

□ SURFACE TENSION

Consider a liquid in contact with its vapour as shown in figure (1). Molecules at the interface experience a net attractive force toward the interior. To extend the area of the interface, molecules must be moved from the interior into interfacial regions and work must be done on the system against cohesive forces of the liquid. The interface is, therefore, at a higher chemical potential than the bulk liquid.

Thomas Young (1805) showed that the mechanical properties of a surface could be related to those of a hypothetical membrane under tension stretched over the surface. A tension is a negative pressure and pressure is force per unit area so that **surface tension** (γ) is *the force per unit length*. The SI unit of surface tension is newton per meter (Nm^{-1}), while in CGS unit it is dyne cm^{-1} . For a plane surface, surface tension is the force acting parallel to the surface and perpendicular to a line of unit length anywhere in the surface. Tension opposes any extension of surface area.

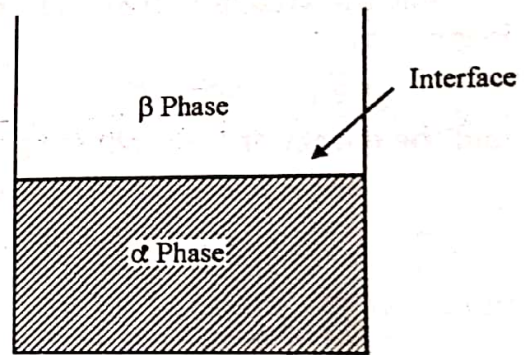


Fig. 1. Two phases and an interface.

Gibbs Dividing Plane. Figure (1) shows a system with two phases and an interface between them. The interfacial region has a finite thickness of a few molecular diameters and in this narrow region properties of the system change markedly over microscopic dimensions. Hence we will be faced with unsolvable problems if we try to treat the interfacial region as another uniform phase. To avoid this difficulty Gibbs defined a plane of zero thickness in the interfacial region which, even though quite artificial, provides an important mathematical tool for the study of real surfaces.

Figure (2) gives the concentration of the substance as a function of height, h , starting at the bottom of the vessel. The concentration changes abruptly as we cross the phase boundary, the transition between the two phases taking place over a few molecular diameters. Imagine a plane of zero thickness perpendicular to h , somewhere in the interfacial region. Let the two bulk phases, with their concentrations unaltered, extend to touch this plane as shown in Fig. 2. The *surface excess concentration*, Γ_σ of this hypothetical surface by the relation.

$$\sigma \Gamma_\sigma = n_\sigma = n_{\text{total}} - c_\alpha V_\alpha - c_\beta V_\beta$$

where σ is the area of the surface, c represents the concentrations, and V the volume. The surface excess moles n_σ is the total number of moles minus the number of moles we assign to each of the

phases. Both n_σ and Γ_σ depend on where the Gibbs dividing plane is drawn, as illustrated in fig. (3) The important point is that for a single component it is possible to draw the Gibbs plane such that $n_\sigma = \Gamma_\sigma = 0$. Hence, in the following derivation we will consider the system in fig. (2) as consisting of two phases and an interface with no molecules.