CEN 207 Physical Chemistry

Text book:

Atkins' Physical Chemistry, Peter Atkins, Julio de Paula, James Keeler, 11th Edition, Oxford University Press.

Reference books

. Physical Chemistry, Robert J. Silbey, Robert A. Alberty, Moungi G. Bawendi

. Physical Chemistry, Ira N. Levine

Physical Transformation of Pure Substance

Phase diagram of pure substances:

Phase: A phase is a form of matter that is uniform throughout in chemical composition and physical state. Solid, liquid and gas

Phase transitions: A phase transition, the spontaneous conversion of one phase into another phase, occurs at characteristic transition temperature, T_{trs}, for a given pressure. At the transition temperature the two phase are in equilibrium and Gibbs energy of the system is a minimum at the prevailing pressure.

Thermodynamic criteria of phase stability: All considerations are based on the Gibbs energy of a substance (G_m). Chemical potential $\mu = G_m$

At equilibrium, the chemical potential of a substance is the same in and throughout every phase in the system.

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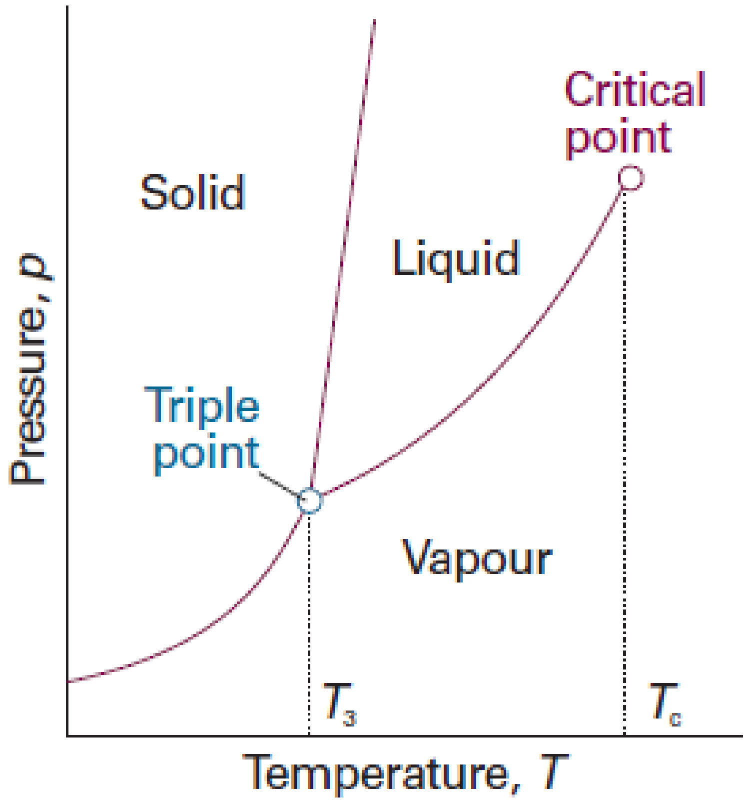
Phase boundaries:



The **phase diagram** of a substance shows the regions of pressure and temperature at which its various phases are thermodynamically stable (see the figure).

The lines separating the regions, which are called **phase boundaries**, show the values of p and T at which two phases coexist in equilibrium.

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Vapour pressure = external pressure, this temperature is boiling temperature

Melting temperature: the liquid and solid phases of a substance coexist in equilibrium (Under a specified pressure).

Melting temperature = freezing temperature

The Phase Rule: The phase rule (deduced by JW Gibbs) gives the number of parameters that can be varied independently (at least to a small extent) while the number of the phases in equilibrium is preserved.

The variance (or number of degrees of freedom), F, of a system is the number intensive variables that can be changed independently without disturbing the number of phases in equilibrium.

Physical Transformation of Pure Substance

A component is a chemically independent constituent of a system

F: the number of degrees of freedom

C: the number of components

P: the number of phases at equilibrium

The phase rule

F = C – P + 2

2: the total number of intensive variables p and T, count as 2.

For C=1→ F = 1 – P+2 = 3-P

For P=1, C=1→ F = 1 – 1+2 = 2

For P=2, C=1→ F = 1 – 2+2 = 1

For P=3, C=1→ F = 1 – 3+2 = 0

Physical Transformation of Pure Substance

Thermodynamic aspects of phase transitions, as reported ($\mu = G_m$)

$$dG = Vdp - SdT$$

$dG = Vdp$, at constant T → $\left(\frac{\partial G}{\partial p}\right)_T = V_m$; $\left(\frac{\partial \mu}{\partial p}\right)_T = V_m$

$dG = -SdT$, at constant p → $\left(\frac{\partial G}{\partial T}\right)_p = -S_m$; $\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m$

The location of phase boundaries

When the phases α and β are in equilibrium

$$\mu(\alpha: p, T) = \mu(\beta: p, T)$$

The solution of this equation for p in terms of T gives an equation for the phase boundary (the coexistence curve).