

GEOL 414/514

CHEMICAL KINETICS

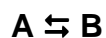
Chapter 2

LANGMUIR

CHEMICAL EQUILIBRIUM & CHEMICAL KINETIC CONCEPTS

- Equilibrium data (ΔG , K_{eq}) denote tendency to react, but give no indication of rate of reaction

- Assume simple first-order reaction:



- Rates of forward and reverse reactions:

$$\text{rate } + = k_+ (A) \quad \text{and} \quad \text{rate } - = k_- (B)$$

- At equilibrium: $k_+ (A) = k_- (B)$, two rates are equal

$$K_{eq} = \frac{k_+}{k_-} = \frac{(B)}{(A)}$$

CHEMICAL EQUILIBRIUM & CHEMICAL KINETIC CONCEPTS

- In an open system, volume mixed, amounts of substances added or removed:

$$t_R = V/Q \quad t_R - \text{residence time; } Q - \text{vol rate of flow}$$

$$t_{1/2} = \ln 2/k_+ = 0.693/k_+$$

$t_{1/2}$ - half-life or half-time of reaction

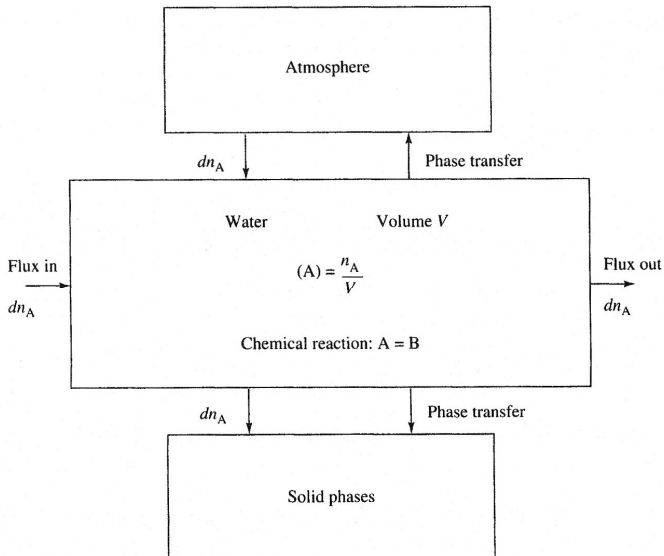
- Assuming that initially (B) = 0:

$$(A)/(B) = 1/K_{eq} + t_{1/2}/0.693 t_R$$

- When $t_R \gg t_{1/2}$, the last term vanishes and we use the expression for K_{eq}
- When $t_R \ll t_{1/2}$, kinetic concepts are needed to explain state of rea'n

CHEMICAL EQUILIBRIUM & CHEMICAL KINETIC CONCEPTS

Schematic
of open
groundwater
system and
reaction of
 $A \rightleftharpoons B$
(Fig 2.1)



CHEMICAL EQUILIBRIUM & CHEMICAL KINETIC CONCEPTS

- When a steady-state system such as that depicted in Fig. 2.1 is governed by reaction rates instead of equilibrium, situation is more complicated.

$$R_+ = k_+(A), \text{ and } R_- = k_-(B) \quad R - \text{rates}$$

- Time rates of change:

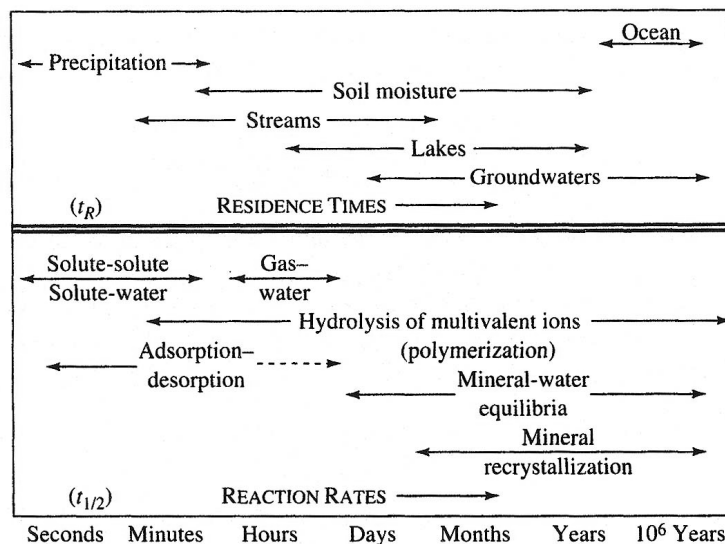
$$\begin{aligned} \text{and} \quad & \frac{d(A)}{dt} = -k_+(A) + k_-(B) \\ & \frac{d(B)}{dt} = +k_+(A) - k_-(B) \end{aligned}$$

$$(A) = \frac{r_A + k_-(A)_0 + (B)_0}{k_+ + k_- + r}$$

$$(B) = \frac{r_B + k_+(A)_0 + (B)_0}{k_+ + k_- + r}$$

V - volume
Q - volume rate of flux (L/sec)
Flux, $r = Q/V$

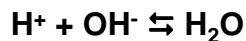
CHEMICAL EQUILIBRIUM & CHEMICAL KINETIC CONCEPTS



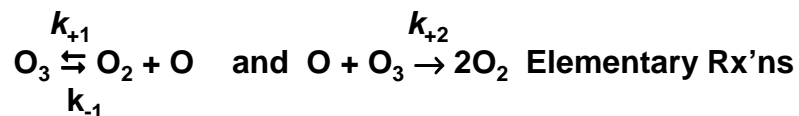
Selected residence times & reaction rates

ELEMENTARY AND OVERALL REACTIONS

- Example elementary reactions:



- Reactants & products of elementary reactions may be solids, ions, or molecular species (gases, radicals, free atoms)



RATE LAWS

For hypothetical elementary reaction $A \rightleftharpoons B$:

Rate of forward rx'n $A \rightarrow B$, $R_+ = dA/dt = k_+(A)$

Rate of reverse rx'n $B \rightarrow A$, $R_- = dB/dt = k_-(B)$

$$R_+ = k_+ \prod_{\text{reactants}} (A_i)^{v_i} \quad \text{and} \quad R_- = k_- \prod_{\text{products}} (A_i)^{v_i}$$

v_i - stoichiometric coefficient

At chemical equilibrium, $R_+ = R_-$, and

$$k_+/k_- = K_{\text{eq}} = \prod_{\text{reactants + products}} (A_i)^{v_i}_{\text{eq}}$$

For simple ele rx'n, $K_{\text{eq}} = k_+(A) / k_-(B)$

RATE LAWS

- The order of an elementary reaction is defined by the number of individual atoms or molecules involved
- The concept of overall reaction order can only be applied to single-term, simple, product rate eq'ns such as:

$$R_+ = k_+ (A)^{n_A}(B)^{n_B}(C)^{n_C}$$

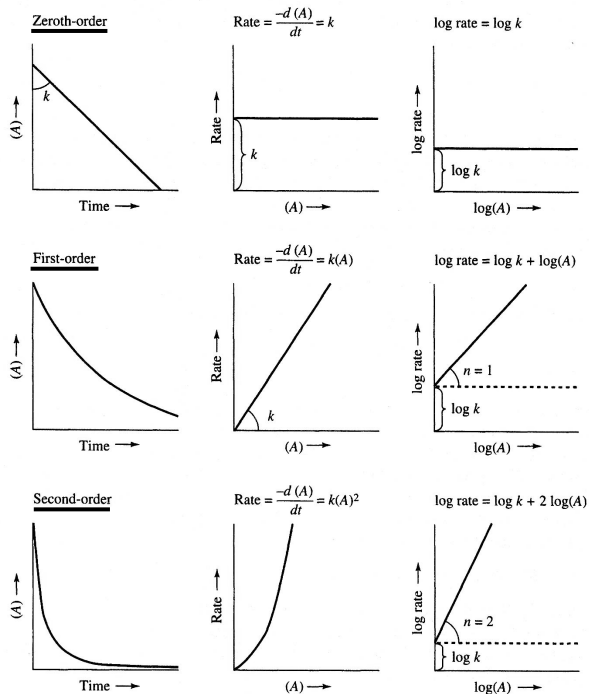
where exponents are whole numbers.

- For example, rate of forward reaction: $A + 2B \rightarrow C$
can be written $-d(C) / dt = k_+ (A) (B)^2$
- Reaction is first-order w/ respect to A & C, second-order w/ respect to B and third-order overall.
- Table 2.2 gives some simple rate laws - look through

RATE LAWS

Concentration
time, rate conc and
log rate-log conc
plots for simple
rate laws involving
reactant A

Note the example
of calcite
dissolution in text



EFFECT OF TEMPERATURE ON REACTION RATES

- The reaction rate constant can be related to T(K) through the Arrhenius expression:

$$k = A_F \exp(-E_a/RT) \quad \text{or} \quad \ln k = \ln A_F - E_a/RT$$

- Where: A_F - constant; E_a - activation energy
- Differentiating:

$$d \log k / dT = E_a / 2.303 RT^2$$

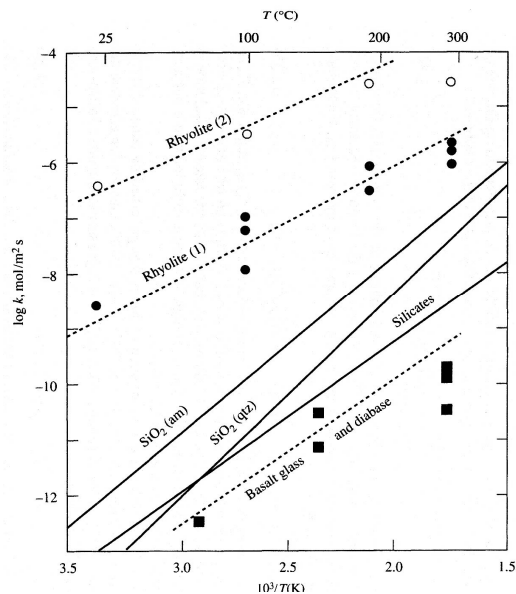
plot of $\log k$ vs $1/T$ is straight line, w/ slope = $-E_a/2.303R$

- Take log of Arrhenius eq'n for T_1 & T_2 and combine:

$$\log \frac{k_1}{k_2} = \frac{E_a}{2.303 R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad \text{Rx'ns 2X as fast at } T_2 \text{ than } T_1$$

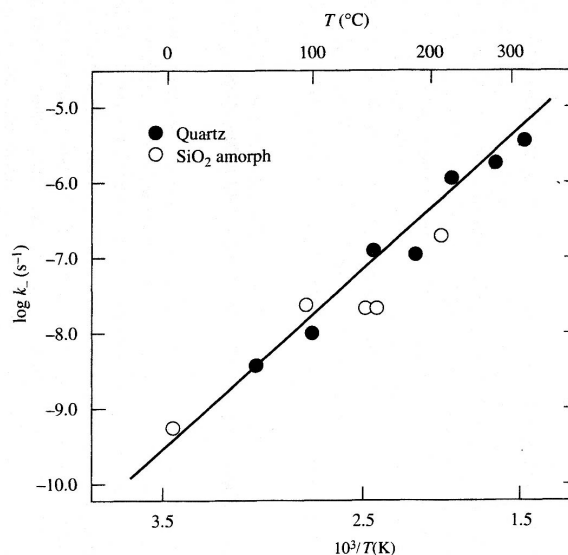
EFFECT OF TEMPERATURE ON REACTION RATES

Arrhenius plot for dissolution rates for various silicate rocks & minerals (Fig 2.5a)



EFFECT OF TEMPERATURE ON REACTION RATES

Arrhenius plot for ppt'n of quartz & amorphous SiO₂ (Fig 2.5b)



EFFECT OF TEMPERATURE ON REACTION RATES

Reaction or process	Typical range of E_a values (kcal/mol)
Physical adsorption	2 to 6
Aqueous diffusion	< 5
Cellular and life-related reactions	5 to 20
Mineral dissolution or precipitation	8 to 36
Mineral dissolution via surface reaction control	10 to 20
Ion exchange	> 20
Isotopic exchange in solution	18 to 48
Solid-state diffusion in minerals at low temperatures	20 to 120

Note differences in E_a values for potentially competing reactions - give us insight into behavior of ions in solution

MINERAL PRECIPITATION/DISSOLUTION REACTION KINETICS

- We know very few of the component elementary reactions of geochemically important reactions
- This is especially for mineral dissolution/precipitation
- In groundwater important factors include mass transport, diffusion control, surface-reaction control; rate of groundwater flow

$$dC/dt = R - k_f C$$

where dC/dt is rate of change of conc in a fixed vol,
R is the rate of dissol'n, k_f is the flushing frequency

MINERAL PRECIPITATION/DISSOLUTION REACTION KINETICS

- For steady-state conditions (when $dC/dt = 0$)

$$C = k_+ C_S / (k_+ + k_f) \quad \text{and} \quad R = k_+ k_f C_S / (k_+ + k_f)$$

- At high groundwater flow ($k_f \gg k_+$), these expressions reduce to:

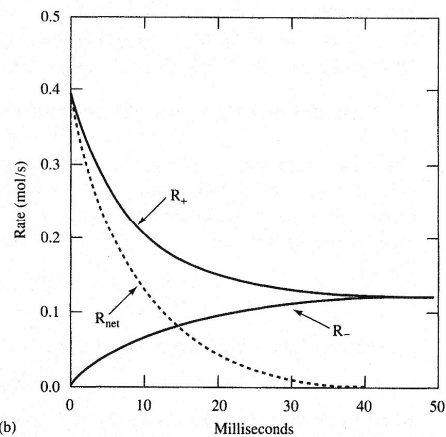
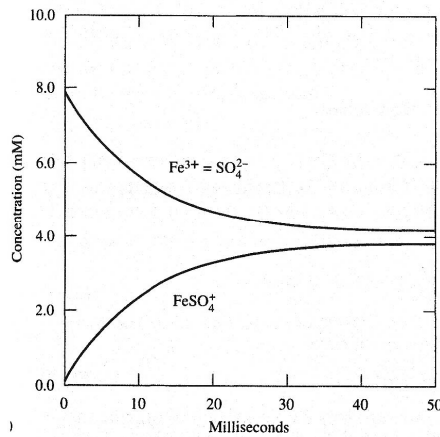
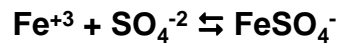
$$C = k_+ C_S / k_f \quad \text{and} \quad R = k_+ C_S$$

- maximum solution rate is reached, independent of flow rate

- At slow groundwater flow ($k_f \rightarrow 0$), $C = C_S$ & $R = k_f C_S$; rate of dissolution is controlled by flow rate
- Aqueous diffusion governs the slowest transport-controlled dissolution/precipitation

KINETIC EXAMPLES OF GEOCHEMICAL INTEREST

The FeSO₄ Complex



KINETIC EXAMPLES OF GEOCHEMICAL INTEREST

Radioactive decay: ¹⁴C

- A first-order, usually irreversibly reaction, rate given by:

$$dn/dt = -k_+ n$$

integrating, we obtain $n = n_0 \exp(-k_+ t)$

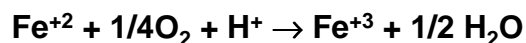
n & n_0 are total no. of molecules present at $t = 0$ & t

- The half-time of radioactive decay is $t_{1/2} = 0.693 / k_+$
- For ¹⁴C, $t_{1/2} = 5570$ y & $k_+ = 0.693 / t_{1/2}$
- Substituting & converting to logs,

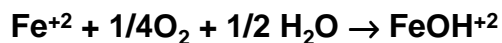
$$t \text{ (y)} = 18,500 \log (13.56/d) \quad d - \text{disintegration rate}$$

KINETIC EXAMPLES OF GEOCHEMICAL INTEREST

Oxidation of ferrous iron:

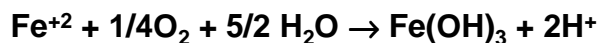


- Between pH 2.2 - 3.5, the overall reaction is:



- rate is up to 10^6 faster in presence of bacteria,
8 minutes vs 15 years

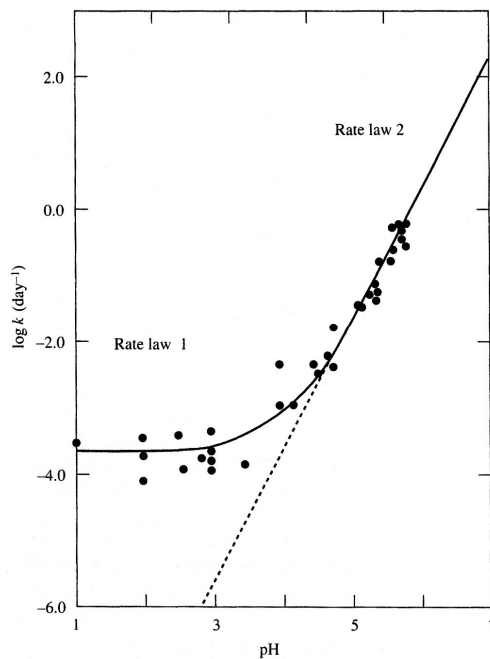
- Above pH = 4, the rate of Fe^{+2} oxidation is related to:



- Since different reactions control rate at different pH ranges, we would expect a nonlinear rate curve.

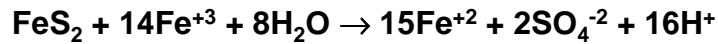
KINETIC EXAMPLES OF GEOCHEMICAL INTEREST

Oxidation of Fe^{+2} at 25°C
as a function of pH (Fig 2.9)



KINETIC EXAMPLES OF GEOCHEMICAL INTEREST

Pyrite & Marcasite Oxidation by Fe⁺³



- The reaction is first-order and follows the empirical rate law:

$$d(\text{Fe}^{+3}) / dt = -k_+ A_w / M (\text{Fe}^{+3})$$

where A_w / M is the wetted surface area of reacting mineral per mass of solution

- k_+ values range from 1×10^{-4} to 2.7×10^{-4} , same for pyrite or marcasite
- Thiobacteria can inc. oxid'n rates by orders of magnitude

SUMMARY OBSERVATIONS

Carbonates weather 10^2 - 10^3 fold faster than silicates

Rates vary widely among silicates

Presence of microbes or surface active trace subst'cs can greatly affect rates

