

7.8: Measuring Work- Non-Pressure-Volume Work

For chemical systems, pressure–volume work is usually important. Many other kinds of work are possible. From our vector definition of work, any force that originates in the surroundings can do work on a system. The force drives a displacement in space of the system or some part of the system. Stretching a strip of rubber is a one-dimensional analog of pressure–volume work. Changing the surface area of a liquid is a two-dimensional analog of pressure–volume work. When only internal forces act, a liquid system minimizes its surface area. We can model this property by attributing a surface-area minimizing force, which we call the surface tension, to the surface of the liquid. We can think of the layer of molecules at the surface as a film that separates the bulk liquid from its surroundings. To increase the area of a liquid system requires an expenditure of work by the surroundings against the surface tension of the film. Gravitational, electrical, and magnetic forces can all do work on particular systems.

In this book, we give little attention to the details of the various kinds of non-pressure–volume work that can be important. (There are two exceptions: Electrical work is important in electrochemistry, which we discuss in Chapter 17. We discuss gravitational work in examples that illustrate reversible processes and some aspects of the criteria for change.) Nevertheless, no development of the basic concepts can be complete without including the effects of non-pressure–volume work. For this reason, we include non-pressure–volume work in our discussions frequently. For the most part, however, we do so in a generalized or abstract way. To do so, we must identify some essential features of any process that does work on a system.

Whenever a particular kind of work is done on a system, some change occurs in a thermodynamic variable that is characteristic of that kind of work. For pressure–volume work this is the volume change. For stretching a strip of rubber, it is the change in length. For gravitational work, it is the displacement of a mass in a gravitational field. For changing the shape of a liquid, it is the change in surface area. For electrical work, it is the displacement of a charge in an electrical field. For magnetic work, it is the displacement of a magnetic moment in a magnetic field. For an arbitrary form of non-pressure–volume work, let us use θ to represent this variable. We can think of θ as a generalized displacement. When there is an incremental change, $d\theta$, in this variable, there is a corresponding change, dE , in the energy of the system.

For a displacement, $d\theta$, let the increase in the energy of the system be dw_θ . The energy increase also depends on the magnitude of the force that must be applied to the system, parallel to the displacement $d\theta$. Let this force be f_θ . Then, for this arbitrary abstract process, we have $dw_\theta = f_\theta d\theta$, or $f_\theta = dw_\theta/d\theta$. Since dw_θ is the contribution to the incremental change in the energy of the system associated with the displacement $d\theta$, we can also write this as

$$f_\theta = \frac{dw_\theta}{d\theta} = \frac{\partial E}{\partial \theta}$$

We can generalize this perspective. θ need not be a vector, and $\partial E/\partial \theta$ need not be a mechanical force. So long as $d\theta$ determines the energy change, dE , we have

$$dw_\theta = \left(\frac{\partial E}{\partial \theta} \right) d\theta$$

We call $\partial E/\partial \theta$ a potential. If we let

$$\Phi_\theta = \left(\frac{\partial E}{\partial \theta} \right)$$

the energy increment becomes $dw_\theta = \Phi_\theta d\theta$. If multiple forms of work are possible, we can distinguish them by their characteristic variables, which we label $\theta_1, \theta_2, \dots, \theta_k, \dots, \theta_\omega$. For each of these characteristic variables, there is a corresponding potential, $\Phi_1, \Phi_2, \dots, \Phi_k, \dots, \Phi_\omega$. The total energy increment, which we also call the non-pressure–volume work, dw_{NPV} , becomes

$$dw_{NPV} = \sum_{k=1}^{\omega} \Phi_k d\theta_k$$

For pressure–volume work, $dw_{PV} = -PdV$. The characteristic variable is volume, $d\theta = dV$, and the potential is the negative of the pressure, $\Phi_V = -P$. For gravitational work, the characteristic variable is elevation, $d\theta = dh$; for a given system, the potential depends on the gravitational acceleration, g , and the mass of the system: $\Phi_h = mg$.

When a process changes the composition of a system, it is often important to relate the work done on the system to the composition change. Formally, we express the incremental work resulting from the k -th generalized displacement as

$$dw_k = \left(\frac{\partial E}{\partial \theta_k} \right) \left(\frac{\partial \theta_k}{\partial n} \right) dn$$

where dw_k and dn are the incremental changes in the work done on the system and the number of moles of the substance in the system. To see how this works out in practice, let us consider the particular case of electrical work. The electrodes of an electrochemical cell can be at different electric potentials. We usually designate the potential difference between the electrodes as \mathcal{E}_{cell} . (We can also write $\Phi_{cell} = \mathcal{E}_{cell}$ when we want to keep our notation uniform. The unit of electrical potential is the **volt**, V. One volt is one joule per coulomb, $1 \text{ V} = 1 \text{ J C}^{-1}$.) We are usually interested in cases in which we can assume that \mathcal{E}_{cell} is constant.

Whenever a current flows in an electrochemical cell, electrons flow through an external circuit from one electrode to the other. By our definition of electrical potential, the energy change that occurs when a charge dq passes through a potential difference, \mathcal{E}_{cell} , is

$$dE = \mathcal{E}_{cell} dq = dw_{elect}$$

We have $\mathcal{E}_{cell} = (\partial E / \partial q)$. Evidently, charge is the characteristic variable for electrical work; we have $\theta_{elect} = q$, and

$$\left(\frac{\partial E}{\partial \theta_{elect}} \right) = \left(\frac{\partial E}{\partial q} \right) = \mathcal{E}_{cell}$$

Letting the magnitude of the electron charge be e , dN electrons carry charge $dq = -e dN$. Then, $dq = (-e\bar{N}) (dN/\bar{N})$. The magnitude of the charge carried by one mole of electrons is the faraday, \mathcal{F} . That is, $1 \mathcal{F} = |e\bar{N}| = 96,485 \text{ C mol}^{-1}$. (See §17-8.)

Letting dn be the number of moles of electrons, we have $dn = dN/\bar{N}$ and

$dq = -\mathcal{F} dn$, so that

$$\left(\frac{\partial \theta_{elect}}{\partial n} \right) = \left(\frac{\partial q}{\partial n} \right) = -\mathcal{F}$$

The work done when dn moles of electrons pass through the potential difference \mathcal{E}_{cell} becomes

$$\begin{aligned} dw_{elect} &= \left(\frac{\partial E}{\partial \theta_{cell}} \right) \left(\frac{\partial \theta_{cell}}{\partial n} \right) dn \\ &= \left(\frac{\partial E}{\partial q} \right) \left(\frac{\partial q}{\partial n} \right) dn = -\mathcal{F} \mathcal{E}_{cell} dn \end{aligned}$$

We find the work done when ions pass through a potential difference \mathcal{E} by essentially the same argument. If ions of species j carry charge $z_j e$, then dN_j ions carry charge $dq = z_j e dN_j = z_j \mathcal{F} dn_j$, and the electrical work is $(dw_{elect})_j = z_j \mathcal{F} \mathcal{E} dn_j$. If ω different species pass through the potential difference, the total electrical work becomes

$$dw_{elect} = \sum_{j=1}^{\omega} z_j \mathcal{F} \mathcal{E} dn_j$$

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