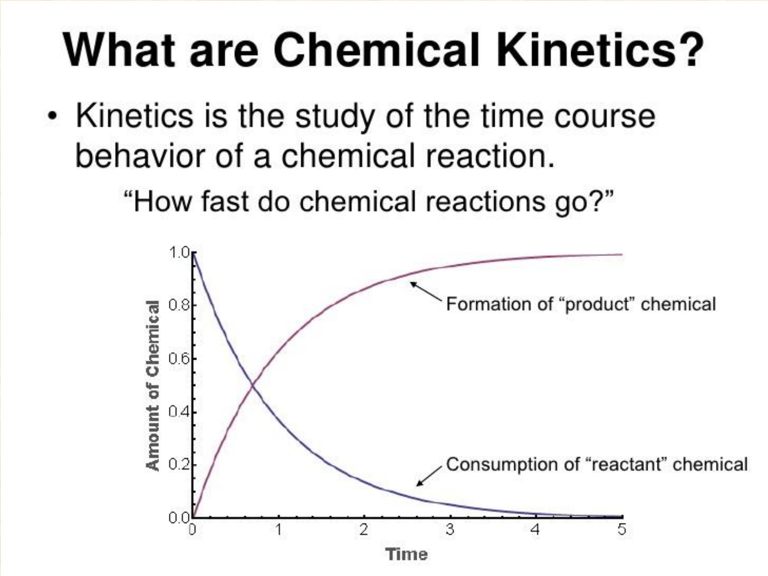
Equilibrium Thermodynamics and Kinetics



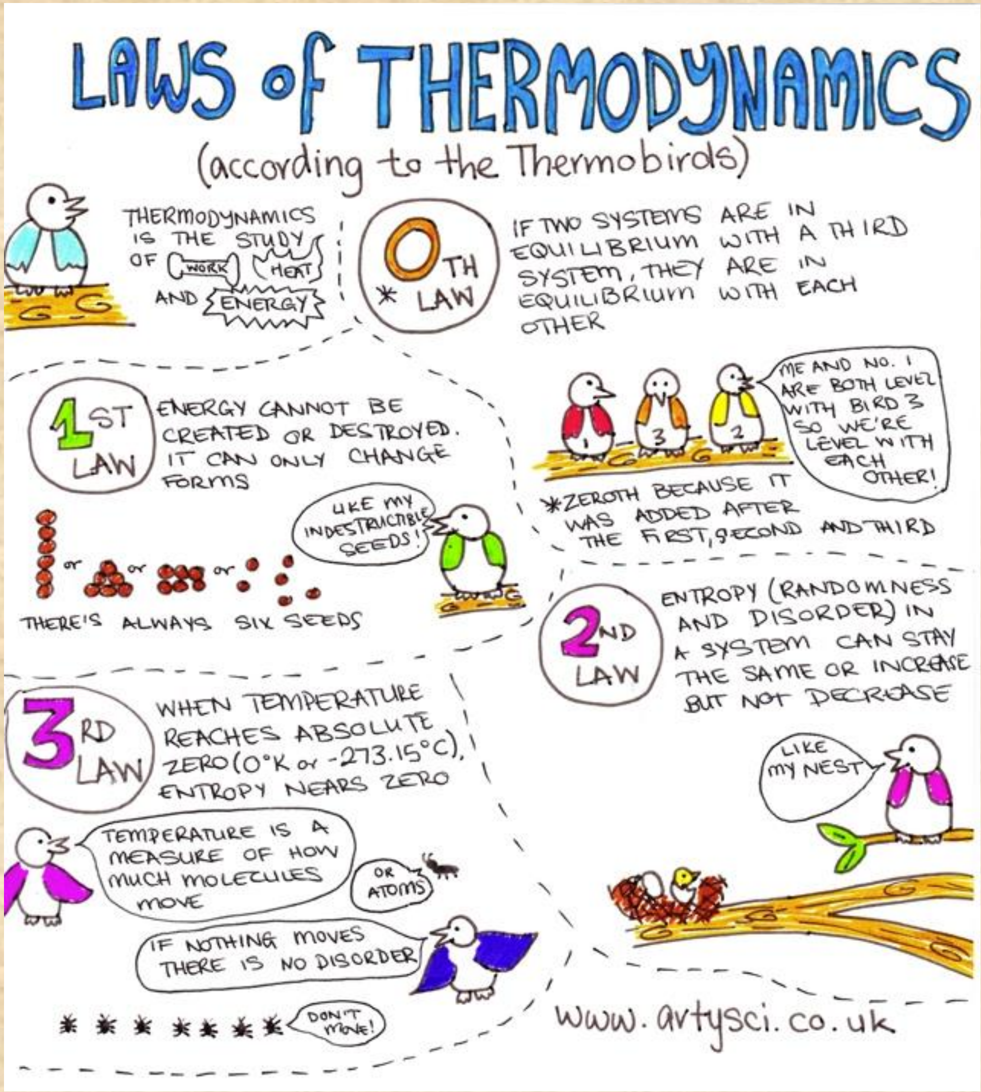
What are Chemical Kinetics?

- Kinetics is the study of the time course behavior of a chemical reaction.

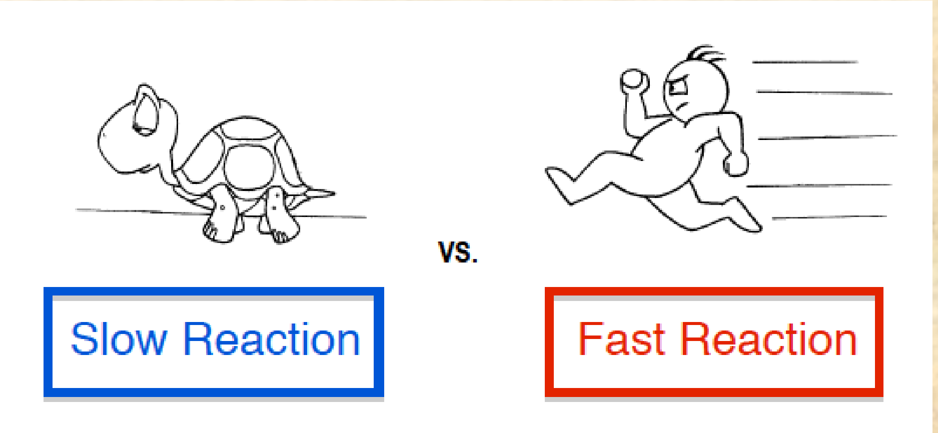
  "How fast do chemical reactions go?"

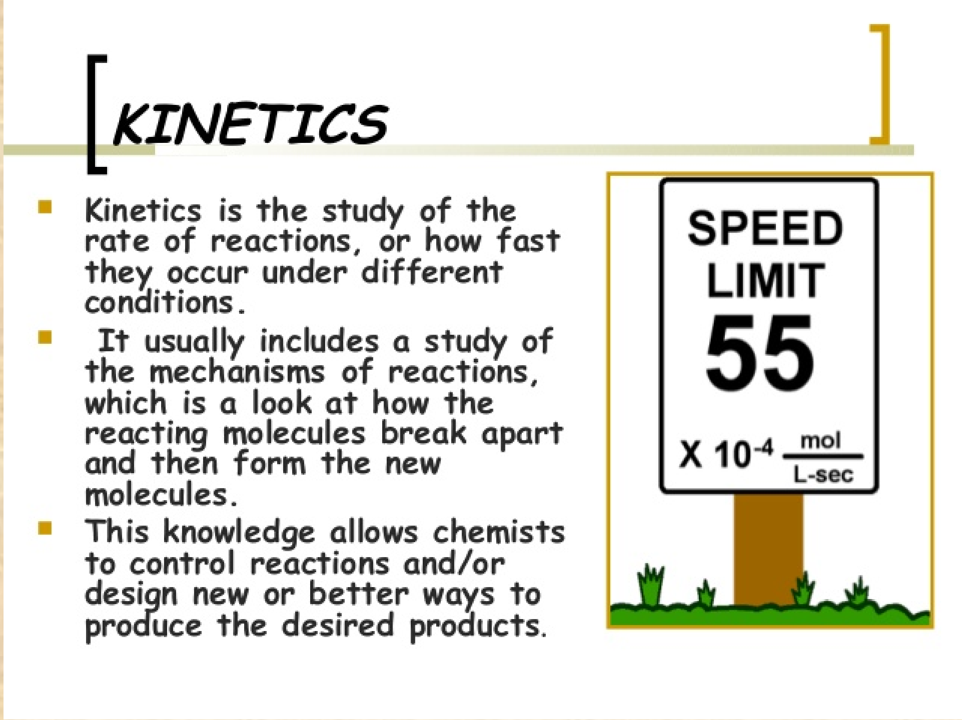
"Now, in the *second* law of thermodynamics . . . "

Equilibrium Thermodynamics: predicts the concentrations (or more precisely, activities) of various species and phases if a reaction reaches equilibrium.



Kinetics tells us how fast, or if, the reaction will reach equilibrium.

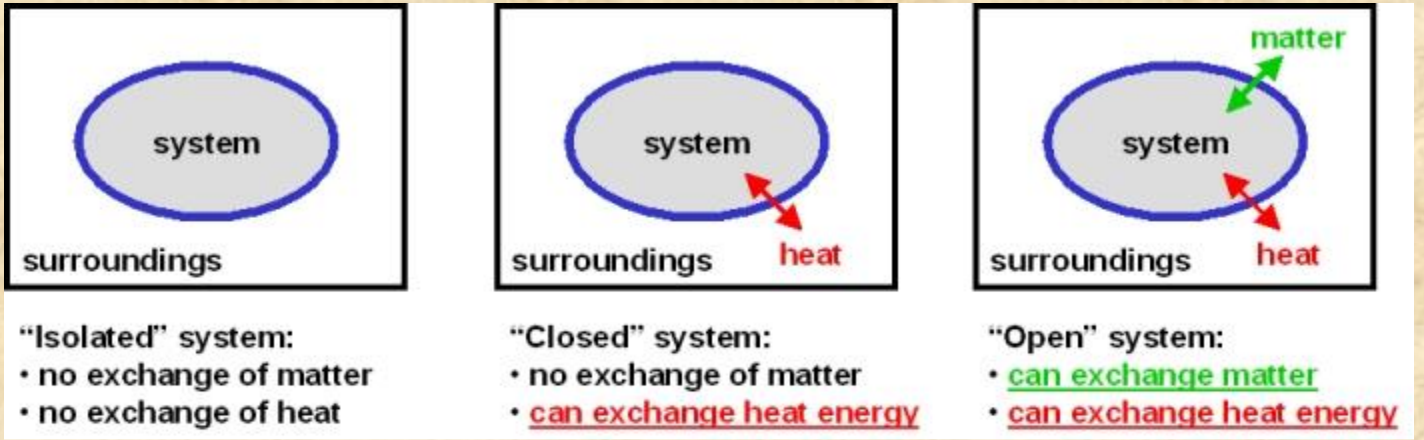




KINETICS

- Kinetics is the study of the rate of reactions, or how fast they occur under different conditions.
- It usually includes a study of the mechanisms of reactions, which is a look at how the reacting molecules break apart and then form the new molecules.
- This knowledge allows chemists to control reactions and/or design new or better ways to produce the desired products.

System: that portion of the universe we wish to study. It could be as simple as a beaker containing solution or as complex as the universe. A system can be ***open*** (exchanging matter and energy with its surroundings), ***closed*** (not exchanging matter with its surroundings), or ***isolated*** (exchanges neither matter nor energy with its surrounding.)



"Isolated" system:
- no exchange of matter
- no exchange of heat

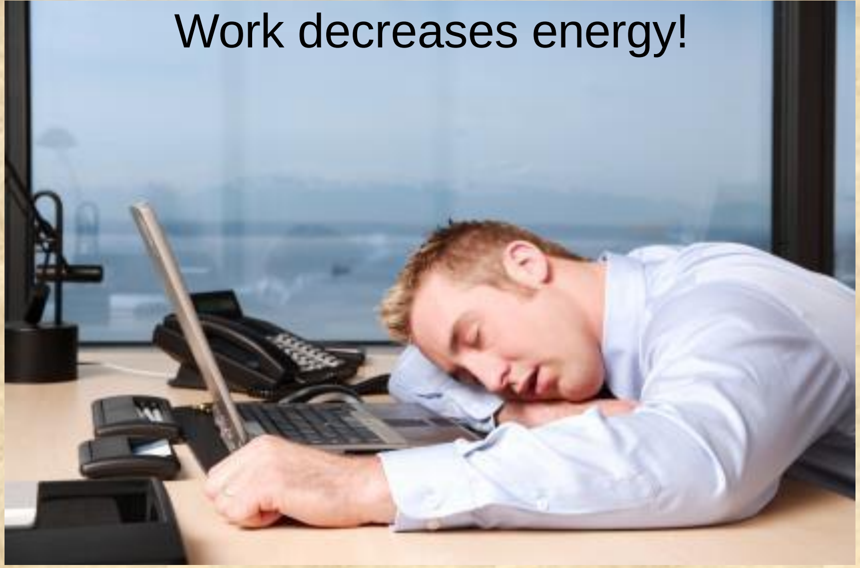
"Closed" system:
- no exchange of matter
- can exchange heat energy

"Open" system:
- can exchange matter
- can exchange heat energy

The First Law of Thermodynamics: (a.k.a. Conservation of Energy) Energy can neither be created nor destroyed, it can only be changed from one form to another.

The change in internal energy of a system is equal to the heat added to the system minus the work done by the system.

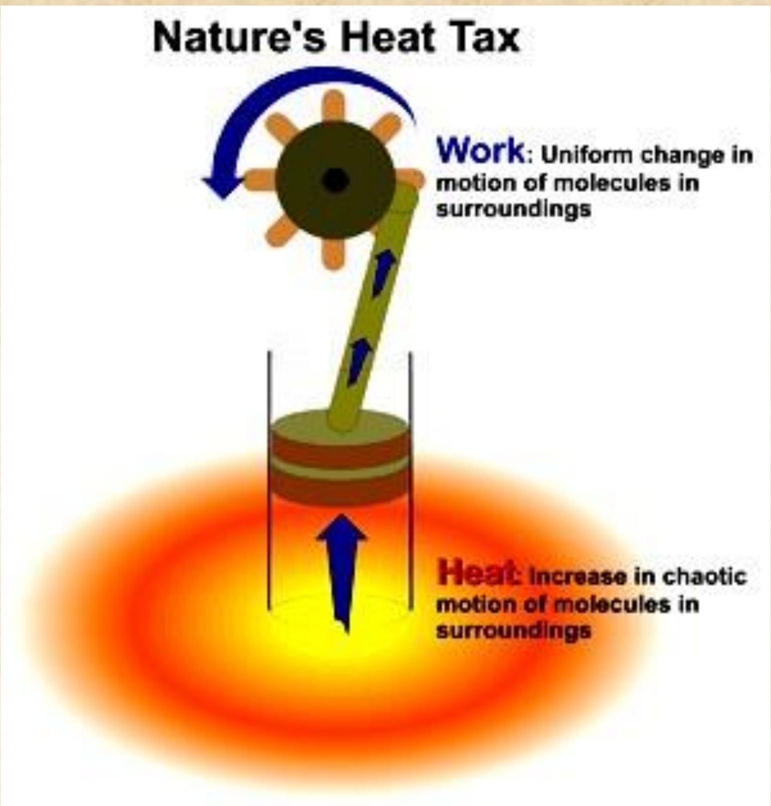
$$\Delta E = q - w$$



Work decreases energy!

Internal energy (E): the energy associated with the random, disordered motion of molecules.

Heat (q): energy in transit from a high temperature object to a lower temperature object.


Nature's Heat Tax

Work (w): forms of energy transfer which can be accounted for in terms of changes in the macroscopic physical variables of the system.

$$\Delta E = q - w$$

Remember: $\Delta E = q - w$

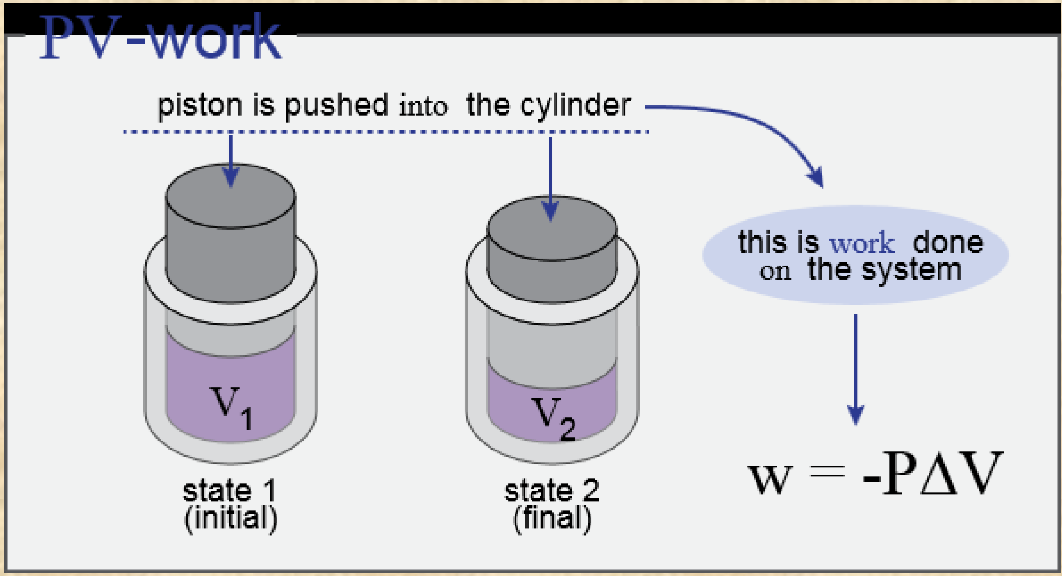
Now to the math…

If the work done by or on a system causes a change in volume at constant pressure, then the equation for ΔE becomes:

$$\Delta E = q - P\Delta V$$

Enthalpy(H) is equal to the heat flow when processes occur at constant pressure and the only work done is pressure- volume work.

$$dH = dE + PdV$$



Exothermic reactions: reactions that release heat energy (*enthalpy is negative for the reaction*).

Reactants → products + heat

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{heat}$$

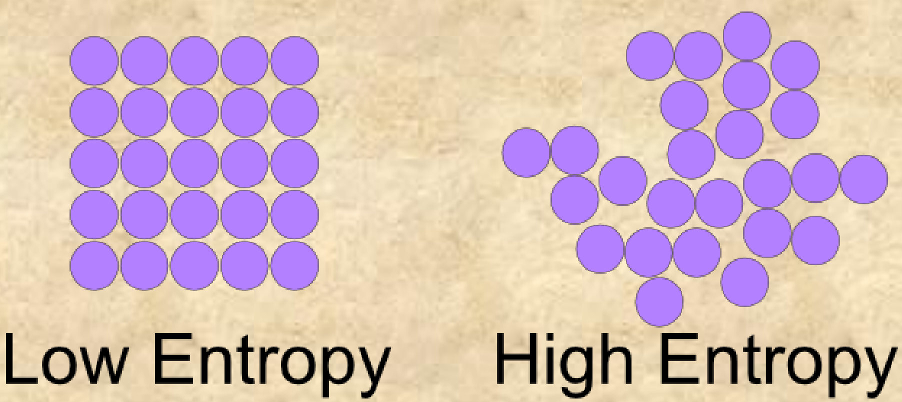
Endothermic reactions: reactions that use heat energy (*enthalpy is positive for the reaction*).

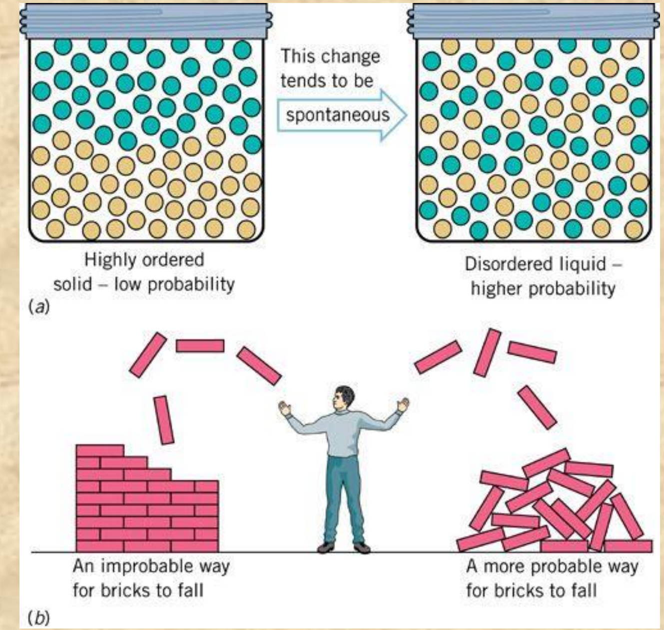
Reactants + heat → products

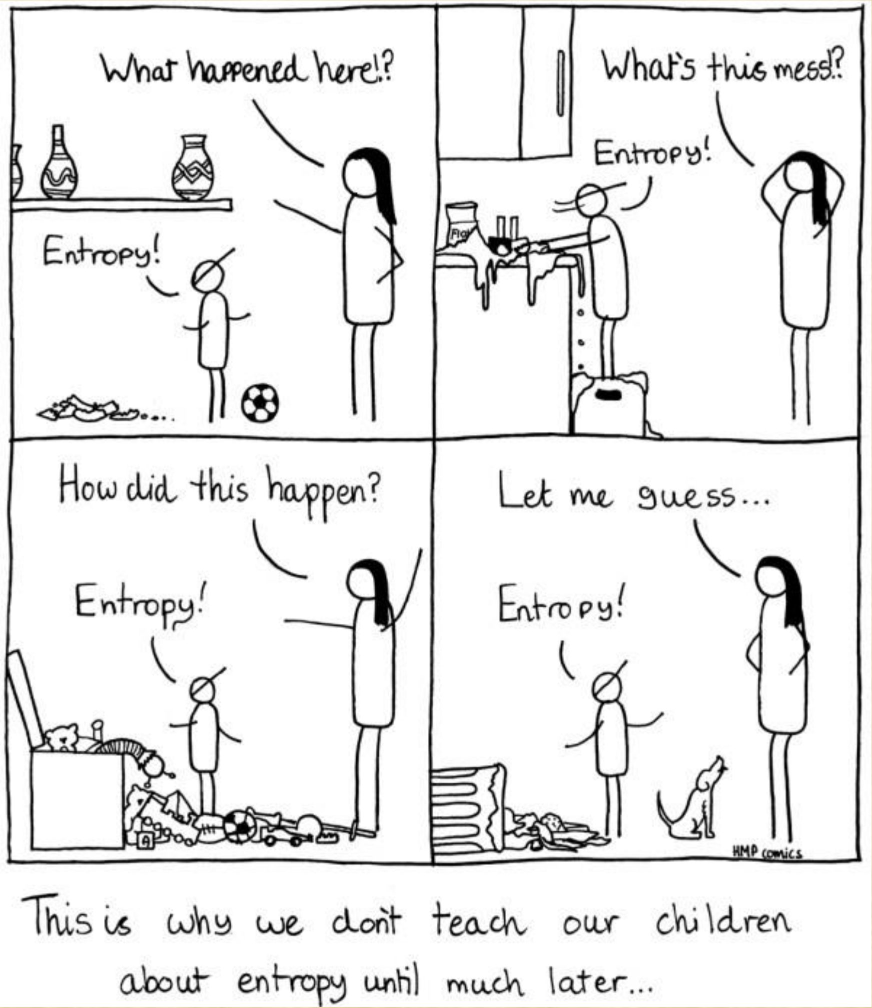
$$Ba(OH)_2 \cdot 8H_2O_{(s)} + 2NH_4SCN_{(s)} \rightarrow Ba(SCN)_{2(s)} + 10H_2O_{(l)} + 2NH_{3(g)}$$

Heat of formation: enthalpy change that occurs when a compound is formed from its elements at a specific (standard) temperature and pressure. The heat of formation for the most stable form of an element is arbitrarily set equal to zero.

Second law of thermodynamics: for any spontaneous process, the process always proceeds in the direction of increasing disorder—entropy.

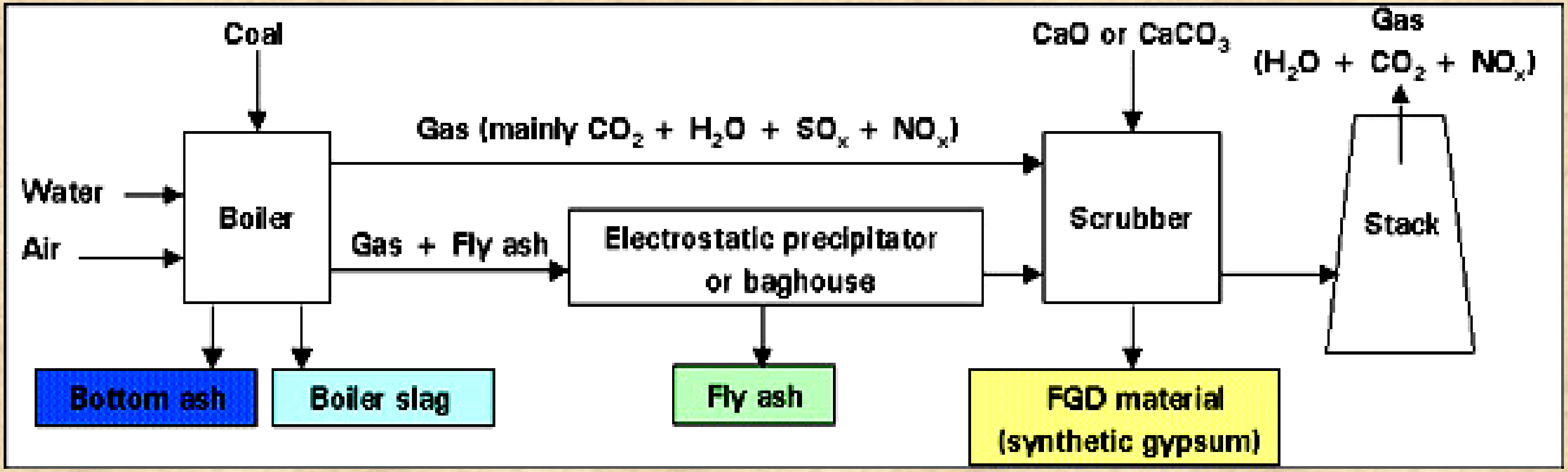






Another way to look at entropy is that during any spontaneous process there is a decrease in the amount of usable energy.

Consider the combustion of coal, an ordered complex organic molecule. Through the process of combustion coal is broken down into ash, CO_2, H_2O, SO_x & No_x, resulting in a dramatic decrease in the amount of usable energy.



The McCormick story.

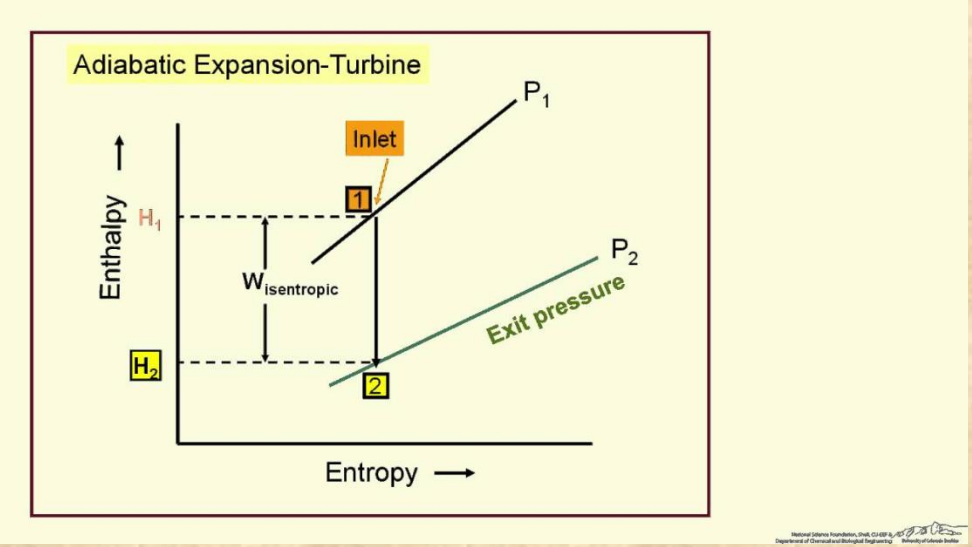
Mathematically, entropy (S) is described in the following equation.

$$\Delta S = q/T$$

Where ΔS is the change in entropy and T is the temperature in Kelvin.

When the entropy equation is combined with the enthalpy equation and only pressure-volume work is considered, then

$$dH = T\,dS + V\,dP$$



National Science Foundation, Shell, CU-EEF & Department of Chemical and Biological Engineering University of Colorado Boulder

Chemical Equilibrium

Chemical equilibrium applies to reactions that can occur in both directions. In a reaction such as

$$CH_{4(g)} + H_2O_{(g)} <\text{--}> CO_{(g)} + 3H_{2(g)}$$

Many chemical reactions are reversible. The products formed react to give back the original reactants, even as the reactants are forming more products. After some time, both the forward and reverse reactions will be going on at the same rate. When this occurs, the reaction is said to have reached equilibrium.

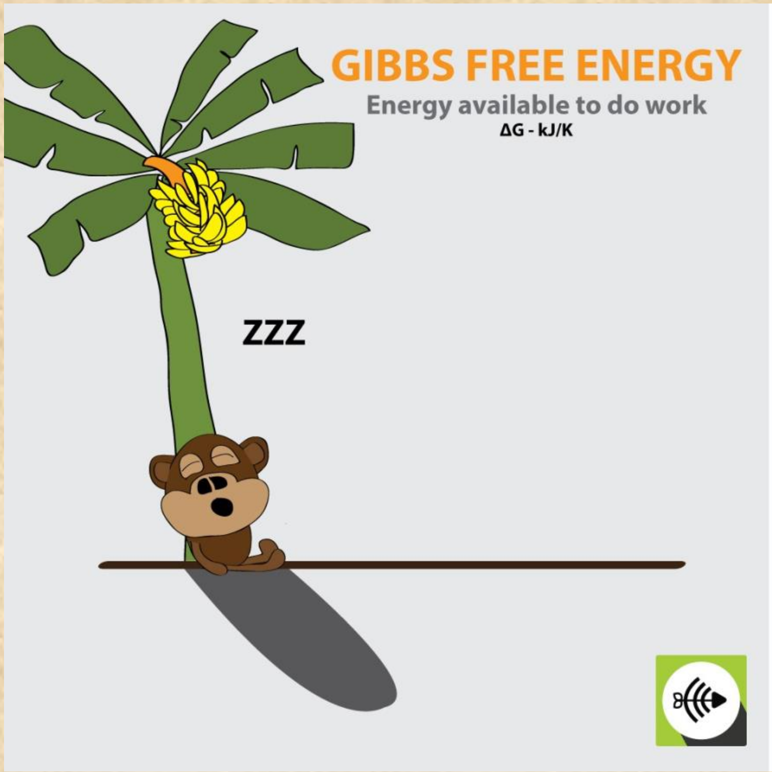
A system at equilibrium is in a state of minimum energy. This energy can be measured as

Gibbs free energy when the reaction occurs at constant temperature and pressure.

For a system *at constant T & P* Gibbs free energy can be written as

$$G = H - TS$$

Where H is enthalpy(kJ mol^{-1}), S is entropy(J $mol^{-1}K^{-1}$) and T is temperature (K).



For ***changes*** that occur at constant T & P the expression for Gibbs free energy becomes

$$\Delta G = \Delta H - T\Delta S$$

If ΔG is (-), the process occurs spontaneously.

If $\Delta G = 0$, the process is at equilibrium

If ΔG is (+), the reaction does not occur spontaneously

To determine ΔG_{R^o} (for the entire reaction) you must subtract

the $\Sigma\Delta G$ of the **reactants** from the $\Sigma\Delta G$ of the **products.**

$$\Delta G_{\text{Reaction}} = \Sigma\Delta G_{\text{Products}} - \Sigma\Delta G_{\text{Reactants}}$$

See appendix II.

So… $\Delta G_R = \Delta H_R - T\Delta S_R$

Note: In the thermodynamic data table (Appendix II) the tabulated values for ΔG_f^0 and ΔH_f^0 are, respectively, the standard free energies and enthalpies of formation for the compounds from the elements in their standard state. S^0 is also tabulated in the thermodynamic data table. Free energy and enthalpy are in kJ mol^{-1} while entropy is in J mol^{-1} K^{-1}. When doing thermodynamic calculations be sure to convert either enthalpy to joules (1 kJ = 1000 J) or entropy to kilojoules ($1 \text{ J} = 1 \times 10^{-3}$ kJ). Temperature is the absolute temperature in Kelvin. To convert centigrade temperatures to Kelvin, add 273.15 to the centigrade value. Failure to change centigrade to Kelvin temperature is one of the most common mistakes made by students on homework and exam problems. By international convention, the accepted units are SI units. In SI units, heat energy is expressed as joules. For years scientists and engineers used the calorie as the unit of heat measurement. Hence, many older tables of thermodynamic data tabulate heat energy in calories. The following conversion factor is used to convert calories to joules:

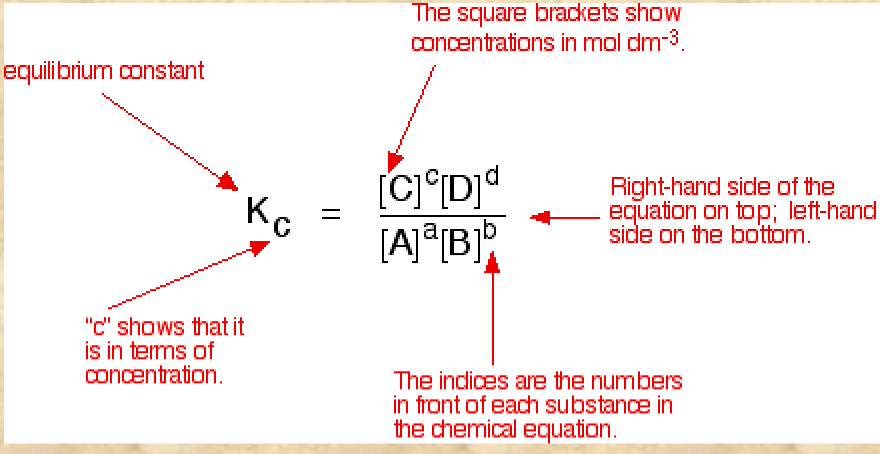
1 calorie = 4.184 joules

Equilibrium Constant

To determine the amount of each compound that will be present at equilibrium you must know the equilibrium constant. To determine the equilibrium constant you must consider the generic equation

$$aA + bB <--> cC + dD$$

The upper case letters are the molar concentrations of the reactants and products. The lower case letters are the coefficients that balance the equation. Use the following equation to determine the equilibrium constant (K_c).



$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

equilibrium constant

The square brackets show concentrations in mol dm^{-3}.

Right-hand side of the equation on top; left-hand side on the bottom.

"c" shows that it is in terms of concentration.

The indices are the numbers in front of each substance in the chemical equation.

The equilibrium constant for a chemical reaction can be determined by using the Kc equation.

Consider the following chemical reaction.

$$N_{2}(g) + 3H_{2}(g) <\!\!-\!\!-\!\!> 2NH_{3}(g)$$

A one-liter vessel contains 1.60 moles NH_3, 0.800 moles N_2, and 1.20 moles of H_2. Calculate the equilibrium constant?

$$K_c = \frac{[1.60]^2}{[.800]\,[1.20]^3} = \quad 1.85$$

Incorporating Gibbs free energy with the equilibrium constant (under standard conditions) yields the following equation

$$\log K_{eq} = -\Delta G_R / 5.708$$

Where 5.708 is a combination of the gas constant (R) and standard temperature of 25°C.

Example 2-1

Calculate the solubility product for gypsum at 25°C

The dissolution of Gypsum is written as follows

$$CaSO_4 \cdot 2H_2O(\text{gypsum}) \leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$$

The equilibrium constant is equal to the solubility constant. $K_{eq} = K_{sp}$

$$K_{sp} = \frac{[Ca^{2+}][SO_4^{2-}][H_2O]^2}{[CaSO_4 \cdot 2H_2O_{(\text{gypsum})}]}$$

The concentration of both water and gypsum is set at 1 as the solution is dilute and the gypsum is a solid in its standard state.

$$K_{sp} = [Ca^{2+}][SO_4^{2-}]$$

If you know the concentrations of calcium and sulfate, you can find the solubility constant with this equation. If not, you may use the free energies of formation from appendix II.

$$\Delta G_R = \Sigma\Delta G_{(products)} - \Sigma\Delta G_{(reactants)}$$

For this problem:

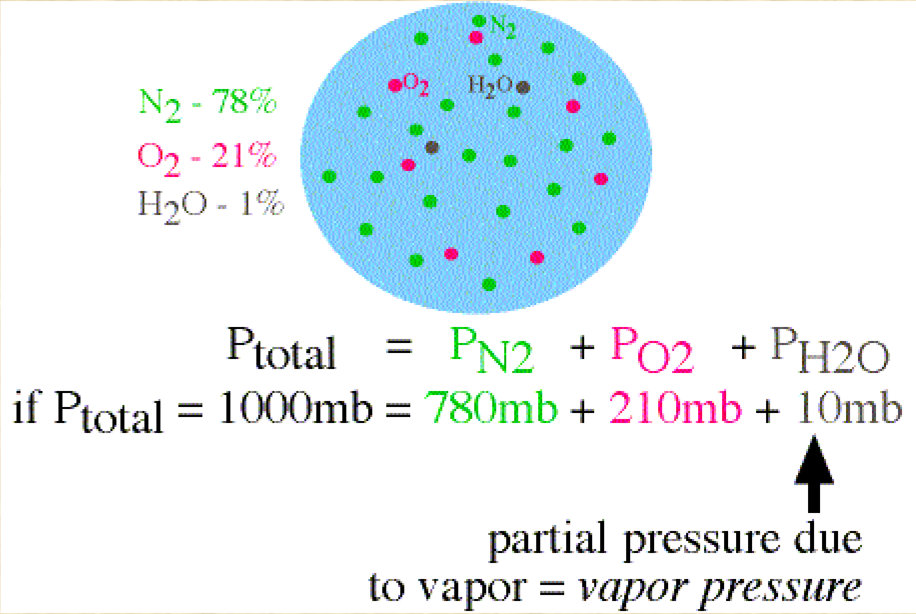
$$\Delta G_R = (-522.8) + (-744.0) + 2(-237.14) – (-1797.36) = 26.28 \text{ kJ mol}^{-1}$$

$$\log K_{sp} = -\Delta G_R / 5.708 = -26.28/5.708 = -4.60 \therefore K_{sp} = 10^{-4.60}$$

Is this a spontaneous reaction?

John Dalton studied the effect of gases in a mixture. He observed that the total pressure of a gas mixture was the sum of the ***partial pressure*** of each gas.

$$P_{(total)} = P_1 + P_2 + P_3 + ...P_n$$



$$P_{total} = P_{N2} + P_{O2} + P_{H2O}$$

$$\text{if } P_{total} = 1000mb = 780mb + 210mb + 10mb$$

partial pressure due
to vapor = *vapor pressure*

Henry's Law: The relationship between the equilibrium constant and the solubility product is used to describe the activity of a dilute component as a function of concentration.

Henry's law relates the fugacity of a gas to its activity in solution. When a gas behaves ideally (1 atm and near surface temperatures) fugacity of a gas equals its partial pressure. Therefore, Henry's law can be written:

$$c_i = K_H P_i$$

Where c_i is the concentration of the gaseous species i in solution, K_H is Henry's law constant in mol L^{-1} atm^{-1} *(see Table 2-1),* and P_i is the partial pressure of gaseous species i.

Get to know this table. You will reference it more than once this semester

Table 2 -1 Henry’s Law constants for gases at 1 bar total pressure in mol L^{-1} bar^{-1}*

T(°C)	O_2	N_2	CO_2	H_2S	SO_2
0	2.18×10^{-3}	1.05×10^{-3}	7.64×10^{-2}	2.08×10^{-1}	3.56
5	1.91×10^{-3}	9.31×10^{-4}	6.35×10^{-2}	1.77×10^{-1}	3.01
10	1.70×10^{-3}	8.30×10^{-4}	5.33×10^{-2}	1.52×10^{-1}	2.53
15	1.52×10^{-3}	7.52×10^{-4}	4.55×10^{-2}	1.31×10^{-1}	2.11
20	1.38×10^{-3}	6.89×10^{-4}	3.92×10^{-2}	1.15×10^{-1}	1.76
25	1.26×10^{-3}	6.40×10^{-4}	3.39×10^{-2}	1.02×10^{-1}	1.46
30	1.16×10^{-3}	5.99×10^{-4}	2.97×10^{-2}	9.09×10^{-2}	1.21
35	1.09×10^{-3}	5.60×10^{-4}	2.64×10^{-2}	8.17×10^{-2}	1.00
40	1.03×10^{-3}	5.28×10^{-4}	2.36×10^{-2}	7.41×10^{-2}	0.837
50	9.32×10^{-4}	4.85×10^{-4}	1.95×10^{-2}	6.21×10^{-2}	——

* Data are from Pagenkopf (1978)

Example

Calculate the solubility of oxygen in water at 20°C.

At sea level (a total atmospheric pressure of 1 bar; where one atm = 1.0135 bar) the partial pressure of oxygen is 0.21bar. At 20°C, the Henry's law constant for oxygen is 1.38×10^{-3} mol/L·bar.

$$C_i = K_H P_i$$

$O_{2(aq)} = (1.38 \times 10^{-3}\ \text{mol/L·bar})(0.21\ \text{bar}) = 2.9 \times 10^{-4}\ \text{mol/L}$

or

$(2.9 \times 10^{-4}\ \text{mol/L})(32.0\ \text{g}O_2\text{/mol}) = 9.28 \times 10^{-3}\ \text{g/L}$ or 9.28 mg/L

The reality we face is that life is rarely ideal. So how do we calculate free energies or solubility constants at temperatures other than 25ºC? Does temperature make a difference in solubility?

Free energies at temperatures other than 25°C.

If the deviations in temperature from 25°C are small (~15°C or less) we can make the assumption that ΔH_R and ΔS_R are constant.

This brings us to the van’t Hoff equation:

$$\ln K_t = \ln K_r + (\Delta H_R/R)(1/T_r - 1/T_t)$$

Where K_t is the equilibrium constant at temperature t, K_r is the equilibrium constant at 25°C, T_t is the temperature t and T_r is 298.15K. Of course, ΔH_R is the enthalpy for the reaction, and R = 8.314×10^{-3} kJ/mol·K.

Example 2-3

Calculate the solubility product of gypsum at 40°C using the van't Hoff equation.

Recall that K_{sp} at 25ºC = $10^{-4.60}$ for the dissolution of gypsum. From Appendix II

$\Delta H_R = (-543.0)+(-909.34)+(2)(-285.83)-(-2022.92) = -1.08 \text{kJ mol}^{-1}$

$\ln K_t = \ln(10^{-4.60}) + [(-1.08/8.314\text{X}10^{-3})/((1/298.15)-(1/313.15))]$

$= -10.61 = e^{-10.61} = 10^{-4.61}$

Le Chatelier's principle

If a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce the change.

To review:

$$CaSO_4 \cdot 2H_2O \leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O + \text{heat}$$

If there is an increase in Ca^{2+}, what will happen?

If the system’s temperature is decreased, what will happen?

$$CaCO_3 + SiO_2 \leftrightarrow CaSiO_3 + CO_{2(g)}$$

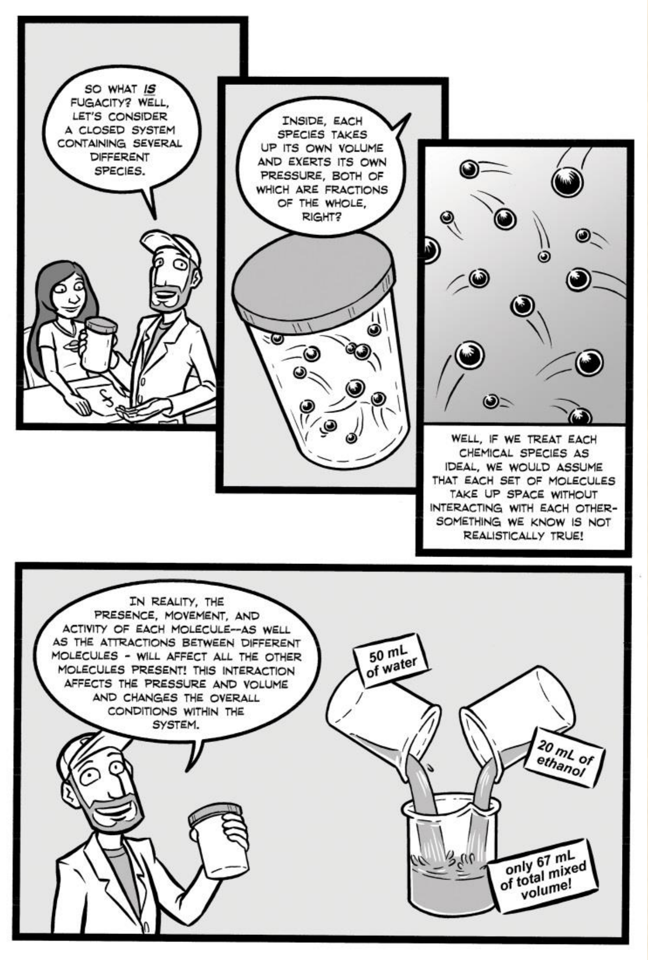
If the pressure on the system is increased, what will happen?

Activity **and** ***Fugacity*** **(for a gas):** the apparent (or effective) concentration of a species as opposed the actual concentration. Activity and fugacity are a measure of the departure of a system from ideal behavior and need to be taken into account even when dealing with relatively dilute solutions.

Activity (or fugacity) is related to concentration through the activity coefficient (γ_i).

$$\gamma_i = a_i / m_i$$

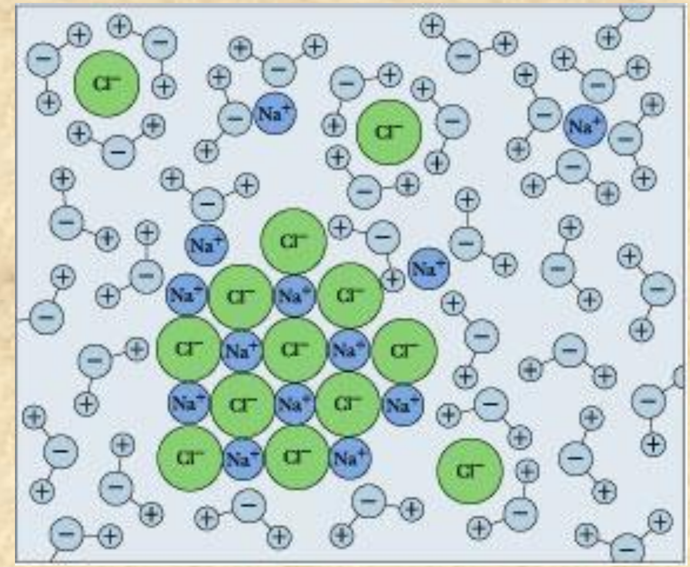
Where a_i is the activity and m_i is the actual concentration.



Activity coefficient (γ): measure of how a specific real system deviates from some reference system that is taken to be *ideal*.

In an ideal solution, activity would equal concentration. The departure from ideal behavior is caused mainly by

- Electrostatic interactions between charged ions.
- The formation of hydration shells around ions.



One factor that is important to understand is ionic strength (I).

$$I = \frac{1}{2} \Sigma m_i z_i^2$$

Where m_i = the moles/liter of ion i and z_i is the charge of ion i.

**The ionic strength is calculated using all the ions in the solution.

Debye-Hückel Model

$$\log\gamma_i = (-Az_i^2(I)^{1/2})/(1 + Ba_i(I)^{1/2})$$

Where A and B are constants depending only on T and P and a_i is the hydrated radius of a particular ion.

Example 2-4

Given the following river water chemistry, calculate the activity coefficient for Ca^{2+} at 25°C, using both the Debye-Hückel and the Truesdell-Jones equations.

We will use the Debye-Hückel equation.

River Water Concentration (mg L^{-1})							
Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	SO_4^{2-}	HCO_3^{-}	SiO_2
14.7	3.7	7.2	1.4	8.3	11.5	53	10.4

We must first calculate I based on all of the ions in the river water.

Recall: $I = \frac{1}{2} \Sigma m_i z_i^2$

Using the Debye Huckel equation for Ca^{2+}

$$\log\gamma_i = (-Az_i^2 (I)_{1/2})/(1 + Ba_i(I)_{1/2})$$

$$\text{Log}\gamma_{(Ca^{2+})} = (-0.5094)(2)^2(0.002005)^{1/2})/(1 + (0.3289)(6.0)(0.002005)^{1/2}) = -0.084$$

$$\gamma_{(Ca^{2+})} = 10^{-0.084} = 0.82$$

What does this imply about the activity of the calcium ion versus the actual concentration? Keep in mind that $a_i = (m_i)(\gamma_i)$

And please……

Do Not Fear the SPREADSHEET!!!!

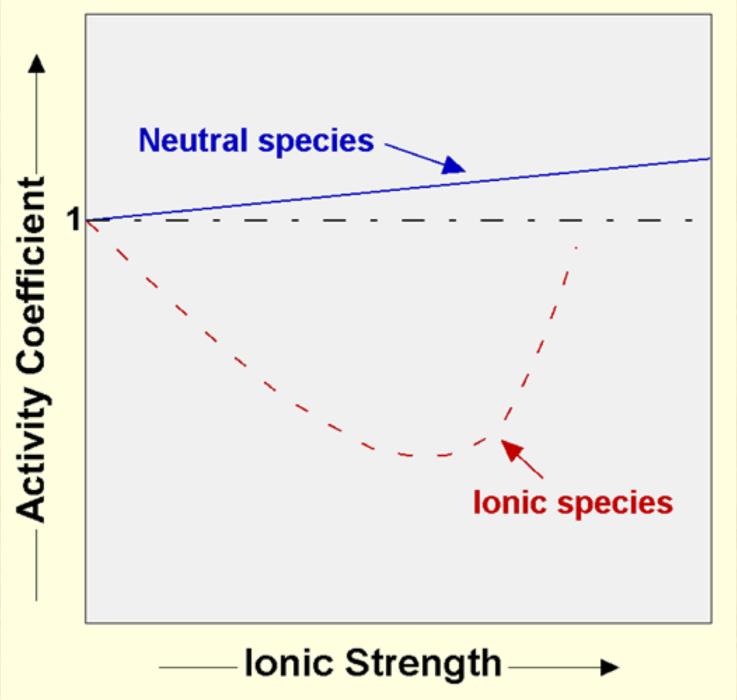
We should be aware of the different types of activity coefficient models and their limitations.

Table 2-4

Appropriate Ranges of Ionic Strengths for Activity Coefficient Models

Model	Ionic Strength (mol/L)
Debye-Hückel	0 to 0.1
Davies	0 to 0.6
Truesdell-Jones	0 to 2
Specific ion interaction	0 to 4
Pitzer	0 to 6

Activity Coefficients for Uncharged Species



Plummer and MacKenzie (1974)

$$\gamma = 10^{0.1I}$$

where *I* is the ionic strength.

Setchenow equation (Millero and Schreiber, 1982)

$$\log \gamma_i = K_i I$$

where K_i is a constant ranging in value from 0.02 to 0.23 at 25°C.

With increasing ionic strength, compounds that yield uncharged species on dissolution (such as quartz, which dissolves to form $H_4SiO_{4\,(aq)}$) become less soluble while ionic compounds (such as NaCl, which dissolves to form Na^+ and Cl^-) become more soluble

Aqueous complex: a dissolved species formed from two or more simpler species, each of which can exist in aqueous solution.

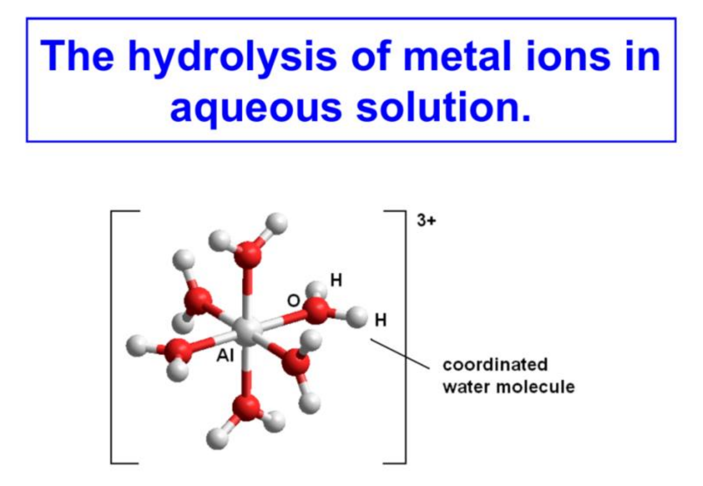
$$A^+ + B^- \rightleftharpoons AB_{(aq)}$$

$$K_{stab} = \frac{\left[AB_{(aq)}\right]}{[A^+][B^-]}$$

$$[AB_{(aq)}] = K_{stab} \cdot [A+][B^-] = K_{stab}\, K_{sp}$$

Why do we care?

1. Complexation of an ion also occurring in a mineral increases solubility
2. Some elements occur as complexes more commonly than as free ions
3. Adsorption of elements greatly determined by the complex it resides in
4. Toxicity/bioavailability of elements depends on the complexation



The hydrolysis of metal ions in aqueous solution.

A Measure of Disequilibrium

Consider the dissolution of gypsum:

$$CaSO_4 \cdot H_2O \leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$$

$$K_{sp} = [Ca^{2+}][SO_4^{2-}]$$

This specific reaction simplifies matters to the point that we can consider the activities of the products when determining K_{sp}. We would call this the activity product [AP] or ion activity product if only charged species are involved [IAP].

If the [AP] = K_{sp}, the system is in equilibrium,.

If the [AP] < K_{sp}, the solution is undersaturated with respect to gypsum.

If the [AP] > than the K_{sp}, the solution is supersaturated with respect to gypsum.

Example 2-6

In a particular solution $[Ca^{2+}] = 10^{-3}$ *mol* L^{-1} *and* $[SO_4^{2-}] = 10^{-2}$ *mol* L^{-1}*. At 25ºC, is the solution over- or under-saturated with respect to gypsum?*

$$IAP / K_{sp} = ((10^{-3})(10^{-2}))/10^{-4.60} = 10^{-0.40}$$

IAP is less than 1 so the solution is under-saturated with respect to gypsum.

Kinetics

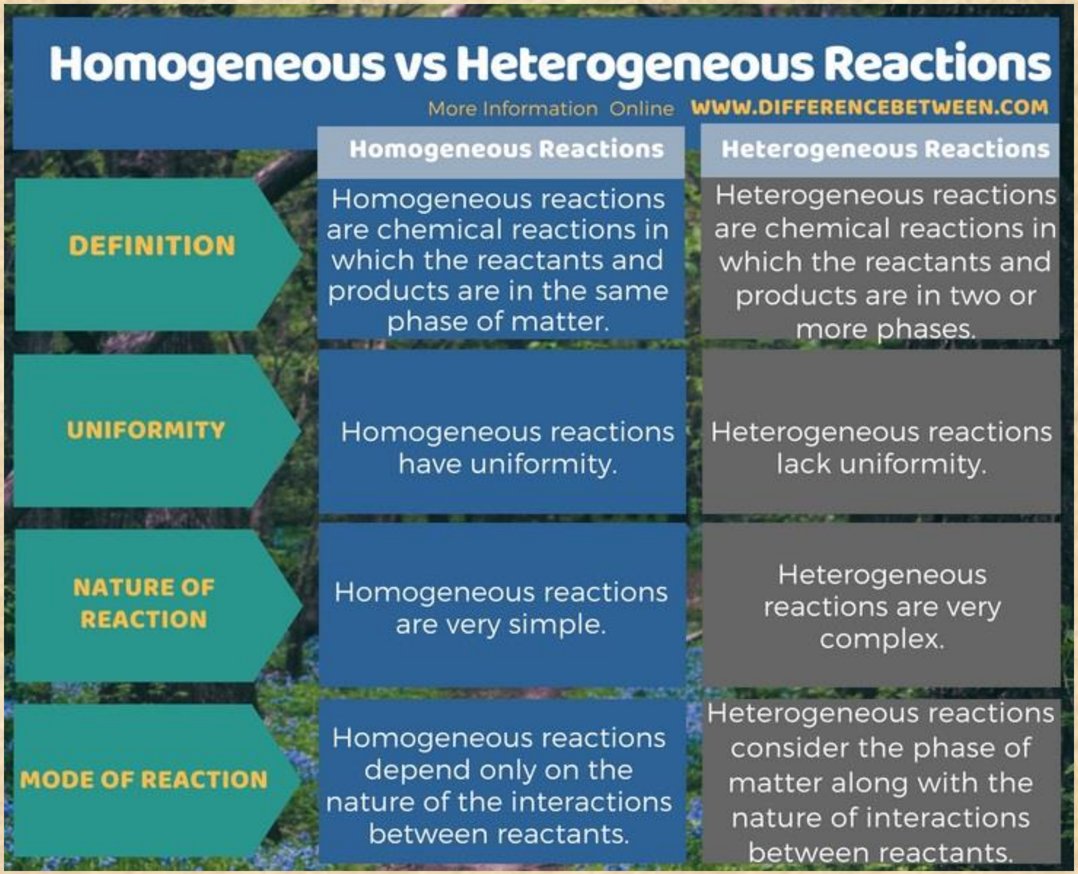
Equilibrium thermodynamics predicts the final state of a system.

Kinetics tells us if the system will actually achieve this state within a reasonable time.

Homogeneous reactions involve one phase (gas, liquid or solid.

Heterogeneous reactions involve two or more phases.

Reactions often occur in a series of steps. The slowest step determines the rate at which the reaction will proceed.

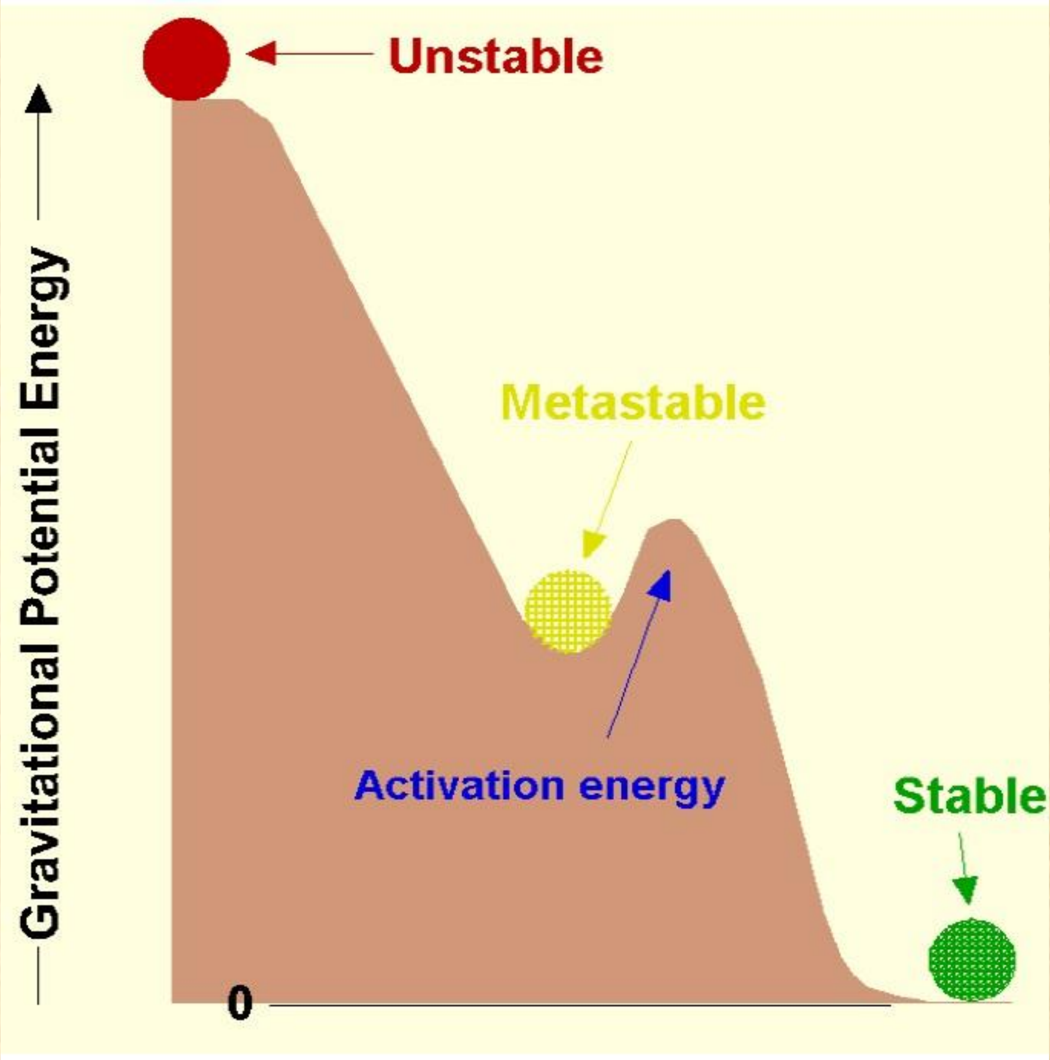


Homogeneous vs Heterogeneous Reactions

More Information Online WWW.DIFFERENCEBETWEEN.COM

	Homogeneous Reactions	Heterogeneous Reactions
DEFINITION	Homogeneous reactions are chemical reactions in which the reactants and products are in the same phase of matter.	Heterogeneous reactions are chemical reactions in which the reactants and products are in two or more phases.
UNIFORMITY	Homogeneous reactions have uniformity.	Heterogeneous reactions lack uniformity.
NATURE OF REACTION	Homogeneous reactions are very simple.	Heterogeneous reactions are very complex.
MODE OF REACTION	Homogeneous reactions depend only on the nature of the interactions between reactants.	Heterogeneous reactions consider the phase of matter along with the nature of interactions between reactants.

Systems can exist in several states: unstable, metastable and stable.



The dissolution of gypsum occurs in two main steps.

1st: energy input is required to free the ions from the crystal structure.

2nd: the ions must diffuse away from the crystal. If they do not, then the microenvironment surrounding the gypsum crystal becomes saturated and the reaction stops.

$CaSO_4 \cdot H_2O \leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$

Which ever these steps is the slowest, will determine the rate at which dissolution proceeds. A common environment for gypsum dissolution is in the presence of ground water. In this case, which step would determine the rate of dissolution?

Order of reactions

Zeroth order: The reaction rate is independent of the concentration of the reactant (A) *–rate of the reaction is constant. When the limiting reactant is completely consumed, the reaction stops. Units for k = mol L^{-1} sec^{-1}*

$$t_{1/2} = 0.5A_0/k$$

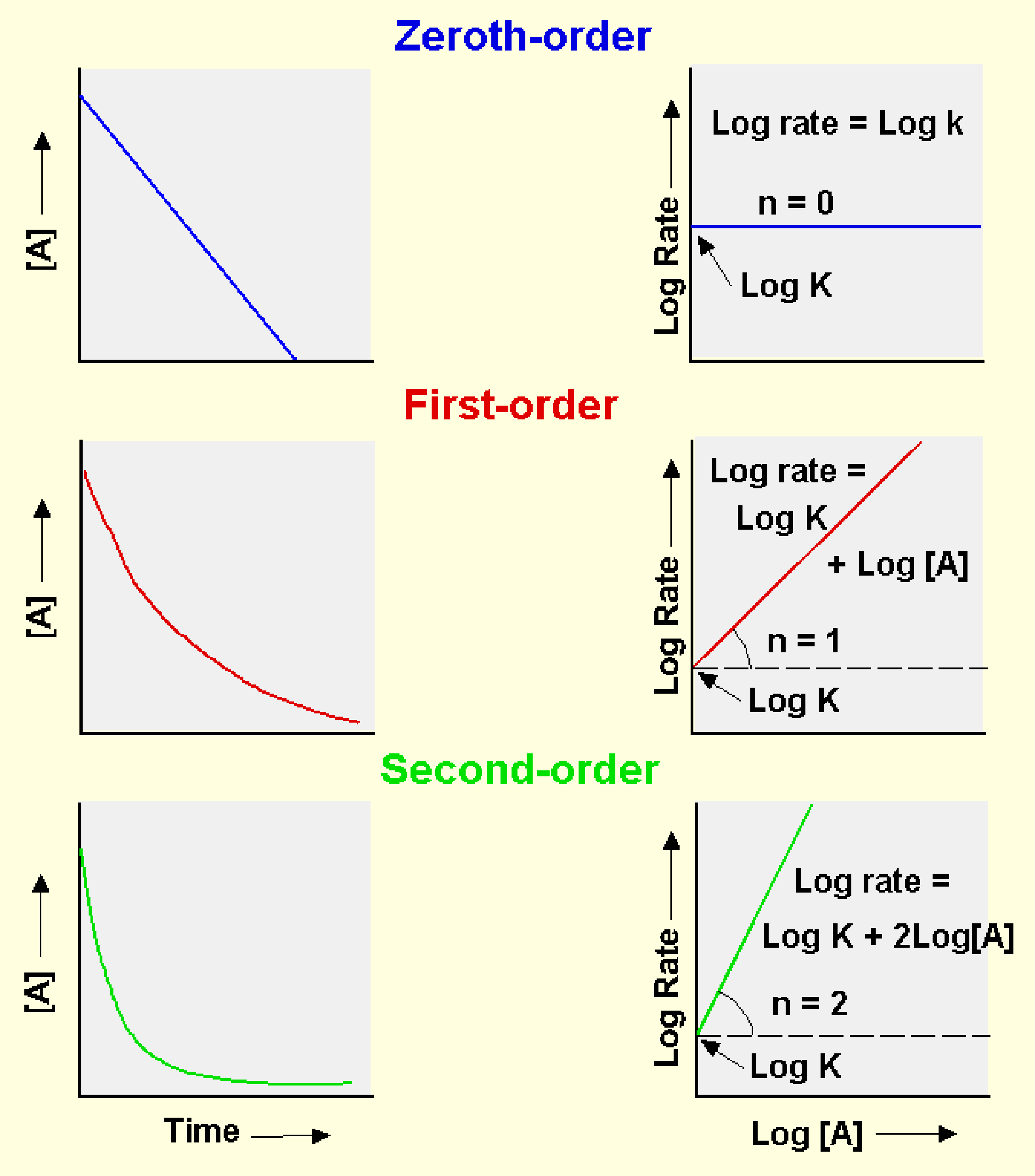
First order: The reaction rate is dependent on the concentration of the reactant A → B. *– The rate of the reaction is directly proportional to the concentration of one of the reactants. Units for k = sec^{-1}*

$$t_{1/2} = 0.693/k$$

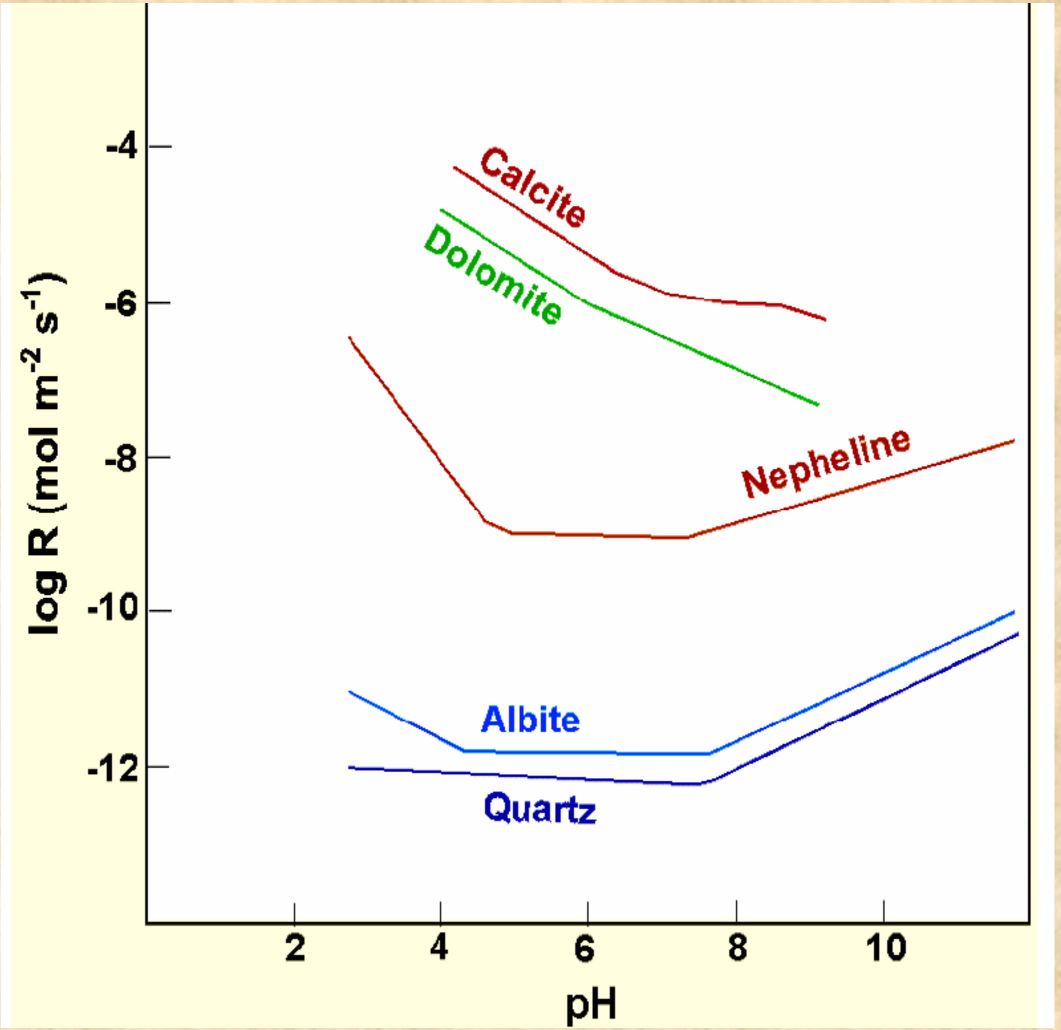
Second order: The reaction rate is dependent on the concentration of the reactant 2A → B. *–The rate of the reaction is directly proportional to the square of the concentration of one of the reactants. Units for k = L mol^{-1} sec^{-1}*

$$t_{1/2} = -1/kA_0$$

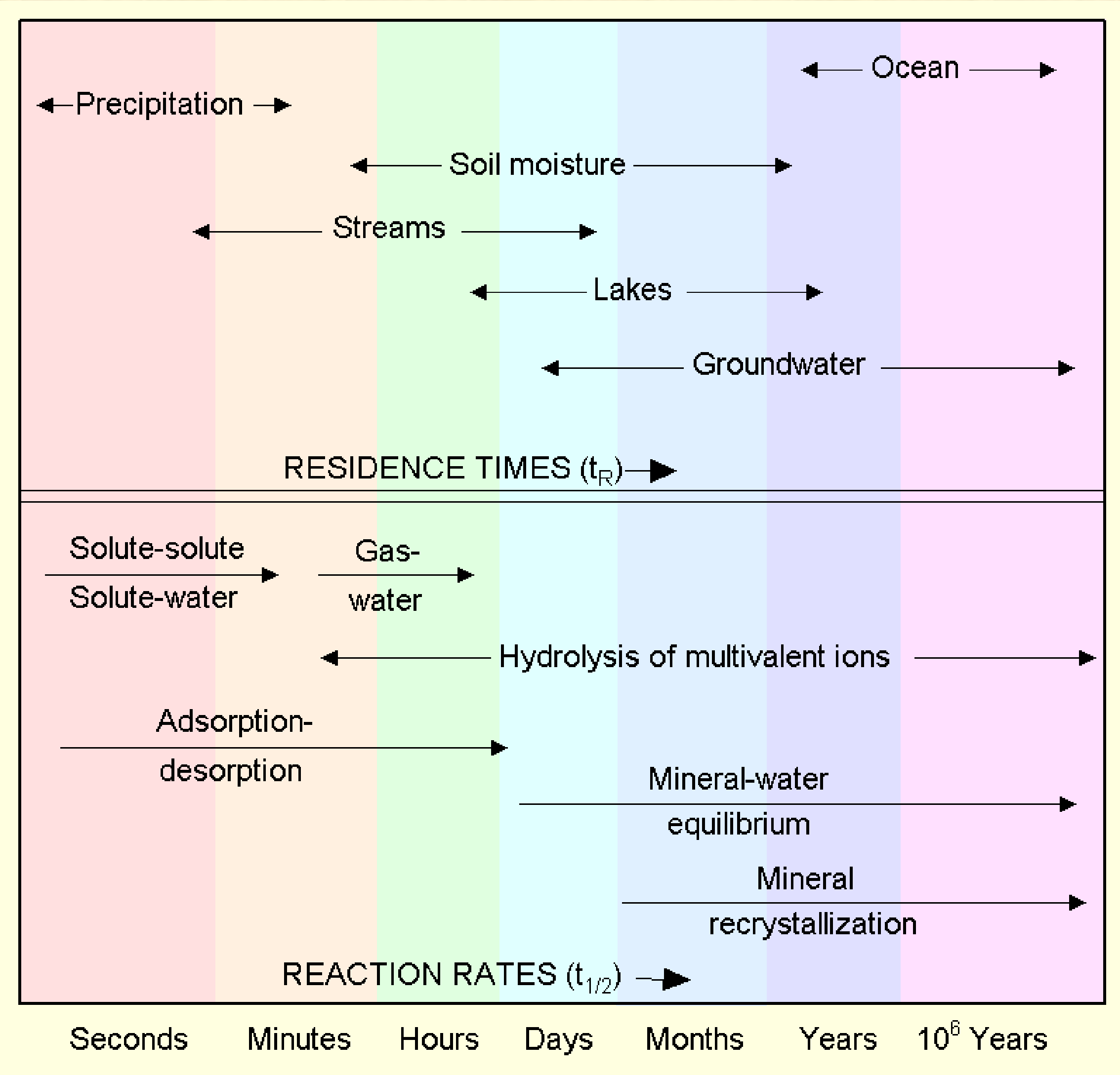
Note that the units for k depend upon the order of the reaction.


Zeroth-order
[A]
Log Rate
Log rate = Log k
n = 0
Log K
First-order
[A]
Log Rate
Log rate =
Log K
+ Log [A]
n = 1
Log K
Second-order
[A]
Log Rate
Log rate =
Log K + 2Log[A]
n = 2
Log K
Time
Log [A]

For many solids, the dissolution rate is affected by the pH of the solution.



Reaction rates & residence times of water for various reservoirs



If $t_{½}$ < residence time. Then the process should reach equilibrium.

The Arrhenius Equation: relates the rate at which a reaction occurs to the temperature.

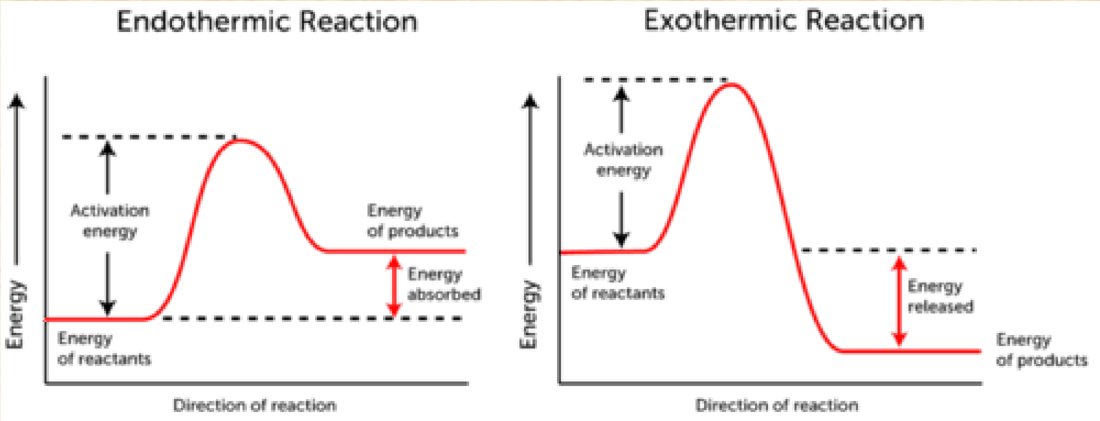
$$k = A \exp(-E_a/RT) = A \times e^{(-Ea/RT)}$$

or

$$\log k = \log A - (E_a/2.303RT)$$

Where A is a experimentally derived factor, E_a is the activation energy for the reaction, R is the ideal gas constant and T is temperature in Kelvin.

Activation energy: the energy that must be overcome in order for a chemical reaction to occur.



Example 2-8

Consider one of the reactions in the carbonate system:

$$CaCO_{3\ calcite} + H_2CO_{3(aq)} \rightarrow Ca^{2+} + 2HCO_3^-$$

The rate constant for this reaction is 3.47 X 10^{-5} s^{-1} and log*k* = -4.46. The activation energy for the reaction us 41.85kJ mol^{-1}. Determine A at 25ºC and then the rate constant for the reaction at 10⁰C.

$\log A = \log k + E_a/(2.303RT) = -4.46 + 41.85/((2.303)(8.314X10^{-3})(298.15)) = 2.87$

$\text{Log } k = \log A – E_a/(2.303RT) = 2.87 – 41.85/(2.303)(8.314x10^{-3})(283.15) = -4.85$

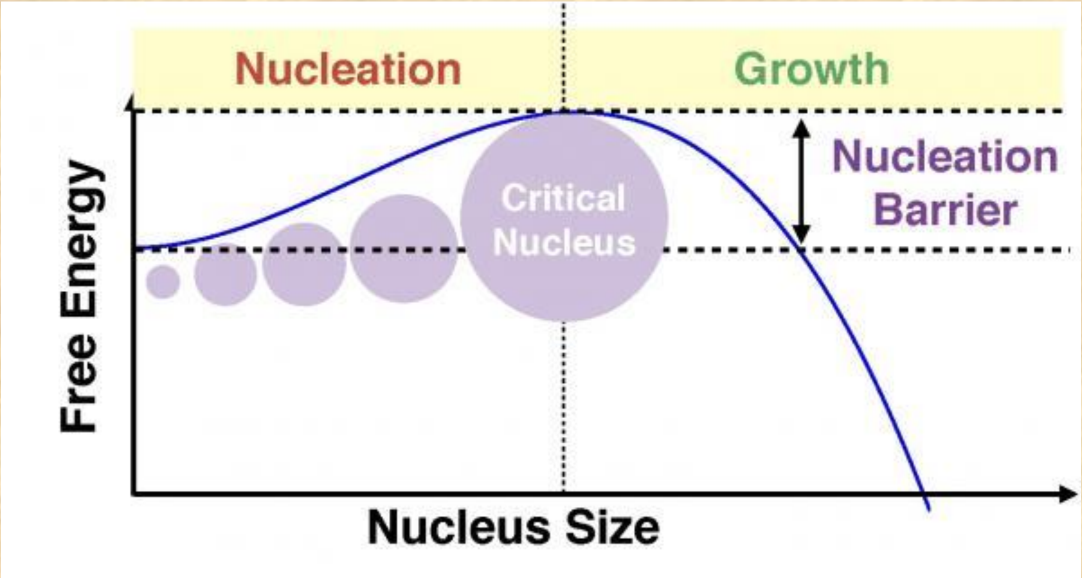
If at 25ºC, k = $10^{-4.46}$ and at 10⁰C, k = $10^{-4.85}$ then it can be said that the reaction rate has decreased by ~2.5 times as a result of the lower temperature.

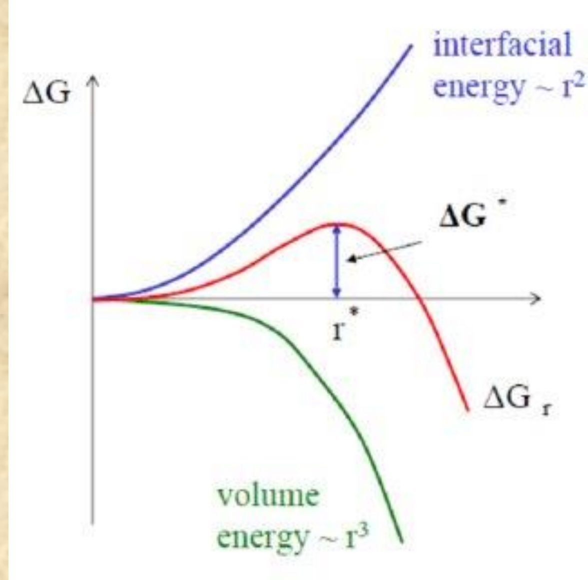
Two types of nucleation:

Homogeneous nucleation occurs when a *nucleus forms spontaneously in an oversaturated solution.*

Heterogeneous nucleation occurs when a *nucleus forms in contact with a*, *usually solid*, *surface*.

Homogeneous nucleation requires a much greater degree of supersaturation than heterogeneous nucleation.





Schematic representation of a mineral reacting with a solution during dissolution. The rate-controlling step can be

1. the diffusion of species through the solution
2. diffusion of species through the reaction zone
3. the rate of the surface reaction.