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**GEOLOGY**
**Paper: Metamorphic and Igneous Petrology**
**Module: Mineralogical Phase Rule in Close and Open Systems**

## Table of Content

1. Introduction
2. Some Basic Definitions
3. Derivation of Phase Rule and Mineralogical Phase Rule in Close and Open System
  - 3.1 Phase Rule in Close System
  - 3.2 Phase Rule in Open System
  - 3.3 Non Compliance of the Phase Rule
  - 3.4 Mineralogical Phase Rule

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## Forewords

This chapter is a continuation of Chapter 4A where I explained the Gibb's Phase Rule and deduced the same in 'Closed' and 'Open' systems. In this chapter the sections 3 and 4 that are listed in Chapter 4A will be discussed. The Chapter 4B is NOT a standalone chapter. The students must read Chapter 4A otherwise Chapter 4B may appear out of place.

To refresh the memory let me state that the forms of the Phase Rule:

$$F = C - P + 2 \text{ (in closed system)} \quad (1)$$

$$F = (C - k) - P + 2 \text{ (in open system)} \quad (2)$$

\*\* Please note that the equations (1) and (2) are the same as equations (1) and (6) mentioned in Chapter 4A.

In the above equations the symbols used represent the following:

C = no. of system components, P = no. of phases, k = number of mobile components

F = degrees of freedom or variance of the system

\*\* I reiterate that an open system will always has less number of phases than a closed system having same variance and no. of system components.

But this is a specific case. When a system (say, a granite) becomes open for a specific no. of system components (say, K and Na), several other components (e.g. U, Th, Fe, H<sub>2</sub>O) can get into the rock and can form U, Th rich veins with muscovite/biotite. Here the no. of phases in the granite will increase (compared to the situation where the granite becomes impervious to fluid and element transfer, i.e. closed system). This observation alone cannot justify that Phase Rule is not obeyed. Since no. of components have increased in the granite and hence, the phases are also increased.

### 3. Derivation of Phase Rule and Mineralogical Phase Rule in Close and Open System

#### 3.3 Non Compliance of the Phase Rule

One fundamental question that haunts the students of earth and material sciences is “What happens if the Phase Rule is not obeyed?”. There is no straight forward answer to this question. There are two scenarios:

##### Scenario 1

Since the phase rule presupposes that the system is in equilibrium, non-compliance of the Phase rule would mean lack of equilibrium. In fact, obedience of the Phase Rule is a confirmative test if the system is not in equilibrium.

Let us consider that I am sipping a hot (60°C) and fuming water from a cup (I have to do this quite often as I have throat problem!). The temperature is certainly above the freezing point. Now if I place a piece of ice in the water and put a thermometer (DO NOT USE CLINICAL THERMOMETER, IT WILL DAMAGE THE THERMOMETER!) in the water, the thermometer will record a decreasing temperature of the hot water though the number of phases becomes 3. The system has one component (H<sub>2</sub>O), phases are three (ice, water and water vapor), the variance is

$$F = 1 - 3 + 2 = 0$$

*If the system were in equilibrium, then the water could not lower its temperature as it is an invariant situation. So the system is out of equilibrium. This is the reason the ice will quickly melt to restore equilibrium.*

One petrological example of this disequilibrium is formation of garnet corona around orthopyroxene separating it from plagioclase. The feature suggests that the rock was in the stability field of garnet and that either plagioclase or orthopyroxene should be in equilibrium (not all the three phases). The number of phases and the system components, in this case, would flout the Phase Rule.

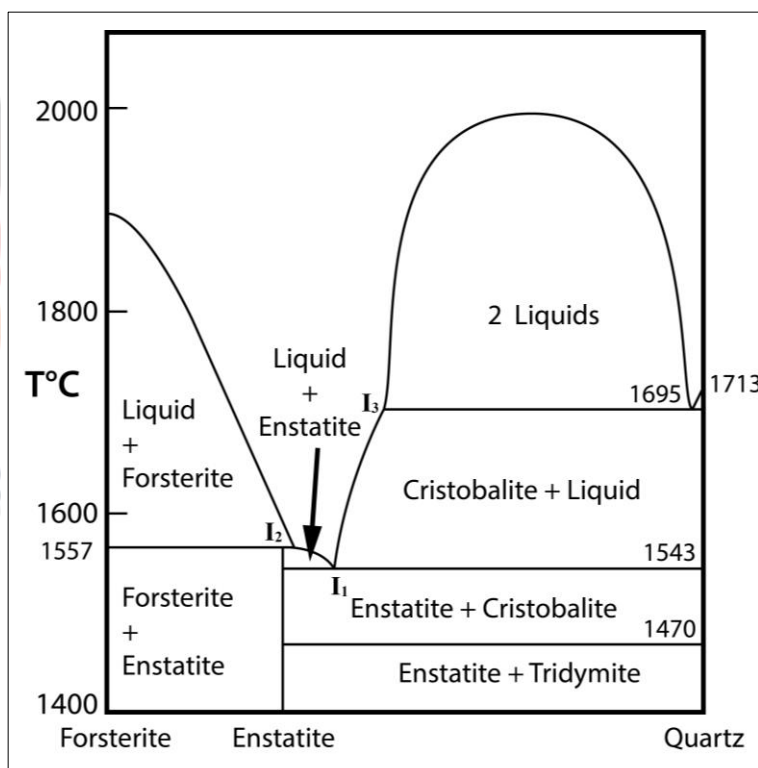
### Scenario 2

Consider that in a closed system ( $Mg_2SiO_4-SiO_2$ ) in equilibrium at constant pressure, there are four phases quartz, forsterite, enstatite and L(liquid).

According to the Phase Rule,

$$F = C - P + 2 = 2 - 4 + 1 = -1$$

Apparently, the Phase Rule is NOT followed as there cannot be a negative value for  $F$  (0 should be the minimum value). Here there is a catch. There is no restriction for a system to have ONLY one invariant point. In strict sense the Phase Rule should be obeyed by one invariant point and the related univariant and bivariant assemblages. The negative value of the variance in this case means that the system is in equilibrium and has more than one invariant points.



**Fig. 2** (Chapter 4A) Two- component system ( $Mg_2SiO_4$  (Forsterite) –  $SiO_2$  (Quartz, tridymite, cristobalite) with eutectic ( $F=0$ ,  $I_1$ ) and peritectic points ( $F=0$ ,  $I_2$ ,  $I_3$ ). Note that both eutectic and peritectic points are invariant points but the former has minimum temperature.

The systems in which there exist more than one invariant point are known as 'Multi Systems'. \*\* In the absence of definitive criteria for disequilibrium, as mentioned in Scenario 1, the possibility of multi system seems to be the cause for noncompliance of the Phase Rule.

### 3.4 Mineralogical Phase Rule

For a long time, the geologists (specially the petrologists) were confronted with the question "Can a system in equilibrium has no. of phases that exceeds the no. of system components". This tricky question was formally addressed by the great Norwegian geologist V. M. Goldschmidt (1911) and his application of the Phase Rule in natural mineral assemblage is known as Goldsmith's Mineralogical Phase Rule (GMPS). GMPS is a corollary of the Gibbs Phase Rule. Goldschmidt's simple but incisive analyses paved the way for quantitative petrology and forms the basis of calculations of the different intensive parameters that led to stabilization of a given mineral assemblage for a given bulk composition.

Any mineral assemblage we encounter in natural rocks having multi components is stabilized over a range of pressure, temperature and bulk composition. Therefore, the variance of the given mineral assemblage has to be more than 2 (as P, T and composition of minerals are changing). If the system is closed, the phase Rule assumes the form,

$$F = C - P + 2$$

Under the circumstances, where  $F > 2$ ,

$$P < C \quad (3)$$

This follows that the no. of phases in natural rocks cannot exceed the number of the system components.

Equation (3) is the form of GMPR under closed system.

\*\* Please note that in closed system,  $P = C - F + 2$ . In many rocks in the world we have kyanite+ Sillimanite (or any two of the three  $Al_2SiO_5$  polymorphs)

are present. In this case,  $P = 1(\text{Al}_2\text{SiO}_5) - 1 + 2 = 2$  and  $P > C$ . This is a special case. Usually, mineral assemblages in natural rocks have variance more than 2 and the GMPR is valid.

In open system the Phase Rule assumes the form (equation 2),

$$F = (C - k) - P + 2$$

For natural assemblages where the variance (F) is  $> 2$ ,

$$P < C - k \quad (4)$$

This is the form of GMPR in open system

\*\* Have a look at eq. (4). Every mobile component in a system will reduce the number of the phases of the system by one. This then follows that a system cannot have all its system components mobile. This is because, under these circumstances,  $P < 0$ , an impractical situation.

### Frequently Asked Questions-

**Q1. Why it is difficult to cook meat (no barbeque, Indian meat curry!) in high altitude if there is no pressure cooker?**

**Hint:** For good cooking of meat the boiling temperature of the water should be  $>95^{\circ}\text{C}$ . Boiling temperature of water decreases with decrease in pressure.

**Q2. Why does a sheared rock show fewer phases than its unsheared equivalent?**

**Q3. A sealed fragile container is half filled with water in which a piece of ice is floating in equilibrium. The container is placed in atmosphere of the Earth. What is the variance of the  $\text{H}_2\text{O}$  system?**

**Hint:** Pay attention to the phrase 'fragile container'

**Q4. Calculate the no. of system component of the assemblage in a calc-silicate rock  
Calcite ( $\text{CaCO}_3$ ), anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ), grossular garnet ( $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ), wollastonite ( $\text{CaSiO}_3$ ) and vapor ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ )?**

**Q5. If the phase meionite ( $3\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot \text{CaCO}_3$ ) is added to the list of minerals given in Q4, will it change the number of components of the system? Justify your answer. Presume that the mineral in the calc silicate rock (Q4) are in equilibrium, can the rock system have only one invariant point? Justify?**

### Multiple Choice Questions-

1. A phase has
- Fixed composition and specific physical properties
  - Fixed physical property but variable composition
  - Variable physical properties and chemical compositions
  - None of the above

**Ans:** a



2. 'Change of heat can change the variance of a system'. This statement is not correct at

- a.  $F=1$
- b.  $F=3$
- c.  $F=2$
- d.  $F=0$

**Ans:** d

3. Mobility of a system component changes the variance if the no. of phases in the system is fixed. The statement is

- a. Valid
- b. Invalid
- c. Valid under certain circumstances
- d. None of the above

**Ans:** a

4. If the fluid pressure is  $>$  load pressure, the variance of the system

- a. Decreases
- b. Increases
- c. Remains the Same
- d. Depends on temperature only

**Ans:** b

5. Mineralogical phase rule is not valid in

- a. Open system
- b. Close system
- c. Partially open system
- d. None of the above

**Ans:** d

**Suggested Readings:**

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