

5.7: Surface Work

Sometimes we need more than the usual two independent variables to describe an equilibrium state of a closed system of one substance in one phase. This is the case when, in addition to expansion work, another kind of work is possible. The total differential of U is then given by $dU = T dS - p dV + Y dX$ (Eq. 5.2.7), where $Y dX$ represents the nonexpansion work $\delta w'$.

A good example of this situation is surface work in a system in which surface area is relevant to the description of the state.

A liquid–gas interface behaves somewhat like a stretched membrane. The upper and lower surfaces of the liquid film in the device depicted in Fig. 5.1 exert a force F on the sliding rod, tending to pull it in the direction that reduces the surface area. We can measure the force by determining the opposing force F_{ext} needed to prevent the rod from moving. This force is found to be proportional to the length of the rod and independent of the rod position x . The force also depends on the temperature and pressure.

The **surface tension** or interfacial tension, γ , is the force exerted by an interfacial surface per unit length. The film shown in Fig. 5.1 has two surfaces, so we have $\gamma = F/2l$ where l is the rod length.

To increase the surface area of the film by a practically-reversible process, we slowly pull the rod to the right in the $+x$ direction. The *system* is the liquid. The x component of the force exerted by the system on the surroundings at the moving boundary, F_x^{sys} , is equal to $-F$ (F is positive and F_x^{sys} is negative). The displacement of the rod results in surface work given by Eq. 3.1.2: $\delta w' = -F_x^{\text{sys}} dx = 2\gamma l dx$. The increase in surface area, dA_s , is $2l dx$, so the surface work is $\delta w' = \gamma dA_s$ where γ is the work coefficient and A_s is the work coordinate. Equation 5.2.7 becomes

$$dU = T dS - p dV + \gamma dA_s \quad (5.7.1)$$

Substitution into Eq. 5.3.6 gives

$$dG = -S dT + V dp + \gamma dA_s \quad (5.7.2)$$

which is the total differential of G with T , p , and A_s as the independent variables. Identifying the coefficient of the last term on the right side as a partial derivative, we find the following expression for the surface tension:

$$\gamma = \left(\frac{\partial G}{\partial A_s} \right)_{T,p} \quad (5.7.3)$$

That is, the surface tension is not only a force per unit length, but also a Gibbs energy per unit area.

From Eq. 5.7.2, we obtain the reciprocity relation

$$\left(\frac{\partial \gamma}{\partial T} \right)_{p,A_s} = - \left(\frac{\partial S}{\partial A_s} \right)_{T,p} \quad (5.7.4)$$

It is valid to replace the partial derivative on the left side by $(\partial \gamma / \partial T)_p$ because γ is independent of A_s . Thus, the variation of surface tension with temperature tells us how the entropy of the liquid varies with surface area.

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