

MSE-204 Thermodynamics for Materials Science

L6. INTRODUCTION TO PHASES OF NON-REACTING SYSTEMS

DEFINITION OF PHASE | FUNDAMENTAL RELATIONS OF MULTIPHASE SYSTEMS | CONDITIONS OF EQUILIBRIUM |
ROLE OF CHEMICAL POTENTIAL | PHASE RULE

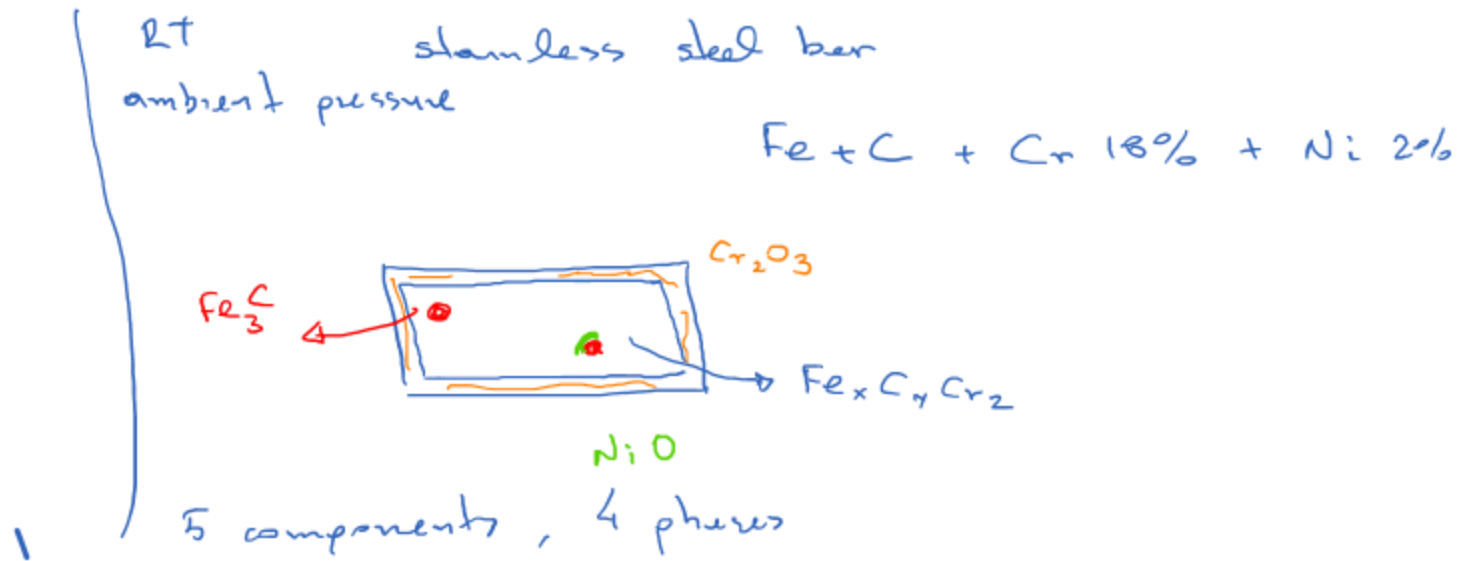
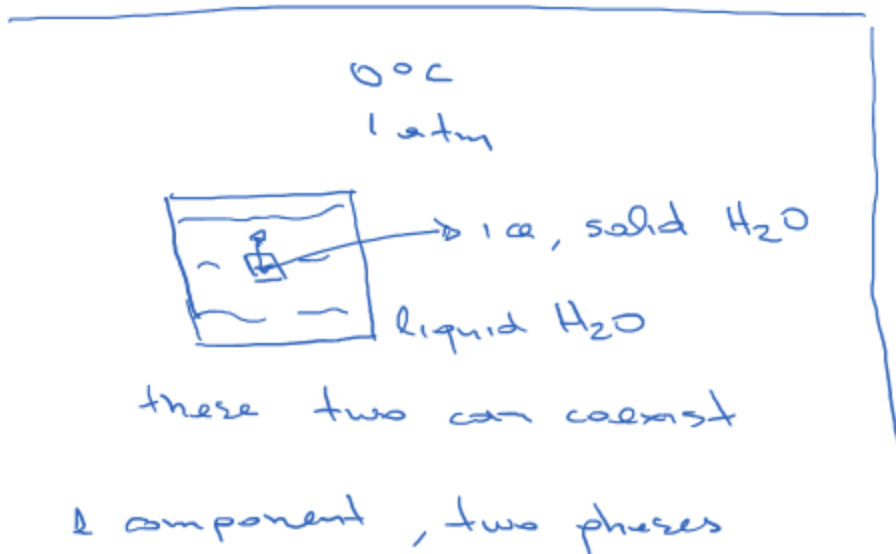
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DEFINITION OF PHASE

In real systems, we often find different materials and within these materials we can find different parts of the same materials coexisting. For example, a glass of water with ice cubes. In materials, this kind of coexistence is quite common.

A phase is a part of a system that on a macroscopic scale can be considered as homogeneous.

- can not be continuous
- need to be able to define a boundary between the phases



FUNDAMENTAL RELATIONS OF MULTIPHASE, CLOSED, NON-REACTING SYSTEMS

$$dU = Tds - p dV + \sum_i \mu_i dn_i$$

What we now need to study is what are the conditions of the multiple phases to coexist and to be at equilibrium.

Let us consider a heterogeneous closed system consisting of the homogeneous phases α, β, \dots . Each phase contains n_i^θ mole of component i .

multi component system $i = 1, 2, 3, \dots, n$

multi phase system $\theta = \alpha, \beta, \gamma, \dots, \varphi$

For the α phase:

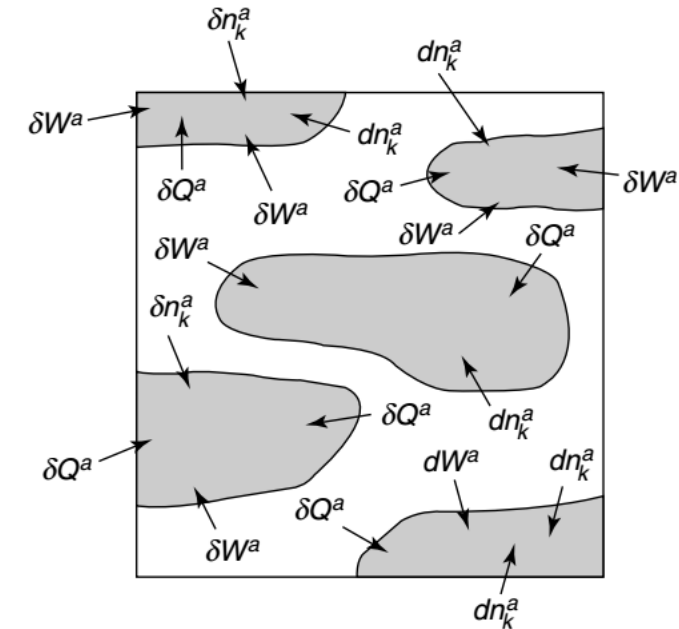
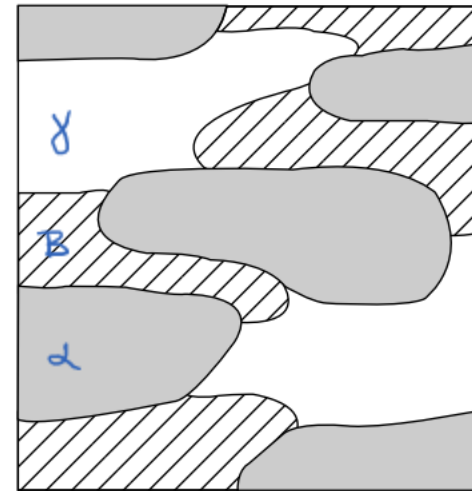
$$dU^\alpha = T^\alpha ds^\alpha - p^\alpha dV^\alpha + \sum_i \mu_i^\alpha dn_i^\alpha$$

For the multiphase system

$$U = \sum_\theta U^\theta, \quad S = \sum_\theta S^\theta, \quad V = \sum_\theta V^\theta, \quad dn_i = \sum_\theta dn_i^\theta$$

At equilibrium:

$$dU = \sum_\theta dU^\theta = 0 \quad \Rightarrow \quad \sum_\theta \left(T^\theta ds^\theta - p^\theta dV^\theta + \sum_i \mu_i^\theta dn_i^\theta \right) = 0$$



TEMPERATURE CONDITIONS FOR EQUILIBRIUM

A possible process can be characterized by the following variations in entropy, volume and composition of the phases:

$$dS^A = -dS^B, \quad dS^Q = 0 \quad \Theta = \gamma, S, \dots, q$$

$$dV^Q = 0, \quad dn_i^Q = 0 \quad \Theta = a, B, \dots, q \quad i = 1, 2, 3, \dots, n$$

$$T^A dS^A + T^B dS^B = 0$$

$$(T^A - T^B) dS^A = 0$$

$$T^A = T^B = \dots = T^Q \quad \text{thermal equilibrium}$$

PRESSURE CONDITIONS FOR EQUILIBRIUM

$$dV^d = -dV^B, \quad dV^\Theta = 0 \quad \Theta = \alpha, S, \dots, q$$

$$dS^\Theta = 0, \quad dn_i^\Theta = 0 \quad \Theta = \alpha, B, \alpha, \dots, q \quad i = 1, 2, 3, \dots, n$$

$$-p^d dV^d - p^B dV^B = 0$$

$$(p^B - p^d) dV^d = 0$$

$$p^d = p^B = \dots = p^q \quad \text{mechanical equilibrium}$$

CONDITIONS ON THE CHEMICAL POTENTIALS FOR EQUILIBRIUM

$$dn_i^A = -dn_i^B, \quad dn_i^\Theta = 0 \quad \Theta = \gamma, \delta, \dots, q \quad i = 1, 2, 3, \dots, r$$

$$dS^\Theta = 0, \quad dU^\Theta = 0 \quad \Theta = A, B, \gamma, \dots, q$$

$$\mu_i^A dn_i^A + \mu_i^B dn_i^B = 0$$

$$(\mu_i^A - \mu_i^B) dn_i^A = 0$$

$$\boxed{\mu_i^A = \mu_i^B = \dots = \mu_i^\Theta}$$

chemical equilibrium / GOLDEN RULE
for material stability

Equilibrium is established when the chemical potential of each component at different phases is equal

cube on liquid water

$$1 \text{ atm}, 0^\circ\text{C} \quad \mu_{\text{H}_2\text{O}}^L = \mu_{\text{H}_2\text{O}}^S$$

stainless steel

RT conditions, ambient pressure

$$\mu_{\text{Cr}}^{\text{Cr}_2\text{O}_3} = \mu_{\text{Cr}}^{\text{Fe}_x\text{Cr}_y\text{Cr}_z} = \mu_{\text{Cr}}^{\text{NiO}}$$

SPONTANEOUS TRANSFER OF A SPECIE FROM ONE PHASE TO ANOTHER

We will now consider a system that can only exchange volume work with its environment. It comprises of two phases and the various species can freely exchange from one phase to another. They do so at constant pressure and temperature.

$$i^d \rightarrow i^B$$

$$dG^\ominus = -S^\ominus dT + V^\ominus dp + \sum_{\ominus} \sum_i \mu_i^\ominus dn_i^\ominus$$

Two phases, isothermal + isobaric

$$dG^{a \rightarrow b} = dG^B - dG^d$$

< 0 spontaneous process

$$\mu_i^B dn_i^B - \mu_i^d dn_i^d < 0$$

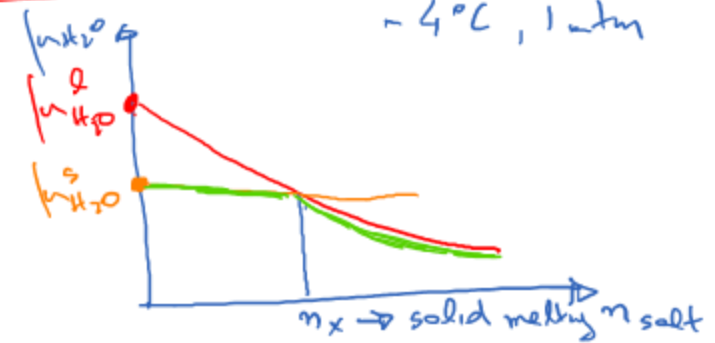
$$(\mu_i^B - \mu_i^d) dn_i^{d \rightarrow B} < 0$$

$$dn_i^{d \rightarrow B} > 0 \quad \mu_i^B - \mu_i^d > 0$$

$$\mu_i^d > \mu_i^B$$

GOLDEN RULE FOR MATERIAL TRANSFORMATION

A component will move from one phase to another, if and only if by doing so its chemical potential will be lower!!!



GIBBS PHASE RULE (FOR NON-REACTING SYSTEMS)

We need to establish a rule, which will allow us to determine the number of intensive variables that can be independently modified. This modification will induce a change in all the other intensive variables in such a way that a new state of equilibrium will be reached.

multicomponent system $n+2$ ^{T, P} + multiphase system $q(n+2)$ TOTAL # of intensive variables

Exclude

1. $\sum_i x_i = 1$

- q

2. Therm. Eq

- $(q-1)$

3. Mech. Eq

- $(q-1)$

4. Chem. Eq

- $n(q-1)$

$F = n + 2 - q$

degrees of freedom
or # of intensive variables
needed to describe the
system



1 atm, ~~0°C~~
coexistence of phases

$F = 1$

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L7.1 SINGLE COMPONENT PHASE DIAGRAMS

PHASE EQUILIBRIA BETWEEN GASES, LIQUIDS, AND SOLIDS | ENTROPY ACCORDING TO BOLTZMANN

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PHASE EQUILIBRIA OF A PURE SUBSTANCE

$$F = 3 - \phi$$

pure substance
 $n = 1$

Let's apply the Gibbs phase rule to single component coexistence of phases.

$F = 0$: three phases coexisting, invariant point in a p - T phase diagram

$F = 1$: two phases coexisting, line or curve in p - T

$F = 2$: one phase existing, surface in the p - T



EQUILIBRIUM OF TWO PHASES OF A PURE SUBSTANCE

Each line on a phase diagram (also called a phase boundary) represents a set of (p,T) points at which two phases are equally stable. We can mathematically calculate these coexistence lines and then we can construct a phase diagram.

$$\mu^{\alpha}(T, p) = \mu^{\beta}(T, p)$$

$$\mu^{\alpha}(T+dT, p+dp) = \mu^{\beta}(T+dT, p+dp)$$

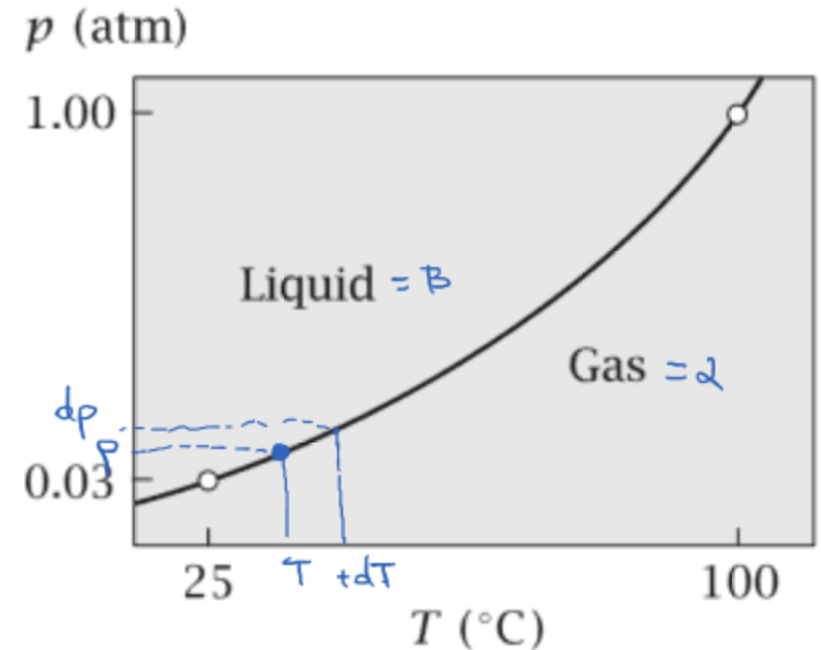
$$\Rightarrow d\mu^{\alpha} = d\mu^{\beta} \Rightarrow \text{the line of coexistence}$$

$$\left(\frac{\partial \mu^{\alpha}}{\partial T}\right)_p dT + \left(\frac{\partial \mu^{\alpha}}{\partial p}\right)_T dp = \left(\frac{\partial \mu^{\beta}}{\partial T}\right)_p dT + \left(\frac{\partial \mu^{\beta}}{\partial p}\right)_T dp$$

$$h = g \quad \left(\frac{\partial h}{\partial T}\right)_p = \left(\frac{\partial g}{\partial T}\right)_p = -s \quad \alpha \quad \left(\frac{\partial h}{\partial p}\right)_T = \left(\frac{\partial g}{\partial p}\right)_T = v$$

$$\Rightarrow -s^{\alpha} dT + v^{\alpha} dp = -s^{\beta} dT + v^{\beta} dp$$

$$\Rightarrow \frac{dp}{dT} = \frac{s^{\alpha} - s^{\beta}}{v^{\alpha} - v^{\beta}}$$



EQUILIBRIUM OF TWO PHASES OF A PURE SUBSTANCE: THE CLAPEYRON EQUATION | CONTINUED

$$g^d = h^d - T s^d \quad \& \quad g^B = h^B - T s^B$$

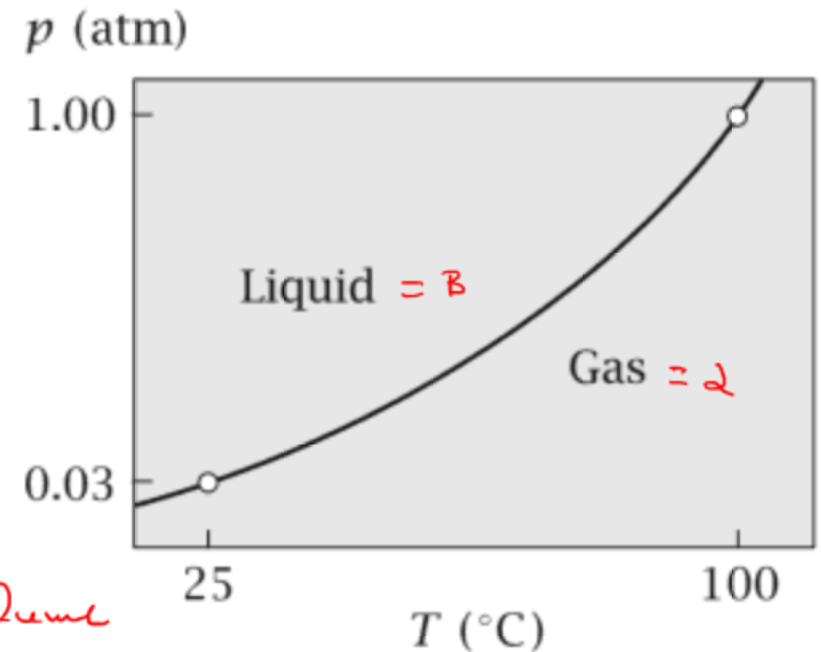
⇒
$$\frac{dp}{dT} = \frac{h^d - h^B}{T (v^d - v^B)} \quad \text{Clapeyron Eq.}$$

By convention $h^d > h^B$ which means
that $\Delta h^{B \rightarrow d} = h^d - h^B > 0$

the slope will be given by the change of volume

$$L = h^d - h^B > 0 \text{ (latent heat)}$$

$$\frac{dp}{dT} = \frac{L}{T (v^d - v^B)}$$



EQUILIBRIUM OF TWO PHASES OF A PURE SUBSTANCE: THE CLAUSIUS CLAPEYRON EQUATION | CONTINUED

In the case when one is gaseous, $\alpha = \text{gaseous}$

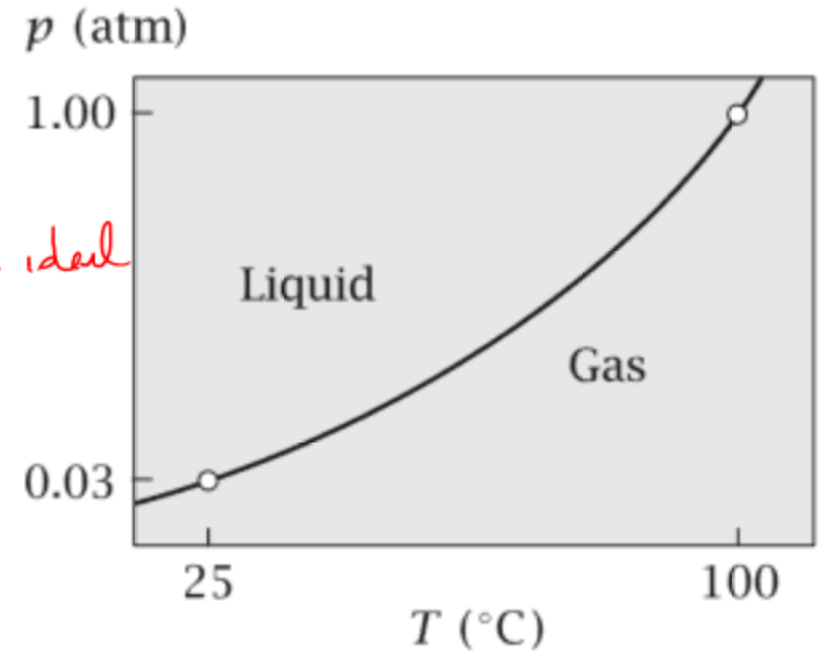
$$v^\alpha - v^\beta \approx v^\alpha$$

$$\Rightarrow \frac{dp}{dT} = \frac{L}{T \cdot v^\alpha}$$

If I consider this gas to be ideal
 $v^\alpha = \frac{RT}{P}$

$$\frac{dp}{dT} = \frac{L \cdot P}{T^2 R}$$

$$\Rightarrow \frac{d(\ln p)}{dT} = \frac{L}{RT^2} \quad \text{or} \quad \frac{d(\ln p)}{d\left(\frac{1}{T}\right)} = -\frac{L}{R}$$



EXAMPLE OF TWO PHASE EQUILIBRIA

THE REFRIGERATOR

In a refrigerator, a “working fluid” is pumped around a system of tubes and undergoes repeated thermodynamic cycles of vaporization and condensation.

Their operation is based on two principles:

- That boiling stores energy by breaking noncovalent bonds and condensation gets that energy back, and
- That a fluid can be boiled at a low temperature and re-condensed at a high temperature by controlling the pressure

