

CHAPTER 9 ENTHALPY

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.

$$dH = dU + P dV + V dP. \quad 9.1.2$$

But $dU = T dS - P dV$, and so the first law becomes

$$dH = T dS + V dP. \quad 9.1.3$$

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

$$dU = dQ - P dV \quad 9.1.4$$

and

$$dH = dQ + V dP. \quad 9.1.5$$

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

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

9.2 Change of State

According to my dictionary, the word "latent" means "present or existing and capable of development but not manifest".

In a liquid at its freezing point there is present or existing some heat, which is capable of development but is not manifest. That is, the liquid secretly holds some latent heat. When the liquid freezes, it gives up this latent heat to its surroundings. The heat is now manifest.

Definition: The *latent heat of freezing* of a quantity of liquid at its freezing point is the heat given up to its surroundings when it freezes. Its SI unit is the joule.

Likewise, we define the *specific latent heat* and the *molar latent heat* of a liquid at its freezing point as the heat given up when unit mass, or a molar amount, respectively, freezes. The SI units are J kg^{-1} and J kilomole^{-1} respectively.

Note: A distressingly large number of people use the words "latent heat" when they mean "specific latent heat". Thus, when you read or hear the words "latent heat" you have to be on guard to decide whether this is really what is meant, or whether "specific latent heat" is intended.

The latent heat of *fusion* of a solid body at its melting point is the heat required to melt it. This is just equal to the heat given up when the liquid freezes, so that, numerically, the latent heats of freezing and of fusion (melting) are the same – though somehow the word "latent" seems less appropriate for freezing, because you are supplying heat to the solid, rather than seeing latent heat being released by a liquid. If you prefer you could refer to the "latent heat" of fusion simply as the "heat of fusion" – or as the "enthalpy of fusion".

Likewise we have a latent heat of condensation of a vapour at its condensation point, and the latent heat of vaporization of a liquid at its boiling point. These are equal in magnitude. We can also define the specific and molar latent heats of condensation and vaporization. The term *latent heat of transformation* will do to cover all four processes. The symbol L (with appropriate subscripts if need be) can be used for any of the latent heats of transformation.

The specific latent heat of fusion of ice at atmospheric pressure is about $3.36 \times 10^5 \text{ J kg}^{-1}$ or about 80 cal g^{-1} .

The specific latent heat of vaporization of water at atmospheric pressure is about $2.27 \times 10^6 \text{ J kg}^{-1}$ or about 540 cal g^{-1} .

Exercise. 70 g of ice at 0 °C are mixed with 150 g of water at 100 °C. What is the final temperature? (I make it 43° C.)

We'll reluctantly, for once, work in calories and grams, and of course the specific heat capacity of water is about 1 calorie per gram per Celsius degree. The heat required to melt the 70 g of ice, and then to raise its temperature from 0 °C to t °C is $70 \times 80 + 70t$ calories. This heat is supplied by the hot water, which cools from 100 °C to t °C, is $150 \times (100 - t)$ calories. Equating the two produces $t = 43^\circ \text{C}$.

Question. Suppose you apply 2.27×10^6 J of energy to a kilogram of water, but, instead of using that energy to vaporize the water, you use it to raise the water from the ground. How high above the ground could you raise it with this energy? It may surprise you – it certainly surprised me! If you were to use the energy, not to vaporize the water, and not to raise it above the ground, but to throw it, how fast, in miles per hour, could you throw it?

For many liquids there is a very rough correlation between molar latent heat of vaporization and boiling point at atmospheric pressure, the ratio L/T usually being in the range 70,000 to 100,000 J kmole⁻¹ K⁻¹.

One last point before proceeding. Generally it is only crystalline solids (including metals) that have a rather definite melting point. Amorphous substances such as plastics and glass generally change from solid to liquid over a rather large range of temperature. Indeed is not obvious when to cease calling such a substance a solid and to start calling it a liquid. Some writers would describe glass as a “liquid” even when it has all the obvious appearances of a solid. See also Section 6.4 of Chapter 6 for a further discussion of this. Mixtures, alloys and solutions, too, do not have such a definite melting point as a crystalline solid, and a salt solution does not have as definite a boiling point (at a given pressure) as a pure liquid does. Thus a salt solution in water at one atmosphere pressure boils at a little higher temperature than 100 °C. When some of the water boils off, the remaining solution is a little more concentrated, and so the boiling point becomes a little higher, and so on.

9.3 Latent Heat and Enthalpy

Consider a liquid of volume V_1 at its boiling point. Suppose a quantity of heat L is supplied, sufficient to vaporize the liquid. The new volume (of what is now vapour) is V_2 . If the vapour has expanded against a constant pressure P (e.g. the pressure of the atmosphere), the work done by it is $P(V_2 - V_1)$. The increase in the internal energy of the system is the heat supplied to the system minus the work done by it (this is the engineer's version of the first law of thermodynamics). That is, $U_2 - U_1 = L - P(V_2 - V_1)$, and so

$$H_2 - H_1 = L. \qquad 9.3.1$$

So, during a change of state at constant pressure the increase or decrease of enthalpy is equal to the latent heat of transformation. This, of course, is just a simple example of our earlier statement, in

Section 9.1, that the increase of enthalpy of a system is equal to the heat supplied to it in an isobaric process.