

2. GEOCHEMICAL KINETICS

Kinetics deals with the *rate* of a chemical reaction, and the reaction mechanism.

Thermodynamic, on the other hand, deals with the state and energetics of a reactions. Thermodynamic principles give us an idea of whether a reaction *is able* to occur in a given system, while kinetics tells us how fast. *Most natural waters are not at equilibrium!!*

2.1. Collision Theory

Basic kinetic theory calls for simple collisions between atoms - more or less like billiard balls – so the more collisions in a certain period of time, the faster the reaction. This conceptual model is surprisingly useful for understanding how fast a reaction occurs. Some of the rules are:

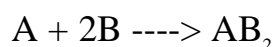
- With few exceptions (Radioactive Decay), **collisions** between reacting species are required for a chemical reaction to occur;
- Not all collisions are successful. The number of *successful* collisions determines the *rate* of the reactions.
- a bimolecular collision is far more likely than a trimolecular.
- Collisions in solution are more often successful because of the rebounding due to the *cage effect*.
- The number of collisions increases with increasing temperature, or in a gas, with increasing pressure. This is a fundamental observation.
- Reactions that require a specific orientation (i.e. S_N2, or the precipitation of sodium acetate from a supersaturated solution) are less likely to occur than others (i.e. ionic reactions).

2.2. Rate Law

- **Elementary reaction** is a fundamental chemical step.
 - **homogeneous reaction** is one with only one *phase*.
 - **heterogeneous reactions** involves more than one phase.
- **Most geochemical reactions are heterogeneous, usually liquid-solid**

2.2.1. Reaction Order

Reaction order is an expression of the dependence of the **elementary** reaction rate on the concentrations of the species involved, i.e.



--If the reactions is independent of A, it is **Zero order to A**

--if the rate is proportional to the concentration of A, the Rx is **1st order** to A

--If the reaction is dependent on both, the reaction is **3rd overall, 1st to A, 2nd to B.**

$$A + 2B + \dots \text{----> } P + 2Q + \dots$$
$$\frac{d[A]}{d t} = -k[A]^a[B]^b[P]^p[Q]^q$$

Where $d[A]/dt$ is the disappearance rate of A, k = rate constant, and a, b, p, q , are individual reaction order constants.

- From the reaction stoichiometry (1 mole of A reacts for every 2 moles of B, etc) we can generalize all the changing concentrations:

$$\frac{d[A]}{dt} = \frac{1}{2} \frac{d[B]}{dt} \dots = \frac{-d[P]}{dt} = \frac{-1}{2} \frac{d[Q]}{dt} \dots$$

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

This reaction would be *first order with respect to A, second order with respect to B, and third order overall.*

2.2.2. Zero Order Reactions:

Consider the irreversible reaction



This would give the general rate law of:

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

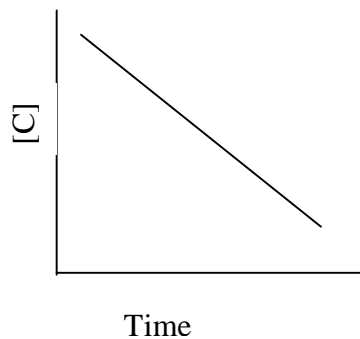
--to determine the behavior of [A] as a function of time, integrate the rate expression with respect to time, according to the value of n. When **n = 0**, the reaction is **zero order**, and

$$\frac{d[A]}{dt} = -k[A]^0 = -k$$

integrating gives us:

$$[A] = [A]_0 - kt$$

Where $[A]_0$ = the concentration of A at t=0



2.2.2.1. Half Life:

The $t_{1/2}$ is the time for 50 percent of the $[A]_0$ to react:

$$t_{1/2} = \frac{0.5[A]_0}{k}$$

2.2.3. First Order Reaction

b) When $n = 1$, the reaction is **first order** with respect to A and overall:

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

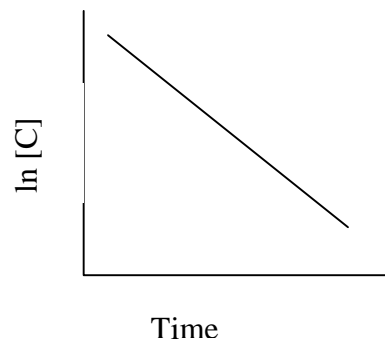
rearranging and solving the integral we get:

$$\ln [A] = \ln[A]_0 - kt$$

or

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

and the half life $t_{1/2} = \frac{\ln 2}{k}$, or **0.693/k**



2.2.4. Second Order Reactions

If the reaction order is greater than first order, we can write

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

integrating to

$$\left(\frac{-1}{n-1}\right)\left(\frac{1}{[A]^{n-1}}\right) - \left(\frac{-1}{n-1}\right)\left(\frac{1}{[A_0]^{n-1}}\right) = -kt$$

$$\frac{1}{n-1}\left(\frac{1}{[A_0]^{n-1}} - \frac{1}{[A]^{n-1}}\right) = -kt$$

if $n = 2$, for example, the reaction is **second order overall and to A**, and

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

and the half-life is $t_{1/2} = \frac{1}{k[A]_0}$

The case of $A + B \rightarrow \text{Products}$ is more complicated, and has the rate law of

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

when $a = 1$ and $b = 1$, the reaction is second order overall and first order with respect to both A and B. There are two general cases for 2nd order reactions:

2.2.4.1. Case 1:

1) When $[A]_0 = [B]_0$:

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

- ◆ For this reaction, for each mole of A that reacts, one mole of B will react. The concentrations of A and B will therefore decrease at the same rate, and will always be equal. The reaction can therefore be rewritten as:

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

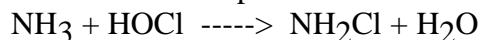
to be solved as described above

2.2.4.2. Case 2: Pseudo First order Reactions

- 2) When the concentrations are not the same, things get messy, except for the case when **one reactant is present in such excess that the concentration remains unchanged over the reaction progress**, and so the rate is expressed in terms of the changing reactant. This is called a *pseudo first-order* reaction.

***An example would be the hydrolysis of a solute in aqueous system.

Example 2-1



- The rate constant k was found experimentally to be 5.1×10^6 liters/mole sec at 25°C
- the rate order was determined to be:

$$\frac{d[\text{HOCl}]}{dt} = -k[\text{HOCl}][\text{NH}_3]$$

1. What is the reaction order with respect to each reactant and overall?
2. What percent decrease in reaction rate occurs if the concentration of each reactant is reduced by 50%
 - a) let the initial concentrations of NH_3 and HOCl be x and y , respectively. The rate of reaction becomes

$$\frac{d[\text{HOCl}]}{dt_0} = -kyx$$

when x and y are each reduced by 50%, the reaction rate becomes

$$\frac{d[\text{HOCl}]}{dt_1} = -k\left(\frac{y}{2}\right)\left(\frac{x}{2}\right) = \frac{1}{4}kyx$$

The new reaction rate is 25% of the original

2.3. Common Units of Rate

| Order: | Units | | Differential form | |
|--------|---------------------------------------------------|---------------------------------|-------------------------|-----------------------------------|
| 0 | mol cm ⁻³ s ⁻¹ | C t ⁻¹ | dC/dt = -k | C=C ^o - kt |
| 1 | s ⁻¹ | t ⁻¹ | dC/dt = kC | C=C ^o e ^{-kt} |
| 2 | cm ³ mol ⁻¹ s ⁻¹ | C ⁻¹ t ⁻¹ | dC/dt = -k ⁿ | Complex |

2.4. Effect of Temperature on Reaction Rates

Experimentally, it has been found that reaction rates increase with temperature increase, and that this increase can be formulated by:

$$k = A e^{\left(\frac{-E_a}{RT}\right)}$$

This relationship is called the Arrhenius equation, where R is the gas constant, A is the pre-exponential *frequency factor*, and E_a is the activation energy.

The relationship of k to T is:

$$\ln k = \ln A - \frac{E_a}{RT}$$

A straight line should be produced by a plot of **ln k vs 1/T**, with the slope equal to.

$$\frac{-E_a}{R}, \text{ or } \frac{d(\ln k)}{d(1/T)} = -\frac{E_a}{R}$$

Activation energy is therefore defined as the slope multiplied by -R. The intercept on the

$$1/T \text{ axis is } \frac{\ln A}{R}, \text{ or on the } \ln k \text{ axis, } \ln A$$

Where

- ◆ A is the pre-exponential factor, or "frequency factor", that is thought to relate to the entropy of the activated complex. A is assumed to be a constant that does not vary with temperature.
- ◆ E_a is the activation energy, also thought to be constant with respect to temperature.

2.5. NUCLEATION:

Nucleation is the formation of a new phase, here the formation of solid phase from a supersaturated solution. The first stage of nucleation is the rapid formation of dimers, trimers, and higher polymers. As the micro-particle forms, however, the surface free energy of the particle becomes an important consideration:

- ◆ The surface free energy of a very small sphere (<0.1 μm) is much higher than for a larger particle. Therefore there is more work associated with overcoming this surface free energy, defined as the interfacial - Free energy liberated

$$W = 4\pi r^2 \gamma - \frac{4}{3}\pi r^3 \Delta G$$

Solving for rate, and using W analogous to activation energy (Even though it is thermodynamic in nature...), we get:

$$\text{Rate} = A \exp\left(\frac{-W_1}{RT}\right) = A \exp\left(\frac{-16\pi\gamma^3}{3\Delta G^2 RT}\right)$$

This suggests that the rate of nucleation and growth is very sensitive to interfacial energy. At low degrees of supersaturation, nucleation can only take place if there is a way of minimizing interfacial energy. This may occur by nucleating on an established surface.

2.6. DISSOLUTION AND GROWTH:

- ◆ There are five primary steps to a surface reaction:
 - 1) Diffusion of reactants to a surface
 - 2) sorption of reactants to the surface
 - 3) reaction forming a transition state complex
 - 4) Decomposition of the transition state complex and desorption
 - 5) diffusion of reactants away from the surface.

Any of these steps, in theory, can be the rate controlling step. In practice, it is usually either surface control, or diffusion/transport control

2.6.1. *Surface Controlled Reactions:*

- ◆ At low degrees of saturation, the rate of dissolution and precipitation is usually surface controlled. Surface control occurs when the rate of dissolution is slower than the rate of diffusion, giving a uniform solution composition with distance from the surface.
- ◆ The nature of the surface controls bulk rate: kinks, steps, dislocations. During dissolution, the atoms with the highest energy react first. Sorbed compounds may *poison* a surface controlled reaction, for example PO₄ on a calcite surface.
- ◆ Surface controlled reactions generally have an activation energy greater than that of diffusion, and are often quite high.

2.6.2. *Diffusion control*

When the rate of reaction is less than the rate of diffusion of products away from the surface, saturation is reached *at the surface*, and the reaction proceeds only as fast as excess products diffuse away. This assumes no advective process, so a standard experimental observation is that an increase in stirring speed should increase the rate.

- ◆ Diffusion-controlled rates have a low activation energy (about 5 kcal/mol) compared to surface controlled reactions (12-17 kcal/mol).

2.6.2.1. *Example: Calcite dissolution in Seawater.*

This experiment used pH stat to control pH during reaction and maintain a constant degree of undersaturation, as long as the added calcium was small compared to sea water

- ◆ Dissolution rate is calculated from the rate and amount of acid added to maintain the pH.
- ◆ SI is calculated as the difference in pH between the actual conditions and the equilibrium pH for that solution composition.

Findings:

- 1) Below pH 4, diffusion controlled, no etch pits formed
- 2) sensitive to pH, pCO₂, possibly reactant sorption controlled (H⁺)
- 3) Surface controlled, dissolving at kinks and dislocations, etch pits formed.

Moral: Even simple calcite dissolution is very complex at the molecular level.

2.6.2.2. ***Kinetics can be used to discern molecular interactions and mechanisms that are invisible in a thermodynamic calculation. Thermo is path independent, kinetics is not!!