

Lecture 4

Thermodynamic considerations

Please read chapter Ch3, Ch4 (McSween et al.)

-or- Ch2, Ch3 (White) – *most detailed*

-or- Ch3 (Brownlow) – *most general*

- Chemical Thermodynamics
 - Into and The Phase Rule
- Enthalpy
- Entropy
- The Gibbs Function
- ΔG and K

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Chemical Thermodynamics

Thermodynamics is the study of the energetics of physical and chemical transformations of matter.

The energetics of a "**system**" are described with

physical (e.g., temperature = T , pressure = P)

and

chemical (e.g., composition = X_1, X_2, X_3, \dots) quantities.

A **system** can contain more than one **chemical component** (e.g., H_2O) and more than one physiochemical **phase** (ice, water vapor, liquid water).

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Definitions

- system - a collection of matter in an identifiable place and condition. A *system* can contain more than one *chemical component* and more than one *physiochemical phase*.
- A component is a chemical entity (e.g., H₂O) that can be used to describe compositional variation in a system.

Normally, we choose the minimum number of components (C) to describe the system: $C = n - r$, where n is the number of chemical species and r is the number of reactions that can occur between these species. A component need not physically exist in a system (e.g., plagioclase can be described as a solid-solution mixture of albite and anorthite components, but neither exists in a plagioclase grain of intermediate composition, like labradorite or andesine).

- A phase is a physical form of that chemical (ice, water vapor, liquid water, e.g., quartz, chert, cristobalite).

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The Phase Rule:

This provides a basis for thermodynamically describing a system by telling us the number of system variables (P, T, composition X₁, X₂, X₃, etc.) we must define for a unique set of conditions to apply

$$F = C - P + 2$$

(Sometimes written as $f = c - \phi + 2$)

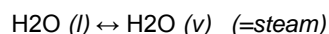
F = degrees of freedom (we want this to be a small number)

C = components (chemical constituents)

P = phases (i.e., minerals)

Some Examples:

- a). A univariant system...
(see figure at right)

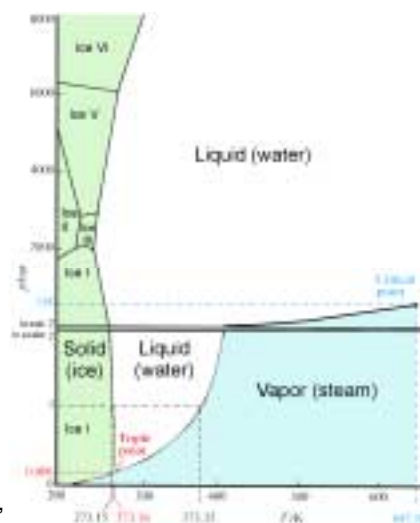


P=2 (aqueous and vapor)

C=1 (water)

F=1 (T or P)

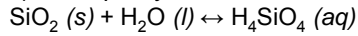
i.e., if we know T, then we can determine P, or vice-versa



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Some More Examples:

b). A simple system... dissolved silica

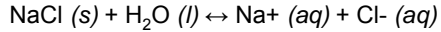


P=2 (aqueous and solid)

C=2 (SiO₂ and water)

F=2 (e.g., T & P)

c). Another simple system... "salt" water



P=2 (aqueous and solid)

C=3 (water, sodium ions, chloride ions)

F=3 (e.g., T & P and either Na⁺ or Cl⁻)

d) The forsterite-fayalite-melt system...

Mg₂SiO₄ + Fe₂SiO₄ form the solid solution mineral olivine, so they count as one phase.

P = 2 (melt + olivine)

C = 2 (forsterite + fayalite)

F = 2 (e.g., T & P)

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In a complex natural system,
such as [sea water](#), or [basaltic melt and crystals](#),

there are **significantly more** components than this (for instance, other minerals with additional chemical elements, gasses such as water and carbon dioxide, etc..)

Many trace elements are present in such fleeting quantities that they don't dramatically alter the energetics of the system or its phases, so they do not contribute to F.

- We USUALLY restrict our system composition to the **major** components and use them to approximate the overall system conditions.

- **Trace constituents** may be used to refine our approximation.

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Chemical Thermodynamics

☛ Please refresh your memory on:

enthalpy (H)

entropy (S)

Gibbs function (G)

and their relationships to measures of chemical equilibrium
(and chemical equilibrium constants, K).

for instance, the last slide of last lecture, inserted after this slide for convenience

In all cases the standard state condition (annotated by "°" next to the variable) is for STP (273.15°C, 1 atm)

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Energy and Chemical Equilibrium

Recall from your prior chemistry classes that the total system energy available for chemical work is known as *Gibbs Free Energy*, ΔG .

☛ $\Delta G_{\text{reaction}} = 0$ at chemical equilibrium, (the total system energy is no longer changing).

$\Delta G^{\circ}_{\text{reaction}}$ is directly related to the equilibrium constant for a chemical reaction:

$$\Delta G^{\circ} = -RT \ln K \quad (\text{the superscript } ^{\circ} \text{ indicates conditions of STP})$$

$$\text{For } aA + bB \rightleftharpoons cC + dD, \quad K = \frac{C^c D^d}{A^a B^b} \quad \dots \text{so } \Delta G^{\circ} = -RT \ln \frac{C^c D^d}{A^a B^b}$$

R is the *Universal Gas Constant* (8.314 J = 0.08206 L-atm = 82.06 cm³-atm = 1.987 calories all per mol °K)

large K (products favored) = negative ΔG°

Small K (reactants favored) = positive ΔG°

☛ What if we are not at chemical equilibrium?

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

remember, AT EQUILIBRIUM (Q=K) and $\Delta G = 0$

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Some Thermodynamic Quantities and Relationships

The laws of thermodynamics and the mathematical relationships that derive from them describe infinitesimal changes to system variables ("variables of state") using differential calculus.

- In this class we will only "break down" the energetics of reactions part of the way.
- You will not have to derive thermodynamic expressions from first principles and partial differential equations.
- The "finite" change versions of various equations will be sufficient (e.g., ΔH , ΔG) for our applications.

Variables such as G , H and S are not measurable as absolute values. Instead, G , H and S are compared to reference materials in the standard state for which arbitrary values (typically 0) are defined.

The variable (G , H or S) is then defined as a Δ (change) relative to that (i.e., ΔG , ΔH or ΔS).

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Enthalpy – H

Enthalpy is a measure of energy in the form of heat (which itself is a measure of molecular vibration or motion).

Enthalpy is important for understanding the energy consumed or released in changes of state of a system.

The relationships between

heat (Q) and
work ($W = -P\Delta V$) to
internal energy (U , e.g., $\Delta U = Q + W$) and
enthalpy (H , e.g., $H = U + PV$)

are details we are going to skip over here
(see equations in the reading if you're interested in the details).

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Enthalpy – H

$$\Delta H = \Delta U + V\Delta P + P\Delta V, \text{ or } \Delta Q + \Delta W + V\Delta P + P\Delta V$$

which reduces to

$$\Delta H = \Delta Q + V\Delta P$$

It is therefore useful to remember that at **constant pressure** :

$$\Delta H = Q$$

(the Enthalpy change of a process is the heat gained or lost in the process)

$$\Delta H = C_p \Delta T \quad (\text{where } C_p = \text{heat capacity})$$

(the Enthalpy change of a process is the heat capacity times the temperature change)

and...

$$\Delta H = T\Delta S + V\Delta P \quad \text{at constant temperature}$$

(the Enthalpy change of a process is relates to changes in entropy, which we define momentarily, and pressure)

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Enthalpy – H

In General, the enthalpy change of a chemical reaction at STP is

$$\Delta H^\circ_{\text{reaction}} = \Sigma \Delta H_f^\circ(\text{products}) - \Sigma \Delta H_f^\circ(\text{reactants})$$

For $A + B \leftrightarrow C + D$

$$\Delta H^\circ_{\text{reaction}} = \Delta H_f^\circ(C) + \Delta H_f^\circ(D) - [\Delta H_f^\circ(A) + \Delta H_f^\circ(B)]$$

The enthalpy of a chemical reaction reflects changes in 3 basic types of system heat:

1. heat that is internal to **chemical bonds** between different atom pairs
2. heat associated with **molecular ordering** in solids versus liquids versus gasses.
3. heat associated with **molecular motion** (kinetic energy)

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Enthalpy – H

1. "Bond Heat"

This energy associated with chemical bonds. The Heat of Formation H_f° of a compound is the heat input or given off when making a molecule from its constituent elements.

We define $H_f^\circ=0$ for the constituent elements in the form that is stable at STP (*i.e.*, for C, the STP form is graphite, and $H_f^\circ=0$)

So C (graphite) \leftrightarrow C (diamond) must involve a transfer of heat

We can learn what is ΔH_f° (standard heat of formation) of diamond relative to this from a table of thermodynamic data:

ΔH_f° of C(diamond) = -453 cal/mol (= -1.897 kJ/mol,
using 1 calorie = 0.0041868 kJ)
453 calories or -1.897 kJ/mol of heat must be added to a mole of graphite to transform it into diamond at STP.

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Enthalpy – H

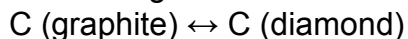
1. "Bond Heat"

If two reactions can be mathematically combined to make a third, we can also combine their ΔH_f° to calculate ΔH_f° of the new reaction.

For example, we might find these two reactions in a table:

1. C (graphite) + O₂ (g) \leftrightarrow CO₂ $\Delta H_f^\circ = 94.051$ kcal/mol
2. C (diamond) + O₂ (g) \leftrightarrow CO₂ $\Delta H_f^\circ = 94.504$ kcal/mol

if we reverse the order of equation 2 and change the sign of ΔH_f° , we can add the two to get



$$\begin{aligned} \Delta H_f^\circ &= (94.051 - 94.504) \text{ kcal/mol} \\ \Delta H_f^\circ &= -0.453 \text{ kcal/mol} &= -1.897 \text{ kJ/mol} \end{aligned}$$

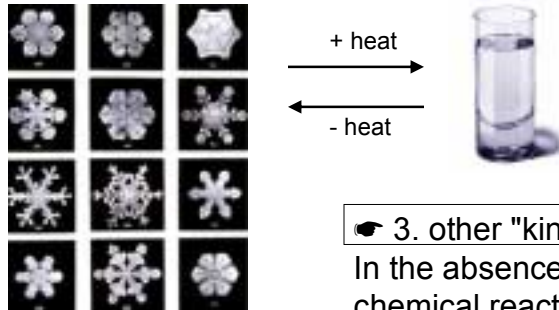
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Enthalpy – H

2. "phase change heat"

Heat of Fusion ΔH_{fus} is the heat absorbed by a solid as it melts.
 $-\Delta H_{\text{fus}}$ is the heat needed to be removed to resolidify

Heat of Vaporization ΔH_{vap} is the heat absorbed by a liquid as it vaporizes.
 $-\Delta H_{\text{vap}}$ is the heat needed to be removed to condense



Snowflake photos by Wilson Bentley
 circa 1902
http://en.wikipedia.org/wiki/Wilson_Bentley

3. other "kinetic energy heat"

In the absence of phase changes and chemical reactions, heat is gained or lost by temperature changes.

$$\Delta H = C_p \Delta T$$

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Entropy - S

Entropy is a measure of system disorder.

In general, systems tend to evolve toward less ordered conditions, reflected in the amount of heat absorbed by a system from its surroundings during any physiochemical change at a given temperature.

$\Delta S = Q_r/T$ in other words, $Q_r = T\Delta S$
 also, at constant P, $\Delta S = C_p/\Delta T$ (where C_p = heat capacity)

The standard state for any compound S° is determined relative to S° of $H^+ = 0$ at STP.

The calculation of $\Delta S^\circ_{\text{reaction}}$ is the same as that for H:

$$\Delta S^\circ_{\text{reaction}} = \sum \Delta S_f^\circ(\text{products}) - \sum \Delta S_f^\circ(\text{reactants})$$

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"Free Energy", or the Gibbs Function – G

Total system energy available for chemical work is known as *Gibbs Free Energy*, ΔG .

☛ $\Delta G_{\text{reaction}} = 0$ at chemical equilibrium, meaning that the net chemical work is no longer occurring.

Like other variables of state, ΔG is additive:

$$\Delta G^{\circ}_{\text{reaction}} = \Sigma \Delta G^{\circ}_{\text{f}}(\text{products}) - \Sigma \Delta G^{\circ}_{\text{f}}(\text{reactants})$$

recall that

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

(where Q is the reaction coefficient, not heat)

Since $Q=K$ and $\Delta G = 0$ AT EQUILIBRIUM, we derive:

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

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"Free Energy", or the Gibbs Function – G

In closed systems, **G** is related to *enthalpy H* and *entropy S* by:

$$\mathbf{G = H-TS.}$$

For isothermal (constant T) conditions:

$$\Delta G = \Delta H - T\Delta S \text{ and } \Delta G^{\circ}_{\text{f}} = \Delta H^{\circ}_{\text{f}} - T\Delta S^{\circ}_{\text{f}}$$

In other words, the free energy change in a closed system reflects the heat and the degree of disorder.

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"Free Energy", or the Gibbs Function – G

another useful general relationship which applies to processes or reactions where T and/or P are changing is

$$\Delta G = V\Delta P - S\Delta T$$

Consider a P-T phase diagram like this one

At any boundary the two phases will be in equilibrium, so that $\Delta G = 0$. Changes in volume (ΔV) and entropy (ΔS) associated with small changes in P and T can be written as

$$d\Delta G = \Delta V dP - \Delta S dT = 0$$

Rearranging, we arrive at the famous Clapeyron Equation

$$\frac{dT}{dP} = \frac{\Delta V}{\Delta S} \quad \text{and because } \Delta S = \Delta H/T, \quad \frac{dT}{dP} = \frac{T\Delta V}{\Delta H}$$



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"Free Energy", or the Gibbs Function – G

Let's solve a problem using the relationship of G and K

What is K_{eq} for the precipitation reaction of the mineral malachite from water?



"copper 2+
cation"

"carbonate
anion"

"hydroxyl
anion"

"malachite"

First, notice how the equation is balanced:

		reactants	products
material:	Cu	2	2
	CO ₃	1	1
	OH	2	2
charge:	Cu	4 (2x2)	--
	CO ₃	-2	--
	OH	-2 (-1x2)	--
	Cu ₂ (OH) ₂ CO ₃	--	0

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"Free Energy", or the Gibbs Function – G

Next, get $\Delta G_{\text{reaction}}^{\circ} = \Sigma \Delta G_f^{\circ}(\text{products}) - \Sigma \Delta G_f^{\circ}(\text{reactants})$ using values for ΔG_f° from a compilation of thermodynamic data.

A word on units:

- Always watch units when solving problems using thermodynamic equations.
- R is the *Universal Gas Constant* (8.314 J = 0.08206
 - L-atm = 82.06 cm³-atm = 1.987 calories all per mol °K).
 - R should be in the same system of units as the thermodynamic data you are using
- Some books give R in non-standard units (cm³-atm/mol-°K) or (cal/mol-°K). Others use the SI units: use J/mol-°K and J/mol, respectively.



$$\Delta G_{\text{reaction}}^{\circ} = -216.44 - (2 \cdot 15.50 + 2 \cdot -37.60 - 126.22) \text{ kcal/mol}$$

$$\Delta G_{\text{reaction}}^{\circ} = -46.02 \text{ kcal/mol} = -46,020 \text{ cal/mol}$$

From $\Delta G^{\circ} = -RT \ln K$, we get $\Delta G^{\circ}/(RT) = -\ln K$

$$-46,020 / (298.15 \cdot 1.987) = -\ln K \quad K = e^{46,020 / (298.15 \cdot 1.987)}$$

$$K = 5.45 \times 10^{33} \text{ or about } 10^{33.7}$$

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