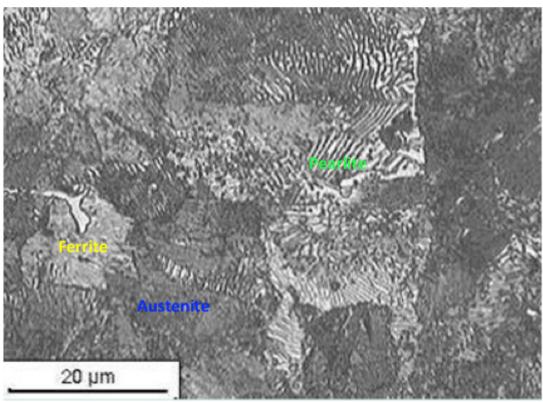
Indian Institute of Technology Bombay Department of Energy Science and Engineering Thermodynamics and Energy Conversion (EN 203) – Autumn 2020-21

PROBLEM SET - 1 Gibbs Phase Rule

Common materials such as steel, Aluminum alloys, Magnesium alloys etc. can exist in multiple phases. For example, Steels are composed of the elements Fe, C, and other impurities such as metallic Cr, Ni etc. and non-metallic such as S, P, B etc. The various phases in steels are *ferrite, austenite, cementite, pearlite bainite* etc. Most of these phases are present in the steel components that are common in our life eg. Steel utensils, tools, frames etc. All the different phases possess different compositions of the above mentioned elements. Thus, they possess different physical and mechanical properties.

A Scanning Electron Microscopy (SEM) image of a steel containing phases such as ferrite (light grey), austenite (dark grey), pearlite (stripes) is shown below. In such a steel block all these different phases co-exist. This means that they are in equilibrium with each other.



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Often, it is a task of the thermodynamicist/materials scientist/engineer to decide on how many independent thermodynamic parameters/properties are needed to establish the state of this steel system containing several such phases uniquely and completely.

This Problem Set teaches us how to decide on the number of independent parameters needed to establish the state of a material system uniquely and completely.

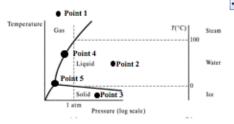
How many independent properties are needed to define a state uniquely and completely?

1.	Let material a system consisting of <i>P</i> phases and <i>C</i> components be at equilibrium	$\begin{array}{c} p^{p}, T^{p}, \mu^{p}_{c=1,2C} \\ \\ p^{1}, T^{1}, \mu^{1}_{c=1,2C} \\ \end{array} \\ \begin{array}{c} p^{3}, T^{3}, \mu^{3}_{c=1,2C} \\ \end{array}$
 3. 	# of independent properties needed = # of independent variables — # of independent equations relating them. This difference is called the <i>degrees of freedom</i> (F).	p ² , T ² , μ ² _{c=1,2} p ³ , T ³ , μ ³ _{c=1,2} p ⁴ , T ⁴ , μ ⁴ _{c=1,2} p ⁵ , T ⁵ , μ ⁵ _{c=1,2}
i.	Procedure: # variables for each phase:	ρ ³ , Τ ³ , μ ³ _{e=1,2} ρ ¹ , Τ ¹ , μ ¹ _{e=1,2}
ii.	Total # variables:	p ¹ , T ¹ , μ ¹ _{c=1,2} p ⁵ , T ⁵ , μ ⁵ _{c=1,2} p ⁵ , T ⁵ , μ ⁵ _{c=1,2}
iv.	Mechanical Equilibrium equations for any phase: Thermal Equilibrium equations for any phase: Chemical Equilibrium equations for any phase:	 Fun Facts The phase rule was deduced by J.W. Gibbs in the 1870s. Today i is popularly known as the Gibbs Phase Rule. Easy way to remember: "Fountain Pepsi = Cops + 2" The eminent Ostwald reminisced in his "Lebenslinien" on hidecision to translate Gibbs' work. After some difficulty procuring a copy, he had even further difficulty understanding it. He soon found that the only way to study Gibbs' papers was to translate word by word because the text was already so tersthat no abbreviated summary of the content was possible Ostwald openly admitted that he had not been able to understand all of the mathematics, and he believed that not one flaw - either in logic, mathematics, or in scientific assumptions had yet been found there Duhem (another hero of thermodynamics), criticized the phase rule because he doubted that the independent variables for the components of each of the phases of the system must be identical with the independent variables of the system. Duhem admitted that Gibbs had dealt with this problem in a few lines but proposed to do it "with all possible rigor". Forty-two page later he concluded: "Thus are rigorously established the variou propositions contained in the phase Rule of J. Willard Gibbs". I
vi.	The total # equations:	is not easy reading! Source: Edward E. Daub; "Gibbs Phase Rule Centenary Retrospect"; Journal of Chemical Education 53 (1976) 747.
vii	. # variables which can be independently chosen	l:
vii	i. The degrees of Freedom F =	
	Gibb's Phas	e Rule

Exercise

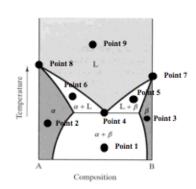
Apply the gibbs phase rule and obtain the number of degree of freedom (F) to the various points.

1. Apply the Gibbs phase rule and obtain the number of degree of freedom (F) to the various points (Point 1 to Point 5) in the $\underline{\text{one-component}}$ (H₂O) phase diagram given below. Write down the Gibbs phase rule for the $\underline{\text{one-component}}$ system. Include the number of the $\underline{\text{component}}$ (C) and the number of phases (P) in your answer.



Gibbs Phase Rule:		(
	No. of Components (C)	No. of Phases (P)	No. of Degree of Freedom (F)				
Point 1	£	()	(
Point 2	(()	(
Point 3	(()	(
Point 4	((()				
Point 5	(((

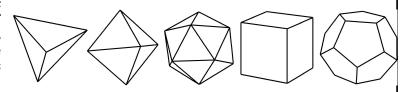
 Apply the Gibbs phase rule and obtain the number of degree of freedom (F) to the various points (Point 1 to Point 9) in the two-components phase diagram given below. Write down the Gibbs phase rule for the two-component system. Include the number of the components (C) and the number of phases (P) in your answer.



Gibbs Phase Rule:		(
	No. of Components (C)	No. of Phases (P)	No. of Degree of Freedom (F)			
Point 1	۲	4	()			
Point 2	(()	(
Point 3	(4	(
Point 4	۲	4	(
Point 5	۲	()	(
Point 6	۲	4	()			
Point 7	۲	()	(
Point 8	۲	()	(
Point 9	(4	(

Interesting!? Are Gibbs Phase Rule and Euler's formula equivalent?

Euler's Formula: Any polyhedron (eg. five platonic solids shown here) with V vertices, E edges, and F faces satisfies V-E+F=2. Eg. the cube has 8 vertices, 12 edges, and 6 faces, and 8-12+6=2. Similarly, the dodecahedron (the polyhedron on the far right) has 20 vertices, 30 edges, and 12 faces, and 20-30+12=2.



Similarity: Euler's Formula: V – E + F = 2; Gibbs Phase Rule: P – C + F = 2

Assume that Vertices ~ Phases; Edges ~ Components; Faces ~ Degrees of Freedom

Answer it for yourself and have fun.

Read the following:

- 1. "Euler's formula and Phase rule", T. P. Radhakrishnan, Journal of Mathematical Chemistry, 5, 381-387 (1990)
- 2. https://divisbyzero.com/2009/02/02/gibbs-phase-rule-and-eulers-formula/