

9.1: Enthalpy

Enthalpy is sometimes known as "heat content", but "enthalpy" is an interesting and unusual word, so most people like to use it. Etymologically, the word "entropy" is derived from the Greek, meaning "turning" (I'm not sure why) and "enthalpy" is derived from the Greek meaning "warming". As for pronunciation, ENtropy is usually stressed on its first syllable, while enTHALpy is usually stressed on the second. Again, I am not sure why.

Definition: *Enthalpy* H is defined as

$$H = U + PV. \quad (9.1.1)$$

You now know the etymology of enthalpy, you know how to spell it, you know its pronunciation, and you even know its definition. But you don't yet know what it *means*. You cannot determine the internal energy of a system to start with (you can only determine an *increase* in it), but what on Earth does it mean to add to the (undetermined) internal energy the product of the pressure and the volume?

Well, let us see how the enthalpy changes if we change the pressure and volume (and hence the internal energy) of a system. We'll just differentiate Equation 9.1.1.

$$dH = dU + PdV + VdP \quad (9.1.2)$$

But $dU = TdS - PdV$, and so the first law becomes

$$dH = TdS + VdP \quad (9.1.3)$$

This helps us to see a little more the meaning of enthalpy. In particular, for a reversible process, $TdS = dQ$, and so Equations 7.3.2 and 9.1.3 become, respectively,

$$dU = dQ - PdV \quad (9.1.4)$$

and

$$dH = dQ + VdP \quad (9.1.5)$$

Thus we can say:

The increase of the internal energy of a system is equal to the heat added to it in an isochoric process,

and

The increase of the enthalpy of a system is equal to the heat added to it in an isobaric process.

Experiments carried out in open beakers on a laboratory bench are isobaric. Thus the heat generated during a chemical reaction in an open beaker represents the generation of enthalpy. You will notice that chemists use the symbol H for heat of reaction, and they are well aware that this means enthalpy. If the reaction were carried out, however, in an autoclave (also known as a pressure cooker), the heat generated represents the generation of internal energy.

I hope that this now gives some meaning to the concept of enthalpy.

Internal energy U and enthalpy H are both functions of state. From Equation 7.3.2 ($dU = TdS - PdV$) we immediately see the relations

$$\left(\frac{\partial U}{\partial S} \right)_V = T \quad (9.1.6)$$

and

$$\left(\frac{\partial U}{\partial V} \right)_S = -P. \quad (9.1.7)$$

From Equation 9.1.3 ($dH = TdS + VdP$) we immediately see the relations

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad (9.1.8)$$

and

$$\left(\frac{\partial H}{\partial P}\right)_S = V. \quad (9.1.9)$$

Also from Equation 7.3.2 ($dU = TdS - PdV$) we obtain (since dU is an exact differential)

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V, \quad (9.1.10)$$

and from Equation 9.1.3 ($dH = TdS + VdP$) we obtain (since dH is an exact differential)

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P. \quad (9.1.11)$$

Equations 9.1.10 and 9.1.11 are two of *Maxwell's Thermodynamic Relations*. (There are two more to come, in a later chapter.)

We also note that, while the heat capacity at constant volume is

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V, \quad (9.1.12)$$

similarly the heat capacity at constant pressure is

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P. \quad (9.1.13)$$

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