VOLUME-14 Part B and C

CONTENTS

V. Thermodynamic and Statistical Physics

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8.1. Phase Transitions

1. Concept of phase

Every substance can exist in distinctly different forms, called phases, which correspond to different types of aggregation of the same molecules. A substance can exist in the form solid, liquid and gases. Different phases are found to exist in different ranges of pressure and temperature.

Gibb's free energy is given by,

$$G = U + PV - TS$$

$$\therefore \quad dG = dU + P.dV - V.dP - TdS - S.dT$$

$$\therefore \quad dG = T.dS - P.dV + PdV - V.dP - T.dS - S.dT$$

$$\therefore \quad dG = -V.dP - S.dT$$

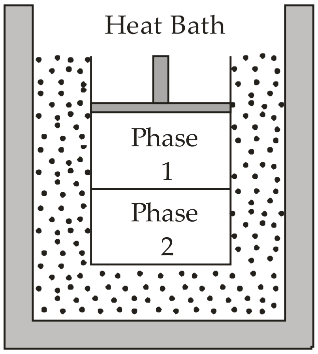
If P and T are constant i.e. an isobaric and isochoric change, $dG = 0$.

A phase change or phase transition is an isothermal and isobaric process. Once a phase change begins, temperature and pressure of the system remains constant till the change is over.

$$dG = 0 \text{ in the process of phase transistion.}$$

Since phase change is an isothermal and isochoric process, we can assume the phase change taking place in a constant temperature bath and imagine a piston enclosing a system which can go up or down to maintain the pressure on the system constant. Different pairs of (P, T) can be obtained of the both and pressure on the piston.

(i) Co-existence of two phases:



Consider one-component system consisting of N-particles in two phases say liquid and gas. Let the two phases coexist in equilibrium at temperature T and pressure P. Let N_1 and N_2 be the number of particles in phase and phase 2 respectively.

Let g_1 and g_2 be the Gibb's energy per particle in the phases respectively.

$$N = N_1 + N_2$$

$$\therefore \qquad G = N_1 g_1 + N_2 g_2$$

If a small number of particles (dN1) are taken from phase 1 to phase 2, then change in Gibb's energy is given by,

$$\begin{aligned} dG &= g_1 dN_1 + g_2 dN_2 \\ &= (g_1 - g_1) dN_1 \qquad (\because dN_1 = -dN_2) \\ &= 0 \qquad (\because dN_1 = -dN_2) \end{aligned}$$

$$\therefore \quad (g_1 - g_2) dN_1 = 0$$

As N_1 is freely variable when two phases coexist $dN_1 \neq 0$

$$\therefore \qquad (g_1 - g_2) = 0$$

$$\therefore \qquad g_1 = g_2$$

g_1 and g_2 are the functions of temperature and pressure.

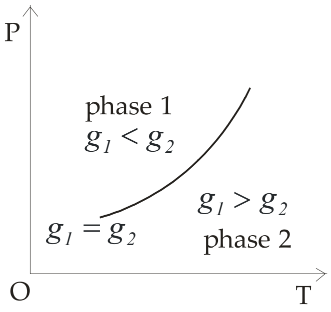
The above equation shows that the existence of phases in equilibrium, Gibb's free energy per particle for the two phases must be the same. When this condition satisfied, the transfer of one particle of the system from one phase to another leaves G unchanged. Hence any number of particles in phase 1 can co-exist with the remaining particle is phase 2.

(ii) Phase Equilibrium Curve:

In reversible process $\Delta\varepsilon = 0$ and in any other process, G decreases till it becomes minimum at equilibrium. Now g_1 and g_2 are functions of T and P. Therefore, T and P are such that, $g_1 > g_2$, G will become minimum when all particles will go to phase 2.

i.e. When $N_1=0$, $N_2=N$.

phase 2 will exist alone at equilibrium.



If T and P are such that $g_1 < g_2$, phase 1 exist alone at equilibrium. For certain set of values of P and T, $g_1 > g_2$, then both the phases co-exist in equilibrium at these (P, T) values. A graph plotted for this set of P, T values is called 'phase' equilibrium curve because at any point on this curve, two phases coexist in equilibrium. This curve is called fusion curve for solid-liquid phase change and sublimation curve for solid-vapour phase change.

At a given temperature, there is only one pressure at which two phases can coexist in equilibrium and vice-versa. For e.g. At 100^0C, water vapour in contact with water always has a pressure of one atmosphere.

(iii) Co-existence of three phases:

Consider a system described by the variables P and T. For a given P and T, the equilibrium state of the system does not necessarily have to be homogeneous. The system can show different state forms (for e.g., for water the possible state forms are liquid/solid/gas). These state forms are called phases. In each phase certain macroscopic properties can show very different values.

Example: water.

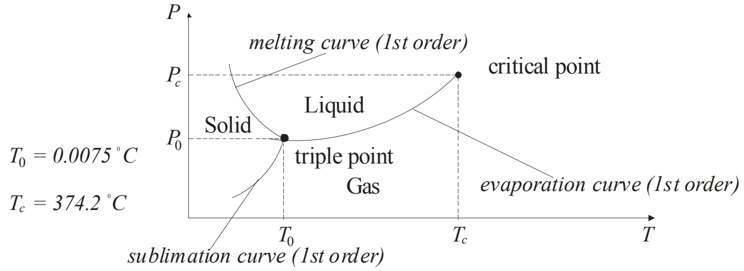


Figure 1 : P – T diagram for water.

The $P - T$ diagram for water shows phase boundaries, or lines of coexistence.

Critical point: At this point, the gas and the liquid have equal densities and specific entropies (entropy per particle). The phase transition becomes second-order at this point. There is no critical point for the liquid-solid transition.

Triple point: At this point (line), gas, liquid and solid coexist.

Note: the melting curve has negative slope, which means that at constant temperature $T < T_0$ ice melts under increasing pressure (we observe this during ice-skating).

1. First-order phase transition

Since we have already started discussing the {P, T} phase diagram for water, let us continue and concentrate first on phase transitions of first order.

When water starts boiling, it undergoes a phase transition from a liquid to a gas phase. For both phases independently, the equation of state is a well-defined regular function, continuous, with continuous derivatives. However, while going from liquid to gas one function ”abruptly” changes to the other function. Such a transition is the first-order phase transition.

The first-order phase transition can be defined more systematically by considering the Gibbs thermodynamic potential. In a ”first-order phase transition”, the first derivative of the Gibbs potential is discontinuous across the phase boundary. Also, according to the relations:

$$V = \left(\frac{\partial G}{\partial P}\right)_T \quad \text{and} \quad S = -\left(\frac{\partial G}{\partial T}\right)_P$$

volume V and entropy S are discontinuous as well.

Let us consider an isotherm drawn in the $P - V$ diagram (Fig. 2).

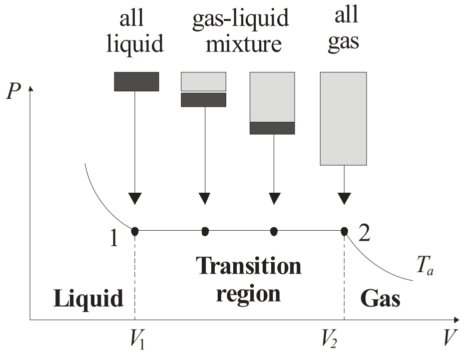


Figure 2 : An isotherm in the P – V diagram for water.