

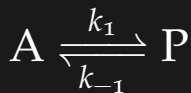
# Reversible reactions and relaxation kinetics

CML103

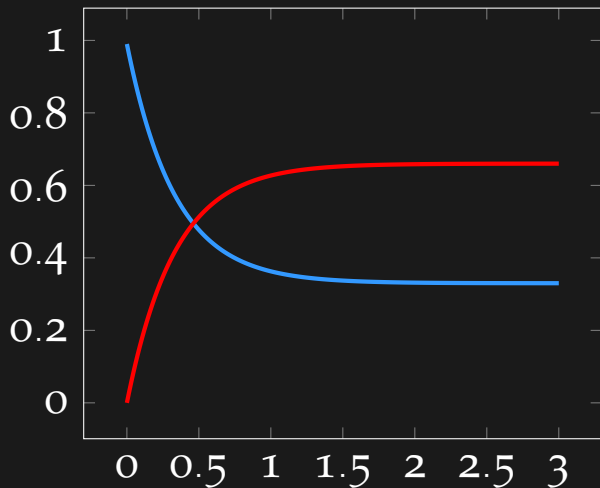
Class 5

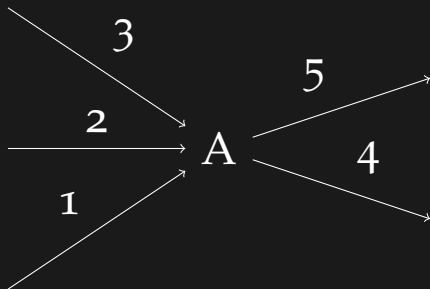
Oct. 06, 2015

All chemical reactions are  
equilibrium reactions



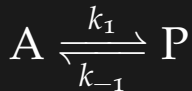
In equilibria concentrations approach equilibrium values over time





$$\frac{d[A]}{dt} = \text{Rate of formation of A}$$
$$- \text{Rate of consumption of A}$$

$$\frac{d[A]}{dt} = \text{Rate}_1 + \text{Rate}_2 + \text{Rate}_3 - \text{Rate}_4 - \text{Rate}_5$$



$$\frac{d[A]}{dt} = k_{-1}[P] - k_1[A]$$



$$\frac{d[P]}{dt} = k_1[A] - k_{-1}[P] = -\frac{d[A]}{dt}$$

Opposing reactions have a simple analytical solution

$$\frac{d[P]}{dt} + \frac{d[A]}{dt} = 0 \implies [A] + [P] = [A]_0$$

$$\frac{d[A]}{dt} = k_{-1}[A]_0 - (k_1 + k_{-1})[A]$$

$$\ln \left( \frac{k_{-1}[A]_0 - (k_1 + k_{-1})[A]}{k_1[A]_0} \right) = -(k_1 + k_{-1})t$$

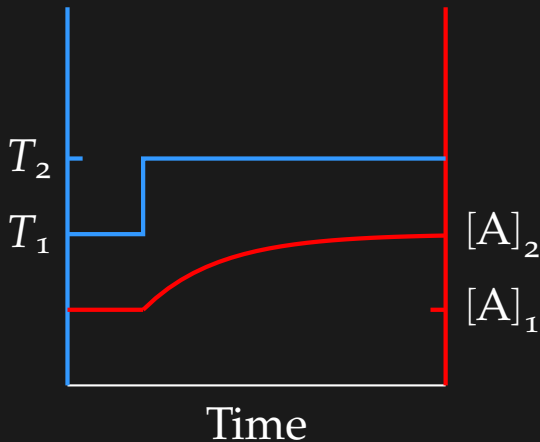
$$[A] = \frac{[A]_0}{k_1 + k_{-1}} \left( k_{-1} + k_1 e^{-(k_1 + k_{-1})t} \right)$$

$\text{H}^+ + \text{OH}^- \xrightleftharpoons[k_{-1}]{k_1} \text{H}_2\text{O}$  is too fast  
to be studied by conventional means

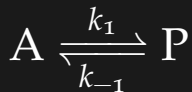
$$k_1 = 1.4 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ and } k_{-1} = 2.5 \times 10^{-5} \text{ s}^{-1} \implies K \approx 10^{15} \text{ dm}^3 \text{ mol}^{-1}.$$

In pure water,  $[\text{H}^+]_0 = [\text{OH}^-]_0 = 1 \times 10^{-7} \text{ dm}^{-3} \text{ mol}$ ,  $t_{1/2} = 7.1 \times 10^{-5} \text{ s}$  is less than mixing time.

# Approach to equilibrium after a perturbation to study fast reactions







$$\frac{d[A]}{dt} = k_{-1}(T)[P] - k_1(T)[A]$$

At equilibrium,

$$0 = k_{-1}(T)[P]_{\text{eq}} - k_1(T)[A]_{\text{eq}}$$

$$K(T) = \frac{k_1}{k_{-1}} = \frac{[P]_{\text{eq}}}{[A]_{\text{eq}}}$$

$$\frac{d[A]}{dt} = k_{-1}[P] - k_1[A]$$

$$[A] = [A]_{\text{eq}} + \Delta A \quad [P] = [P]_{\text{eq}} + \Delta P$$

$$\begin{aligned} \frac{d([A]_{\text{eq}} + \Delta A)}{dt} &= k_{-1}([P]_{\text{eq}} + \Delta P) \\ &\quad - k_1([A]_{\text{eq}} + \Delta A) \end{aligned}$$

Stoichiometry of the reaction demands that  $\Delta A = -\Delta P$ .

$$\frac{d\Delta A}{dt} = -(k_{-1} + k_1)\Delta A$$

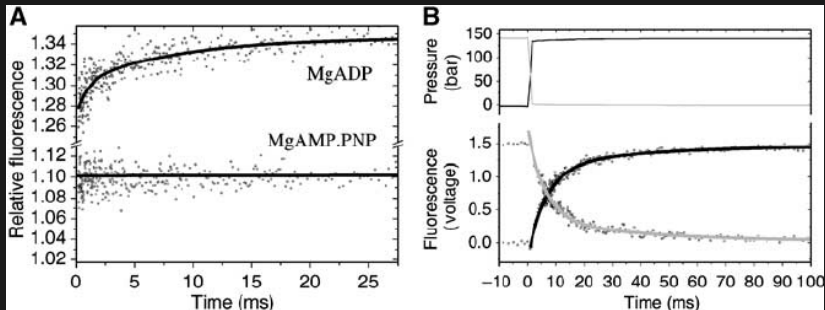
Exponential approach of the displacement from equilibrium to its equilibrium value.

$$\Delta A = \Delta A_0 e^{-t/\tau},$$

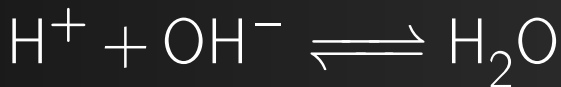
with a time-constant (relaxation time)

$$\tau = \frac{1}{(k_{-1} + k_1)}$$

# Experimental results from a pressure jump relaxation study



Relaxation time for



$$\frac{d[\text{H}_2\text{O}]}{dt} = k_1[\text{H}^+][\text{OH}^-] - k_{-1}[\text{H}_2\text{O}]$$

Steps:

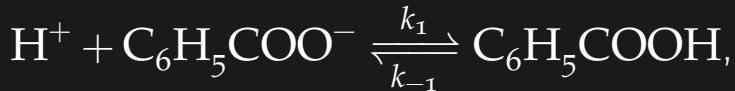
1  $[\text{H}^+] = [\text{H}^+]_{\text{eq}} + \Delta\text{H}^+$  and ....

2 Use  $\Delta\text{H}^+ = \Delta\text{OH}^- = -\Delta\text{H}_2\text{O}$

relaxation time,  $\tau$ ,  $\frac{1}{(k_{-1} + k_1([\text{H}^+]_{\text{eq}} + [\text{OH}^-]_{\text{eq}}))}$

# Quiz on relaxation kinetics

Calculate the relaxation time when 0.015 M benzoic acid is subjected to a temperature-jump experiment to a final temperature of 298 K. For the reaction



the rate constants are  $k_1 = 3.5 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $k_{-1} = 2.2 \times 10^6 \text{ s}^{-1}$ .