L10: Thermodynamics

Thursday, July 30, 2020   16:55

Time on task: 2 hours (material posted on Oct 10th, Student hour: Monday Oct 26st)

Goals:
This lecture is an introduction to phase diagrams. Upon completion of lecture 10 to 12, you should
1. Know how to determine the stability range of a mineral assemblage
2. Understand the effects of a change of parameters (P, T, fluids) on a stable mineralogical assemblage
3. Know how to use a simple phase diagram to understand natural systems.

1. Thermodynamics.

1.1. Introduction

The Oxford Dictionary definition: "Thermodynamics: the theory of the relations between heat and mechanical energy, and of the conversion of either into the other."
In other words, thermodynamics is the science that tells is which minerals or mineralogical assemblages are stable for a given set of conditions.
It is also the science that allows us to use mineral assemblages and compositions to determine a condition at which a rock formed = **thermobarometry**.

In the following lectures, we are going to look at simple systems. We usually consider than we can manually solve a thermodynamics system with up to 6 different components. However, natural systems usually require more components to accurately describe them. (for instance, you list of main oxides in lecture 8 involved 13 different oxides). To treat more complex system we can use thermodynamics software.

Popular Computer Programs for Thermodynamic Calculations and Modeling:
- **TWQ**: allows the calculations of the position of phase equilibria in P-T, T-X_{CO2}, and P-X_{CO2} space. (Windows – easy to use)
- **Thermocalc**: performs the same calculations as TWQ for a much larger number of phases and includes more complicated types of calculations. (not free but demo version available)
- **MELTS family**: allows thermodynamic calculations to be made for equilibria involving magmas. (free, the windows version is called alphaMELTS)
- **Perplex**: thermodynamic calculation package suitable for "rapidly" creating phase diagrams of all types (free, not intuitive to start with but easy to use with some training).

1.2. Definitions.

A system is a portion of the universe your wish to study.
A change in the system always results into a change of energy.
Natural systems tend toward states of minimal energy.

The Gibbs free energy of formation is the energy associated with the formation of a phase (mineralogical or not), ΔG_f
It varies with the pressure and temperature (P-T) conditions and the composition of the phase.

The Gibbs free energy of reaction, ΔG_r is the sum of the ΔG_f on the right side of the reaction **minus** the sum of ΔG_f on the left side of the reaction.
- If $\Delta G_r < 0$, reaction proceeds to the right
- If $\Delta G_r > 0$, reaction proceeds to the left

Example: albite = jadeite + quartz
ΔGr(1bar)>0
⇒ albite is stable, the assemblage
jadeite + quartz is unstable.

ΔGr varies with P-T and X ⇒
the various fields of stability in **phase diagram are representation of the phase assemblage with the lowest ΔG_f.**

The Gibbs free energy of a mineral, G:
Unit: joules/mole (or calorie/mole)
Convention: **ΔGf (pure element) = 0** : other values of Gibbs free energy are **relative values.**
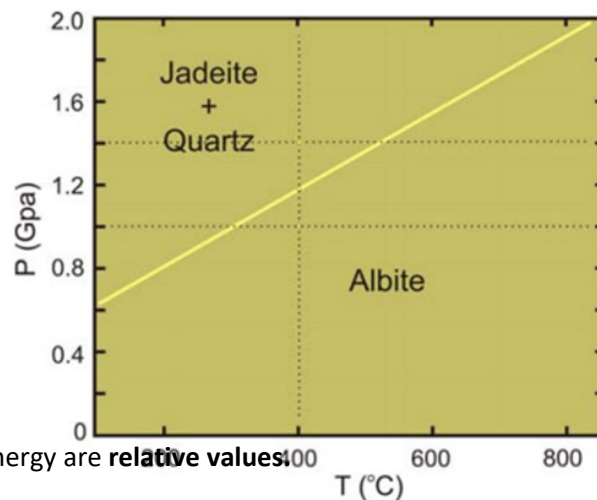
e.g, albite = jadeite + quartz
ΔGr = ΔGf(jadeite,elmt) + ΔGf(quartz, elmt) – ΔGf(albite, elmt)
   = ΔGf(jadeite,oxide) + ΔGf(quartz, oxide) – ΔGf(albite, oxide)
At 400°C and 1 Gpa, ΔGr >0
At 400°C and 1.4 Gpa ΔGr <0

- **Equation:**

G = E + PV – TS = H-TS,
with:
  P and T: pressure and temperature,
  V: volume,
  E: internal energy,
  H: enthalpy, such as: **H = E + PV**
  S: entropy,
of the phase.

Note that we do the demonstration from Eq(1) to Eq(2) in Petrology.
This is beyond the scope of this lecture.

The **Gibbs free energy of a reaction** is then:

$$ΔG_r = ΔE_r + PΔV_r – TΔS_r = ΔH-TΔS \quad (1)$$

Constant (depend on the present phases)

More voluminous phase = greater Gibbs free energy

High volume phases are unstable at high pressure

High S phase are more stable at higher T

Measure of the disorder

or dG_r = VdP – SdT (2)

P and T are **intensive variables** = do not depend on the size of the system or the amount of material present.
G,E, H, V and S are **extensive variables** = depend on the size of the system or the amount of material present

- **Units:**
P: bar, kbar, Pa, GPa
G, E, H: J/mole
V: cm³/mole
S: J/(K*mole)

- **Meanings:**
ΔGr: tells us if a reaction will take place
ΔHr: tell us how much heat will flow in or out of the reaction:
    If ΔHr < 0: **exothermic** reaction (e.g. $C + O_2 = CO_2$)
    If ΔHr > 0: **endothermic** reaction (e.g. $H_2O(ice) = H_2O(water)$)

ΔSr: tell us whether the products or reactants are more disordered
ΔVr: tell us whether the products or reactants have greater volumes (e.g., ΔVr (graphite = diamond) <0)
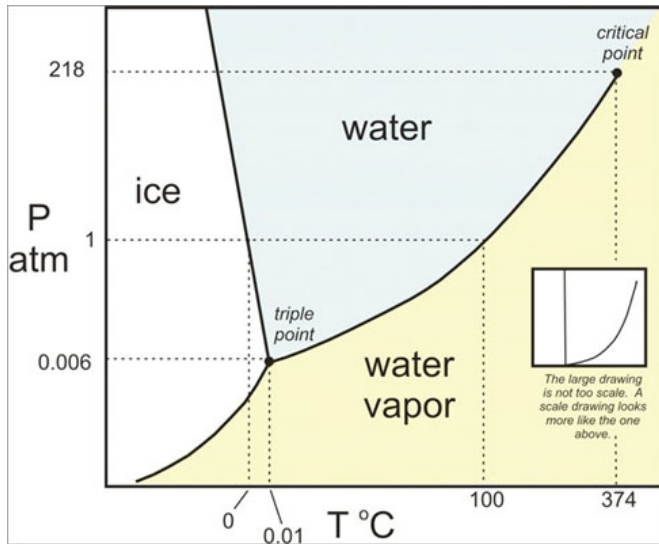
L10: Phase diagrams
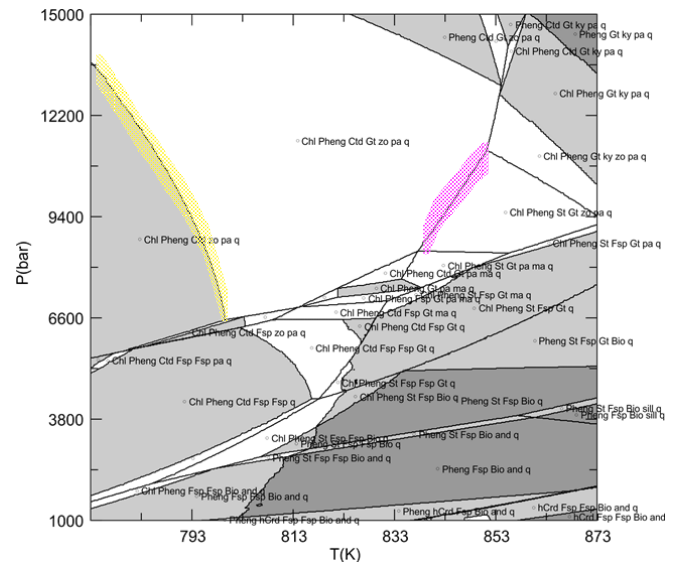
Monday, August 3, 2020   9:38

2. Phase diagrams

2.1. Introduction

Phase diagrams are the results of thermodynamic calculations. They are the graphical representations of equilibrium relationships between minerals.

Phase diagrams can be as simple as a one component system or projection of multicomponent complex systems.

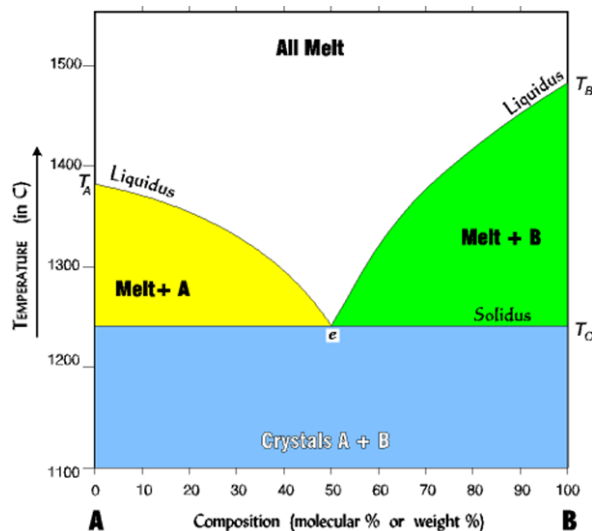<div align="center">One component</div>

<div align="center">Multi-component.</div>

The most common variables used in phase diagrams are the intensive variables P and T. However, we can also represent a phase diagram by changing only one intensive variable (usually T), but by looking at the effect of the composition.

<div align="center">Two component T-composition phase diagram
(we will look at this particular type of phase diagram in details in the next lecture)</div>

2.2. Clausius-Clapeyron equation.

If you look at the phase diagram for H2O, you can see that the p-T slope between water and vapor is positive, while the slope ice/water is negative. Similarly, on the multi-component diagram. The slope between the phase assemblages with and without garnet (Gt) is negative, while the slope between the Gt-bearing assemblages with and without Staurolite (St) is positive.

The **Clausius-Clapeyron equation** describes this P-T slope that describes the limit of stability between two phases (or two phase assemblages):

$$dG_r = VdP - SdT$$

On the reaction curve, $dG_r = 0 \Rightarrow dP/dT = dS_{P,T}/dV_{P,T}$: slope of the reaction – define equilibrium between reactants and products in terms of volume and entropy

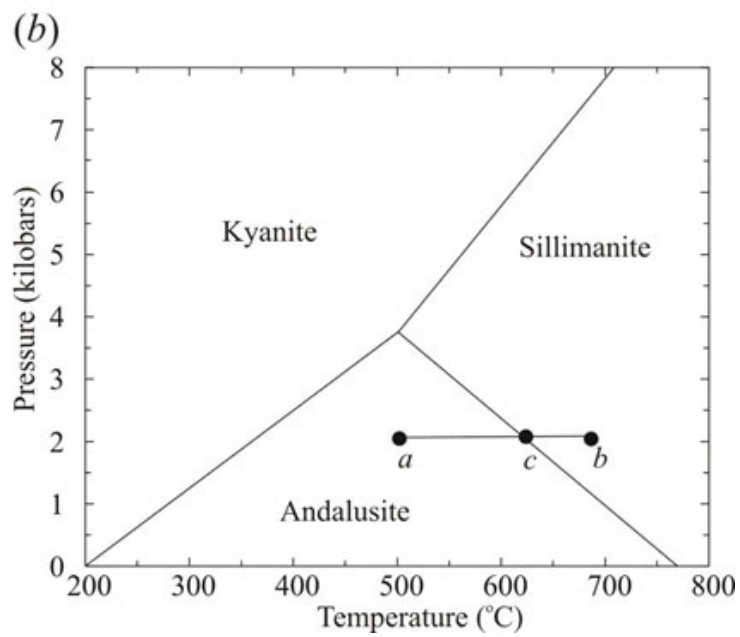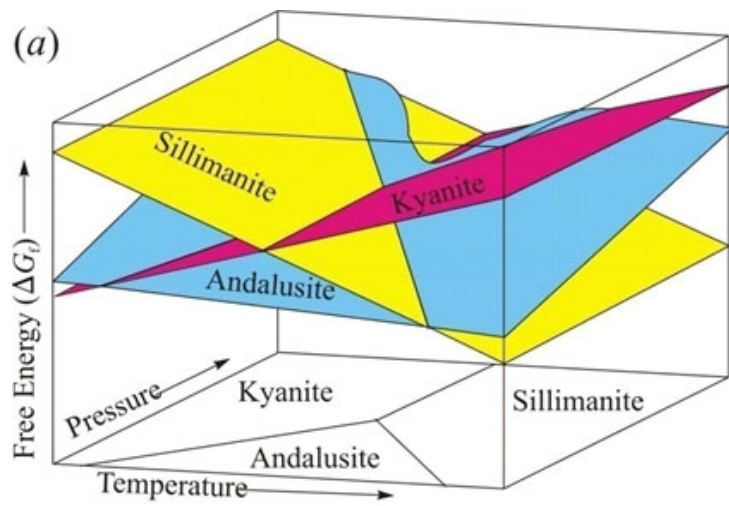**Slope: positive if both ΔV and ΔS increase (or decrease)**

Your turn! Considering the reaction olivine = liquid. In a P-T diagram, do you expect the slope of the reaction being positive or negative? (keys at the end of the assessment).

A - Positive

olivine

melt

P

T

B - negative

olivine

melt

P

T
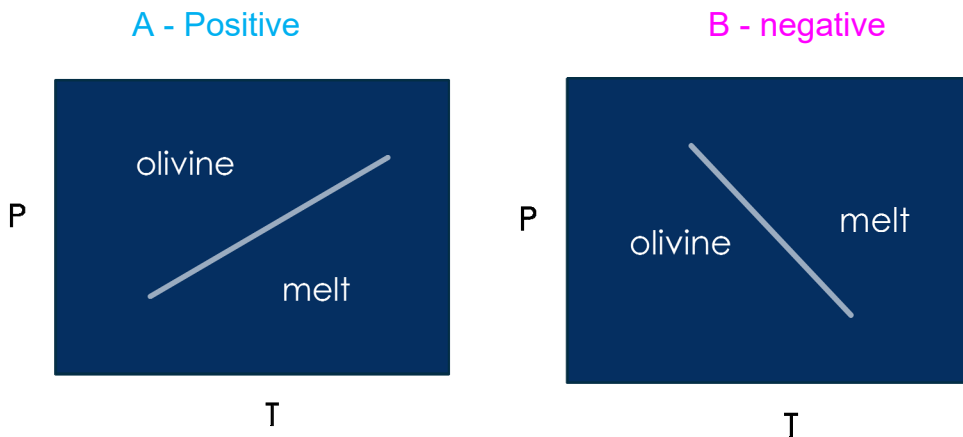
2.3. Phase diagram construction

The Gibbs and Clapeyron Equations allow us to estimate phase diagrams with extrapolations from laboratory measurements. The lines show where equilibrium conditions (ΔG = 0) occur. Clapeyron tells us the slope.

Our experiments and calculations allow us to construct the 3-D plot (a), and to project the mineral with the <u>lowest free energy</u> at each P-T onto the graph (b).

(a)

Free Energy (ΔG_f)

Sillimanite

Kyanite

Andalusite

Pressure

Kyanite

Sillimanite

Andalusite

Temperature

(b)

Pressure (kilobars)

Kyanite

Sillimanite

Andalusite

a   c   b

Temperature (°C)

L10: Phase Rule

2.4. Definitions

A system: a portion of the universe that you wish to study
e.g. salt + water in a beaker

- **Isolated system**: cannot exchange mass or energy with the surroundings
  we sealed the beaker with a lid and enclosed it in a perfect thermal insulator
- **Closed system:** can exchange energy but not mass
  no thermal insulator but still sealed
- **Open system:** can exchange both mass and energy
  beaker is open to the air and not insulated

Phase (Φ)= a **physically separable** part of the system with distinct physical and chemical properties. A system must consist of one or more phases.

Ex1: system: salt-water: one phase (sodium choride – water solution or salt crystals), two phases (sodium choride – water solution and salt crystals) or three phases (sodium choride – water solution, salt crystals, gas phase – mostly water)

Ex2: magma with crystals of olivine and plagioclase: 3 phases because melt, olivine and plagioclase are physically and chemically distinct

Component ©: Each phase in the system may be considered to be composed of one or more components. The number of components (i.e., chemical formula) in the system must be **the minimum required to define all of the phases**.

Ex: salt-water system
Possible list of components:
- Na, Cl, H, and O: four components
- NaCl, H, and O: three components
- NaCl and H2O : two components
- NaCl-H2O: one component.

Possible phases: NaCl crystal, H2O (liquid or vapor), and NaCl-H2O solution

⇒ only two components (NaCl and H2O) are required to define the three phases (NaCl - H2O solution).

3. Gibbs Phase rule

Fundamental relation between the minimum number of components (c) in a chemical system, the number of phases present (Φ), and the number of parameters that can be independently varied while maintaining equilibrium, i.e the variance or the degrees of freedom (ƒ)

$$f = c + n - Φ$$

n: intensive variables (can be changed independently) ⇔ P , T, fugacity of water, ect…

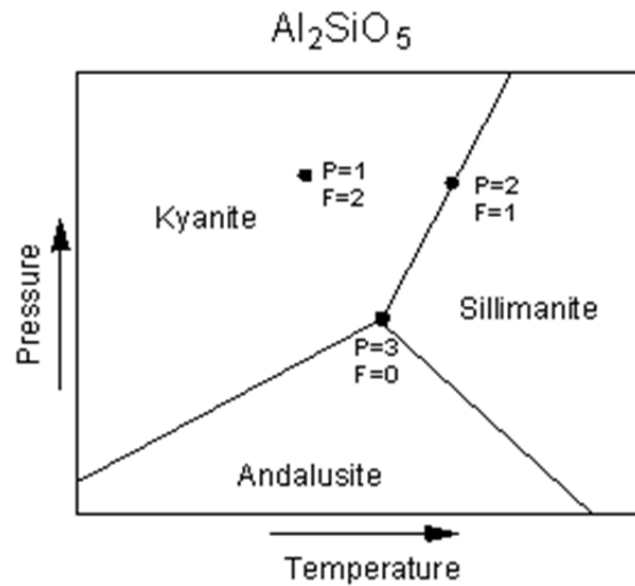*For the purpose of this class, we will only look at Pressure and/or Temperature.*

f ≥ 0 ⇔ c + n ≥ Φ ⇒ there can never be more than c + n phases in equilibrium.
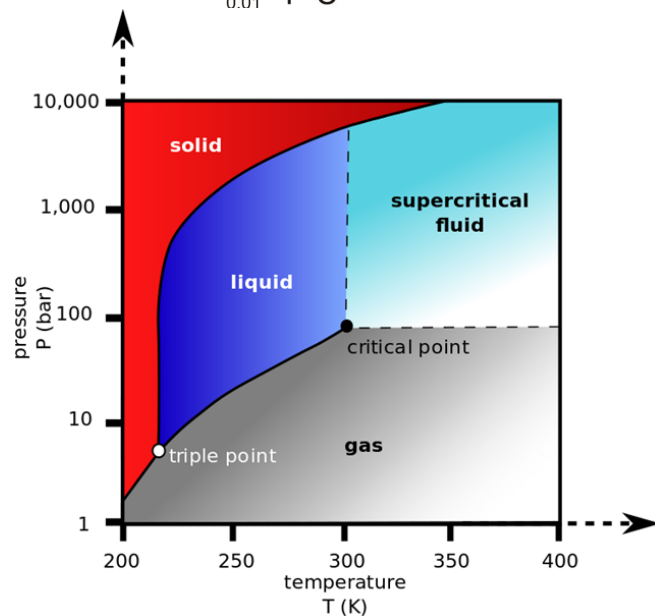
Example: One component system

C = 1: Al2SiO5 (all the phases can be described with the same chemical formula)

- P1: $\Phi = 1 \Rightarrow f = 2$: this field stability is **divariant**
- P2: $\Phi = 2 \Rightarrow f = 1$: the phase assemblage is **univariant**
- P3: $\Phi = 3 \Rightarrow f = 0$: the point is **invariant**

3.1 Examples of one-component diagrams
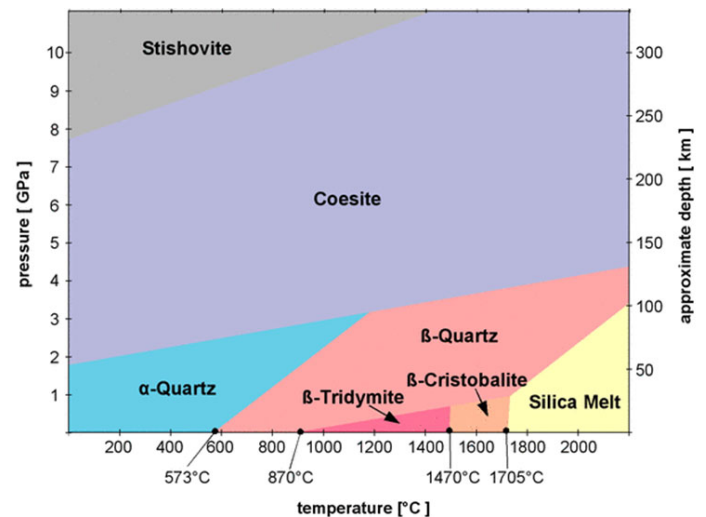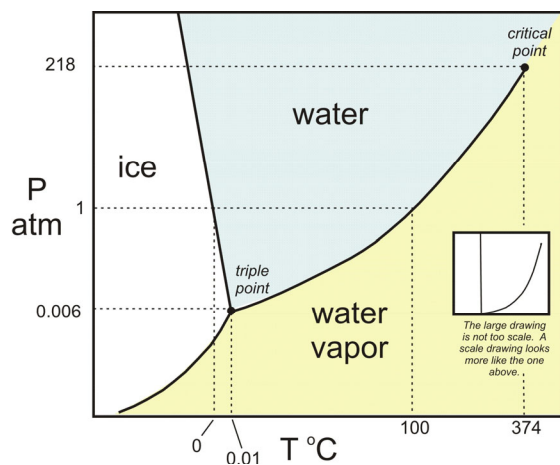
Critical point: end point of a phase equilibrium curve

Supercritical fluid: any substance at a temperature and pressure above its critical point where liquid and gas phases do not exist.

Identify the degree of freedom (=variance) at various points in each of these diagrams.

L10: Personal assessment

Tuesday, August 25, 2020   10:54 AM

After reviewing this material, you should be able to answer these questions:

****Multiple choices possible!****

1) **Assuming the reaction, Mg2SiO4(solid) <=> Mg2SiO4(liquid), which of these four diagrams is/are correct.**

A

Energy = G   const T   liq / sol   P

B

Energy = G   const T   sol / liq   P

C

Energy = G   const P   liq / sol   T

D

Energy = G   const P   sol / liq   T
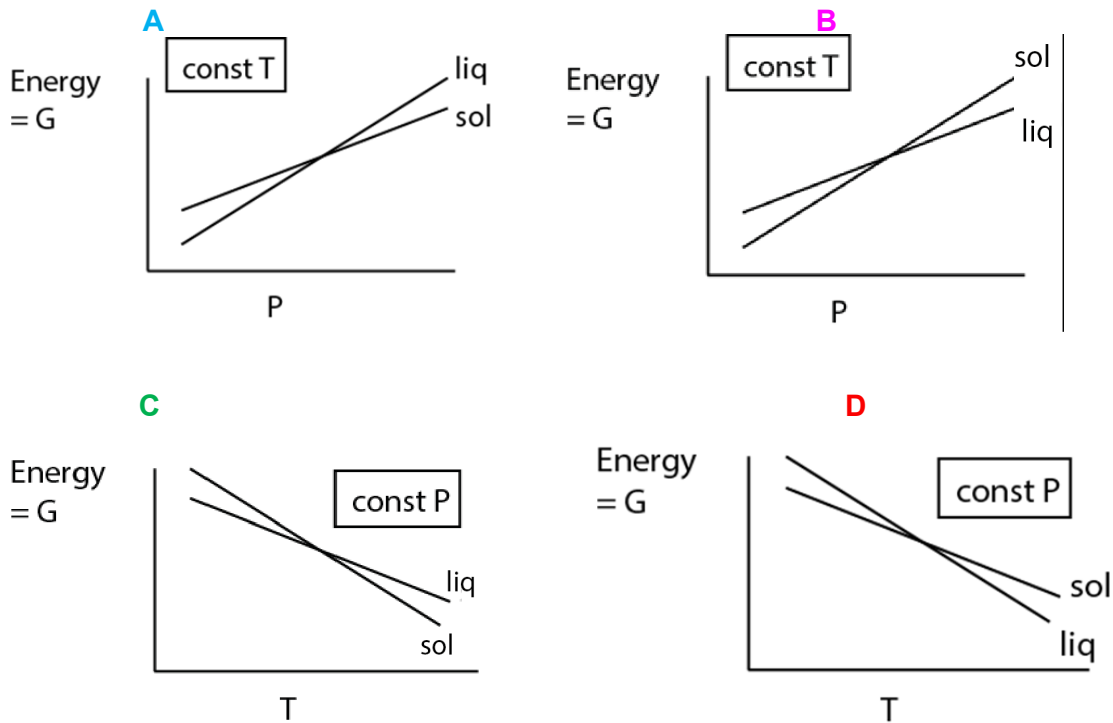
2) **The Gibbs free energy of sillimanite at 530°C and 1300 bars has been determined experimentally as G = -2.031 ± 0.2 kcal/mol. At higher temperature, you expect G to be:**

A – Lower
B – Higher
C – The same
D – We can't know

Al_2SiO_5

P=1 F=2   P=2 F=1

Kyanite

Sillimanite

P=3 F=0

Andalusite

Pressure

Temperature
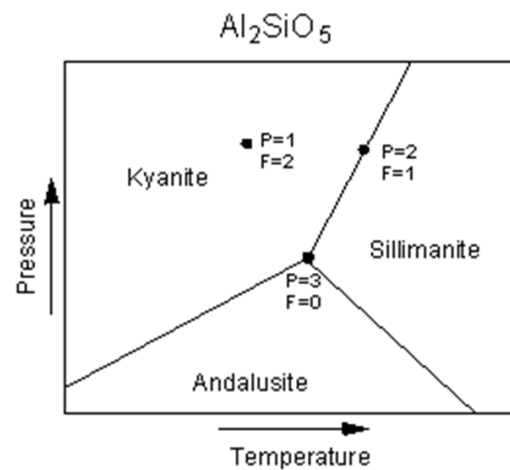
3) Looking at this phase diagram:

The phase diagram (P(bar) vs T(K)) with many mineral assemblage fields labeled:

- Pheng Ctd Gt ky pa q
- Pheng Ctd Gl zo pa q
- Pheng Gt ky pa q
- Chl Pheng Ctd Gt ky pa q
- Chl Pheng Gt ky pa q
- Chl Pheng Ctd Gt zo pa q
- A
- Chl Pheng Gt ky zo pa q
- Chl Pheng St Gt zo pa q
- Chl Pheng Ctd zo pa q
- Chl Pheng St Fsp Gt pa q
- Chl Pheng St Gt pa ma q
- Chl Pheng Ctd Gt pa ma q
- Chl Pheng Gt pa ma q
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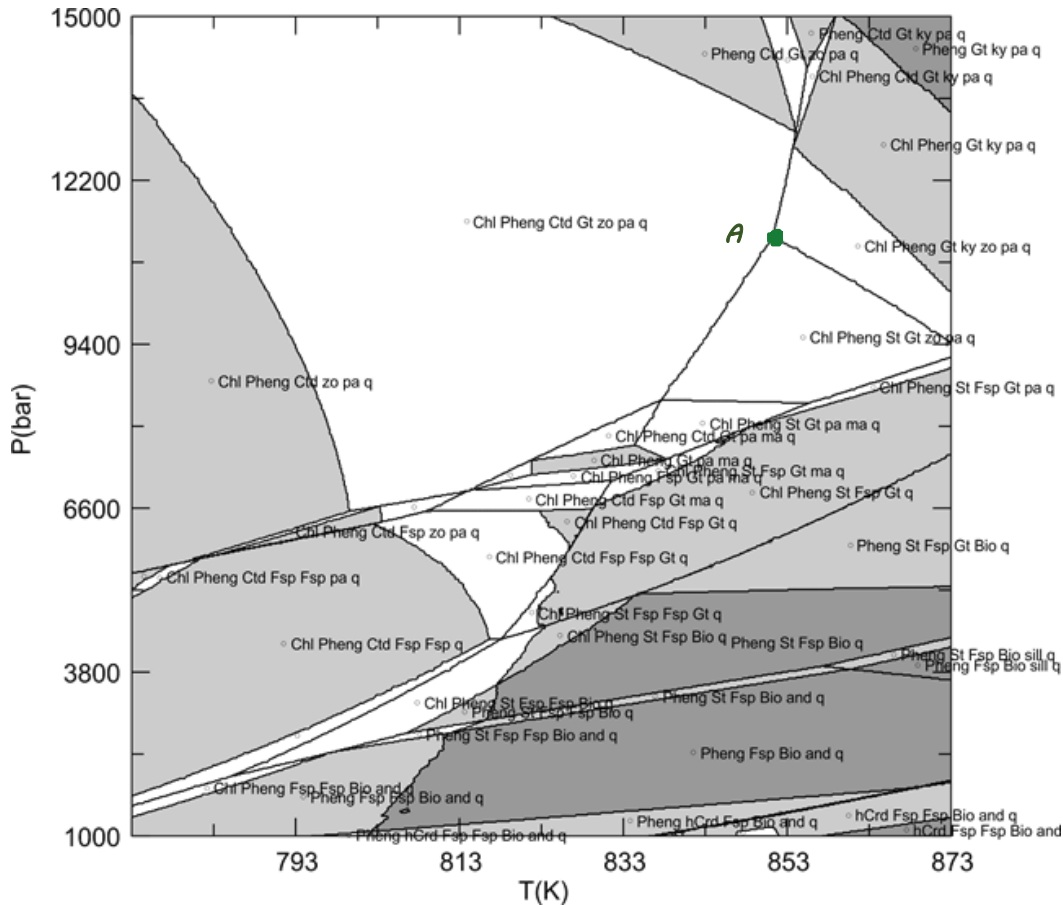- Pheng St Fsp Gt ma q
- Chl Pheng Ctd Fsp Gt ma q
- Chl Pheng St Fsp Gt q
- Chl Pheng Ctd Fsp Gt q
- Chl Pheng Ctd Fsp zo pa q
- Chl Pheng Ctd Fsp Fsp Gt q
- Pheng St Fsp Gt Bio q
- Chl Pheng Ctd Fsp Fsp pa q
- Chl Pheng St Fsp Fsp Gt q
- Chl Pheng St Fsp Bio q
- Pheng St Fsp Bio q
- Chl Pheng Ctd Fsp Fsp q
- Pheng St Fsp Bio sill q
- Pheng Fsp Bio sill q
- Chl Pheng St Fsp Fsp Bio q
- Pheng St Fsp Fsp Bio q
- Pheng St Fsp Bio and q
- Pheng St Fsp Fsp Bio and q
- Pheng Fsp Bio and q
- Chl Pheng Fsp Fsp Bio and q
- Pheng Fsp Fsp Bio and q
- Pheng hCrd Fsp Fsp Bio and q
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- hCrd Fsp Fsp Bio and

T(K) axis values: 793, 813, 833, 853, 873
P(bar) axis values: 1000, 3800, 6600, 9400, 12200, 15000

a. The degree of freedom of the point A is?

A – 0
B – 1
C – 2
D – 3

b. What is the number of components of this system.

A – 1
B – 5
C – 7
D – we can't know

Practice keys:

Melting curve: dP/dT = ΔS / ΔV   Clapeyron equation
1. Does the liquid or solid have the larger volume/unit mass? Usually liquid. (except H2O)
2. High pressure favors low volume, so which phase should be stable at high P? Solid
3. Does liquid or solid have a higher entropy? Liquid
High temperature favors randomness, so which phase should be stable at higher T?
Liquid is more random, expect at high T.

Both ΔV and ΔS increase to right. We can thus predict that the slope of solid-liquid equilibrium should be positive and that increased pressure raises the melting point.