The Gibbs Phase Rule

The phase rule allows one to determine the number of degrees of freedom (F) or variance of a chemical system. This is useful for interpreting phase diagrams.

\[ F = 2 + C - P \]

Where F is the number of degrees of freedom, C is the number of chemical components and P is the number of phases in the system. The number two is specified because this formulation assumes that both T and P can be varied.
The Gibbs Phase Rule

- **Phases:** Part of a system that is chemically and physically homogeneous, bounded by a distinct interface with other phases and physically separable from other phases.

- **Components:** Smallest number of chemical entities necessary to describe the composition of every phase in the system.

- **Solutions:** Homogeneous mixture of two or more chemical components in which their concentrations may be freely varied within certain limits.
The Gibbs Phase Rule

The phase rule was originally derived from thermodynamic principles by J. Willard Gibbs and hence it is commonly known as the **Gibbs Phase Rule**. It is widely used in both igneous and metamorphic petrology to predict the number of phases that can be present in equilibrium assemblages.

Phase assemblages with **zero** degrees of freedom are **invariant** \( f = 0 \)

Phase assemblages with **one** degree of freedom are **univariant** \( f = 1 \)

Phase assemblages with **two** degrees of freedom are **divariant** \( f = 2 \)

Phase assemblages with **three** degree of freedom are **trivariant** \( f = 3 \), etc.

Important principles of crystallization and melting can be demonstrated by examining a few, relatively simple, systems. Phase diagrams for one-, two-, three-component and higher order systems are widely used by petrologists to understand and illustrate the details of crystallization and/or melting. It is important to keep in mind, however, that natural systems are compositionally much more complex and will consequently show somewhat more complex behavior.
Mole Fractions

\[ X_A = \frac{n_A}{\sum n_i} = \frac{n_A}{(n_A + n_B + n_C + \cdots)}, \]

where \( X_A \) is called the “mole fraction” of component \( A \) in some phase.

If the same component is used in more than one phase, then we can define the mole fraction of component \( A \) in phase \( i \) as \( X_A^i \)

For a simple binary system, \( X_A + X_B = 1 \)
Phase Rule Significance for Phase Diagrams

- For two dimensional phase diagrams:
  - **Stability fields:** Areas (T-P, T-X, P-X space) where a phase or phase assemblage (more than one phase) is stable.
  - **Equilibrium boundary lines:** These define the limits of stability fields. These represent values of parameters where phases in adjacent fields coexist.
  - **Triple points:** Points where equilibrium boundary lines meet. All phases in the adjacent stability fields must coexist.
Silica Phase Diagram and Phase Rule

Single Component System:

\[ F = 2 + C - P = 3 - P \]

Stability Field:
- \( P = 1; F = 2; \) divariant

Boundary Line:
- \( P = 2; F = 1; \) univariant
- \( P = 3; F = 0; \) invariant

From Swamy et al., 1994
Binary Phase Relations - Definitions

**Liquidus line**: the line that represents the locus of depressed freezing points as a second component is added to the system. Solid phases are not stable at temperatures above those defined by the liquidus line or surface.
Binary Phase Diagram Definitions

- **Eutectic point:** Lowest T point on the liquidus at which a unique melt of fixed composition is in equilibrium with two or more phases.
- **Isopleth:** line of constant chemical composition.
- **Isotherm:** line of constant temperature
- **Tie line:** portion of isotherm that connects two stable coexisting phases, in this case L (representing the silicate liquid) and S (pure crystalline anorthite feldspar)
Di-An Binary Eutectic Phase Diagram

- **Diopside** ($\text{CaMgSi}_2\text{O}_6$)
- **Anorthite** ($\text{CaAl}_2\text{Si}_2\text{O}_8$)

**Phase Regions**:
- **Liquid (L)**
- **Diopside + Anorthite Crystals**
- **Diopside + Liquid (L)**
- **Anorthite + Liquid (L)**

**Isopleth**

**Temperature (°C)**:
- 1600
- 1553
- 1400
- 1392
- 1374
- 1274
- 1200
- 1000

**Composition (wt. %)**
- 0
- 20
- 40
- 60
- 80
- 100

**Example Isotherm**

**Diopside + Anorthite Region**

**Diopside Region**

**Anorthite Region**

**P = 1 atm**
The Lever Rule

Follows directly from the Law of Conservation of Mass. Allows one to calculate either algebraically or graphically the modal abundance of each phase at every temperature.

\[
L = \frac{y}{(x + y)} \\
S = \frac{x}{(x + y)}
\]

MASS OF LIQUID

MASS OF SOLID
PHASE EQUILIBRIA AND PHASE DIAGRAMS

Experimentally determined phase diagrams are used extensively by petrologists to elucidate the details of crystallization and/or melting phenomena in igneous systems. At the present time there are basically two approaches used by experimental petrologists:

[1] Detailed studies of “simple” systems containing fewer than 5 components. These are called model or analog systems. Simple systems have the advantage that the phase equilibria can be accurately expressed in a phase diagram and a large number of compositions can be examined. In addition, compositional variables can be well controlled. The main deficiency of simple systems is that they may not adequately model the phase equilibria occurring in natural systems.

[2] Melting and crystallization studies on “real” rocks, i.e., naturally occurring samples. In this approach, the results can be directly applied to the particular rocks being studied but they are limited in the sense that only one composition is being studied. In addition, the fact that real rocks contain at least 10 major components makes the graphical depiction of phase equilibria rather difficult.

With modern experimental equipment, petrologists are able to control all the important variables, i.e., T, P, and the partial pressures (actually fugacity) of volatile species such as H₂O, CO₂, SO₂ and O₂. In this introduction to phase equilibria we will consider temperature (T), and composition (X) as the main variables. The appropriate pressure is noted at the top of each diagram.
Follows directly from the Law of Conservation of Mass.

Allows one to calculate either algebraically or graphically the modal abundance of each phase at every temperature.

PHASE EQUILIBRIA AND PHASE DIAGRAMS

Before we start looking at simple systems, let’s look at natural examples to provide some context of what it is that we are trying to explain by spending huge amounts of time and energy doing difficult experiments in the lab.

Photomicrographs of thin sections of samples collected from variable depths and temperature from Makaopuhi lava lake, Hawaii.

Note:
1. Increasing crystallinity with decreasing T
2. Crystallization sequence: ol→plag→cpx→FeTi-ox
3. Color change in glass (increasingly dark to 1075°C, clear at 1020°C)
Follows directly from the Law of Conservation of Mass. Allows one to calculate either algebraically or graphically the modal abundance of each phase at every temperature.

Note: (1) olivine increases then decreases in amount as $X^n$ proceeds.
(2) Change in comp$^n$ of the phenocrysts as $X^n$ proceeds--Ferromag. minerals become increasingly Fe rich and plagioclases become more Na rich.
A. One component system \((c = 1)\)

Example: \(\text{SiO}_2\) system. Since all phases in this system have the same composition, there are no compositional variables to consider. Phase equilibria can be shown completely on a pressure \((P)\) versus temperature \((T)\) diagram.

Some other one component systems of interest to petrologists are:

- \(\text{Al}_2\text{SiO}_5\) system [andalusite-kyanite-sillimanite]
- \(\text{CaCO}_3\) system [calcite I-calcite II-aragonite]
- \(\text{MgSiO}_3\) system [orthoenstatite-clinoenstatite-protoenstatite]
- Alkali feldspars: \(\text{KAISi}_3\text{O}_8\) system [sanidine-orthoclase-microcline]

The slope of the univariant lines in a \(P-T\) diagram is given by the Clapeyron Equation:

\[
\frac{dT}{dP} = \frac{\Delta V}{\Delta S}
\]

where \(\Delta V\) is the volume change of the reaction and \(\Delta S\) is the entropy change.

The low quartz (\(\alpha\)) to high quartz (\(\beta\)) is a non-quenchable (displacive) transition. The others are all reconstructive transitions.

In stishovite Si is in octahedral (VI) coordination.
First Law of Thermodynamics

The increase in internal energy as a result of heat absorbed is diminished by the amount of work done on the surroundings:

\[ dE_i = dq - dw = dq - PdV \]

By engineering convention, heat added to the system, \( dq \), is positive and work done by the system, \( dw \), on its surroundings is positive.

\[ E = \text{energy of the system} \]
\[ q = \text{heat flowing into the system} \]
\[ w = \text{work is being done by the system} \]

This is also called the Law of Conservation of Energy
Definition of Enthalpy

We can define a new **state variable** (one where the path to its current state does not affect its value) called enthalpy:

\[ H = E_i + PV \]

**Enthalpy = Internal Energy + PV**

E = energy of the system  
P = pressure of the system  
V = volume of the system
Definition of Enthalpy

\[ H = E_i + PV \]

Enthalpy = Internal Energy + PV

Upon differentiation and combining with our earlier definition for internal energy:

\[ dH = dE_i + PdV + VdP \]

\[ dE_i = dq - PdV \]

\[ dH = dq + VdP \]
Enthalpy, Melting, and Heat

For isobaric (constant pressure) systems, \( dP = 0 \) and then the change in enthalpy is equal to the change in heat:

\[
dH_p = dq_p
\]

Three possible changes in a system may occur:

1) Chemical reactions (heterogeneous)
2) Change in state (e.g. melting)
3) Change in \( T \) with no state change

Heat capacity is defined by the amount of heat that may be absorbed as a result of temperature change at constant pressure:

\[
C_p = \frac{dH}{dT}_p
\]
Heating of Crystals and Enthalpy of Melting

\[ \Delta H_m = 144 \text{ kJ/mol} \]

\[ (dH/dT)_p = C_p = 0.28 \text{ kJ/mol°C} \]

580°C
How to calculate heats of reaction

\[ \Delta H = \sum nH \text{ (products)} - \sum nH \text{ (reactants)} \]

\[ n = \text{molar coefficient of each reactant/product} \]

When \( \Delta H \) is positive, the reaction is endothermic (heat flows from the surroundings to the system);

When \( \Delta H \) is negative, the reaction is exothermic (heat flows from the system to the surroundings)
How to calculate heats of reaction

$$\Delta H = \Sigma nH \text{ (products)} - \Sigma nH \text{ (reactants)}$$

For example, evaporation: $H_2O(l) \rightarrow H_2O(g)$

$$\Delta H = H_{(H_2O(g))} - H_{(H_2O(l))}$$
$$\Delta H = (-57.80) - (-68.32) = 10.52 \text{ kcal}$$

The reaction is *endothermic* (i.e., sweating is a mechanism for cooling the body)

$H = 0$ for pure elements in their natural states
How to calculate heats of reaction

\[ \Delta H = \sum nH \text{ (products)} - \sum nH \text{ (reactants)} \]

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\[ \Delta H = H_{(H_2O(g))} - H_{(H_2O(l))} \]
\[ \Delta H = (-57.80) - (-68.32) = 10.52 \text{ kcal} \]

The reaction is *endothermic* (i.e., sweating is a mechanism for cooling the body)
Second Law of Thermodynamics

- One statement defining the second law is that a **spontaneous** natural processes tend to even out the energy gradients in a **isolated** system.
- Can be quantified based on the **entropy** of the system, $S$, such that $S$ is at a maximum when energy is most uniform. Entropy can also be viewed as a measure of disorder.

\[ \Delta S = S_{\text{final}} - S_{\text{initial}} > 0 \]
Change in Entropy

Relative Entropy Example:

\[ S_{\text{steam}} > S_{\text{liquid water}} > S_{\text{ice}} \]

Entropy can also be viewed as a measure of disorder.
Change in Entropy

In any reversible process: \( \text{d}S = \frac{\text{d}q}{T} = C \frac{\text{d}T}{T} \)
Integration if \( C \) is constant for \( S \) at any given \( T \):
\( S_2 - S_1 = C \ln \left( \frac{T_2}{T_1} \right) \)

In any irreversible process: \( \text{d}S > \frac{\text{d}q}{T} \)

\( S \): entropy
\( q \): heat
\( T \): temperature
\( C \): heat capacity

**Third Law Entropies:**
All crystals become increasingly ordered as absolute zero is approached (\( 0K = -273.15^\circ C \)) and at \( 0 \) K all atoms are fixed in space so that entropy is zero.


How to calculate entropy change of reaction

\[ \Delta S = \Sigma nS \text{ (products)} - \Sigma nS \text{ (reactants)} \]

- \( n \) = molar coefficient of each reactant/product

  When \( \Delta S \) is positive, the entropy increases
  When \( \Delta S \) is negative, the entropy decreases

For example, evaporation: \( \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g) \)

\[ \Delta S = S_{\text{H}_2\text{O}(g)} - S_{\text{H}_2\text{O}(l)} \]

\[ \Delta S = 45.10 - 16.71 = +28.39 \text{ cal/deg} \]

Increase in the entropy \( \rightarrow \) water molecules in the gas phase are more randomly distributed than those of liquid water
Gibbs Free Energy

Gibbs free energy is a measure of chemical energy

All chemical systems tend naturally toward states of minimum Gibbs free energy

\[ G = H - TS \]

Where:

- \( G \) = Gibbs Free Energy
- \( H \) = Enthalpy (heat content)
- \( T \) = Temperature in Kelvins
- \( S \) = Entropy (can think of as randomness)
Gibbs Free Energy

The change in some property, such as G for a reaction of the type:

\[ 2 \text{A} + 3 \text{B} = \text{C} + 4 \text{D} \]

\[ \Delta G = \sum (n \ G)_{\text{products}} - \sum (n \ G)_{\text{reactants}} \]

\[ = G_C + 4G_D - 2G_A - 3G_B \]

The side of the reaction with lower G is more stable

\[ \Delta G < 0, \text{reaction: left} \rightarrow \text{right} \]

\[ \Delta G > 0, \text{reaction: left} \leftarrow \text{right} \]
Gibbs Free Energy

For a phase we can determine V, T, P, etc., but not G or H

We can only determine changes in G or H as we change some other parameters of the system

Example: measure $\Delta H$ for a reaction by calorimetry - the heat given off or absorbed as a reaction proceeds

Arbitrary reference state and assign an equally arbitrary value of H to it:

Choose 298.15 K and 0.1 MPa (lab conditions)

...and assign $H = 0$ for pure elements (in their natural state - gas, liquid, solid) at that reference
Gibbs Free Energy

In our calorimeter we can then determine $\Delta H$ for the reaction:

$$\text{Si (metal)} + \text{O}_2 \text{ (gas)} = \text{SiO}_2 \quad \Delta H = -910,648 \text{ J/mol}$$

= molar enthalpy of formation of quartz (at 298, 0.1)

It serves quite well for a standard value of H for the phase

Entropy has a more universal reference state: entropy of every substance = 0 at 0K, so we use that (and adjust for temperature)

Then we can use $G = H - TS$ to determine G of quartz

= -856,288 J/mol
Gibbs Free Energy

For other temperatures and pressures we can use the equation

\[ G = E_i + PV - TS \]

\[ dG = dE_i + PdV + VdP - TdS - SdT \]

\[ dw = PdV \quad \text{and} \quad dq = TdS \]

\[ dG = VdP - SdT \]

(for pure phases)

At equilibrium: \( dG_{P,T} = 0 \)
Change in Gibbs Free Energy

\[ G_{\text{diamond}} \]

\[ G_{\text{graphite}} \]

\[ G_{\text{graphite}} - G_{\text{diamond}} = \Delta G_{P,T} < 0 \]
Melting Relations for Selected Minerals

\[ dG_c = dG_l \]

\[ V_c dP - S_c dT = V_l dP - S_l dT \]

\[ (V_c - V_l) dP = (S_c - S_l) dT \]

Clapeyron Equation

\[ \frac{dP}{dT} = \frac{(S_c - S_l)}{(V_c - V_l)} = \frac{\Delta S}{\Delta V} \]
Follows directly from the Law of Conservation of Mass. Allows one to calculate either algebraically or graphically the modal abundance of each phase at every temperature.