Advanced Redox Technology (ART) Lab
고도산화환원 환경공학 연구실

http://artlab.re.kr

Environmental Chemistry-3

-Thermodynamics and Kinetics

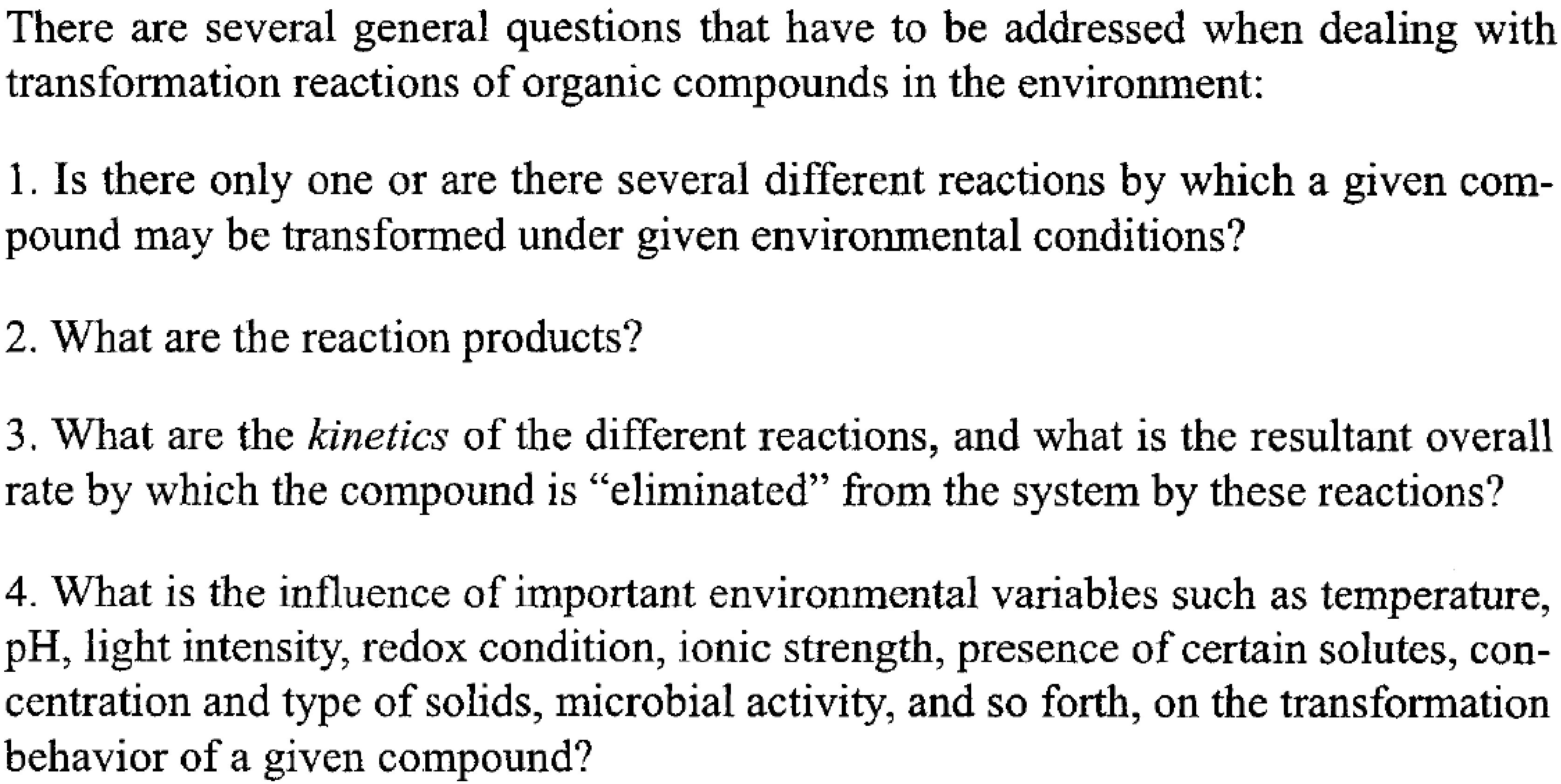
(from *Environmental Organic Chemistry* by Schwarzenbach et al.)

Changha Lee

School of Chemical and Biological Engineering
Seoul National University

Transformation Reactions

√ Transformation reactions in environment



There are several general questions that have to be addressed when dealing with transformation reactions of organic compounds in the environment:

1. Is there only one or are there several different reactions by which a given compound may be transformed under given environmental conditions?

2. What are the reaction products?

3. What are the *kinetics* of the different reactions, and what is the resultant overall rate by which the compound is "eliminated" from the system by these reactions?

4. What is the influence of important environmental variables such as temperature, pH, light intensity, redox condition, ionic strength, presence of certain solutes, concentration and type of solids, microbial activity, and so forth, on the transformation behavior of a given compound?

Thermodynamics

√ Chemical potential

μ_i : chemical potential of a compound, *i*

$= (\partial G/\partial n_i)_{P,T,n(others)}$

$= \mu_i^o + RTln\{i\}$

G : Gibbs free energy (= H – TS)

μ_i^o : Standard chemical potential

$= \Delta G_{f,i}^{\mathrm{o}}$: standard Gibbs free energy of formation

*Standard Gibbs free energy of formation ($\Delta G_{f,i}^{\mathrm{o}}$)

: the Gibbs free energy of the standard reaction for the formation of a compound (*i*) from its elements in their reference state

e.g., $\Delta G_{f,}^{\mathrm{o}}$ of $O_{2(g)}$, $N_{2(g)}$, $Fe_{(s)}$, $Cu_{(s)}$, … = 0

Thermodynamics

√ Gibbs free energy of reaction

$$aA + bB + \ldots \rightleftharpoons pP + qQ + \ldots$$

Total potential of reactants: $a\mu_A + b\mu_B + \ldots.$

Total potential of products: $p\mu_P + q\mu_Q + \ldots.$

The reaction proceeds in the direction of decreasing the potential!

Potential difference: $(p\mu_P + q\mu_Q + \ldots.) - (a\mu_A + b\mu_B + \ldots.)$

$= \Delta G_r$ (Gibbs free energy of reaction)

$= \Delta G_r > 0$ (endergonic)

$= \Delta G_r < 0$ (exergonic) : thermodynamically favored, spontaneous

Thermodynamics

$$\Delta G_r = (p\mu_P + q\mu_Q) - (a\mu_A + b\mu_B) \qquad \text{using } \mu_i = \mu_i^o + RTln\{i\}$$

$$= p(\mu_P^o + RTln\{P\}) + q(\mu_Q^o + RTln\{Q\}) - a(\mu_A^o + RTln\{A\}) + b(\mu_B^o + RTln\{B\})$$

$$= \underbrace{p\mu_P^o + q\mu_Q^o - (a\mu_A^o + b\mu_B^o)}_{\Delta G_r^o\ \text{(standard Gibbs free energy of reaction)}} + RT\ ln\,\frac{\{P\}^p\{Q\}^q}{\{A\}^a\{B\}^b}$$

$$\overbrace{p\Delta G_{f,P}^o + q\Delta G_{f,Q}^o - (a\Delta G_{f,A}^o + b\Delta G_{f,B}^o)} \qquad \text{Because } \mu_i^o = \Delta G_{f,i}^o$$

$\text{Activity of } i:\ \{i\} = \gamma_i[i]$

γ_i : *Activity coefficient* (≈ 1 for dilute solution)

$[i]$: *molar concentration*

$$\Delta G_r = \Delta G_r^o + RT\ ln\,\frac{[P]^p[Q]^q}{[A]^a[B]^b} \longrightarrow Q_r$$

Reaction quotient

Thermodynamics

In equilibrium,

$$aA + bB + \ldots \rightleftharpoons pP + qQ + \ldots$$

$$\Delta G_r = 0$$

$$\Delta G_r = \Delta G_r^o + RT\, ln \frac{[P]^p[Q]^q}{[A]^a[B]^b} = 0$$

$$\Delta G_r^o = -RT\, ln \underbrace{\frac{[P]^p[Q]^q}{[A]^a[B]^b}}_{K_r}$$

Equilibrium constant

$$\Delta G_r^o = -RT\, lnK_r$$

$$lnK_r = -\Delta G_r^o /RT$$

$$K_r = exp(-\Delta G_r^o /RT)$$

High ΔG_r^o ⇒
The forward reaction is unfavored
⇒ Low K_r

Kinetics

√ First-order kinetics

$$\mathbf{A} \rightarrow \mathbf{P}$$

k : first-order rate constant (s^{-1})

$$\frac{d[\mathrm{A}]}{dt} = -k[\mathrm{A}]$$

$$[\mathrm{A}]_t = [\mathrm{A}]_0 \cdot e^{-kt}$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

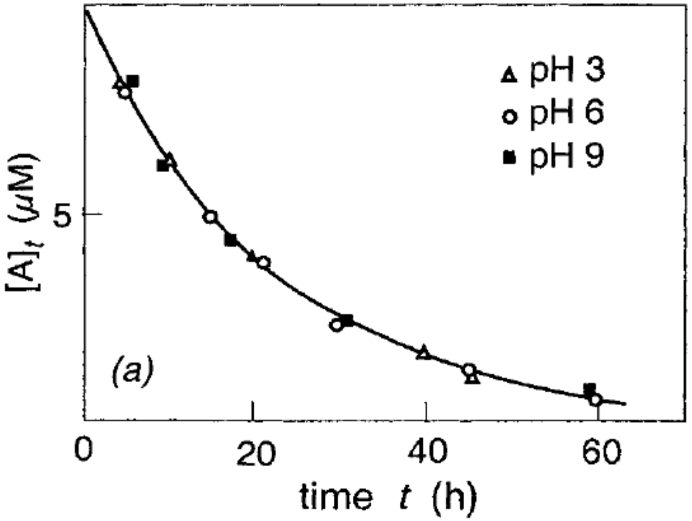


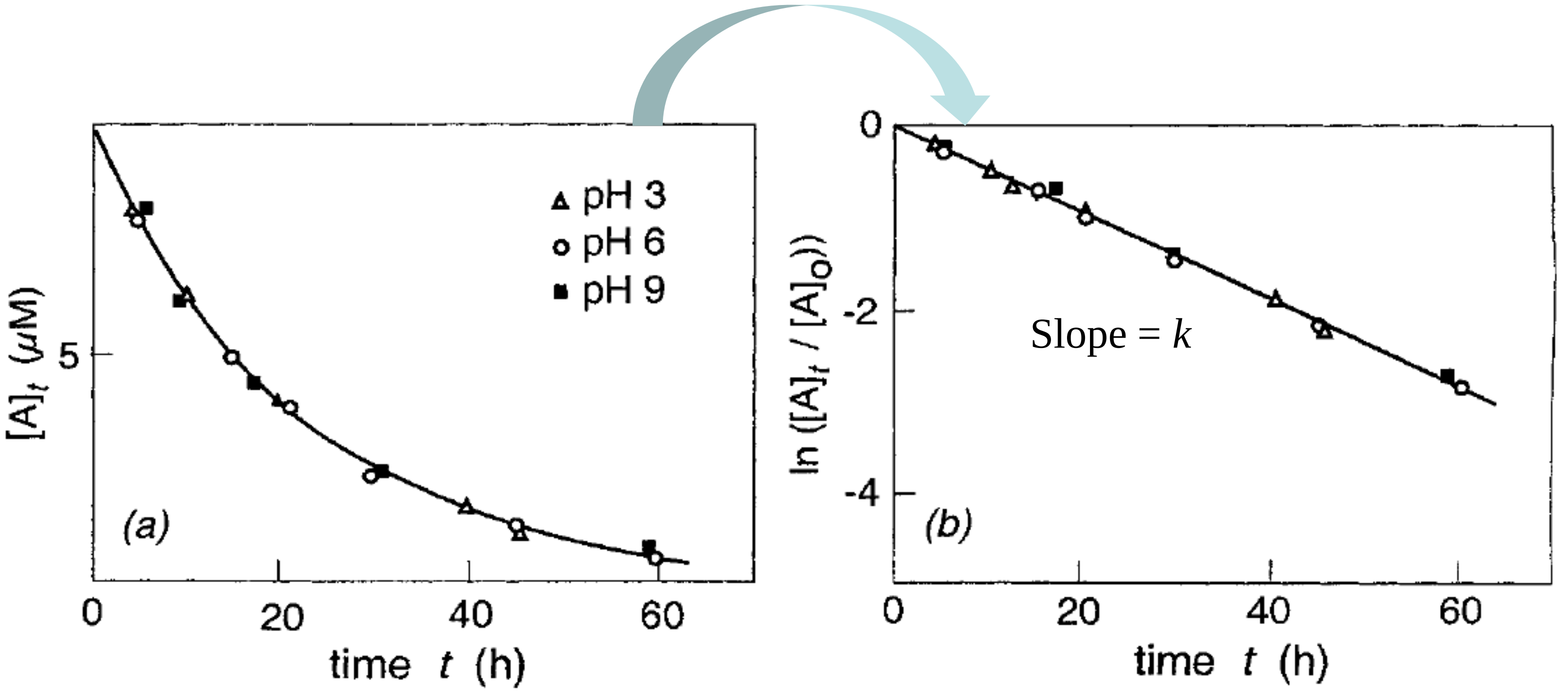
Figure 12.2 Decrease in benzyl chloride concentration (*a*) plotted directly and (*b*) plotted logarithmically as a function of time in aqueous solution at three different pHs.

Kinetics

How to determine the first-order rate constant in the lab?

A → P

k : first-order rate constant (s^{-1})



Slope = k

Plot $\ln([A]_t/[A]_0)$ vs. t ⇒ the slope is k

Kinetics

√ Second-order kinetics

$$\mathbf{A + B \rightarrow P + Q}$$

k : second-order rate constant ($M^{-1}\ s^{-1}$)

$$\frac{d[A]}{dt} = -k[A][B] = \frac{d[B]}{dt} = -\frac{d[P]}{dt} = -\frac{d[Q]}{dt}$$

* Let's determine $[A] = f(t)$

$$\frac{d[A]}{dt} = -k[A][B]$$

Assume $[B] = [A] + C$

$$\text{C : constant} \begin{cases} C = 0 \ \ ([A]_0 = [B]_0) \\ C > 0 \ \ ([A]_0 < [B]_0) \\ C < 0 \ \ ([A]_0 > [B]_0) \end{cases}$$

Kinetics

i) If C = 0 ($[A]_0 = [B]_0$),

$$\frac{d[A]}{dt} = -\,k[A][B] \quad = -\,k[A]^2$$

$$\frac{d[A]}{[A]^2} = -\,k\,dt \quad \Rightarrow \quad -\left.\frac{1}{[A]}\right|_{[A]_0}^{[A]} = -\,k\,t\,\Big|_{0}^{t}$$

$$\Rightarrow \quad -\frac{1}{[A]} + \frac{1}{[A]_0} = -\,k\,t$$

$$\Rightarrow \quad [A] = \frac{[A]_0}{1 + kt[A]_0} \qquad [B] = \frac{[B]_0}{1 + kt[B]_0}$$

$t_{1/2} = \;?$ Put $[A] = 1/2[A]_0$

$$\Rightarrow \quad \frac{1}{[A]_0} = k\,t \quad \Rightarrow \quad t_{1/2} = \frac{1}{k[A]_0}$$

Kinetics

i) If $C \neq 0$ ($[B] = [A] + C$),

$$\frac{d[A]}{dt} = -k[A][B] = -k[A]([A] + C)$$

$$\frac{d[A]}{[A]([A]+C)} = -k\,dt \Rightarrow \frac{1}{C}\left(\frac{1}{[A]} - \frac{1}{[A]+C}\right)d[A] = -k\,dt$$

$$\Rightarrow \frac{1}{C}\ln\frac{[A]}{[A]+C}\Bigg|_{[A]_0}^{[A]} = -k\,t\Bigg|_{0}^{t} \Rightarrow [A] = \frac{C[A]_0\exp(-kCt)}{C + [A]_0(1-\exp(-kCt))}$$

$[B] = ?$, $t_{1/2} = ?$

Kinetics

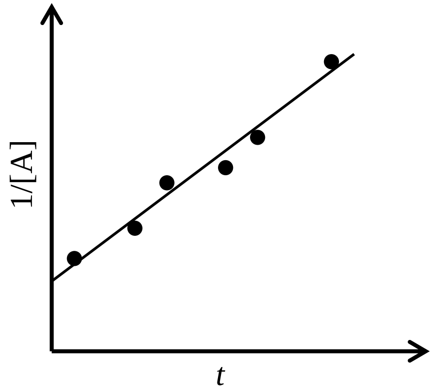
How to determine the second-order rate constant in the lab?

$$\mathbf{A + B \rightarrow P + Q}$$

k : second-order rate constant ($M^{-1}\ s^{-1}$)

Use of same concentrations of A and B

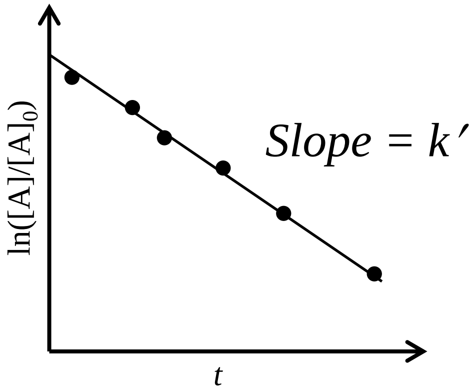
$$\frac{1}{[A]} - \frac{1}{[A]_0} = k\,t$$



Plot 1/[A] vs. t $\Rightarrow$ the slope is k

Use of excess B compared to A

$$\begin{aligned}\frac{d[A]}{dt} &= -k[A][B] \\ &= -k[A][B]_0 \quad ([B] \approx [B]_0) \\ &= -k'[A] \qquad (k' = k[B]_0)\end{aligned}$$



Kinetics

√ First-order reaction including back reaction

$$\mathbf{A} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathbf{D}$$

k_1 & k_2 : first-order rate constants

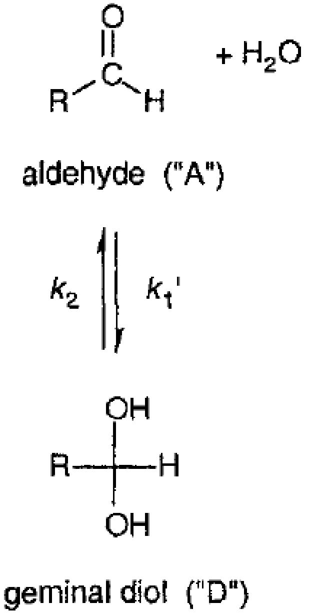


Figure 12.3 Many aldehydes react substantially with water in a reversible fashion to yield a diol (see also Bell and McDougall, 1960).

* Let's determine [A] = $f(t)$

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_2[\mathrm{D}]$$

$$[\mathrm{A}]_0 = [\mathrm{A}] + [\mathrm{D}]$$

⇒ $$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_2([\mathrm{A}]_0 - [\mathrm{A}])$$
$$= k_2[\mathrm{A}]_0 - (k_1 + k_2)[\mathrm{A}]$$

⇒ $$[\mathrm{A}] = [\mathrm{A}]_0 \frac{k_2 + k_1\exp(-(k_1+k_2)t)}{k_2 + k_1}$$

Kinetics

Equilibrium constant (K_r)

$$[\mathrm{A}] = [\mathrm{A}]_0 \frac{k_2 + k_1 \exp(-(k_1+k_2)t)}{k_2 + k_1}$$

$$[\mathrm{D}] = [\mathrm{A}]_0 - [\mathrm{A}] = [\mathrm{A}]_0 \frac{k_1 - k_1 \exp(-(k_1+k_2)t)}{k_2 + k_1}$$

$$t \rightarrow \infty$$

$$[\mathrm{A}]_{\mathrm{eq}} = [\mathrm{A}]_0 \frac{k_2}{k_2 + k_1} \qquad [\mathrm{D}]_{\mathrm{eq}} = [\mathrm{A}]_0 \frac{k_1}{k_2 + k_1}$$

$$K_r = [\mathrm{D}]_{\mathrm{eq}}/[\mathrm{A}]_{\mathrm{eq}} = k_1/k_2$$

Or, (easier way)

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_2[\mathrm{D}] = 0$$

$$-k_1[\mathrm{A}]_{\mathrm{eq}} + k_2[\mathrm{D}]_{\mathrm{eq}} = 0$$

$$[\mathrm{D}]_{\mathrm{eq}}/[\mathrm{A}]_{\mathrm{eq}} = k_1/k_2$$

Kinetics

√ Catalyzed reactions

What is “Catalyst”?

“Catalyst” does not participate in the reaction, but accelerates the reaction rate?

“Catalyst” does participate in the reaction, accelerating the reaction rate, but, it just does not appear in the overall reaction!

“Catalyst” lowers the activation barrier (energy) of the reaction.

e.g., Michaelis-Menten enzyme kinetics

$$\mathbf{A} \rightarrow \mathbf{P} \quad \text{(slow)}$$

But, in the presence of enzyme, E

$$\mathbf{A} + \mathbf{E} \rightleftarrows \mathbf{AE} \quad \text{(ultra-fast)}$$

$$\mathbf{AE} \rightarrow \mathbf{P} + \mathbf{E} \quad \text{(fast)}$$

Overall reaction: $\mathbf{A} \rightarrow \mathbf{P}$ (fast)

Kinetics

$$\mathbf{A} + \mathbf{E} \underset{k_b}{\overset{k_f}{\rightleftarrows}} \mathbf{AE}$$

$$\mathbf{AE} \xrightarrow{k_E} \mathbf{P} + \mathbf{E}$$

* Let's determine [A] = $f(t)$

$$K_E = \frac{k_f}{k_b} = \frac{[AE]}{[A][E]}$$

$$\frac{d[A]}{dt} = -k_f[A][E] + k_b[AE] \qquad (1)$$

$$\frac{d[AE]}{dt} = k_f[A][E] - k_b[AE] - k_E[AE] = 0 \qquad (2)$$

(steady-state approximation)

$$(1) + (2) \Rightarrow \qquad \frac{d[A]}{dt} = -k_E[AE]$$

Kinetics

$$\boxed{\frac{d[\mathrm{A}]}{dt} = -k_E[\mathrm{AE}]}$$

$$\begin{aligned}[\mathrm{E}]_0 &= [\mathrm{E}] + [\mathrm{AE}] \\ &= [\mathrm{AE}](1 + [\mathrm{E}]/[\mathrm{AE}]) \\ &= [\mathrm{AE}](1 + 1/K_\mathrm{E}[\mathrm{A}])\end{aligned}$$

$$K_\mathrm{E} = \frac{[\mathrm{AE}]}{[\mathrm{A}][\mathrm{E}]}$$

$$\Rightarrow [\mathrm{AE}] = [\mathrm{E}]_0/(1 + 1/K_\mathrm{E}[\mathrm{A}])$$

$$\begin{aligned}\Rightarrow \frac{d[\mathrm{A}]}{dt} &= -k_E[\mathrm{E}]_0/(1 + 1/K_\mathrm{E}[\mathrm{A}]) \\ &= -k_E[\mathrm{E}]_0[\mathrm{A}]/([\mathrm{A}] + 1/K_\mathrm{E})\end{aligned}$$

If $[\mathrm{A}] \gg 1/K_\mathrm{E}$

$$\Rightarrow \frac{d[\mathrm{A}]}{dt} = -k_E[\mathrm{E}]_0 \text{ (zero-order kinetics)}$$

$$[\mathrm{A}] = [\mathrm{A}]_0 - k_E[\mathrm{E}]_0 t$$

If $[\mathrm{A}] \ll 1/K_\mathrm{E}$

$$\Rightarrow \frac{d[\mathrm{A}]}{dt} = -k_E K_E[\mathrm{E}]_0[\mathrm{A}] \text{ (first-order kinetics)}$$

$$[\mathrm{A}] = [\mathrm{A}]_0\exp(-k_E K_E[\mathrm{E}]_0 t)$$