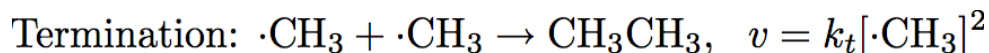
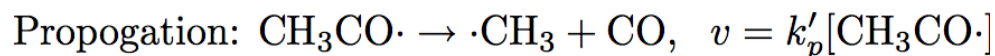
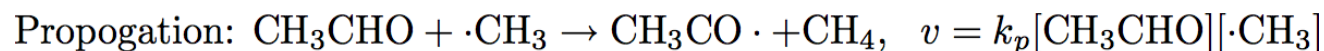
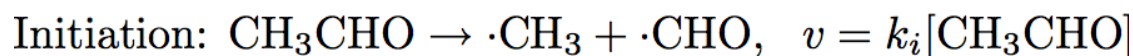
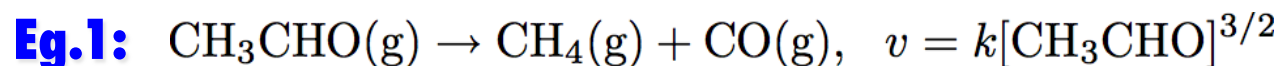


# Chap. 10. The kinetics of complex reactions

## Chain reaction

**A chain of reactions where the intermediates generated in one step generate inrmediates in a subsequent reaction**

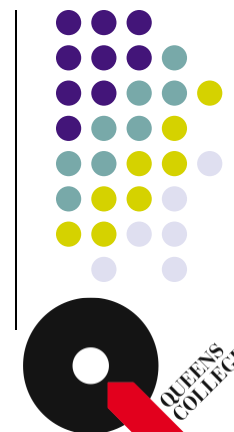
**Examples: radical chain reaction, explosion, polymerization**

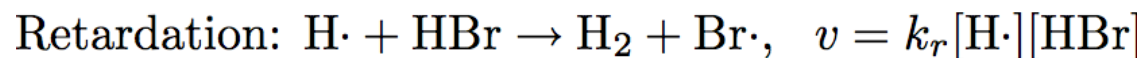
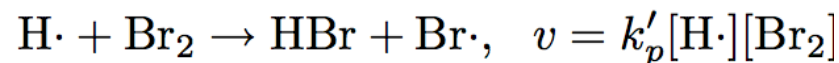
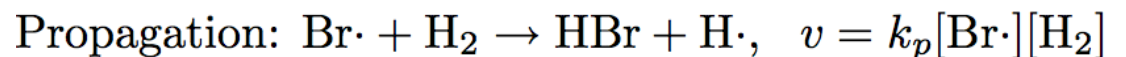
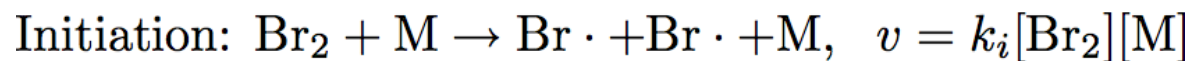
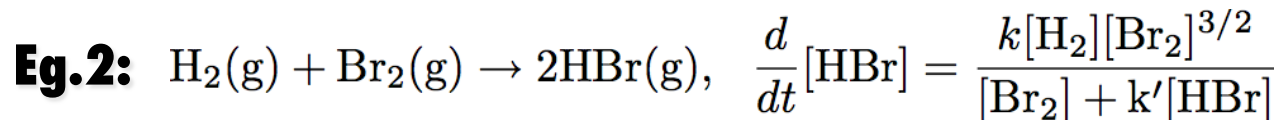


## **Steady state approximations**

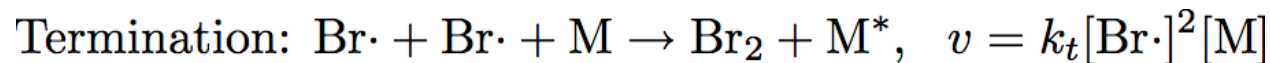
$$\frac{d}{dt}[\cdot\text{CH}_3] = k_i[\text{CH}_3\text{CHO}] - k_p[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] + k'_p[\text{CH}_3\text{CO}\cdot] - 2k_t[\cdot\text{CH}_3]^2 = 0$$

$$\frac{d}{dt}[\text{CH}_3\text{CO}\cdot] = k_p[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] - k'_p[\text{CH}_3\text{CO}\cdot] = 0$$





**reduces the net rate of formation of product**



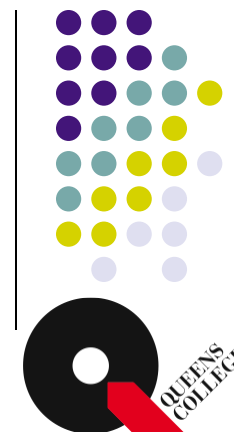
**↑  
quencher, removes the energy of recombination**

$$\frac{d}{dt}[\text{H}\cdot] = k_p[\text{Br}\cdot][\text{H}_2] + k'_p[\text{H}\cdot][\text{Br}_2] - k_r[\text{H}\cdot][\text{HBr}]$$

## Steady state approximations

$$\frac{d}{dt}[\text{H}\cdot] = k_p[\text{Br}\cdot][\text{H}_2] - k'_p[\text{H}\cdot][\text{Br}_2] - k_r[\text{H}\cdot][\text{HBr}] = 0$$

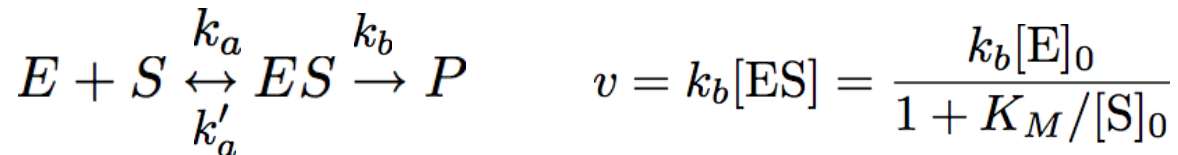
$$\frac{d}{dt}[\text{Br}\cdot] = 2k_i[\text{Br}_2][\text{M}] - k_p[\text{Br}\cdot][\text{H}_2] + k'_p[\text{H}\cdot][\text{Br}_2] + k_r[\text{H}\cdot][\text{HBr}] - 2k_t[\text{Br}\cdot]^2[\text{M}] = 0$$



# Enzyme - Biological Catalyst

**Reduces the activation energy with great specificity**

## **Michaelis-Menten mechanism**



## **Steady state approximation**

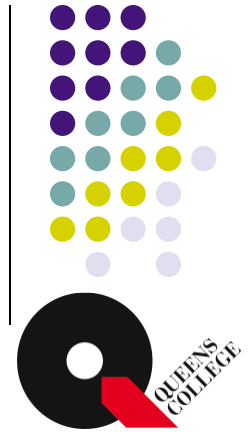
$$\frac{d}{dt}[ES] = k_a[E][S] - k'_a[ES] - k_b[ES] = 0$$

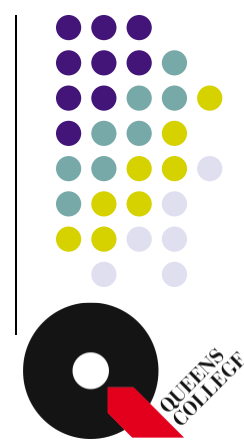
**Michaelis constant:** 
$$K_M = \frac{k'_a + k_b}{k_a} = \frac{[E][S]}{[ES]} = \frac{([E]_0 - [ES])[S]}{[ES]}$$

$$\rightarrow [ES] = \frac{[E]_0[S]}{K_M + [S]} \approx \frac{[E]_0[S]_0}{K_M + [S]_0}$$

For  $[S]_0 \gg K_M$ ,  $v \rightarrow v_{max} = k_b[E]_0$

**Lineweaver-Burk plot:** 
$$\frac{1}{v} = \frac{1}{v_{max}} + \frac{K_M}{v_{max}} \frac{1}{[S]_0}$$





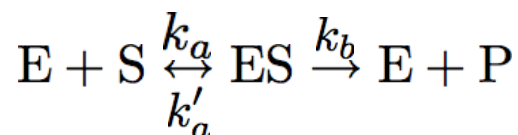
## Catalytic constant or turnover frequency

**# of catalytic cycles (turnovers) performed by the active site in a given interval divided by the duration of the interval.**

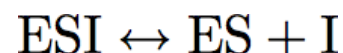
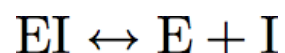
$$k_{cat} = k_b = \frac{v_{max}}{[E]_0}$$

**Catalytic efficiency:**  $\mathcal{E} = \frac{k_{cat}}{K_M} = \frac{k_a k_b}{k'_a + k_b}$

## Mechanism of Enzyme Inhibition



**Inhibition steps:**



$$K_I = \frac{[E][I]}{[EI]}$$

$$K'_I = \frac{[ES][I]}{[ESI]}$$

$$[E]_0 = \alpha[E] + \alpha'[ES], \text{ where } \alpha = 1 + \frac{[I]}{K_I} \text{ and } \alpha' = 1 + \frac{[I]}{K'_I}$$

$$[ES] = \frac{[E]_0}{(\alpha K_M/[S]_0 + \alpha')} \quad \rightarrow \quad v = k_b[ES] = \frac{v_{max}}{(\alpha K_M/[S]_0 + \alpha')}$$

# Photochemistry

## Quantum Yield

$$\phi = \frac{\text{number of events}}{\text{number of photons absorbed}} = \frac{\text{rate of process}}{\text{rate of photon absorption}}$$

$$\sum_i \phi_i = \sum_i \frac{v_i}{I_{abs}} = 1$$

**Without photochemical reaction,**  $\phi_f + \phi_{IC} + \phi_{ISC} + \phi_P = 1$

**With photochemical reaction,**  $\phi_f + \phi_{IC} + \phi_{ISC} + \phi_P + \phi_R = 1$

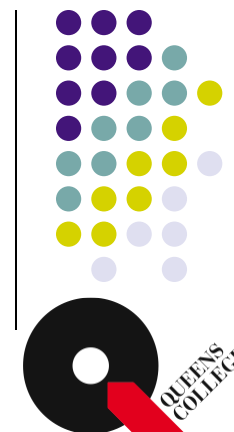
Absorption:  $S + h\nu_i \rightarrow S^*$  ,  $v_{abs} = I_{abs}$

Fluorescence:  $S^* \rightarrow S + h\nu_f$  ,  $v_f = k_f[S^*]$

Internal conversion:  $S^* \rightarrow S$  ,  $v_{IC} = k_{IC}[S^*]$

Intersystem crossing:  $S^* \rightarrow T^*$  ,  $v_{ISC} = k_{ISC}[S^*]$

**After light is turned off,**  $[S^*] = [S^*]_0 e^{-t/\tau_0}$  ,  $\tau_0 = \frac{1}{k_f + k_{ISC} + k_{IC}}$



## In the presence of steady radiation,

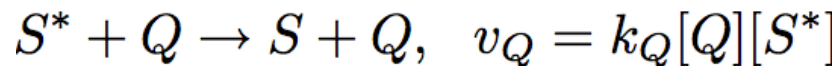
$$\frac{d[S^*]}{dt} = I_{abs} - k_f[S^*] - k_{ISC}[S^*] - k_{IC}[S^*] = 0$$

$$\rightarrow I_{abs} = (k_f + k_{ISC} + k_{IC})[S^*]$$

$$\phi_f = \frac{k_f[S^*]}{(k_f + k_{ISC} + k_{IC})[S^*]} = \frac{k_f}{k_f + k_{ISC} + k_{IC}}$$

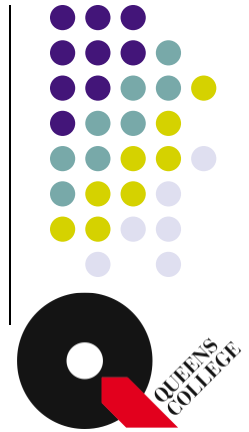
$$\rightarrow \tau_0 = \frac{\phi_f}{k_f}$$

## In the presence of quenching and steady radiation,



$$I_{abs} = (k_f + k_{IC} + k_{ISC} + k_Q[Q])[S^*]$$

$$\phi_f = \frac{k_f[S^*]}{I_{abs}} = \frac{k_f}{k_f + k_{ISC} + k_{IC} + k_Q[Q]}$$

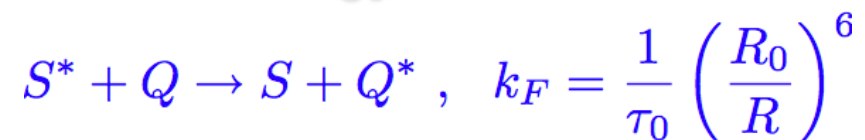


## Stern-Volmer equation

$$\frac{\phi_{f,0}}{\phi_f} = 1 + \left( \frac{k_Q}{k_f + k_{ISC} + k_{IC}} \right) [Q] = 1 + \tau_0 k_Q [Q]$$

$$\rightarrow \frac{1}{\tau} = \frac{1}{\tau_0} + k_Q [Q]$$

## Resonance energy transfer



$$E_T = 1 - \frac{\phi_f}{\phi_{f,0}} = 1 - \frac{\tau}{\tau_0} = 1 - \frac{R^6}{R_0^6 + R^6} = \frac{R_0^6}{R_0^6 + R^6}$$

