

GEOL 414/514

INTRODUCTORY GEOCHEMISTRY

Lecture = 2 hrs/week

Lab = 3hrs/week

Course = 3 credits

Text:

Langmuir

Aqueous Environmental Geochemistry

CHEMICAL EQUILIBRIUM

A REVIEW

EQUILIBRIUM CONSTANTS

- Nature of interaction when two substances are mixed:
 - reaction - ?
 - how far and how fast - ?
- Early work by Guldberg & Waage attributed reaction dynamics to a “driving force” and “mass” of substances
- “Mass” should be labeled concentration
- “Law of mass action” - “The rate of a reaction is directly proportional to the concentration of each reacting substance”
- This is NOT a a general law for reaction rates

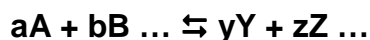
EQUILIBRIUM CONSTANTS

- Guldberg & Waag’s work allowed recognition that many reactions were incomplete because they are reversible
$$A + B \rightleftharpoons Y + Z$$
- Mix equal amounts of A & B in one container and equal amounts of Y & Z in another container:
 - when all reactions stop, there are equal amounts of all four substances in both containers
- Driving force of forward reaction = $k_1[A][B]$
- Driving force of reverse reaction = $k_2[Y][Z]$
- Equality requires that: $k_1[A][B] = k_2[Y][Z]$

EQUILIBRIUM CONSTANTS

$$\frac{[Y][Z]}{[A][B]} = \frac{k_1}{k_2} = K$$

- K - equilibrium constant
- General equation for a chemical reaction:

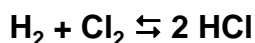


$$K = \frac{[Y]^y[Z]^z \dots}{[A]^a[B]^b \dots}$$

- Should use activities, [], instead of concentrations

Remember, $K = \frac{\text{Products}}{\text{Reactants}}$

EXAMPLE OF EQUILIBRIUM: HCl



$$K = \frac{[HCl]^2}{[H_2][Cl_2]}$$

- Units of concentration - ? : g L⁻¹; mols L⁻¹, mols kg⁻¹
 - use partial pressure in bars (used by convention)
- Dalton's law of partial pressures: the total pressure of a mixture is the sum of all partial pressures
- At equilibrium, a change in the partial pressure of one component forces change in the other components

EXAMPLE OF EQUILIBRIUM: HCl

- Whatever change occurs in a reaction, K remains constant
- Add H₂ to an equilibrium mixture, the forward reaction,
$$\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$$
is favored, while the reverse reaction is unaffected:
$$2\text{HCl} \rightarrow \text{H}_2 + \text{Cl}_2$$
- Note that an equilibrium constant has no meaning except in terms of a specified chemical equation

THE EFFECT OF TEMPERATURE

- Temperature is a very important factor to consider for chemical reactions
- Temperature may affect stability of reactants or products and may affect kinetics
- Remember that the K_{eq} does not give us information on the reaction kinetics
- How to determine experimentally if a mixture is at equilibrium?
 - bake it or boil it!
 - take a system of interest and raise the temp; measure all components before & after temp rise
 - also mix components at different initial temps

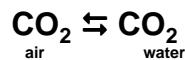
THE EFFECT OF TEMPERATURE

- Most reaction rates increase by a factor of 2X - 3X for each 10 °C rise in temperature
- Generally, to see if a mixture of compounds is an equilibrium assemblage, we set up experiments to see whether the same mixture can be obtained by starting with pure components at each end of the reaction
- Many reactions involving polyatomic molecules react slowly at room temperature & reach equilibrium readily only at temps of a few hundred degrees
- Reactions involving ions in aqueous solution are almost instantaneous; those of ions in silicate melts may be slow

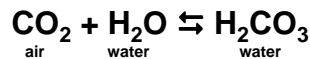
SECOND EXAMPLE: CO₂ IN H₂O

The example of H₂, Cl₂ & HCl involved a single phase, or homogeneous system

A heterogeneous system, involving substances in different states, is geologically common



Then:



$$K = \frac{[\text{H}_2\text{CO}_3]}{[\text{CO}_2][\text{H}_2\text{O}]}$$

The equilibrium will respond to increased P_{CO₂} (add CO₂), decreased P_{CO₂} (heat, create vacuum)

SECOND EXAMPLE: CO₂ IN H₂O

- Solubility of CO₂ = 0.76 L/L H₂O at t = 25 °C, P_{CO₂} = 1 bar
- 0.75 L CO₂; 0.76L/24.5 L/mole = 0.31 moles CO₂
- [Notice that H₂O = 1000/18.016 = 55.5 m]
- For CO₂ above: K = [H₂CO₃]/[CO₂] = 0.031/1 = .031 ≈ 10^{-1.5}
- How much H₂CO₃ in water exposed to ordinary air?
- Air contains 0.03% CO₂ by volume; volume fraction = 0.0003 & partial pressure = 0.00003 bar

$$K = 0.031 = [\text{H}_2\text{CO}_3] / 0.0003$$

$$[\text{H}_2\text{CO}_3] = 0.031 \times 0.0003 = 10^{-1.5} \times 10^{-3.5} = 10^{-5} \text{ m}$$

A THIRD EXAMPLE: CaSO₄

- Add CaSO₄ to water:



- After time, equilibrium appears to have been reached; conc of Ca⁺² & SO₄⁻² does not change
- In another container, add Ca⁺² & SO₄⁻²; a precipitate forms immediately; find that conc's of Ca⁺² & SO₄⁻² are the same as in the first solution
- Have now established existence of an equilibrium:



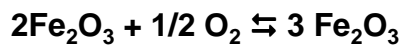
$$K_{\text{eq}} = \frac{[\text{Ca}^{+2}][\text{SO}_4^{-2}]}{[\text{CaSO}_4]}$$

A THIRD EXAMPLE: CaSO_4

- Concentrations of Ca^{+2} and SO_4^{-2} can be expressed in terms of mols/kg or mols/L;
- What about conc of CaSO_4 ? By convention, the conc or activity of a pure solid = 1

• So:
$$K_{\text{eq}} = [\text{Ca}^{+2}][\text{SO}_4^{-}]$$

- Example of formation of hematite from magnetite:



$$K_{\text{eq}} = 1/[\text{O}_2]^{1/2}$$

- Both solids exist together only at one P_{O_2}
- (How could you use this info in paleointerpretation?)

SOLUBILITY PRODUCT

- $\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$ Solubility product = $K = m_{\text{Ag}^+} m_{\text{Cl}^-}$

$$K \text{ of } \text{CaSO}_4 = 3.4 \times 10^{-5}$$

- $[\text{Solubility}]^2 = [\text{Ca}^{+2}][\text{SO}_4^{-2}] = K_{\text{sp}} = 3.4 \times 10^{-5}$

- Solubility = $5.8 \times 10^{-3} m$

- For the most simple case, assuming that no other ions form, the solubility is just the $\sqrt{\quad}$ of the K_{sp}

- What happens if we add CaCl_2 to an equilibrium mixture of CaSO_4 ?

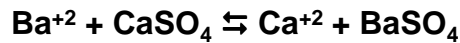


COMMON-ION EFFECT

- Common-ion effect – the decrease in solubility of a salt due to the presence of one of its own ions in solution



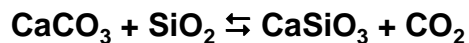
- Add BaCl_2 (soluble salt)



- $K' = [\text{Ca}^{+2}][\text{SO}_4^{-2}] = 3.4 \times 10^{-5}$
- $K'' = [\text{Ba}^{+2}][\text{SO}_4^{-2}] = 1.0 \times 10^{-10}$
- Divide the equations, $K = [\text{Ca}^{+2}] / [\text{Ba}^{+2}] = 3.4 \times 10^5$
- The equilibrium conc of Ca is 340,000 X that of Ba

LE CHATELIER'S RULE

- A chemical equilibrium responds to any disturbance by trying to undo the effects of the disturbance
- If one reaction is exothermic, the reverse must be endothermic
- Endothermic reactions are favored by a rise in temp
- Exothermic reactions are favored by a fall in temp
- Note muscovite-quartz-K-feldspar-sillimanite example
- Equilibria involving gases are especially sensitive to P



- Forward reaction produces a large volume increase; high P would tend to prevent formation of wollastonite

STABILITY

- A stable substance is one that does not react readily in a particular environment.
- At ordinary STP: Au is stable and Fe oxidizes (rusts)
- K-feldspars: - sanidine is stable at high temps
- adularia is stable at low temps
- Supersaturated solutions are unstable
- A qualifying phrase is always implied: stable with respect to particular conditions
- Stability may also be defined with respect to either equilibrium or reaction rate
- Stability of galena: $\text{PbS} \rightleftharpoons \text{PbSO}_4$
- Apparent stability of galena due to slow reaction rate

GEOL 414/514

**THERMOCHEMICAL
PRINCIPLES**

**CHAPTER 1
LANGMUIR**

THERMODYNAMIC SYSTEMS

- Dimensions of system are chosen to suit specific geochemical problems
- There are three types of systems:
 - isolated - cannot exchange energy or matter
 - closed - can exchange energy but not matter
 - open - can exchange both energy and matter
- The material in a system is composed of phases, each phase having distinct physical & chemical properties
- Phases: minerals plus fluids (vapor, water, magma), each described by discrete chemical components
 $\text{NaAlSi}_3\text{O}_8$: K_2O , Al_2O_3 , SiO_2 , H_2O & HCl

THERMODYNAMIC SYSTEMS - 2

System properties:

- Extensive - defined by the system as a whole - these properties are additive: internal energy (E), entropy (S), enthalpy (H), Gibbs free energy (G) & number of mols of chem components
- Intensive - take well-defined values at each point within the system - these properties are not additive: T, P, chemical potential (μ_i)
- The thermodynamic state of a system is described by a specified group of independent intensive and/or extensive variables
- A property that can be expressed in terms of these variables is called a function of the state of the system

THERMODYNAMIC SYSTEMS - 3

Example:

- System with one phase, a gas, in a confined cylinder that allows variable volume.
- Specify the T & P and the V will be a function of the state of the system, represented by:

$$V = F(T,P) \text{ or } V = RT/P$$

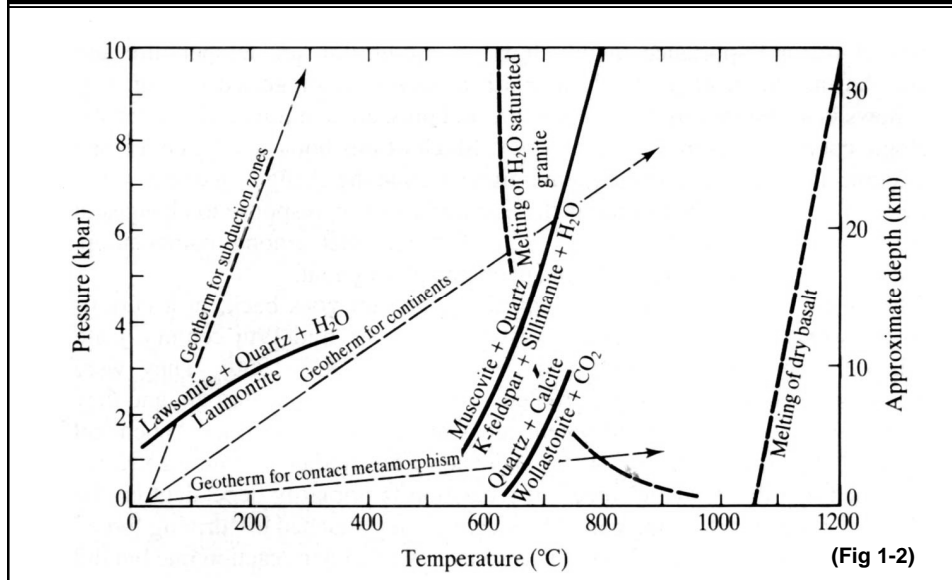
- Read derivation in text
- We will describe chemical equilibrium in terms of T, P & composition, using a function of the state of a system, Gibbs free energy(G)

$$G = F(T, P, n_i)$$

THE PHASE RULE

- We have studied the calculation of equilib phase relationships among minerals & solutions
- Variables used: T, P, molal conc's, mol fractions
- How many thermodynamic variables must be fixed to establish equilib in an assemblage of phases?
- For the equilib of muscovite, quartz, K-feldspar, sillimanite & water shown in Fig 1-2 (axes of P vs T), how many variables must be fixed to ensure that equilib exists?
- Here we ponder, meditate & discuss - but not too long
- Answer is one; fix T & P is automatically fixed

TYPICAL GEOTHERMS FOR THREE METAMORPHIC REACTIONS



THE PHASE RULE - 2

- A general answer to questions about the number of variables that must be fixed to establish equilib lies in a relationship called the phase rule.
- The number of phases (p) & number of chem components (c) needed to describe the comp of all phases deter's the number of intensive variables that must be specified at equilibrium.

$$f = c + 2 - p$$

- Using the previous example:
- Muscovite-quartz-K-feldspar-sillimanite-water - 5 phases
- K_2O , Al_2O_3 , SiO_2 & H_2O are the 4 components

$$f = 4 + 2 - 5 = 1$$

THE PHASE RULE - 3

- The quartz-water equilibrium has 2 phases & 2 components (SiO_2 & H_2O), so

$$f = 2 + 2 - 2 = 2$$

- If we fix T & P, the equilib value of $m_{\text{SiO}_2(\text{aq})}$ is determined
- Note the derivation proof for the phase rule in the text
- The phase rule has many uses in geochemistry, esp in evaluating experimental observations & constructing theoretical phase diagrams
- Application to geologic systems is complicated:
 - large number of components needed to describe all of the phases
 - system is open to transport of chem components

THE LAWS OF THERMODYNAMICS

First Law: Conservation of Energy

- Absolute values of energy are difficult to obtain, but mostly we are interested in changes in E
- Add heat (Q) to a system which does work (W) on the surroundings

$$\Delta E = E_{\text{final}} - E_{\text{initial}} = Q - W, \text{ or}$$

$$dE = dQ - dW$$

- Substituting for the W function,

$$dE = dQ - PdV$$

- E is a property of the system, Q & W are not properties of the system

THE LAWS OF THERMODYNAMICS-2

Second Law: Creation of Entropy

Entropy (S) is a measure of disorder or randomness; highly disordered substances have high S & low S is associated with strongly ordered substances

- The second law states that the change in S of a closed system due to a reversible process is equal to:

$$dS = dQ / T$$

- For an irreversible process:

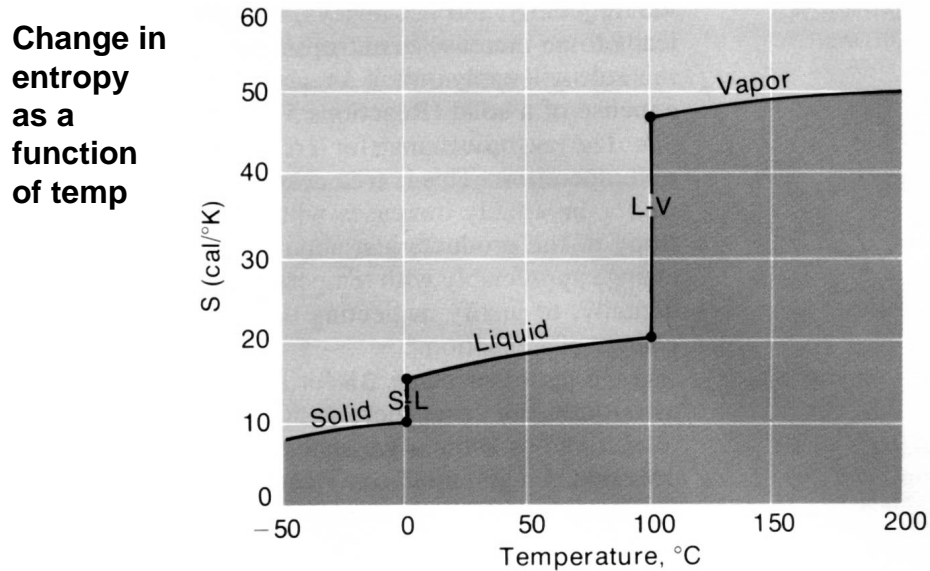
$$dS > dQ / T$$

- Consider a process that can be carried out either reversibly or irreversibly

THE LAWS OF THERMODYNAMICS-3

- For reversible process, dS of a closed system is proportional to heat exchange with surroundings
- For an irreversible process, dS is defined by some change in the system, expansion of gas to greater volume
 - the measure of dS is still the heat that would be absorbed if the process were carried out reversibly
- Adding heat to a system always increases its entropy:
 - gas expands
 - solids melt
 - liquids evaporate

THE LAWS OF THERMODYNAMICS-4



THE LAWS OF THERMODYNAMICS-5

Combined Laws: Thermodynamic Potentials

- Combining equations representing the first & second laws gives (for reversible process, closed system):

$$dE = TdS - PdV$$

- Combining Eqs. For entropy, we obtain

$$dQ = TdS - TdS_{int.}$$

- Substituting into Eq'n relating heat & energy:

$$dE = TdS - PdV - TdS_{int}$$

- Where $dS = dV = 0$ and $dE = -TdS_{int}$

$$(dE)_{S,V} \leq 0 \quad [\text{constant } S, V]$$

ENTHALPY

Definition

- Enthalpy (H) is an extensive property of a system, closely related to energy, defined as

$$H = E + PV \quad \text{or} \quad dH = dE + PdV + VdP$$

- For a process at constant pressure:

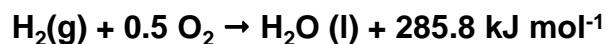
$$dH = dE + PdV = dQ$$

- H is often called the “heat content” of a system, although the term as defined above has a broader meaning

ENTHALPY - 2

Heats of Reaction

- At constant T & P, this is the heat taken up or given off by a chemical reaction



$$\Delta H = H_{\text{products}} - H_{\text{reactants}} = -285.8 \text{ kJ mol}^{-1}$$

- The H for the system becomes less during the reaction, so ΔH must have a negative sign
- The absolute H of a substance or mixture is difficult to obtain so, as with S, we are more interested in ΔH of reactions
- If two moles react, the $\Delta H = -571.5 \text{ kJ}$; for reverse reaction, $\Delta H = +571.5 \text{ kJ}$

ENTHALPY - 3

Computing Reaction Enthalpy

- The ΔH for the formation of a compound from its elements is the heat of formation of the compound.
- The ΔH for elements = 0
- Heats of reaction given in tables are for elements & compounds at standard states ($t = 25^\circ\text{C}$, $P = 1 \text{ bar}$) and are designated by ΔH_f° .
- The heat of reaction, ΔH_r , can be determined by adding & subtracting the heats of formation of the compounds.

$$\Delta H_r = \Delta H_f^\circ(\text{products}) - \Delta H_f^\circ(\text{reactants})$$

FREE ENERGY

Definition

- Enthalpy is not the only factor of importance in making a reaction take place.
- Take the example of a reaction where $\Delta H = 0$
$$A + B \rightarrow A - B$$
- The reaction occurs because the mixture represents a state of greater disorder or randomness, so
tendency to react = $\Delta H + \text{change in disorder}$
change in disorder = $T\Delta S$
- Describe “tendency to react” as “change in free energy”

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

FREE ENERGY - 2

- G is Gibbs free energy, an extensive property, defined as

$$G \equiv H - TS \quad \text{or} \quad G = E - TS + PV$$

- As with H & E, absolute values for G are difficult to obtain; fortunately the change in G during reactions are most important:

$$\Delta G = G_{\text{products}} - G_{\text{reactants}}$$

Free Energy as a Criterion of Equilibrium

- Since ΔG expresses the ability of substances to react & extent of reaction, it is important in making predictions about many geochemical processes

FREE ENERGY - 3

Free Energy as a Criterion of Equilibrium

$$dG = dE - TdS + VdP + PdV$$

- Substituting from heat (Q) and energy (E) relationships:

$$dE = TdS - PdV - TdS_{\text{int}}$$

- Using equilibrium condition relationships:

$$dG = -SdT + Vdp - TdS_{\text{int}}$$

- For a chem rea'n occuring in a closed system, at const. T & P, so that $dT = dP = 0$; Eq. above reduces to

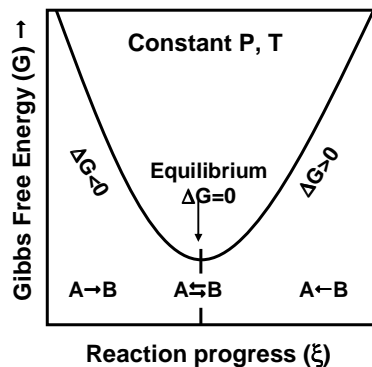
$$(dG)_{T,P} = -TdS_{\text{int}}$$

- or from $dS \geq 0$ at equilibrium:

$$(dG)_{T,P} \leq 0$$

FREE ENERGY - 4

Gibbs free energy as an indicator of equilibrium.



For a chemical reaction:

1. If $\Delta G = 0$, the reaction mixture is at equilibrium
2. If $\Delta G < 0$, reaction will take place spontaneously
3. If $\Delta G > 0$, reaction cannot take place without added E

FREE ENERGY - 5

- Values of ΔG are calculated for reactions as written!
- Can combine ΔG 's for simple reactions to obtain values for complex reactions.
- ΔG_f° , standard free energy of formation, is defined in a manner analogous to ΔH_f° .

$$\Delta G_f^\circ \text{ of } S_{(\text{orthorhombic})} = 0$$

$$\Delta G_f^\circ \text{ of } S_{(\text{monoclinic})} = +0.097 \text{ kJ mol}^{-1}$$

$$\Delta G_f^\circ \text{ of } H^+(\text{aq}) = 0 \text{ by convention}$$

- See Appendix Handout, for ΔG° , ΔH° & S° values

FREE ENERGY - 6

Measurement of ΔG

- Direct measurement of ΔG for most reactions is difficult
- For many oxidation-reduction reactions:

$$\Delta G^\circ = -W' = nFE^\circ$$

- Can measure activities of reactants & products at equilibrium for many reactions:

$$\Delta G^\circ = -RT \ln K$$

- Can also determine ΔG° from heat measurements:

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

- Determine ΔH from measuring heat of reaction in calorimeter & ΔS from heat capacity measurements

FREE ENERGY - 7

Measurement of ΔG

- Entropy diff's between various crystal forms becomes smaller & smaller as T drops towards absolute 0
- Assume zero entropy at T = 0 for one crystal form and the entropy of other crystal forms is also 0
- Entropy differences in reactions involving combinations of crystalline elements to form pure crystalline compounds also fall toward 0 as T approaches 0.
- If the entropy of each element in some crystal state is assumed to be zero at T = 0, the entropy of other pure crystalline solids is also zero at this temp

This is the Third Law of Thermodynamics

FREE ENERGY - 7

Free Energy: Conventions and Qualifications

1. Gibbs free energy refers only to processes taking place at constant T & P
2. Numerical values of free energies are known only as relative quantities, not absolute ones
3. Free energies are expressed in joules (J) or (kJ)
4. ΔG_f is free energy change for formation of 1 mol of compound from its elements
 ΔG_f° is free energy change when reaction occurs with all substances in their standard states
5. Substances in solution are assigned an activity of unity
6. By definition, the formation of H^+ has $\Delta G^\circ = 0$
7. ΔG_f° can be added & subtracted to determine ΔG_r°

THE EQUILIBRIUM CONSTANT

- Where dT and dP are zero,

$$0 = \sum_i n_i d\mu_i \quad (n - \text{no. of moles; } \mu - \text{chem potential})$$

$$dG = \sum_i n_i d\mu_i$$

- For a chem reaction:

$$\Delta G = \sum_i \mu_i \nu_i \quad (\nu - \text{stoichiometric rea'n coeff})$$

- Substitute for μ_i the standard state & activity relations defined by Eq. (8-34),

- Noting that:

$$\Delta G^\circ = \sum_i \mu_i^\circ \nu_i$$

THE EQUILIBRIUM CONSTANT - 2

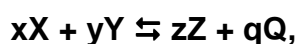
- After substitution, we obtain:

$$\Delta G = \Delta G^\circ + RT \sum_i \nu_i \ln a_i$$

- Equilibrium at constant T & P requires that $\Delta G = 0$, so

$$-\Delta G^\circ = 2.303 RT \sum_i \nu_i \log a_i$$

- For a chemical reaction:



$$\Delta G^\circ = -2.303 RT (\log a_Z^z + \log a_Q^q - \log a_X^x - \log a_Y^y)$$

- Rearrange:

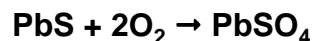
$$-\Delta G^\circ / 2.303 RT = \log (a_Z^z \cdot a_Q^q / a_X^x \cdot a_Y^y)$$

THE EQUILIBRIUM CONSTANT - 3

- A very useful expression that relates K, standard Gibbs free energy and activities of components in a reaction is:

$$\Delta G^\circ = -2.303 RT \log K$$

- Example:



$$\Delta G^\circ = -714 \text{ kJ} \quad \text{and} \quad K = 10^{125}$$

- Both of these values indicate that this reaction goes practically to completion to the right
- Describe the condition/state of the galena sample provided by the instructor with respect to the above data