

# Kinetics

EAR 419/619 Environmental Aqueous Geochemistry

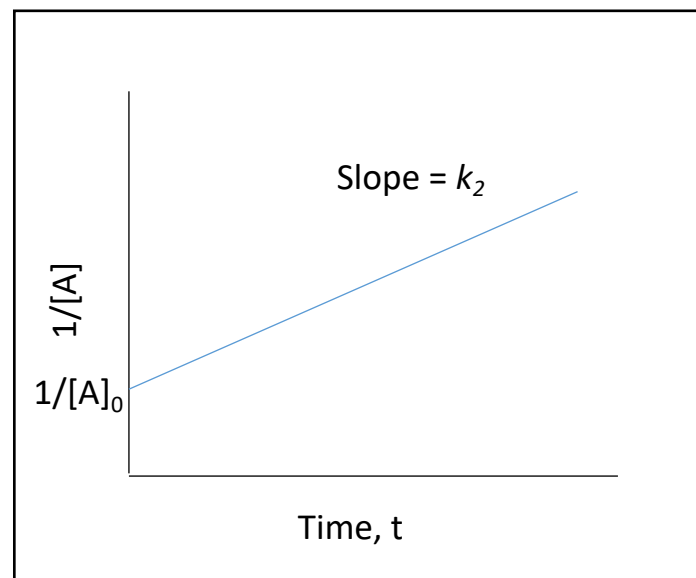
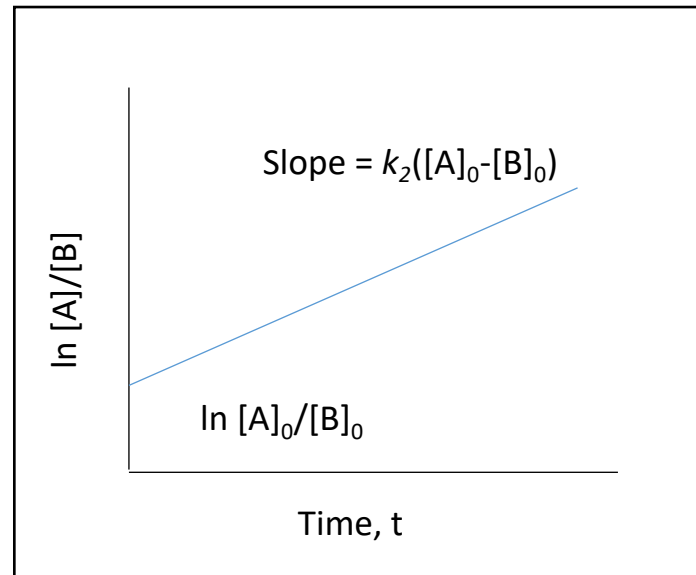
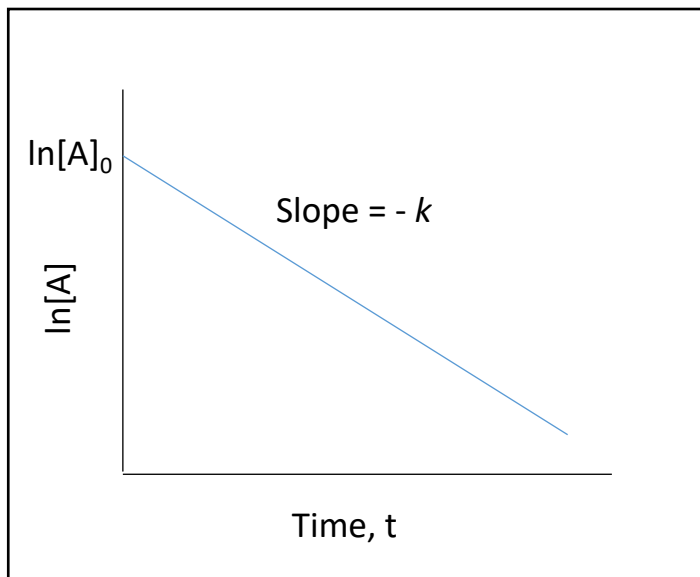
# What is kinetics?

- 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 vs. Multistep reactions



- 1) breaking CaCO<sub>3</sub> bonds
- 2) diffusion of ions away from mineral surface and into solution
- 3) conversion of CO<sub>3</sub>(<sup>2-</sup>) to HCO<sub>3</sub>(<sup>-</sup>)
- 4) conversion of HCO<sub>3</sub>(<sup>-</sup>) to H<sub>2</sub>CO<sub>3</sub>
- 5) CO<sub>2</sub> degassing
- 6) formation of water



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

What are the partial and full orders of reaction?

1:  $d[M]/dt = k[A]$

2:  $d[M]/dt = k[A][B]$

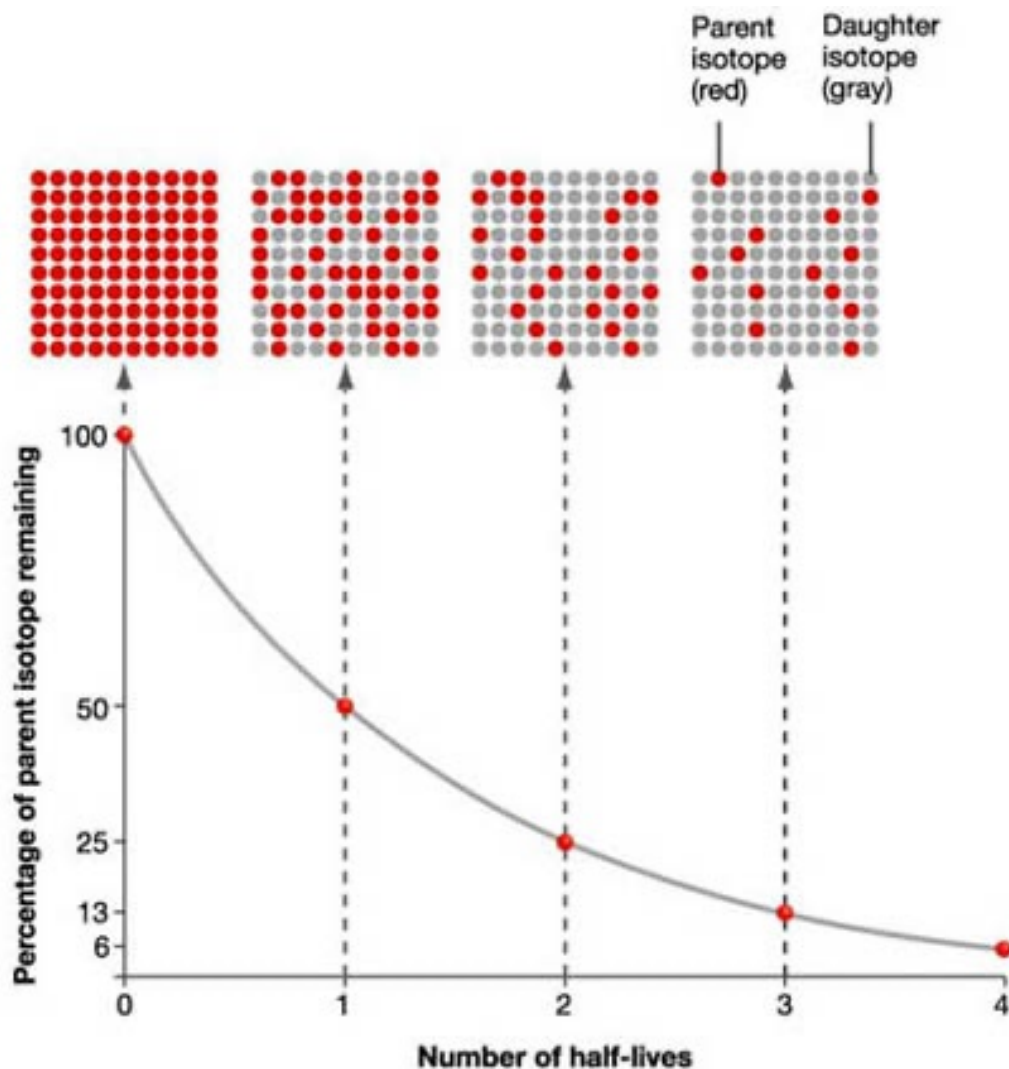
3:  $d[M]/dt = k[A][B]^2$

4:  $d[M]/dt = k[A]^2[B]^2$

5:  $d[M]/dt = k$

Radioactive decay is an example of first-order kinetics:

$$-d[A]/dt = k[A]$$



To predict  $[A]$  remaining after a given time,  $t$ :

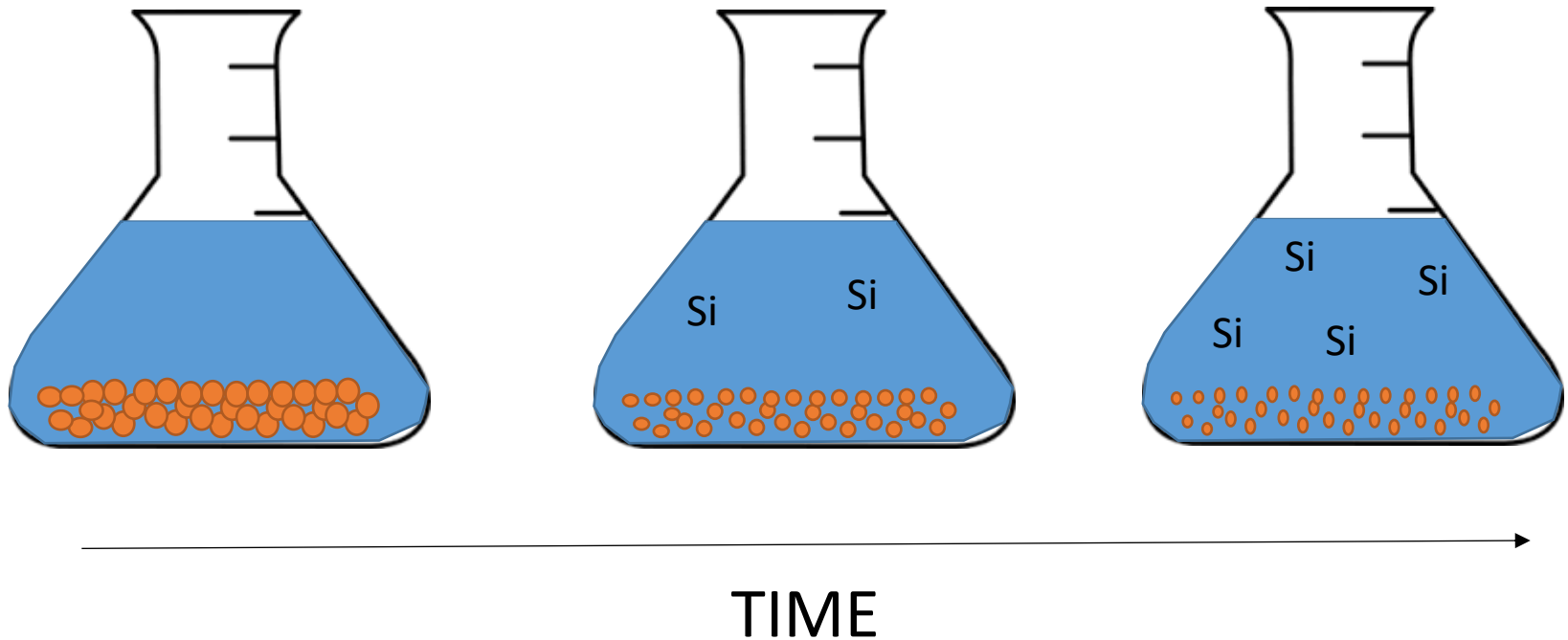
$$[A] = [A]_0 e^{-kt}$$

The half-life ( $t^{1/2}$ ) of M:

$$t^{1/2} = \frac{\ln(2)}{k}$$

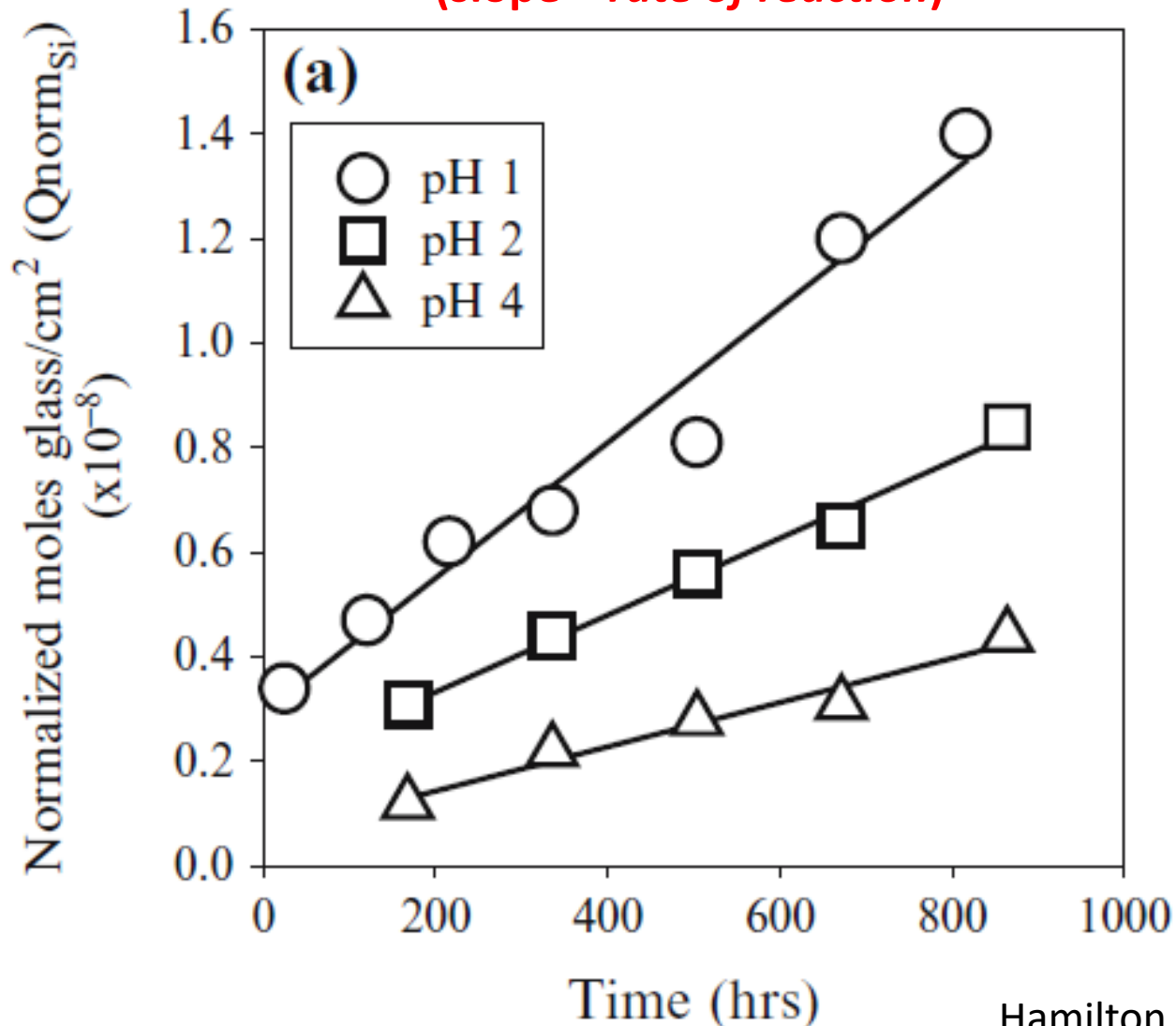
How can we determine the rate of reaction, order of reaction, etc?

Kinetics of mineral dissolution: Measure release of dissolved species as a function of time in well-mixed *batch reactors* (e.g., acid-promoted dissolution of glass to release Si)



# Rate of reaction: measure product formation over time

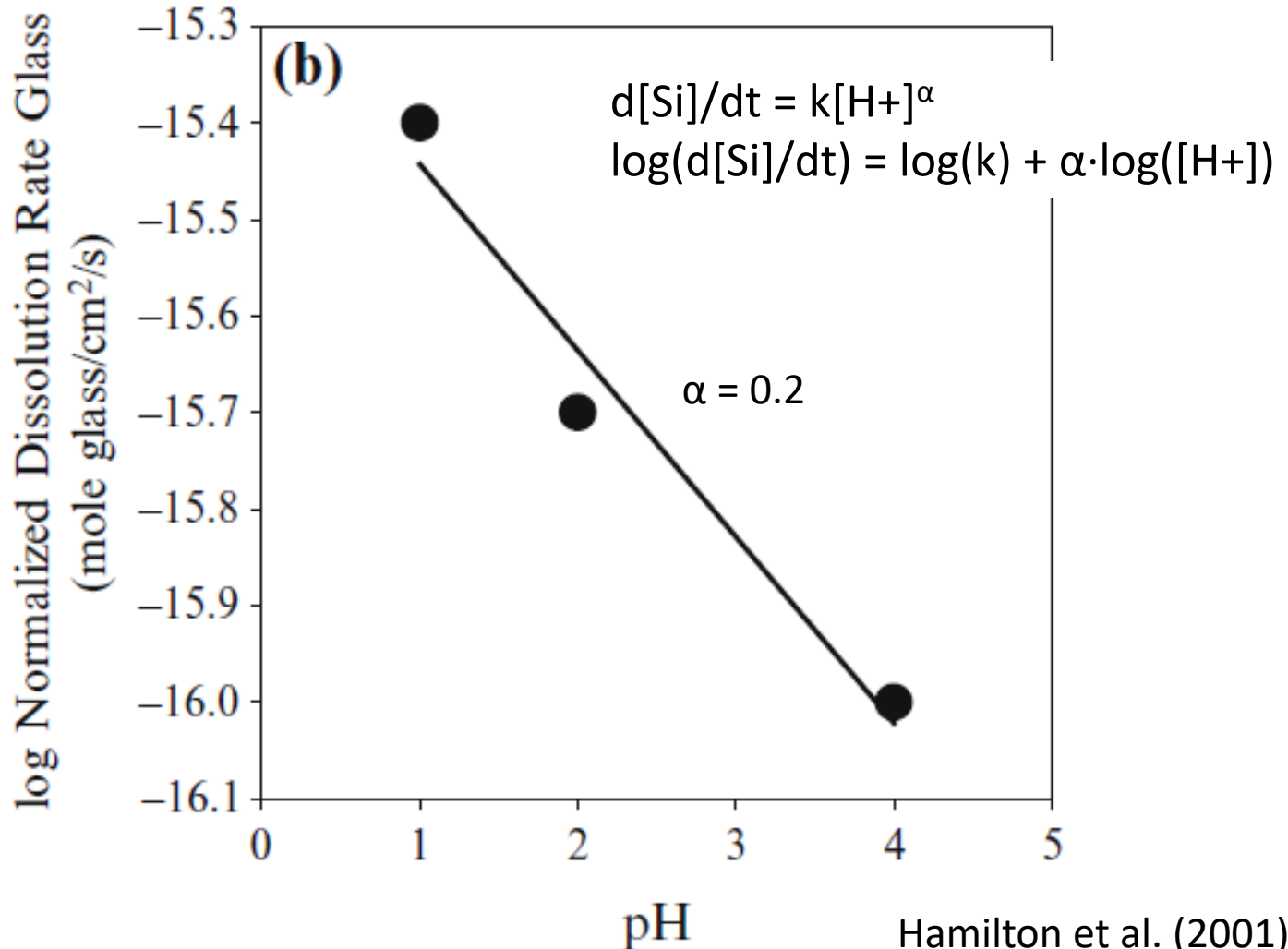
**Si release from glass dissolution**  
**(slope = rate of reaction)**





Reaction order: Plot rate of reaction as a function of reactant concentration

**Rate of glass dissolution as a function of [H+]**



# Kinetics beyond second order is more complicated

- One complication factor is reversible reactions, i.e., product is converted back to the reactant at a significant rate
- The reverse reaction, e.g.,  $[P] \rightarrow [A]$ , must be considered when a reaction approaches equilibrium
- The reaction orders described so far are calculated far from equilibrium (back reaction is negligible)

# Effects of temperature on reaction rates and rate constant

- 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

$$k = Ae^{-Ea/RT}$$

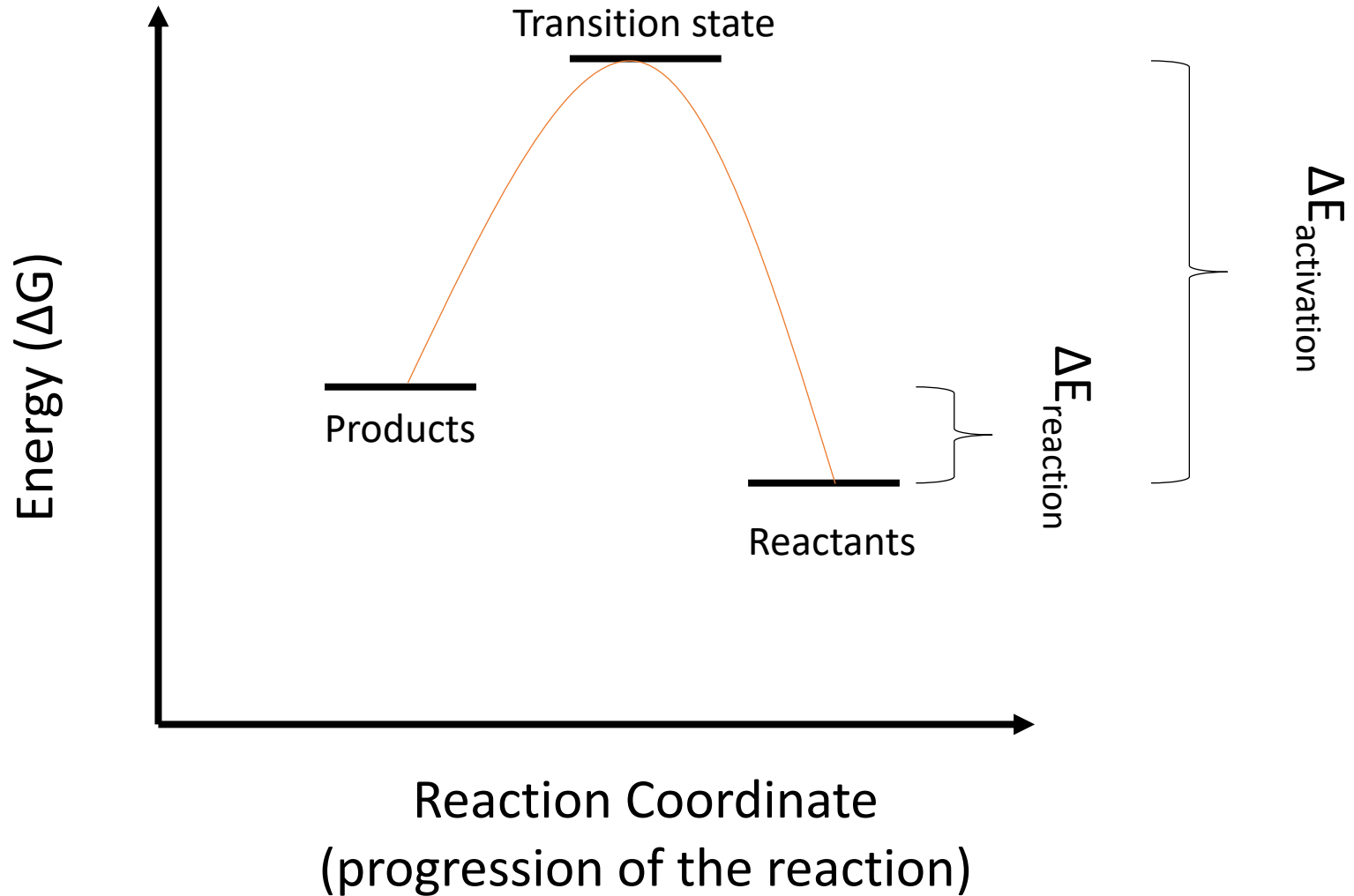
A = empirical pre-exponential factor

Ea = 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

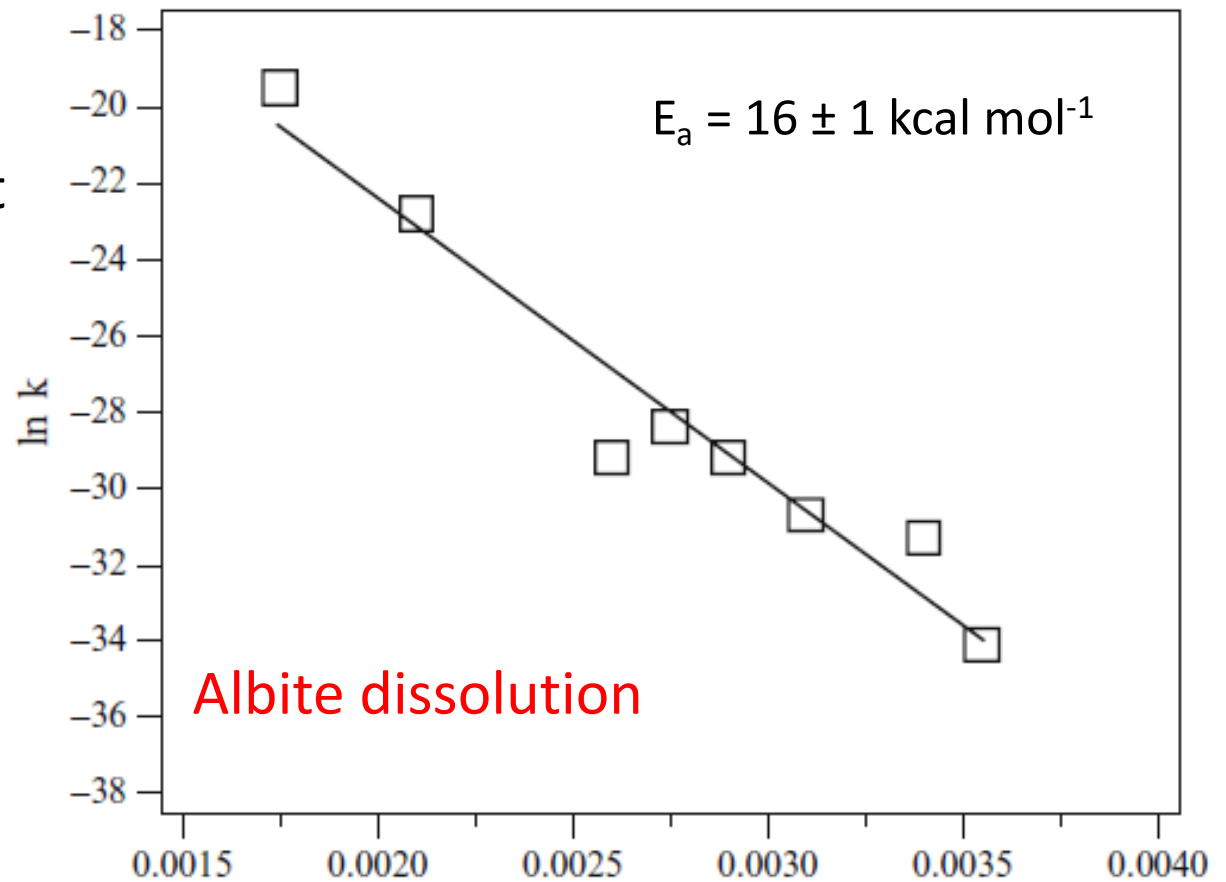


The *Arrhenius plot* can be used to determine the activation energy ( $E_a$ ) of a chemical reaction

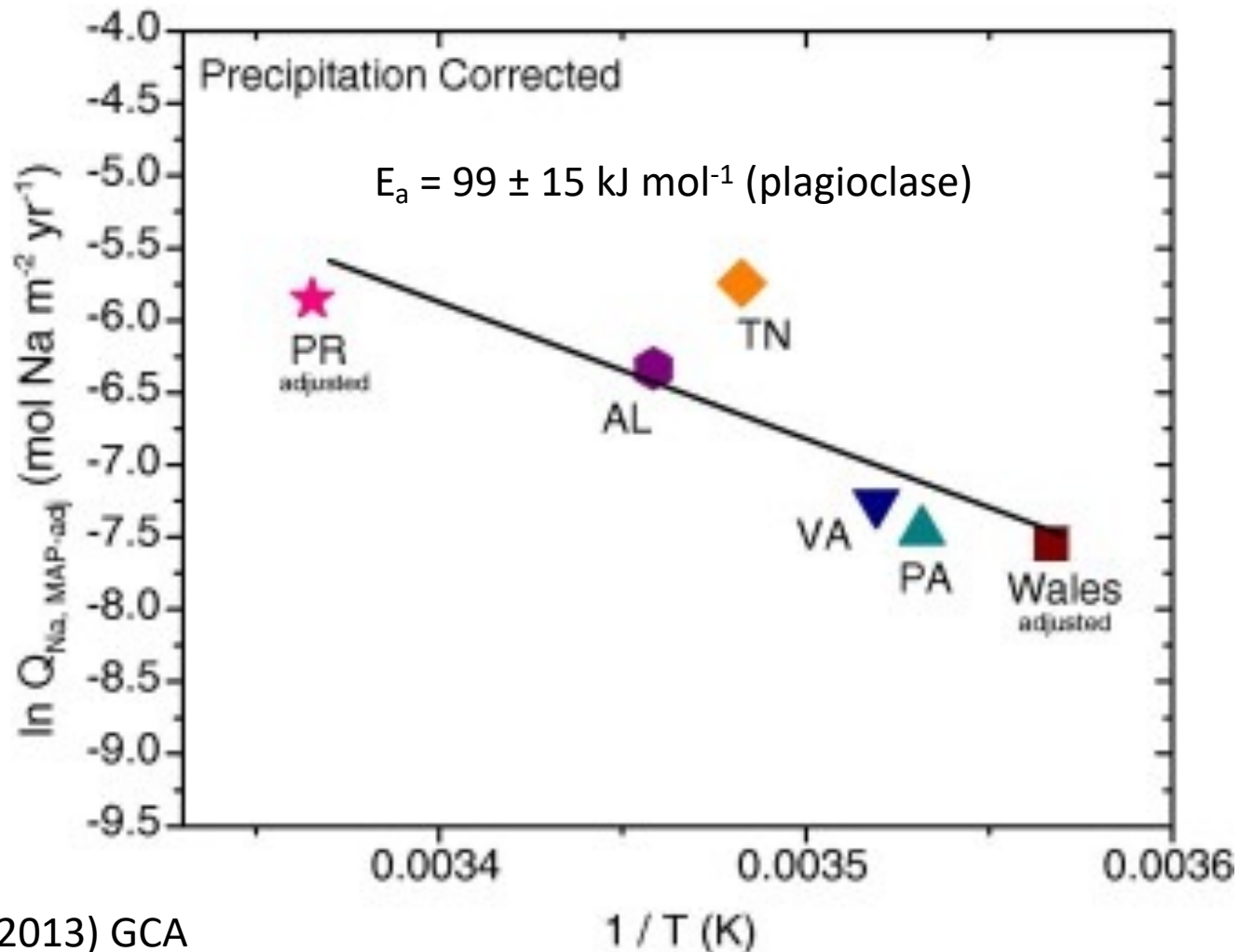
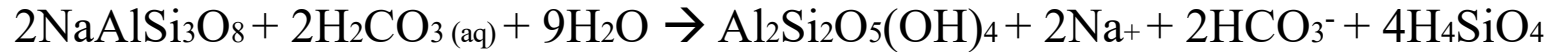
$$k = Ae^{-E_a/RT} \rightarrow \ln k = \ln(A) - \left(\frac{E_a}{R}\right) \times \left(\frac{1}{T}\right)$$

Albite dissolution

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



The temperature-dependence of Na loss from soils can be modeled with the Arrhenius equation to derive  $E_a$



## Kinetics summary:

1. Kinetics describe the rates of chemical reactions and depend on the series of steps required to convert reactants to products
2. Reaction rates are  $n$ th-order with respect to the concentration of reaction species
3. The temperature-dependence of rate constants (and hence, rates) is described by the Arrhenius equation
4. Life is easier when trends are linear

Want to learn more  
about kinetics?

# Kinetics of Water-Rock Interaction

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