Lecture 12/13: Kinetics of Water-Rock Interaction

Kinetics is the study of the *rates* of chemical reactions, factors affecting rates, and mechanisms by which reactions proceed
- Reaction rates are determined by a series of chemical reaction and transport steps
    Reaction – rates of bond formation and breakage
    Transport – physical movement of species to and from the site of reaction

Elementary Reactions – proceed in one step
Multistep reactions – a series of elementary steps that

What are the reaction and transport elementary steps involved in the multistep dissolution of calcite?
$$CaCO_{3(s)} + 2H^+ \rightarrow CO_{2(g)} + Ca^{2+} + H_2O$$
1) breaking $CaCO_3$ bonds
2) diffusion of ions away from mineral surface and into solution
3) conversion of $CO3(2-)$ to $HCO3(-)$
4) conversion of $HCO3(-)$ to $H2CO3$
5) CO_2 degassing
6) formation of water

One of these will be the **rate-determining step** – the slowest step in a multistep reaction that determines the rate of the overall reaction

Outline
    (1) Using *rate equations* to predict concentrations of reactants and products over time
    (2) Basic theory of how chemical reactions occur
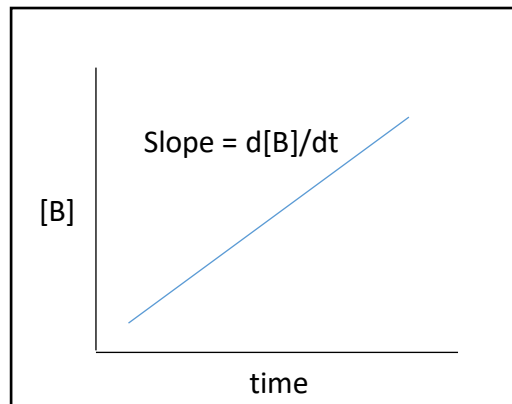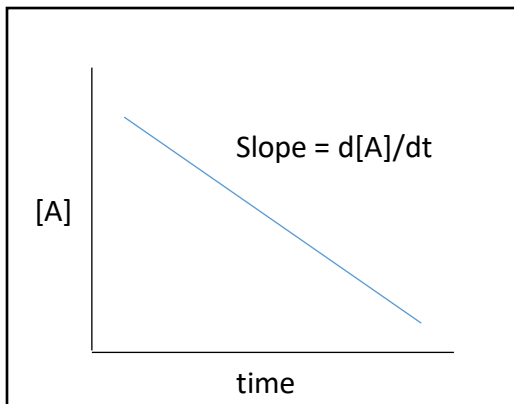   **(3) Effects of physical factors on rates and rate constants**

For a chemical reaction: $A \rightarrow B$
The rate of formation of B is expressed as: $r_B = d[B]/dt$
The rate of loss of A is expressed as: $r_A = -d[A]/dt$

Slope = d[A]/dt   [A]   time

Slope = d[B]/dt   [B]   time

A *rate equation* relates the change in concentration of a species versus time to species concentration

For the reaction: A + B → M
The rate equation is: $r = d[M]/dt = k[A]^\alpha [B]^\beta$

Rate (r = d[M]/dt): the change in concentration of species M with respect to time (t)
Rate constant (k): time-independent value that relates rate to concentrations of A and B
Partial orders of reaction (exponents): dependence of r on the concentration of each species
- Zeroth-order – rate is independent of species concentration
- First-order – rate is proportional to the concentration of a species (X_i)
- Second-order – rate is proportional to the squared concentration of a species (X_i^2)
- Third-order, etc.

Reaction Order – described by the sum of the exponents; expresses the dependence of the overall reaction rate on the concentration of species involved

Examples of different reaction orders:
1) Oxidation of pyrite by O_2 is first-order with respect to $FeS_{2(s)}$
   $-d[FeS_2]/dt = k[FeS_2]$
2) Oxidation of arsenite (AsO_3^{3-}) by MnO_2 is second-order with respect to arsenite
   $-d[AsO_3^{3-}]/dt = k[AsO_3^{3-}]^2$
3) Oxidation of ferrous iron on the surface of silicate minerals by O_2 is first-order with respect to each ferrous iron and O_2 (i.e. second order overall rate)
 $-d[Fe^{2+}]/dt = k[Fe^{2+}][O_2]$

How can we predict concentrations of a chemical species as a function of time?
- Need to determine the value of the rate constant (k) and the orders of each reactant
- Integrate rate equations to express concentrations [C] as a function of time (t) in a linear fashion
- Typically collect data of [C] vs t and use empirical fits to determine reaction order

First-Order Kinetics: rate depends linearly on the concentration of a single reactant
$$d[C]/dt = k[C]$$
Radioactive decay is first-order with respect to the concentration of the radioactive element
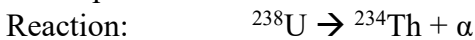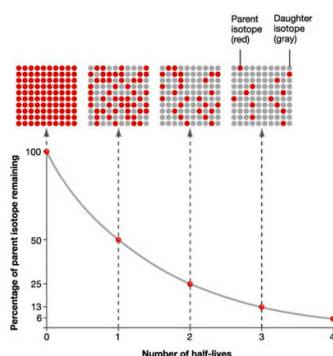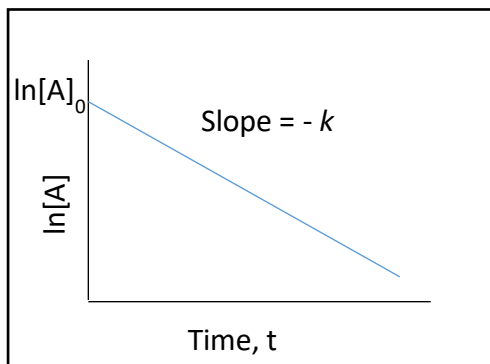

Reaction: $^{238}U → ^{234}Th + \alpha$
Reaction rate: $-d[^{238}U]/dt = k[^{238}U]$
To predict $[^{238}U]$ after a given time, t: $d[^{238}U]/[^{238}U] = -kdt$
Integrate to solve for $[^{238}U]$: $[^{238}U] = [^{238}U]_0 e^{-kt}$

The linear form of the equation, $\ln[A] = \ln[A]_0 - kt$, can be plotted as follows:

Half-life: time it takes for half of the material to decay (or react, for non-radioactive species)
For first-order reactions: $t^{1/2} = (1/k) \times \ln([A]_0/0.5[A]_0) = \ln(2)/k$

Example 5.2 (Brezonik and Arnold) – see Excel sheet
Reactions can be made *pseudo-first order* by experimentally holding the concentrations of all reactants constant except for one

Oxidation of ferrous iron by oxygen gas can be described by the following rate equation:
$$- d[Fe^{2+}]/dt = k[Fe^{2+}]P_{O2}[OH^-]^2$$
When the partial pressure of O_2 is held constant, and pH is buffered, the equation becomes:
$$- d[Fe^{2+}]/dt = k_{obs}[Fe^{2+}]$$
Where $k_{obs} = kP_{O2}[OH]^2$

Plotted as $\ln[Fe^{2+}]$ versus time, we obtain $\ln[Fe^{2+}] = 6.2 - 0.045(t)$, so $k_{obs} = 0.045$

Since we know that $k_{obs} = kP_{O2}[OH]^2$, and we know P_{O2} and $[OH]$ for our controlled system, we can determine k for the initial reaction.

Second-order kinetics
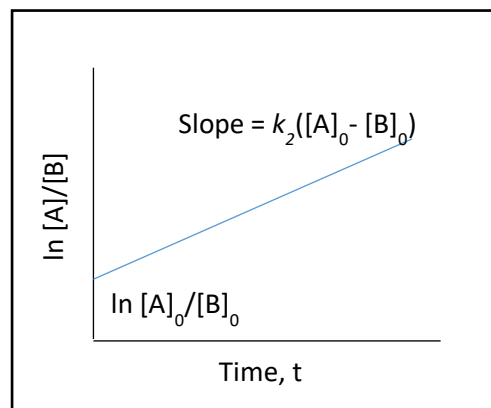For a second-order reaction, $A + B \rightarrow P$,
Rate $= - d[A]/dt = - d[B]/dt = d[P]/dt = k_2[A][B]$

We represent $d[A]$ and $d[B]$ as $d[x]$ (x = the concentration of each species reacted at time t):
$$dx/dt = k_2[A][B] = k_2([A]_0 - x)([B]_0 - x)$$

The integrated, linearized form of this equation is as follows:
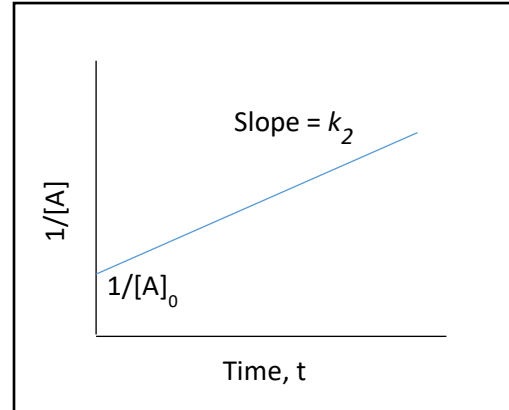$$\ln([A]/[B]) = k_2([A]_0 - [B]_0)t + \ln([A]_0/[B]_0)$$

For a second-order reaction, 2 A → P, we represent d[A] as d[x]:

$$dx/dt = k_2[A]^2 = k_2([A]_0 - x)^2$$

The integrated, linearized form of this equation is as follows:

$$(1/[A]) = k_2 t + (1/[A]_0)$$

Slope = k_2

$1/[A]_0$

1/[A]

Time, t

Zero-order reactions

Zero-order reactions are independent of concentration, such that $-d[A]/dt = k_0[A]^0 = k_0$
The integrated form of this equation is as follows: $[A] = [A]_0 - k_0 t$

Zero-order reactions occur when something other than concentration (such as binding to active sites on enzymes or minerals) controls the rate of reaction; **only occurs for multistep reactions**

Kinetics of mineral dissolution: measure the release of dissolved species as a function of time in well-mixed batch reactors
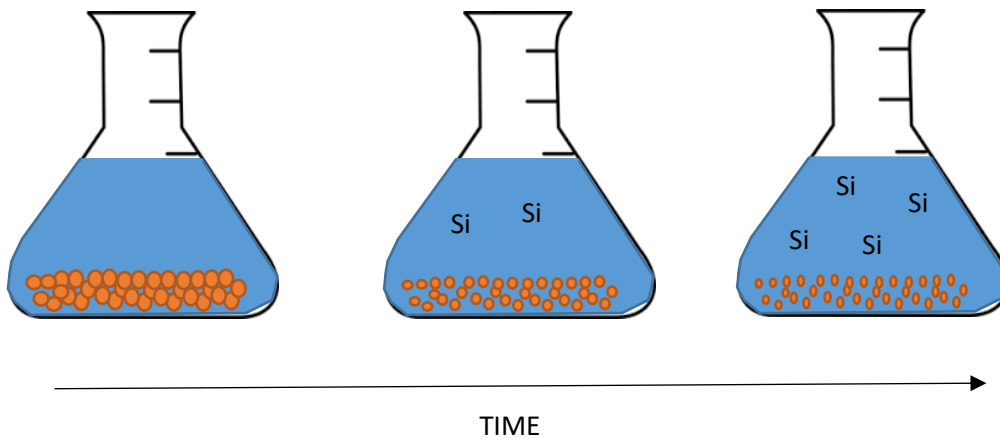
TIME

To determine the rate of reaction, measure product formation over time, such as release of Si from glass dissolution; here, slope of each line = *rate of reaction*
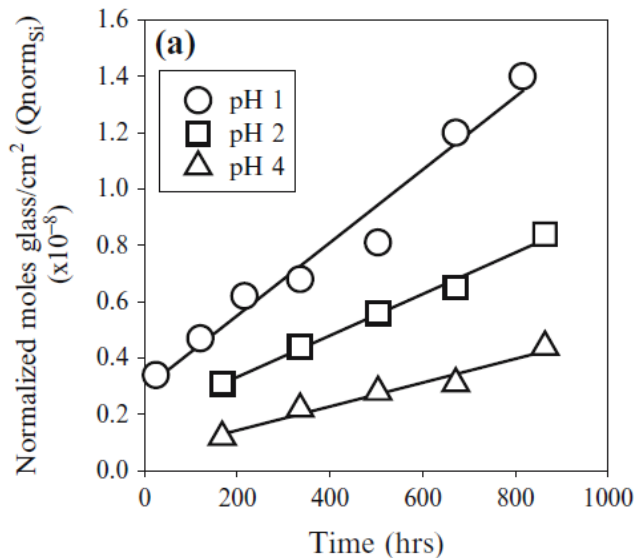
Or, plot the rate of reaction (d[Si]/dt) as a function of a reactant concentration (rate of dissolution vs pH)

$$d[Si]/dt = k[H+]^{\alpha}$$
$$\log(d[Si]/dt) = \log(k) + \alpha \cdot \log([H+])$$

$$\alpha = 0.2$$
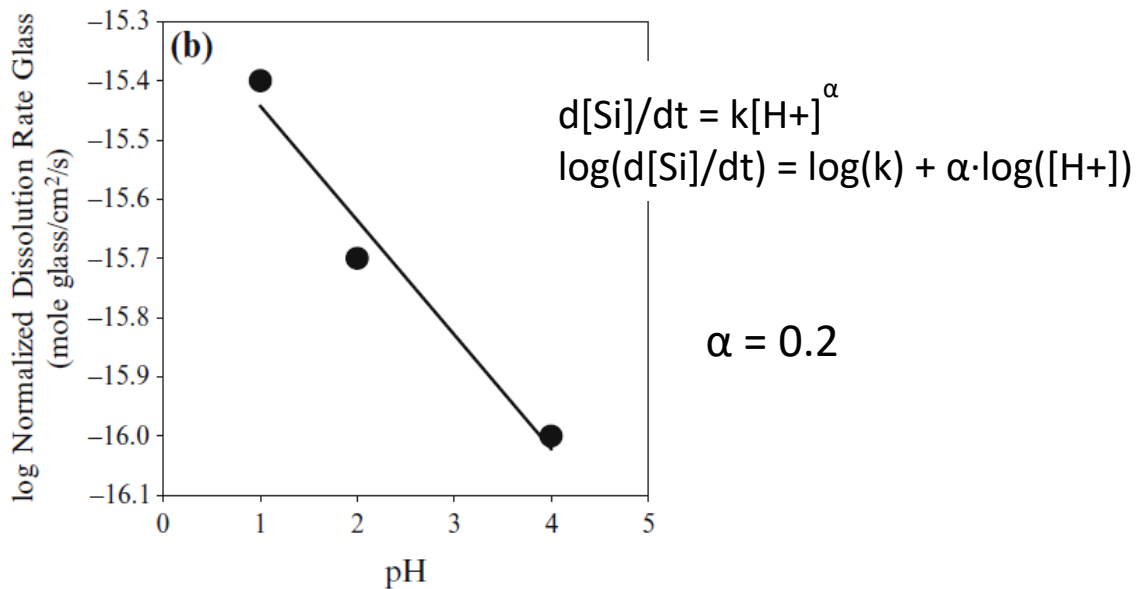
Kinetics becomes ever more complicated beyond second-order reaction kinetics. One complicating factor is *reversible reactions*, where the product is converted back to the reactant at a significant rate.

- The reverse reaction, e.g., [P] → [A], must be considered when a reaction approaches equilibrium
- The reaction orders described above are calculated far from equilibrium (back reaction is negligible)

Effects of temperature on reaction rates
- Rates are often strongly temperature dependent
- Rate constants are independent of *time*, but not temperature (or other physical factors)
- Rate constants vary as a function of temperature according to the *Arrhenius equation*
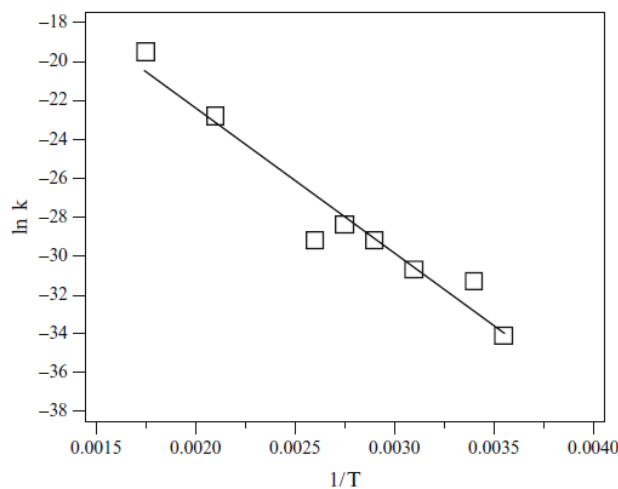
$$k = Ae^{-E_a/RT}$$

A = empirical pre-exponential factor, E_a = activation energy, R = gas constant, T = temperature

The activation energy (E_a) is the energy that must be input into a system to drive the chemical reaction
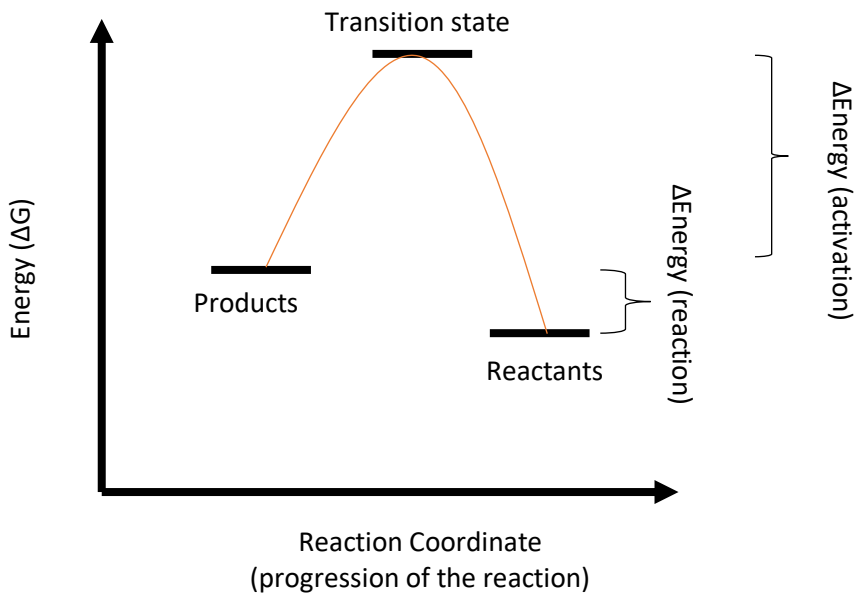
An *Arrhenius plot* can be used to determine the activation energy (Ea) of a chemical reaction:

Example: Albite (feldspar) dissolution

1) Measure *k* for albite dissolution at different temperatures
2) Plot *k* as a function of inverse temperature (in Kelvin)

ln k = ln(A) − (E_a/R)*(1/T)

$E_a = 16 \pm 1$ kcal mol^{-1}