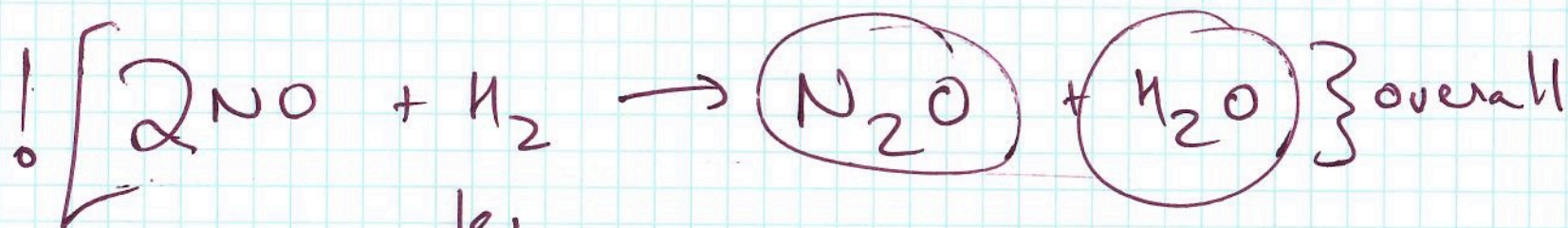


Class 4

①



$\frac{d[M]}{dt} = 0$ is the steady-state approximation



production $\frac{d[N_2O_2]}{dt} = k_1 [NO]^2$

(2)

loss
(consumption) $-\frac{d[N_2O_2]}{dt} = k_{-1}[N_2O_2] + k_2[N_2O_2][H_2]$

S.S. approximation \Rightarrow

$$k_1[NO]^2 = k_{-1}[N_2O_2] + k_2[N_2O_2][H_2]$$

$$[N_2O_2] = \frac{k_1[NO]^2}{k_{-1} + k_2[H_2]}$$

overall rate (production of N_2O)

is $k_2[N_2O_2][H_2]$

$$\text{rate} = \frac{k_2 k_1 [NO]^2 [H_2]}{k_{-1} + k_2 [H_2]}$$

simplifications

if $[H_2]$ is very large, then

$$k_2 [H_2] \gg k_{-1}$$

\Rightarrow denominator is

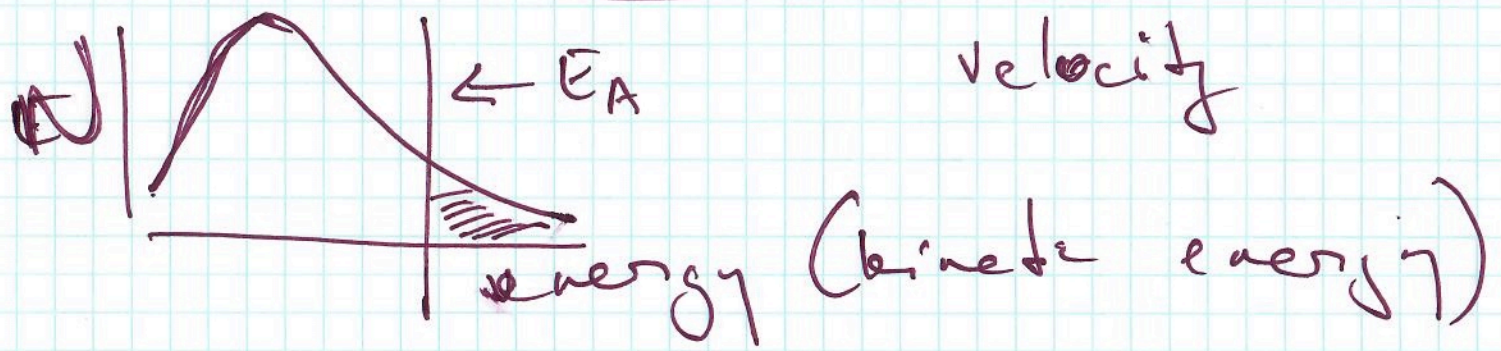
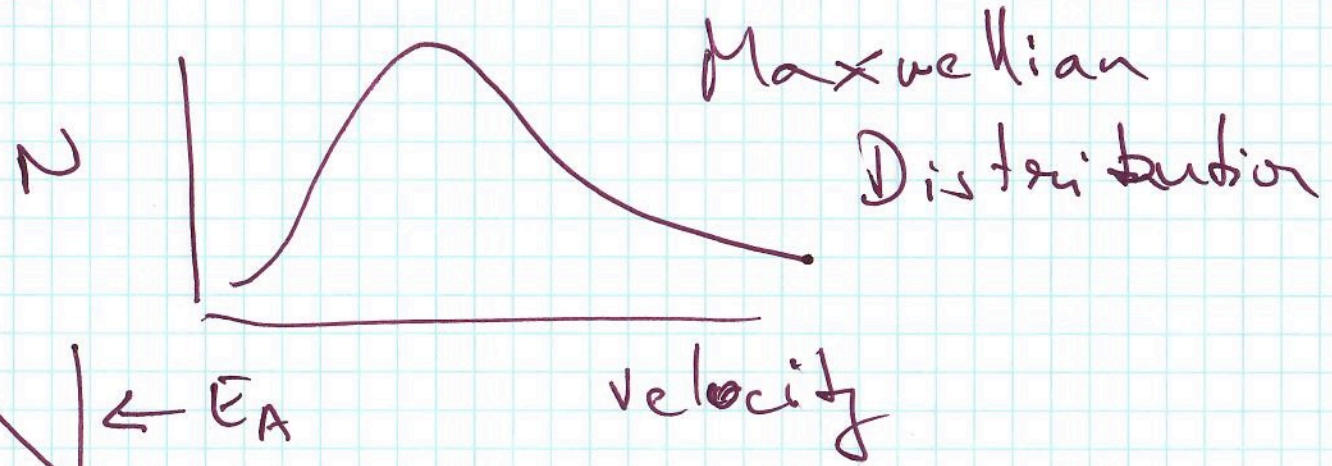
$$k_2 [H_2]$$

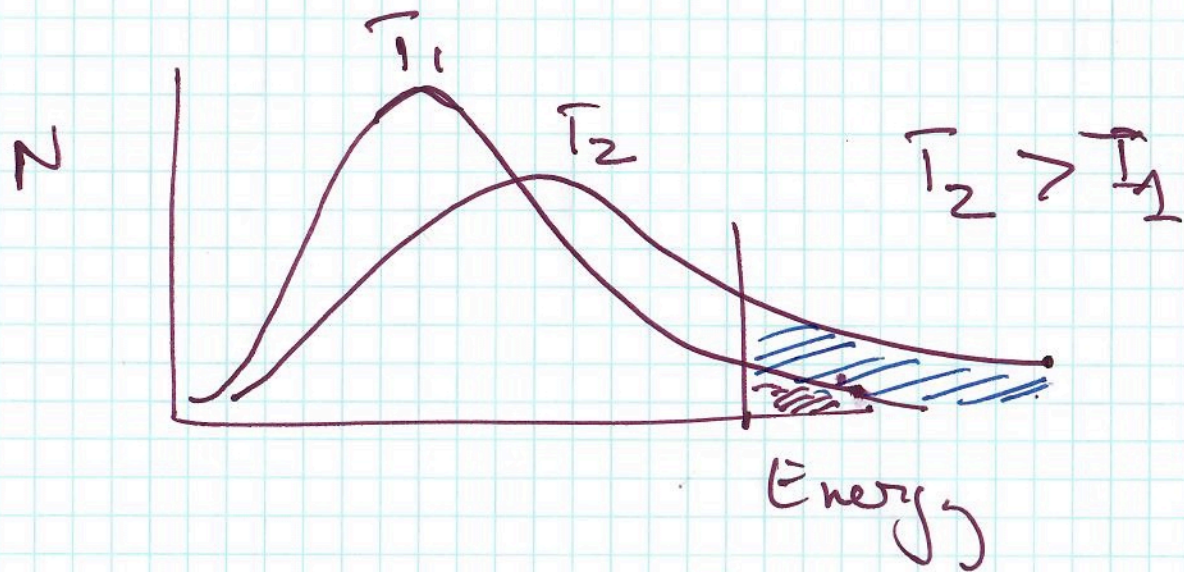
$$\text{rate} = k_1 [NO]^2$$

~~if~~ if $[H_2]_0$ is very small $\Rightarrow [H_2]$ is very small
then $k_{-1} + k_2[H_2] \approx k_{-1}$

$$\Rightarrow \text{rate} = \frac{k_2 k_1 [NO]^2 [H_2]}{k_{-1}}$$

Temperature dependence of rate constants





$$k = z p e^{-E_A/RT}$$

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

↑
prefactor

Arrhenius

$$\ln k = \ln A - \frac{E_A}{RT}$$

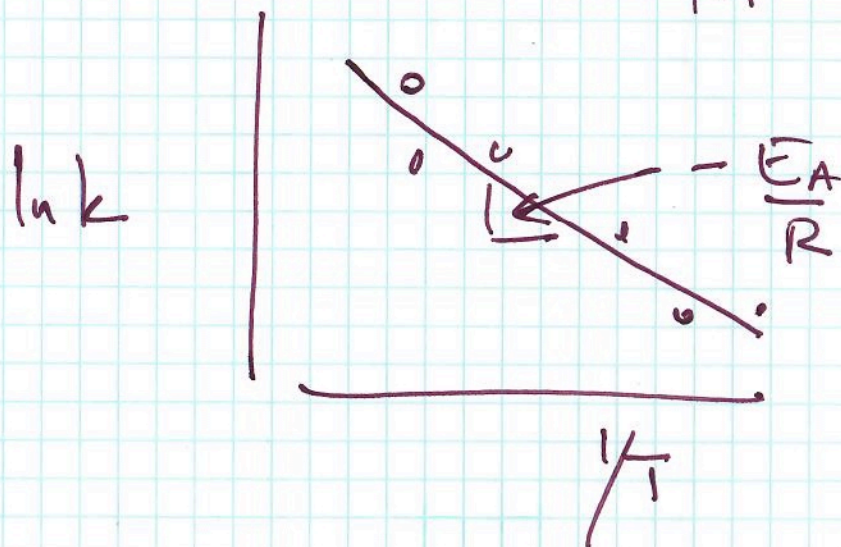
$$R$$

$$k_B$$

$$f = N_A k_B$$

5

$$\ln k = \ln A - \frac{E_A}{RT}$$



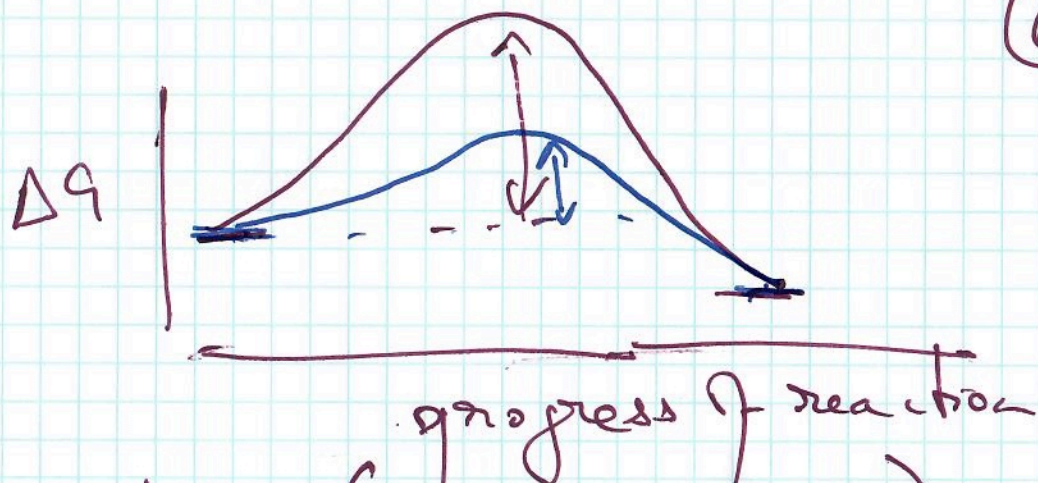
$$T_1 \Rightarrow k_1$$
$$T_2 \Rightarrow k_2$$

$$\ln(k_2) = \ln(A) - \frac{E_A}{RT_2} ; \ln(k_1) = \ln(A) - \frac{E_A}{RT_1}$$

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_A}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

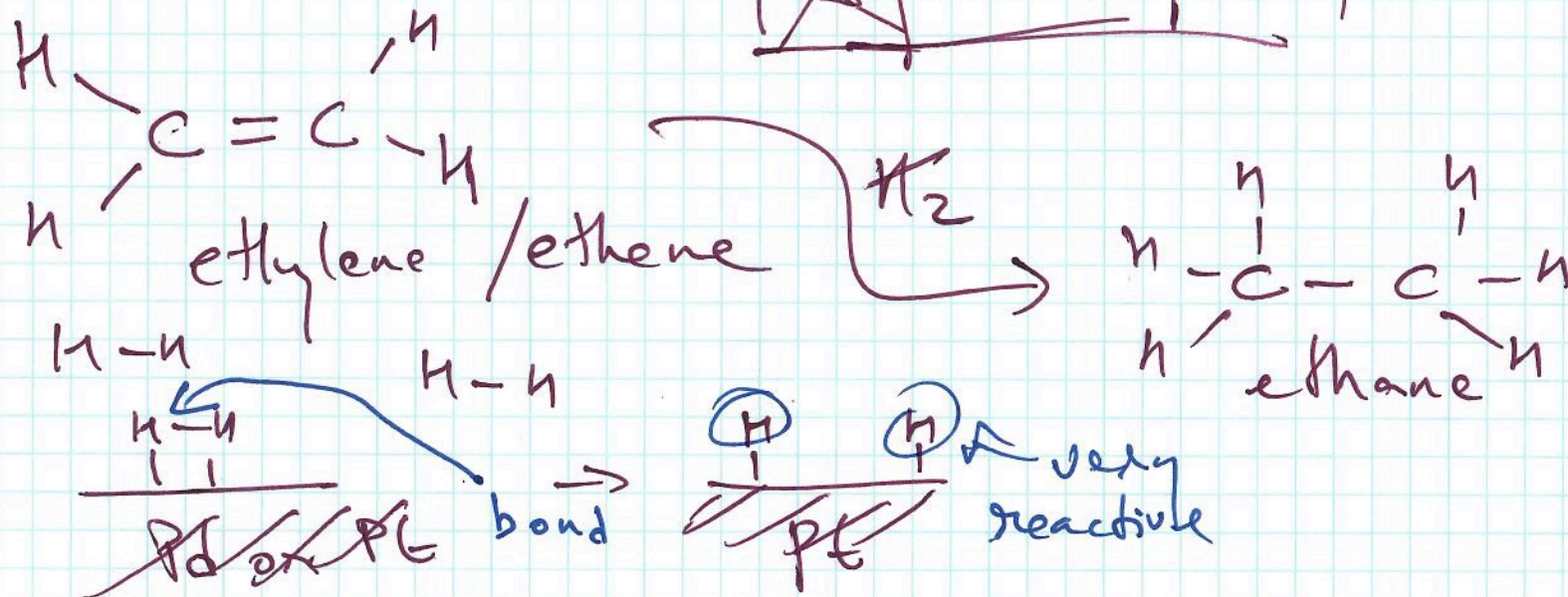
Catalysis

6

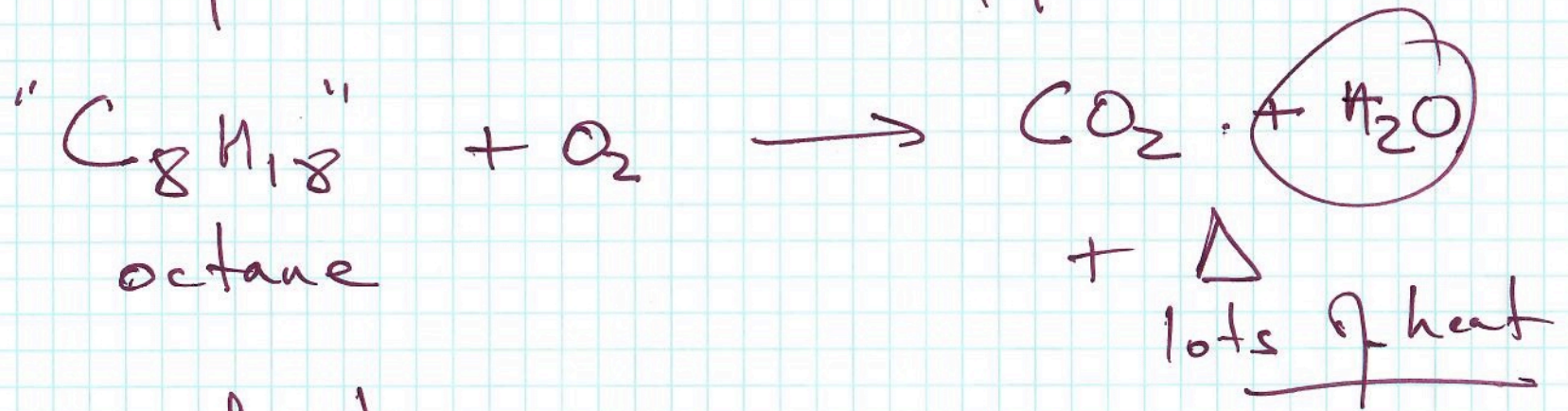


use of noble metals (like Pd, Pt)

Pu	Rh	Pd	Au
Os	Ir	Pt	Au

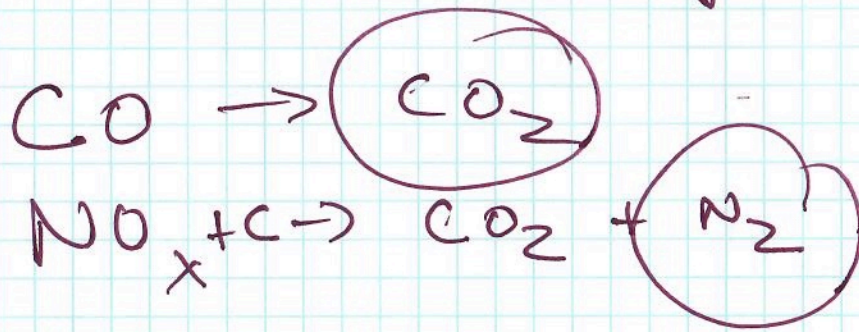


3-way automotive catalysis



products

unburnt hydrocarbons

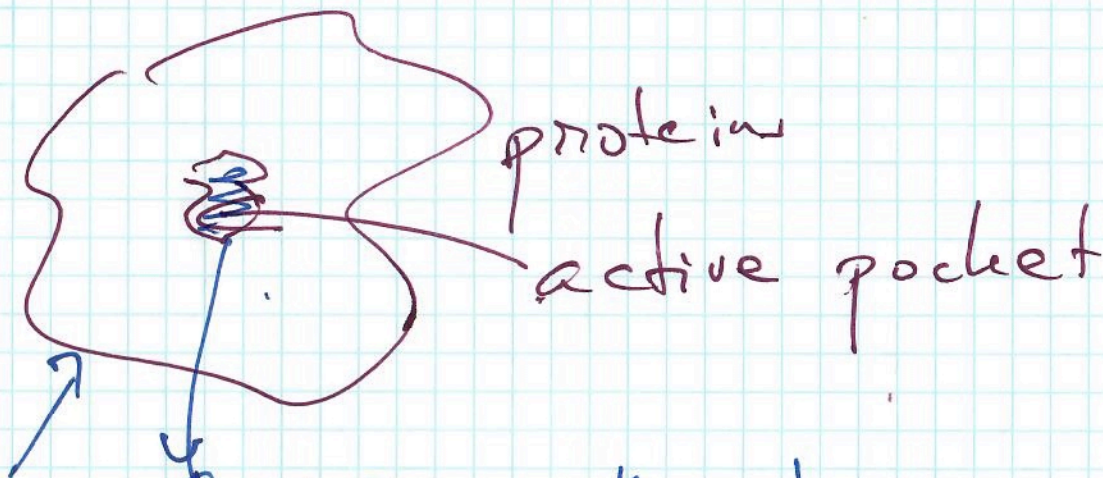
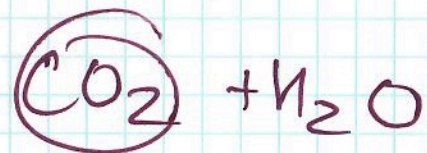
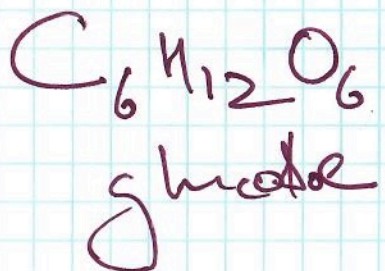


- CH_x
- CO
- NO_x
- C

Pd & Pt catalysts

Rh (diesel engines)

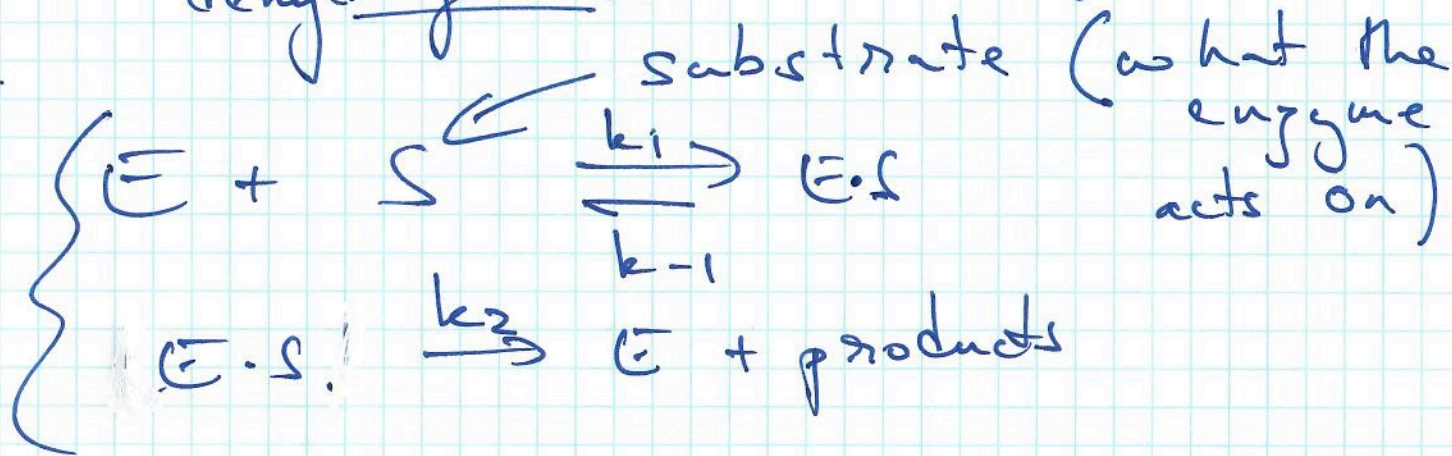
Enzymes



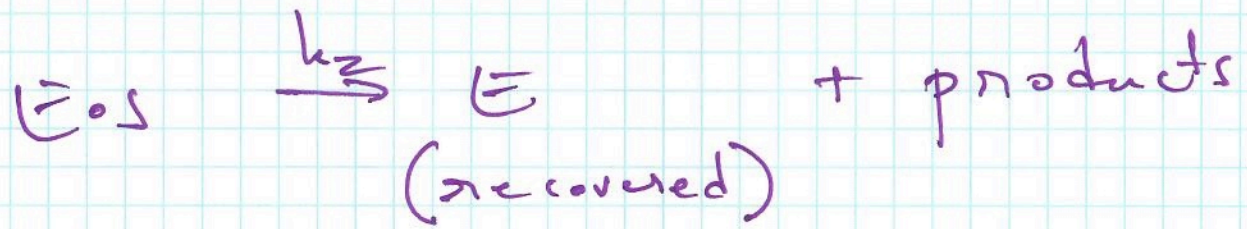
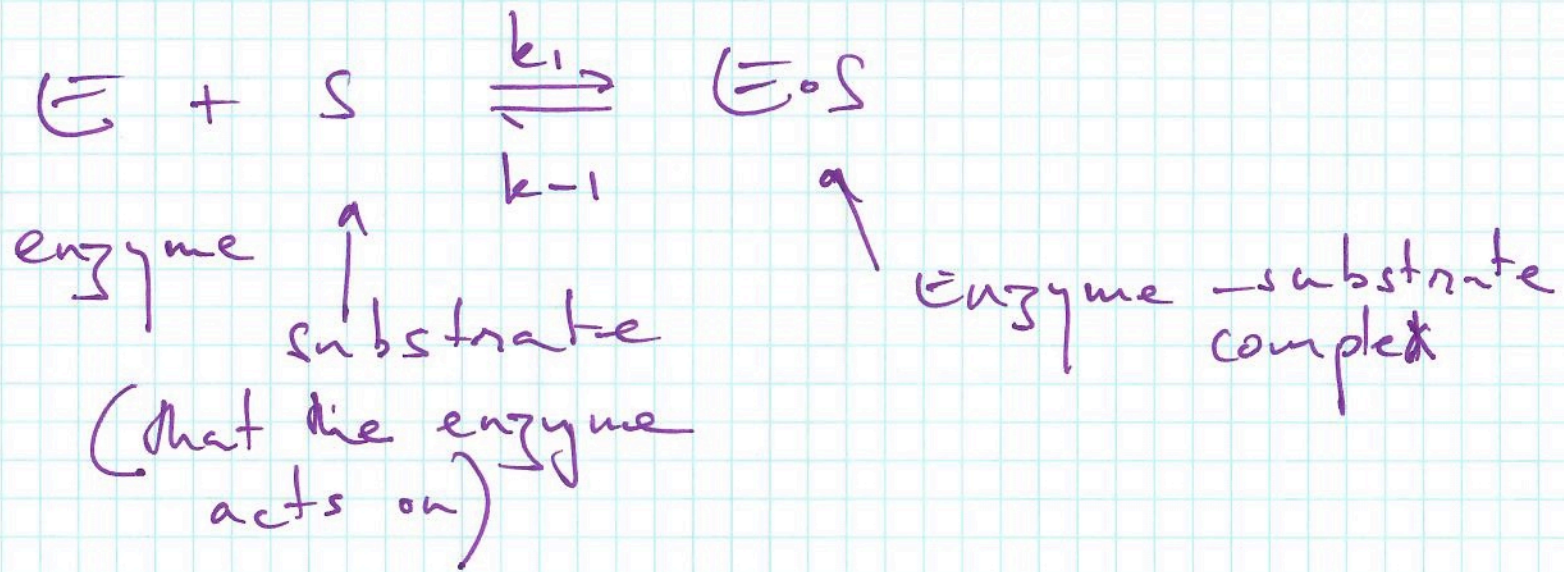
alcohol
dehydrogenase

C_2H_5OH ethanol
ethyl alcohol

Michaelis-Menten
Kinetics



Michaelis - Menten Kinetics



overall rate = $k_2 [E \cdot S]$

Steady state approximation applied to $[E \cdot S]$ (production = use & $\frac{d(E \cdot S)}{dt} = 0$)

Production of $E \cdot S$

$$\equiv k_1 [E] [S]$$

Use of $E \cdot S$

$$= k_{-1} [E \cdot S] + k_2 [E \cdot S]$$

but $[E] = [E]_0 - [E \cdot S]$ (enzyme is conserved)

↑
instantaneous

↑ original

↑ used to form complex

$$S_0 = A_0$$

$$\Rightarrow \frac{d[E \cdot S]}{dt} = 0 \Rightarrow k_1 [E] [S] = k_{-1} [E \cdot S] + k_2 [E \cdot S]$$

$[E] = [E]_0 - [E \cdot S]$ Enzyme conservation
 ↑ at time t ← original ← used up by Enzyme-Substrate complex

$$\Rightarrow k_1([E]_0 - [E \cdot S])[S] = k_{-1}[E \cdot S] + k_2[E \cdot S]$$

$$k_1[E]_0[S] - k_1[E \cdot S][S] = k_{-1}[E \cdot S] + k_2[E \cdot S]$$

$$k_1[E]_0[S] = (k_{-1} + k_2 + k_1[S])[E \cdot S]$$

$$[E \cdot S] = \frac{k_1[E]_0[S]}{k_1[S] + k_{-1} + k_2}$$

$$\text{Overall rate} = k_2[E \cdot S] = \frac{k_2 k_1 [E]_0 [S]}{k_1 [S] + k_{-1} + k_2}$$

Special cases

① $[S]$ is very large & $k_1[S] \gg k_{-1} + k_2$

$$\Rightarrow \text{rate} \approx \frac{k_2 k_1 [E]_0 [S]}{k_1 [S]} = k_2 [E]$$

& the reaction becomes 0th order in $[S]$

② $[S]$ is very small & $k_1[S] \ll k_{-1} + k_2$

$$\Rightarrow \text{rate} \approx \frac{k_2 k_1 [E]_0 [S]}{k_{-1} + k_2} \approx k [E]_0 [S]$$

& the rate is first-order in $[E]_0$ & $[S]$