Fundamentals of Thermodynamics
Lecture 7. Enthalpy

7.1. 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 "enthalpy" is derived from the Greek meaning "warming".

Definition: *Enthalpy* H is defined as

$$H = U + PV \qquad (1)$$

But what does Enthalpy *mean?*. 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 will just differentiate equ. 1.

$$dH = dU + PdV + VdP \qquad (2)$$

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

$$dH = TdS + VdP \qquad (3)$$

This helps us to see a little more the meaning of enthalpy. In particular, for a reversible process, $TdS = dQ$, and so the equation ($dU = TdS - PdV$) and equ. 3 become, respectively,

$$dU = dQ - PdV \qquad (4)$$

and

$$dH = dQ + VdP \qquad (5)$$

Thus we can say:

> | *The increase of the internal energy of a system is equal to the heat added to it in an isochoric (constant volume) 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.

This now gives some meaning to the concept of enthalpy.

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

$$(\frac{\partial U}{\partial S})_V = T \qquad (6)$$

and

$$(\frac{\partial U}{\partial V})_S = -P \qquad (7)$$

From equ.3 ($dH = TdS + VdP$) we immediately see the relations

$$(\frac{\partial H}{\partial S})_P = T \qquad (8)$$

and

$$(\frac{\partial H}{\partial P})_S = V \qquad (9)$$

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

$$(\frac{\partial T}{\partial V})_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad (10)$$

and from the equ. 3 ($dH = TdS + VdP$) we obtain (since dH is an exact differential)

$$(\frac{\partial T}{\partial P})_S = -\left(\frac{\partial V}{\partial S}\right)_P \qquad (11)$$

Equations 10 and 11 are two of *Maxwell's Thermodynamic Relations*.

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

$$C_V = (\frac{\partial U}{\partial T})_V \qquad (12)$$

similarly the heat capacity at constant pressure is

$$C_P = (\frac{\partial H}{\partial T})_P \qquad (13)$$

7.2 Change of State

According to the 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 (sensible).

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.

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 3.36×10^5 J kg^{-1} or about 80 cal g^{-1}.

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

Example

70 g of ice at 0 °C are mixed with 150 g of water at 100 °C. What is the final temperature?

Solution

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 × 80 + 70 T calories. This heat is supplied by the hot water, which cools from 100 °C to T °C, is 150 % (100 − T) calories. Equating the two produces T = 43 °C. (Show in details)

7.3 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

$$H_2 - H_1 = L \qquad (14)$$

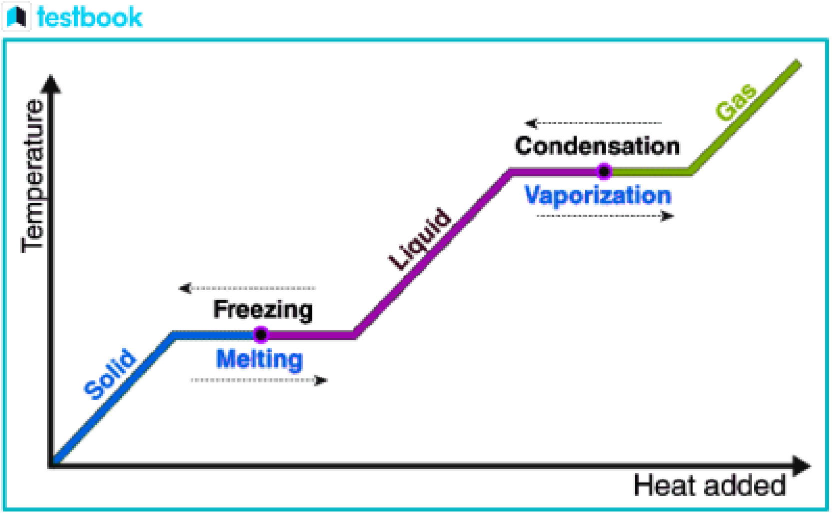
So, during a change of state at constant pressure the increase or decrease of enthalpy is equal to the latent heat of transformation. This, of course, is just a simple example of our earlier statement, in Section 7.1, that the increase of enthalpy of a system is equal to the heat supplied to it in an isobaric process.

7.4 Understanding Latent Heat

The term **latent heat** refers to the energy absorbed or released during a phase change of a substance. This phase change could occur in any form - from a gas to a liquid, a liquid to a solid, or vice versa. Latent heat is closely related to a heat property known as enthalpy.

A crucial aspect of latent heat is that the substance's temperature remains constant during the phase change. In essence, latent heat represents the energy required to overcome the attractive forces that bind molecules and atoms together in a substance.

For instance, when a solid substance transitions into a liquid, it needs to absorb energy to expand the molecules into a broader, more fluid volume. Similarly, a substance transitioning from a gas phase to a liquid phase needs to release energy to bring the molecules closer together due to the change in density levels. This energy, required for a substance to freeze, melt, or boil, is what we call latent heat.



Sensible Heat

Sensible heat, often confused with latent heat, is not related to constant temperature situations or phase changes. Sensible heat refers to the heat transfer between an object and its surroundings. This heat can be "sensed" as a change in the object's temperature.

https://phys.libretexts.org/Bookshelves/Thermodynamics_and_Statistical_Mechanics/Heat_and_Thermodynamics_(Tatum)/09%3A_Enthalpy/9.01%3A_Enthalpy