REACTION KINETICS

different type of reactions
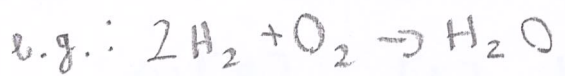→ different relationships between $t, [A](t), [A]_0, k(T), T$

rate of reaction: two definitions

THEORETICAL	EXPERIMENTAL

(const. T, V) $\dfrac{1}{v_A} \dfrac{d[A](t)}{dt} = v(t) = k(T) \cdot [A]^{\alpha}(t) \cdot [B]^{\beta}(t) \cdot \ldots$

e.g.: $2H_2 + O_2 \rightarrow H_2O$ generally, $\alpha \neq v_A$ etc.

$\qquad v = -2 \quad v = -1 \qquad v = 1$

$\qquad \dim v = \dfrac{\text{concentration}}{\text{time}}$ → determines dim k

FIRST ORDER REACTIONS

$A \xrightarrow{k} P + \ldots \qquad -\dfrac{d[A](t)}{dt} = k \cdot [A](t) \Rightarrow \boxed{[A](t) = [A]_0 \cdot e^{-kt}}$
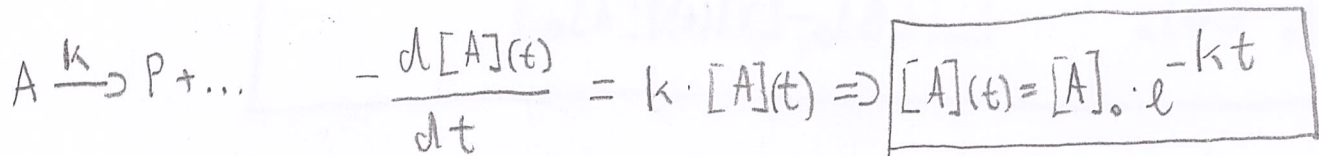
$\dim k = \dfrac{1}{\text{time}}$) <u>K and t must be in matching units</u>❗

$\boxed{\dfrac{[A](t)}{[A]_0} = e^{-kt}}$: how much of $[A]_0$ is still there?

$\boxed{1 - \dfrac{[A](t)}{[A]_0} = 1 - e^{-kt}}$: how much of $[A]_0$ was converted?

half-life: $\boxed{\tau = \dfrac{\ln 2}{k}}$ $\Bigg\}$ not dependent on $[A]_0$!

generally: $\boxed{t_{1/n} = \dfrac{\ln n}{k}}$

SECOND ORDER REACTIONS

a) $A + A \xrightarrow{k} P + \dots$ $\qquad -\frac{1}{2}\frac{d[A](t)}{dt} = k \cdot [A]^2_{(t)}$

$\qquad \llcorner \Rightarrow \boxed{\dfrac{1}{[A]_{(t)}} - \dfrac{1}{[A]_0} = 2 \cdot k \cdot t}$, $\quad \dim k = \dfrac{1}{conc. \cdot time}$

$\qquad \boxed{\tilde{J} = \dfrac{1}{2k[A]_0}}$

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b) $A + B \xrightarrow{k} P + \dots$ $\qquad -\dfrac{d[A](t)}{dt} = k \cdot [A]_{(t)} \cdot [B]_{(t)}$
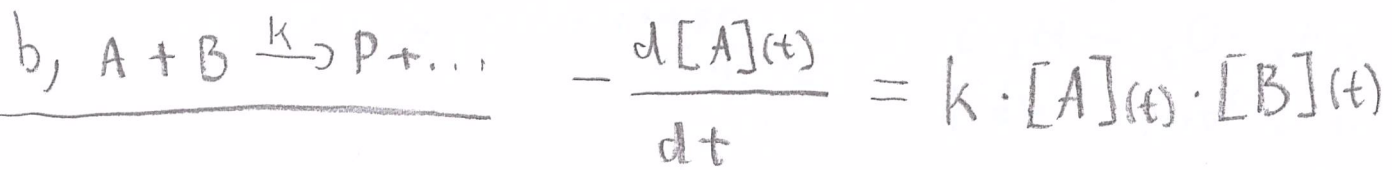
$\qquad [A](t) = [A]_0 - [X](t)$, $[B](t) = [B]_0 - [X](t)$

$\qquad \llcorner \Rightarrow \boxed{\dfrac{1}{[A]_0 - [B]_0} \cdot \ln\left[\dfrac{([A]_0 - [X](t))[B]_0}{([B]_0 - [X](t))[A]_0}\right] = k \cdot t}$

$\dim k = \dfrac{1}{conc. \cdot time}$

$\tilde{J}$: which half-life is the question?

half-life of A: $[X](\tilde{J}_A) = 0,5 [A]_0$

$\qquad \llcorner \Rightarrow \boxed{\tilde{J}_A = \dfrac{1}{k} \cdot \dfrac{1}{[A]_0 - [B]_0} \cdot \ln\left[\dfrac{0,5[B]_0}{[B]_0 - 0,5[A]_0}\right]}$

NOTES: -Eqs. for b) only valid when $[A]_0 \neq [B]_0$

$\qquad$ - general case: $\mu A + \nu B \xrightarrow{k} P + \dots$: slightly different equations

PSEUDO FIRST ORDER REACTIONS

$A + B \xrightarrow{k} P + \ldots$ $\qquad V(t) = k \cdot [A](t) \cdot [B](t)$

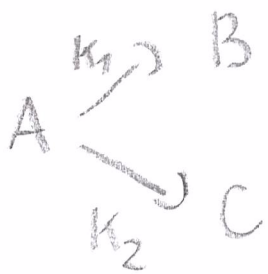BUT: if $[B]_0 \gg [A]_0$, then B remains approx. constant

$\llcorner \rightarrow [B](t) \approx [B]_0 \longrightarrow V(t) \approx \underbrace{k \cdot [B]_0}_{k'} \cdot [A](t) = k' \cdot [A](t)$

now formally first order:

$$\boxed{[A](t) = [A]_0 \, e^{-k't}} \qquad \boxed{\mathcal{T}_A = \frac{\ln 2}{k'}}$$

PARALLEL REACTIONS

$A \overset{k_1}{\underset{k_2}{\lessgtr}} \begin{array}{c} B \\ C \end{array}$

$$-\frac{d[A](t)}{dt} = k_1 [A](t) + k_2 [A](t) = \overbrace{(k_1 + k_2)}^{k'} [A](t)$$

$\llcorner \rightarrow \boxed{[A](t) = [A]_0 \, e^{-k't}} \qquad \boxed{\mathcal{T}_A = \frac{\ln 2}{k'}}$

if: $[B]_0 = [C]_0 = \varnothing$

$\llcorner \rightarrow \boxed{\dfrac{[B](t)}{[C](t)} = \dfrac{k_1}{k_2}} \qquad \boxed{[A]_0 = [A](t) + [B](t) + [C](t)}$

$$\boxed{[C](t) = \frac{k_2 [A]_0}{k'} \left(1 - e^{-k't}\right)}$$ for B: k_1 instead of k_2 in the nominator

$$\boxed{[C]_{max} = [C](t \rightarrow \infty) = \frac{k_2 [A]_0}{k'}}$$

OPPOSING REACTIONS
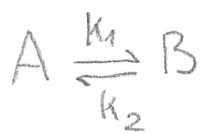
$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \qquad -\frac{d[A](t)}{dt} = \frac{d[B](t)}{dt} = k_1[A](t) - k_2[B](t)$$

In equilibrium: $-\frac{d[A](t)}{dt} = \frac{d[B](t)}{dt} = 0 = k_1[A]_e - k_2[B]_e$

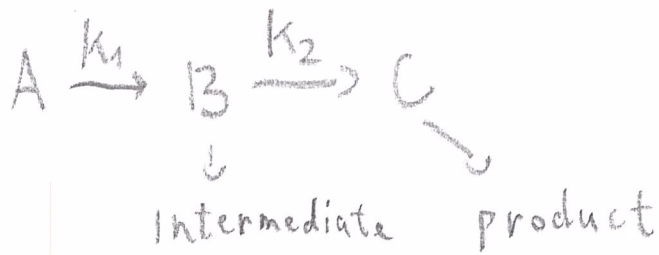$$\downarrow \quad \boxed{\frac{[B]_e}{[A]_e} = \frac{k_1}{k_2} = K}$$

if: $[B]_0 = \emptyset$ and $[A]_0 > 0$, then $\boxed{[B](t) = [A]_0 - [A](t)}$

and also $\boxed{[B]_e = [A]_0 - [A]_e}$

$$\downarrow \quad \boxed{[A]_e = \frac{[A]_0 k_2}{k_1 + k_2}} \qquad \boxed{[B]_e = \frac{[A]_0 k_1}{k_1 + k_2}}$$

$$\boxed{\ln\left[\frac{[A](t) - [A]_e}{[A]_0 - [A]_e}\right] = -(k_1 + k_2)t}$$

CONSECUTIVE REACTIONS

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$\downarrow$

intermediate   product

$$[A](t) = [A]_0 \, e^{-k_1 t}$$

$$\frac{d[B](t)}{dt} = k_1 [A](t) - k_2 [B](t)$$

if $k_2 \neq k_1$, then

$$[B](t) = \frac{k_1 [A]_0}{k_2 - k_1} \left(e^{-k_1 t} - e^{-k_2 t} \right)$$

if $[B]_0 = [C]_0 = \emptyset$, then

$$[C](t) = [A]_0 - [A](t) - [B](t)$$

when will $[B]$ reach its maximum?

$$t_{B_{max}} = \frac{\ln k_1 - \ln k_2}{k_1 - k_2}$$

$$[B]_{max} = [A]_0 \left(\frac{k_1}{k_2} \right)^{\frac{k_2}{k_2 - k_1}}$$

$$[C](t) = [A]_0 \left(1 + \frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2 - k_1} \right)$$
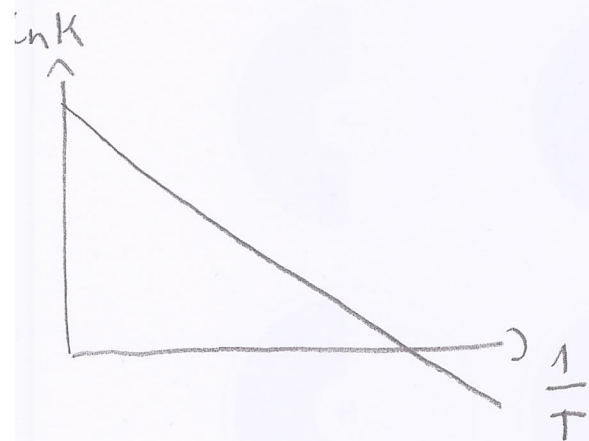
ARRHENIUS EQUATION

empirical formula for thermally activated reactions

$$k(T) = A \cdot e^{-\frac{E_a}{R \cdot T}}$$

$$\ln k(T) = \ln A - \frac{E_a}{R \cdot T}$$

E_a: activation energy, $\underline{\underline{J/mol}}$

A: preexponential factor, same dim as K

$\left.\begin{array}{l} \end{array}\right\}$ We will treat both of these as $\underline{independent}$ of T

according to the model $A = K(\infty)$
$\downarrow$
usually a large number

$$\left.\begin{array}{l} \ln k(T_1) = \ln A - \dfrac{E_a}{R T_1} \\[4mm] \ln K(T_2) = \ln A - \dfrac{E_a}{R T_2} \end{array}\right\}$$

$$\boxed{E_a = \frac{R\left(\ln K_1 - \ln K_2\right)}{\dfrac{1}{T_2} - \dfrac{1}{T_1}}}$$

$\underline{\text{NOTES}}$: $\ln K_1 - \ln K_2 = \ln \dfrac{K_1}{K_2}$

E_a and A are both positive!