EVROPSKÁ UNIE
Evropské strukturální a investiční fondy
Operační program Výzkum, vývoj a vzdělávání

MINISTERSTVO ŠKOLSTVÍ,
MLÁDEŽE A TĚLOVÝCHOVY

Geochemistry on the Earth’s surface for analytical geochemists

3b. Speed of processes

Tento učební materiál vznikl v rámci projektu Rozvoj doktorského studia chemie
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Questions

1. How can we determine which processes will take place spontaneously in nature?
2. What will tell us in which direction?
3. From what can we determine the equilibrium state of the system/process?
4. Which processes will not reach equilibrium, but will run (more or less) completely?

Reaction kinetics

- It studies the rate of reactions that are feasible from thermodynamic point of view.
- The rate of a reaction is basically the rate at which the reactants are consumed and the products are formed.
- How reactions occur is explained by the **collision theory**

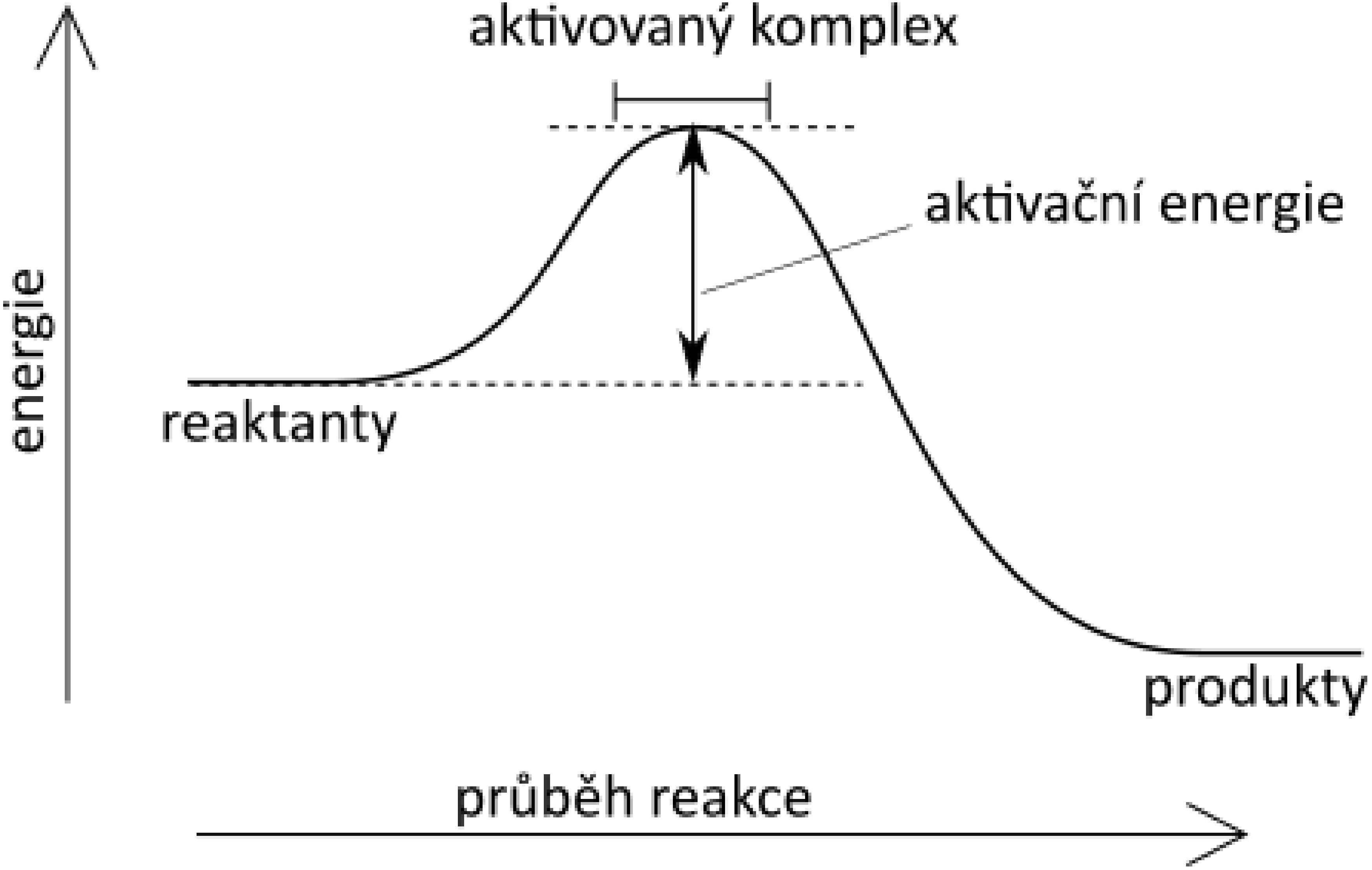
Collision theory

- For the reaction to take place, several conditions must be met:

1. The reactant particles must collide.
2. The colliding particles must have sufficient energy to react.
3. In some cases, particles need to collide with a specific orientation (e.g., a functional group).

Activation energy

- The minimum total kinetic energy that the particles must have for a reaction to occur.
- Each reaction has a different value of $\mathbf{E}_\mathbf{A}$.
- In the case of slow reactions, the activation energy is much higher than the average energy of the particles – collisions rarely lead to the reaction.
- Sometimes the activation energy can be supplied externally as an initiator, and then the reaction continues to be driven by the energy released during it.


aktivovaný komplex
aktivační energie
energie
reaktanty
produkty
průběh reakce

Factors affecting reaction rate

- What factors will play a role in the final rate of chemical reactions?
- How will this be reflected in geological processes?

Factors affecting reaction rate

- There are several, but 4 generally apply to all reactions:
  1. Physical nature of reactants.
  2. Concentration.
  3. Temperature.
  4. The presence of catalysts.

Physical nature of reactants

- State, but also the size of the particles.
- Reaction rate: gas > liquid > solid
- Solids react on the surface:
  - The larger the surface, the faster the reaction.
  - The smaller the grains, the faster the reaction.
- **Ex.:** Consider the burning of the same amount of wood in different forms

Increase in surface area = increase in contact between reactants →

Trunk - boards - chips - sawdust

→ Increase in burning rate

Concentration

- An increase in reactants leads to an increase in the reaction rate.
- Substances burn faster in pure oxygen than in air.
- A higher concentration increases the chance of particle collision.
- The effect of concentration varies depending on the substance, there is no general relationship and each substance needs to be tested experimentally.
- **E.g.:** Influence of the content of CO_2, O_2 or organic acids in the soil on weathering and soil-forming processes.

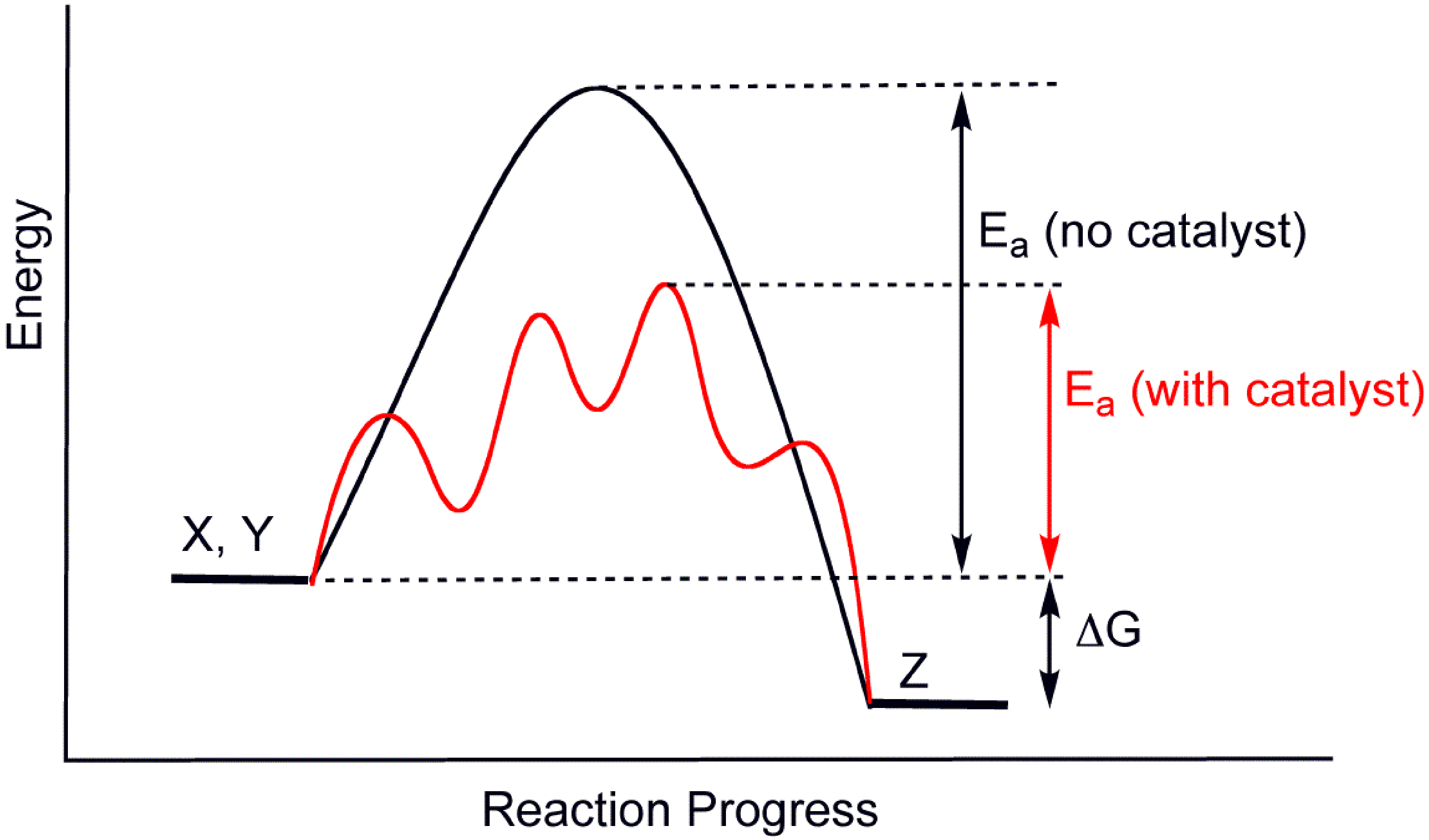
Temperature

- Increases the probability of collisions because the particles have higher kinetic energy.
- Particles with higher energy are closer to exceeding the activation energy (E_A).
- The reaction rate roughly doubles for every 10°C.
- **Ex.**: Food is refrigerated to slow down decomposition processes.
- Weathering in cold/warm climates.

The presence of catalysts

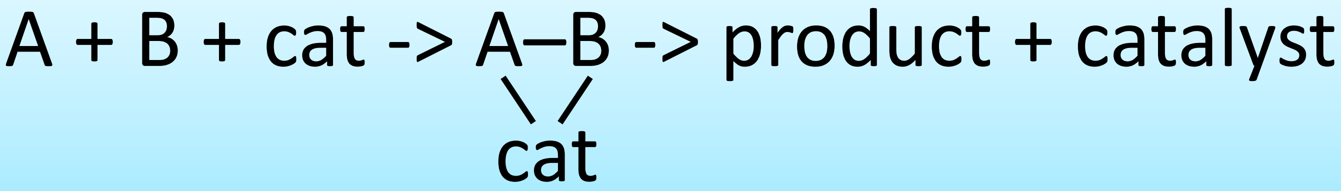
- A catalyst is a substance that increases the rate of a reaction but is itself unchanged after the reaction is complete.
- They provide alternative reaction pathways with lower activation energy.
- It is part of the reaction in the same way that a table is part of the lunch – it provides space and the right conditions, but the reaction does not consume it.

Catalysis


Energy
X, Y
Z
E_a (no catalyst)
E_a (with catalyst)
ΔG
Reaction Progress

Homogeneous catalyst

- Same phase as the reactants, usually forming an intermediate.



$$\text{A + B + cat -> } \underset{\text{cat}}{\text{A–B}} \text{ -> product + catalyst}$$

Heterogeneous catalyst

- A separated phase, usually a solid.
- It is assumed to provide the environment for the reaction.
  - The reactants bind to the surface of the solid phase at a certain angle and thus facilitate the reaction.

Use of catalysts

- Intensive use in the chemical industry in the production of chemicals -> low energy consumption during reactions is economically very advantageous.
- High temperatures are demanding and expensive!
- Exhaust gas cleaners in combustion engines of cars.
- Enzymes are important in biochemistry.
- Ozone depletion.

SPEED OF PROCESSES

A natural process

- We observe that the concentration of a substance in a solution changes over time
- There is a process going on
- How can I find out and express its speed?

Process speed

- We usually use the change in content over time – concentration, weight, amount of substance, volume

$$\mathrm{d}[\mathrm{A}]/\mathrm{d}t$$

- The tangent of the concentration-time curve

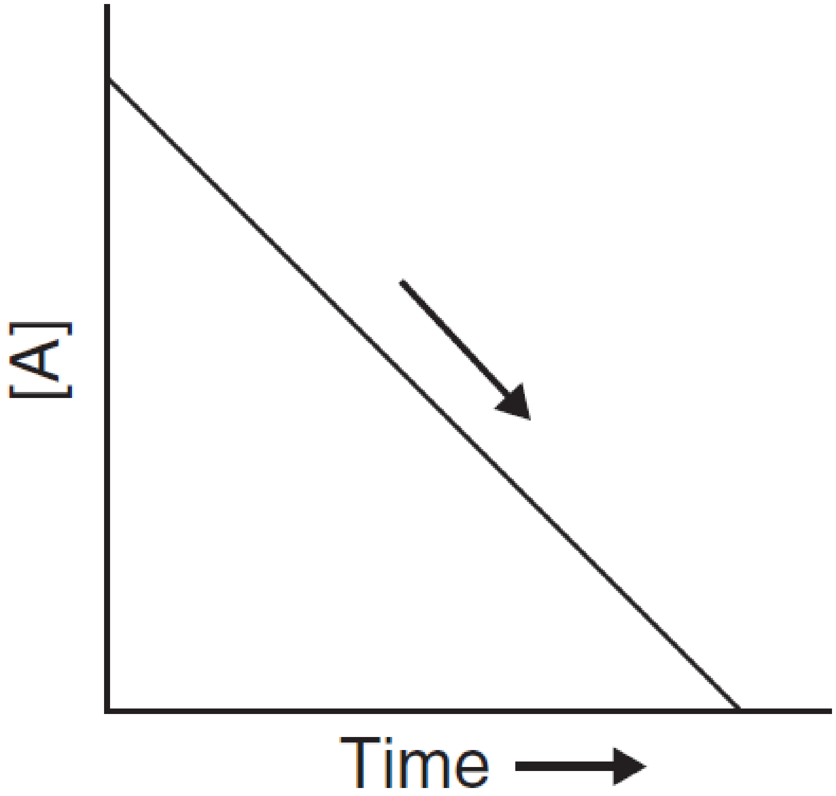
0th order reaction

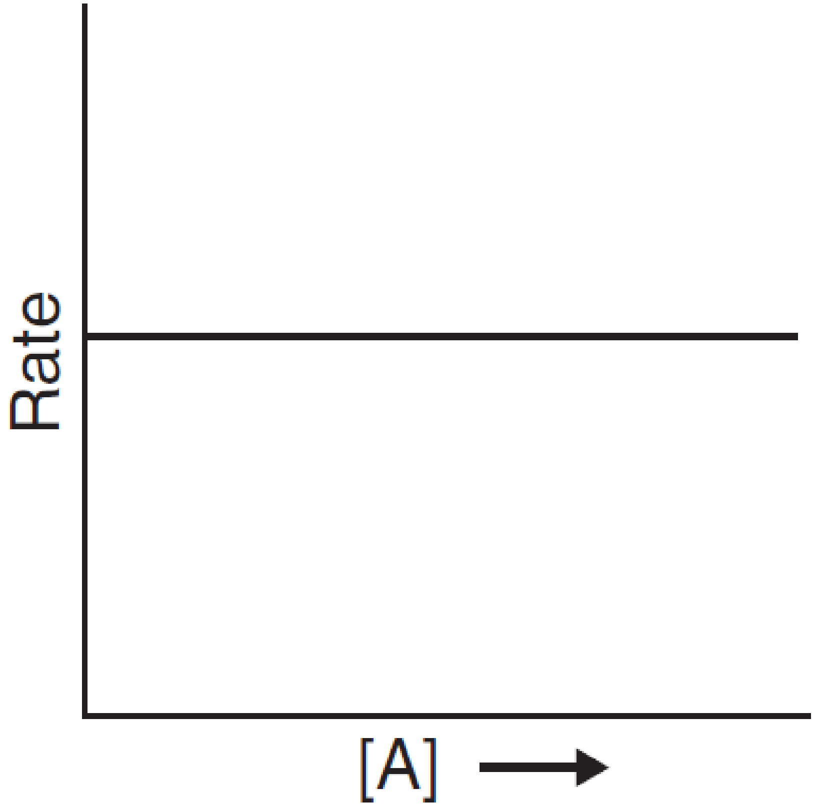
$$\mathrm{A} \Rightarrow \mathrm{B}$$

$$\mathrm{d}[\mathrm{A}]/\mathrm{d}t = -k$$

$$[\mathrm{A}] = [\mathrm{A}]_o - kt$$

0th order reaction





Adapted from Ryan (2014)

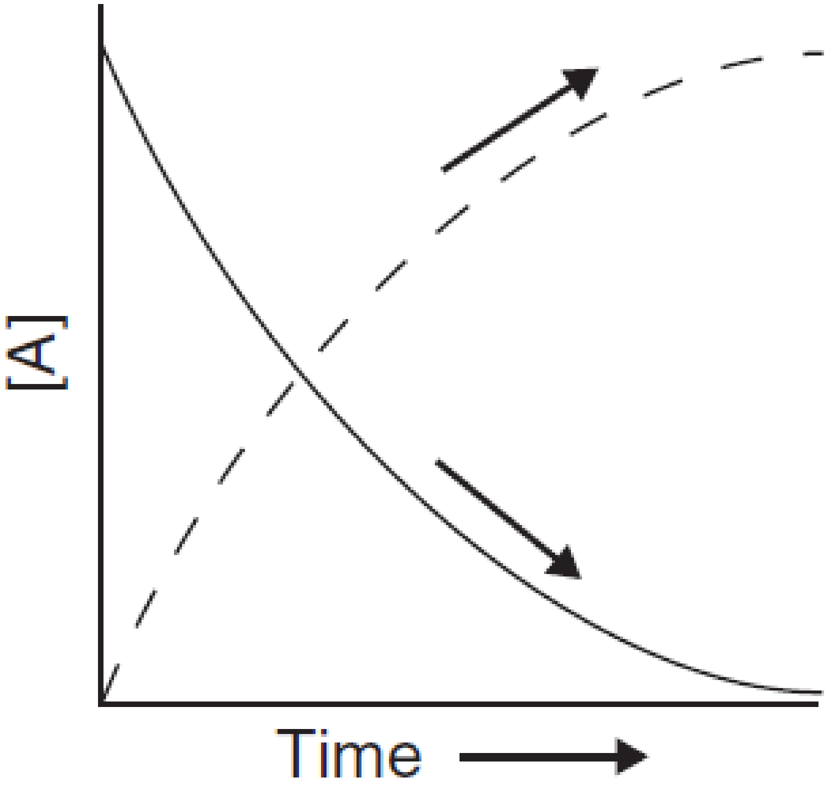
1st order reaction

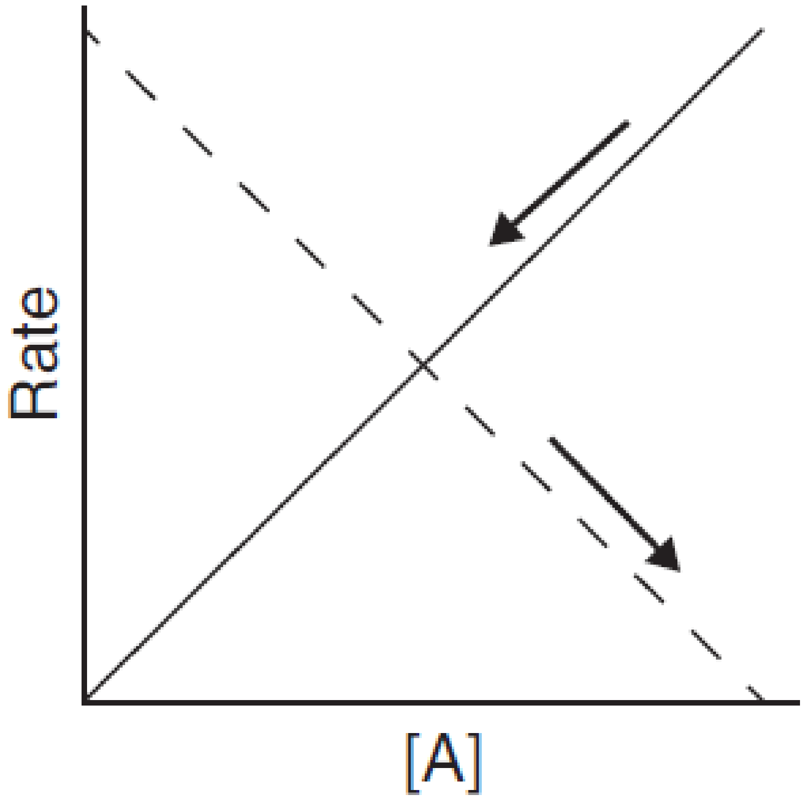
$$A => B$$

$$\mathrm{d}[\mathrm{A}]/\mathrm{d}t = -k\mathrm{A}$$

$$[\mathrm{A}] = [\mathrm{A}]_{\mathrm{o}} * e^{-kt}$$

1st order reaction





Adapted from Ryan (2014)

2nd order reaction

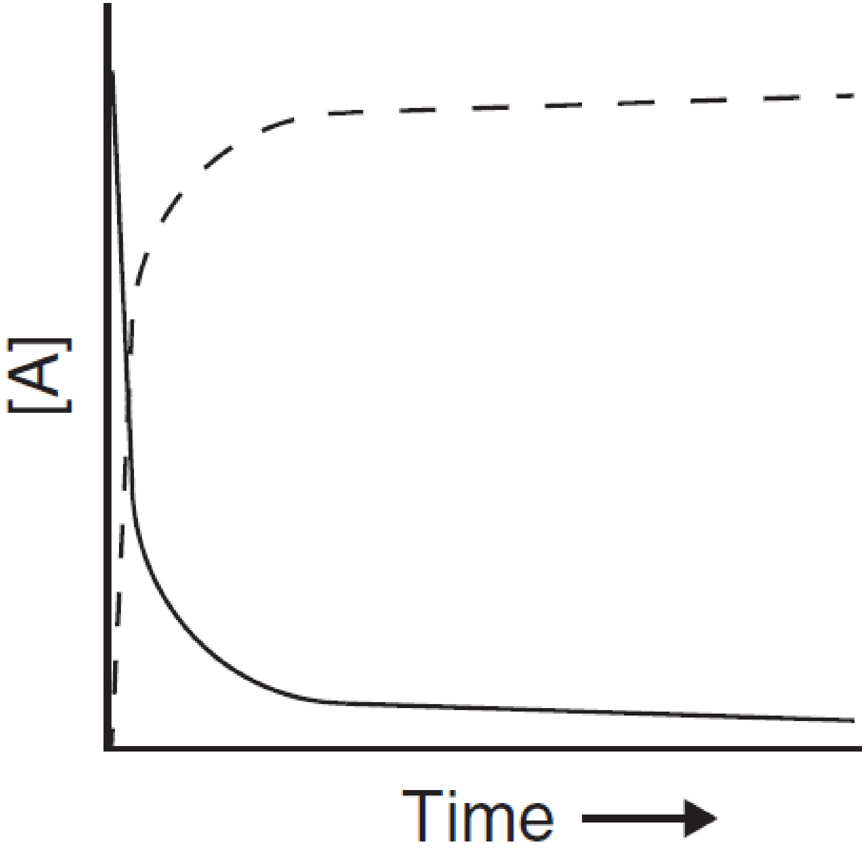
$$2A => B$$

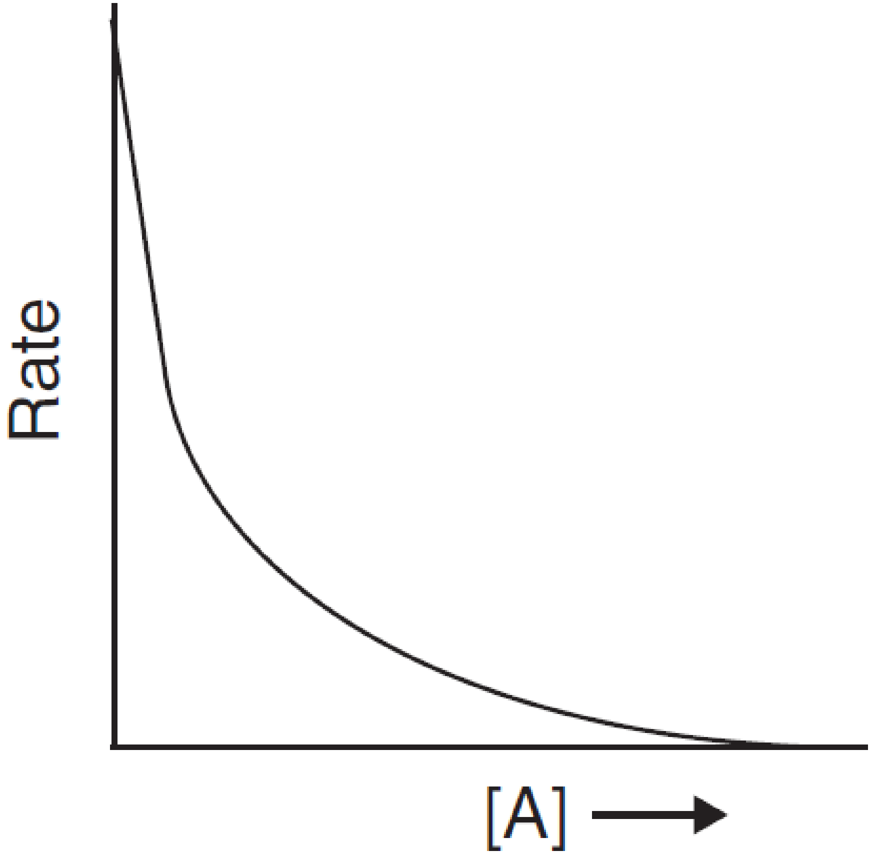
$$A + B => C$$

$$1/[\mathrm{A}] = k * t + \mathrm{C}$$

$$1/[\mathrm{A}] - 1/[\mathrm{A_o}] = k * t$$

2nd order reaction





Adapted from Ryan (2014)

Dependence of *k* on temperature

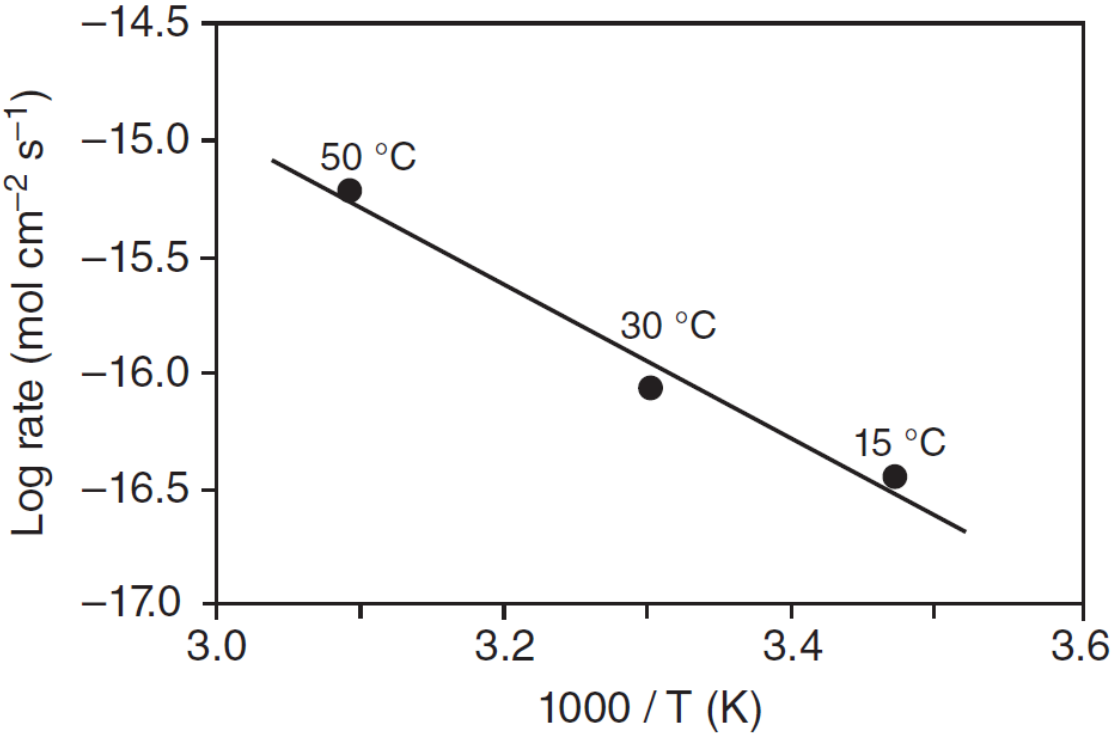


Fig. 1.19 Effect of temperature on chemical weathering rate of rhyolite as a function of temperature. (Yokoyama and Banfield 2002. Reproduced with permission of Elsevier.)

$$k = A * e^{-\mathrm{Ea}/RT}$$

Adapted from Ryan (2014)

Retention time

- Inverse of the rate constant

$$k = 1/\tau$$

Example process

CALCITE DISSOLUTION

Dissolution/precipitation

$$\begin{array}{c} \mathrm{CaCO_{3\,(s)}} \xrightarrow{\ \Re_{\mathrm{d}}\ } \mathrm{Ca^{2+}} + \mathrm{CO_3^{2-}} \\ \xleftarrow[\ \Re_{\mathrm{p}}\ ]{} \end{array}$$

$$\Omega = \frac{Q}{K} = \frac{[Ca^{2+}][CO_3^{2-}]}{K}$$

An empirical model

Dissolution $\Re_d = k_d(1 - \Omega_{cal})^{n_d}$

Precipitation $\Re_p = k_p(\Omega_{cal} - 1)^{n_p}$

$$\log \Re_d = n_d \log (1 - \Omega_{cal}) + \log k_d$$

$$\log \Re_p = n_p \log (\Omega_{cal} - 1) + \log k_p$$

- They can vary significantly

$$\Re_d(\%\ \mathrm{day}^{-1})_{\text{Indian ocean}} = 10^{4.3}(1 - \Omega_{\mathrm{cal}})^{5.2}$$

$$\Re_d(\%\ \mathrm{day}^{-1})_{\text{Pacific ocean}} = 10^{2.7}(1 - \Omega_{\mathrm{cal}})^{3.0}$$

$$\Re_d(\%\ \mathrm{day}^{-1})_{\text{Atlantic ocean}} = 10^{3.1}(1 - \Omega_{\mathrm{cal}})^{4.5}$$

- Effect of particle size or mineral surface condition?

Mechanical model

- The dissolution mechanism is pH dependent

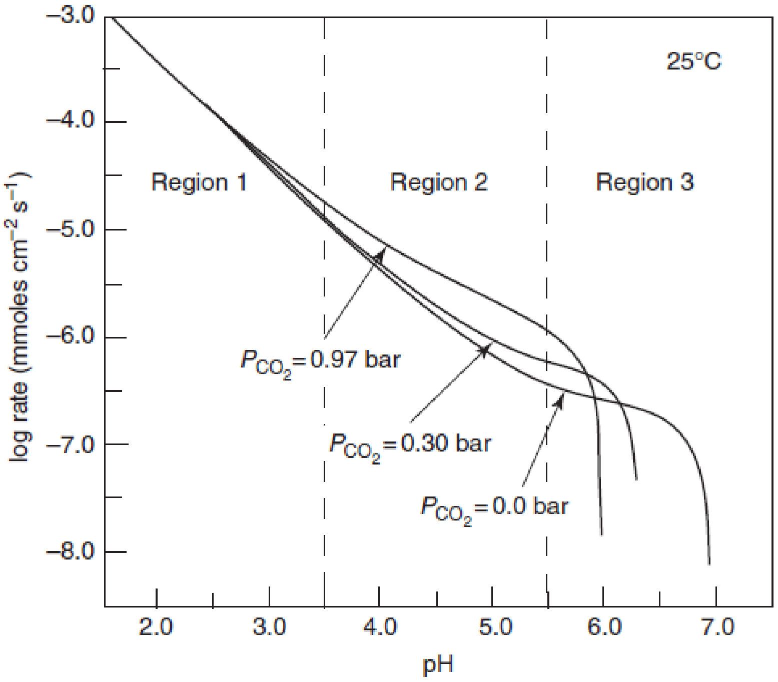
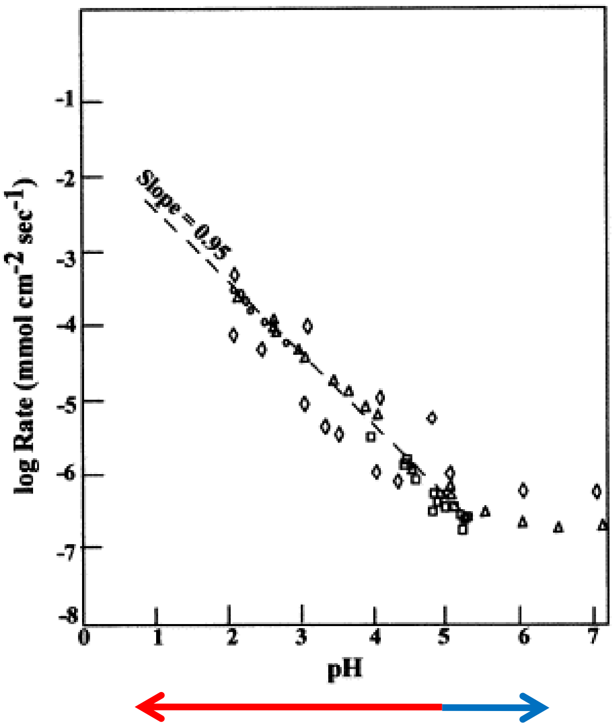


Fig. 9.11 Experimentally determined dissolution rates of calcite (Iceland spar) as a function of bulk fluid pH and P_{CO_2} at 25°C. The results can be divided into three regions: a pH-dependent regime (Region 1), a transition region (Region 2), and a pH-independent region (Region 3) (see text for explanation). The boundaries between the regimes are shown for dissolution at P_{CO_2} = 1 atm but, in general, the boundaries are a function of P_{CO_2} and reaction progress. (After Plummer *et al.*, 1978, Figure 1, p. 186.)



(Edited of Parkhurst et al. al. 1979)

pH dependentindependent of pH

Processes on the surface of calcite

1. $CaCO_3 + H^+ \xrightarrow{k_1} Ca^{2+} + HCO_3^-$
2. $CaCO_3 + H_2CO_3^* \xrightarrow{k_2} Ca^{2+} + 2HCO_3^-$
3. $CaCO_3 + H_2O \xrightarrow{k_3} Ca^{2+} + CO_3^{2-} + H^+ \rightarrow Ca^{2+} + HCO_3^- + OH^-$
4. $Ca^{2+} + HCO_3^- \xrightarrow{k_4} CaCO_3 + H^+$

$$\boxed{\mathfrak{R} = k_1\, a_{\mathrm{H}^+} + k_2\, a_{\mathrm{H_2CO_3^*}} + k_3\, a_{\mathrm{H_2O}} - k_4\, a_{\mathrm{Ca}^{2+}}\, a_{\mathrm{HCO_3^-}}}$$

Driven by diffusion of H+ to the surface

pH < 5

Controlled by diffusion of products from the surface

pH > 5

Extension to the natural environment

A RESERVOIR AS A REACTOR

Rezervoár

Photo by Adam Vradenburg.

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Reservoir balance

$$A = \sum_i I + \sum_i P - \sum_i O - \sum_i L$$

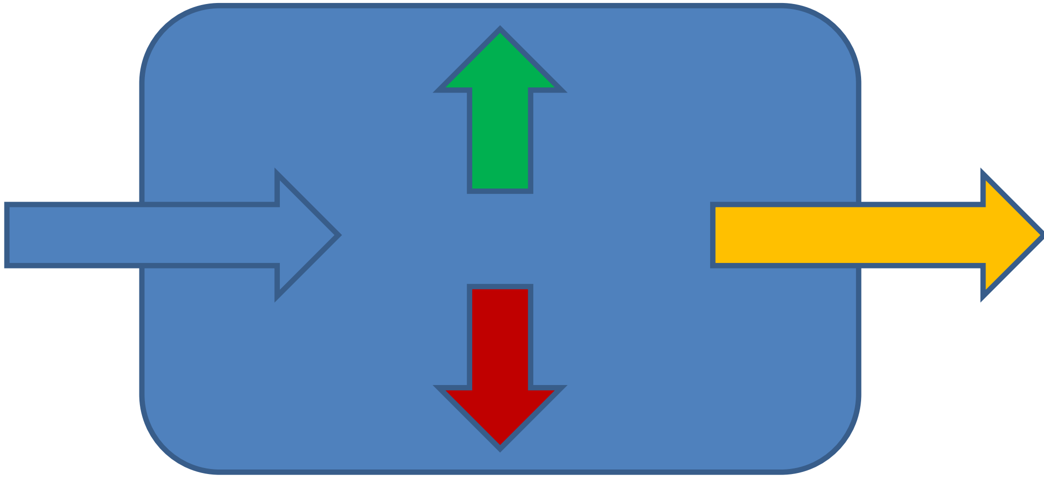
A … increase/decrease of substance in the system

I … input

P … production

O … output

L … loss/consumption



Balance

- If A is zero, the system is in dynamic equilibrium (steady state)

- Will the content of the system grow?
- Will system content go down?
- How long will it take to reach balance?

Retention time in the reactor

- The average time spent by the particle in the system
- At a steady state, transport by advection only

$$\tau = \frac{\text{celková hmota}}{\text{hmotová výměna}} = \frac{M_{tot}}{dM_{in(out)}/dt} = \frac{V}{F}$$

τ … retention time

M_{tot} … total content of the reactor

$M_{in(out)}$ … quantity entering/exiting the reactor

V … reactor volume

F … flux to/from the reactor (they are in equilibrium)

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Resources

- Images without credit are mine or with a free license.
- RYAN, Peter Crowley. Environmental and low-temperature geochemistry. Chichester, West Sussex, UK: Wiley Blackwell, 2014. ISBN 978-1-118-86735-8.