

12.1: Review of Internal Energy and Enthalpy

We are by now familiar with the equations

$$dU = TdS - PdV \text{ and } dH = TdS + VdP,$$

and with the ideas that the increase in the internal energy is the heat added at constant volume and the increase in enthalpy is the heat added at constant pressure, and that U is constant in an adiabatic isochoric process and H is constant in an adiabatic isobaric process. I am now going to examine these equations and statements a bit more critically. In particular I am going to consider that there may be several types of configuration work involved in addition to just PdV work of compression or expansion.

The First Law of thermodynamics is $dU = dQ + dW$.

The work done on a system may comprise an irreversible component dW_I (such as stirring with a paddle, or forcing an electric current through a resistor) plus some reversible components dW_R . The irreversible component is dissipated as heat and is tantamount to adding heat to the system. The heat and the irreversible work contribute to the increase in entropy of the system, according to $dS = (dQ + dW_I)/T$. Thus we have $dQ = TdS - dW_I$.

The reversible component of the work may consist of work done in compressing the system, $-PdV$, but there may also be other kinds of work, such as the work required to create new area, $\Gamma d\sigma$, or the work required to twist a rod, $\tau d\theta$, or the work required to charge a battery, Edq , or the work required to magnetize a specimen, BdM , and perhaps others. In general the expression for each of these forms of reversible work is of the form XdY , where X is an intensive state variable and Y is an extensive state variable. All of these forms of nondissipative work can collectively be called *configuration work*.

The total work done on the system is therefore of the form

$$dW = dW_I - PdV + \sum XdY. \quad (12.1.1)$$

The first law therefore takes the form

$$dU = dQ + dW_I - PdV + \sum XdY. \quad (12.1.2)$$

If the system is held at constant volume (e.g. in a pressure cooker or in an autoclave), then no PdV work of expansion or compression is done. And if no other sort of work is done either (either non- PdV reversible work or irreversible work dW_I) then the increase in internal energy of the system is just equal to the heat added to it.

Enthalpy is defined as $H = U + PV$, so that $dH = dU + PdV + VdP$. From this, we obtain

$$dH = dQ + dW_I + VdP + \sum XdY. \quad (12.1.3)$$

If heat is added to a system at constant pressure, then the system expands and does external work. However, provided that the pressure is held constant and if no other sort of work is done either (either non- PdV reversible work or irreversible work dW_I) then the increase in the enthalpy of the system is just equal to the heat added to it.

In summary, the well-known equations $dU = TdS - PdV$ and $dH = TdS + VdP$ are valid for reversible and for irreversible processes, provided that the only nondissipative work is PdV work; but in general, if there are other types of work being done (e.g. $\Gamma d\sigma$, or $\tau d\theta$, etc.), the required relations are

$$dU = TdS - PdV + \sum XdY \quad (12.1.4)$$

and

$$dH = TdS + VdP + \sum XdY. \quad (12.1.5)$$

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