

First Law, Heat Capacity, Latent Heat and Enthalpy

Stephen R. Addison

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Introduction

In this section, we introduce the first law of thermodynamics and examine sign conventions.

Heat and Work

Heat is the spontaneous flow of energy from one object to another caused by a difference in temperature. Work is defined as any other transfer of energy into or out of the system. Examples of work are: pushing on a piston, stirring a cup of coffee, passing current through a resistor, etc. In each case the temperature will rise as the system's energy is increased. We don't say that the system is being heated because the flow of energy is not spontaneous.

Heat and work refer to energy in transit, we can talk about how much energy is in a system, talking about how much work is in a system is meaningless.

The First Law of Thermodynamics

Let U be the internal energy of a system then

$$\Delta U = (\text{Energy input by Heating}) + (\text{Work done on system}).$$

This is called the first law of thermodynamics, clearly it is just a statement of the law of conservation of energy. We will use Q , and W to denote large or finite changes, we'll use dQ , and dW to denote infinitesimal changes. Thus we will write

$$\Delta U = Q + W,$$

or

$$dU = dQ + dW.$$

Where Q , dQ are negative if heat leaves the system, W , dW are negative if work is done by the system. Many authors write dQ and dW to denote inexact differentials, and to emphasize that Q or W to take the differential of. That is Q and W are not state functions. When a system changes from state 1 to state 2, while ΔU is determinate, Q and W are path dependent.

Other Sign Conventions

There are other sign conventions in use. Many authors define $\Delta U = Q - W$ so that any work done by the system is positive.

Heat capacity and specific heat

In this section we will explore the relationships between heat capacities and specific heats and internal.

Heat Capacity

The heat capacity of an object is the energy transfer by heating per unit temperature change. That is,

$$C = \frac{Q}{\Delta T}.$$

In this expression, we will frequently put subscripts on C , C_p , or C_v for instance, to denote the conditions under which the heat capacity has been determined. While we will often use heat capacity, heat capacities are similar to mass, that is their value depends on the material and on how much of it there is. If we are calculating properties of actual materials we prefer

to use specific heats. Specific heats are similar to density in that they depend only on material. Specific heats are tabulated. When looking them up, be careful that you choose the correct specific heat. As well as tabulating specific heats at constant pressure and constant volume, specific heats are given as heat capacity per unit mass, heat capacity per mole, or heat capacity per particle. In other words, $c = C/m$, $c = C/n$, or $c = C/N$. In elementary physics mass specific heats are commonly, while in chemistry molar specific heats are common. Be careful!

Heat Capacities at Constant Volume and Pressure

By combining the first law of thermodynamics with the definition of heat capacity, we can develop general expressions for heat capacities at constant volume and constant pressure. Writing the first law in the form $\Delta U = Q - p\Delta V$, and inserting this into $C = \frac{Q}{\Delta T}$, we arrive at

$$C = \frac{\Delta U + p\Delta V}{\Delta T}.$$

We can now evaluate this at constant volume, and we arrive at

$$C_v = \left(\frac{\Delta U}{\Delta T} \right)_v.$$

For an infinitesimal process we write this as

$$C_v = \left(\frac{Q}{dT} \right)_v = \left(\frac{dQ}{dT} \right)_v$$

or

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v.$$

Where as usual the “d” is used to denote an “inexact” differential. (By an inexact differential we mean that there is no function to take the differential of, instead the symbol is used to denote a small amount.) Similarly we can calculate the heat capacity at constant pressure. So the heat capacity at constant pressure is given by

$$C_p = \left(\frac{\Delta U + p\Delta V}{\Delta T} \right)_p = \left(\frac{\partial U}{\partial T} \right)_p + p \left(\frac{\partial V}{\partial T} \right)_p.$$

If we examine the expressions for heat capacity, apart from the quantity held constant we see that the expression for C_p contains an extra term. It isn't too difficult to figure out what is going on. Most materials expand when they are heated. The additional term keeps track of the work done on the rest of the universe as the system expands.

Heat Capacities of an Ideal Gas

For an ideal gas, we can write the average kinetic energy per particle as

$$\frac{1}{2}m\langle v^2 \rangle = \frac{3}{2}kT.$$

From this, we calculate C_v and C_p for N particles.

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v = \frac{3}{2}Nk$$

To calculate C_p , we make use of the ideal gas law in the form $pV = NkT$.

$$C_p = \left(\frac{\partial U}{\partial T} \right)_p + p \left(\frac{\partial V}{\partial T} \right)_p$$

So,

$$C_p = \frac{3}{2}Nk + p \frac{\partial}{\partial T} (NkT/p)_p = \frac{3}{2}Nk + Nk = \frac{5}{2}Nk$$

Comparing the expressions for C_p and C_v , we see that we can write

$$C_p - C_v = Nk.$$

So in terms of the ideal gas constant, R , we can write

$$C_p - C_v = nR.$$

This is an interesting result. It's independent of pressure, in other words, at high external pressures, the gas will expand less in such a way that the work done on the environment is independent of p .

Latent heat and enthalpy

In this section we will develop the relationship between latent heat and enthalpy.

Latent Heat

As we have noted, you can transfer energy by heating without increasing temperature. This happens during *phase changes*. In a phase change, the heat capacity becomes infinite. The appropriate term to consider is now *latent heat*. We want to know how much energy is transferred by heating during phase changes. We can define the *latent heat* as

$$L = \frac{Q}{m} = \frac{Q}{N}.$$

Some books like to use to use the latent heat per molecule, I have a preference for using the latent heat per unit mass. The reason isn't deep, latent heats per unit mass are easier to find! The definitions that I have given for latent heat are a little ambiguous, in the same way that the definition for heat capacity was ambiguous until I stated the conditions under which it was to be evaluated. By convention, we assume that latent heats are calculated under conditions of constant pressure, and normally that that pressure is one atmosphere. Constant pressure processes are common enough that we introduce a new variable to simplify calculations under constant pressure conditions. That quantity is *enthalpy*.

Enthalpy

Enthalpy, H , is defined through

$$H = U + pV.$$

It is possible to use enthalpy to purge heat from our vocabulary. I won't do that because most people still use heat, and you'll need to communicate with others. Basically, the pV term in enthalpy keeps track of expansion/compression related work for us. Starting from the first law in the form

$$dU = dQ - p\Delta V$$

(Let's call this the first law for hydrostatic processes) and the definition

$$C_p = \left(\frac{\partial U}{\partial T} \right)_p + p \left(\frac{\partial V}{\partial T} \right)_p,$$

and inserting H , we can rewrite the expression for C_p in terms of enthalpy. Thus,

$$C_p = \left(\frac{\partial(H - pV)}{\partial T} \right)_p + p \left(\frac{\partial V}{\partial T} \right)_p,$$

or

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p - p \left(\frac{\partial V}{\partial T} \right)_p + p \left(\frac{\partial V}{\partial T} \right)_p,$$

producing the result

$$C_p = \left(\frac{\partial U}{\partial T} \right)_p + p \left(\frac{\partial V}{\partial T} \right)_p = \left(\frac{\partial H}{\partial T} \right)_p.$$

This expression is often taken as the definition of C_p .

Enthalpy and latent heat are simply related. Which, of course is reason that I introduced latent heats in the previous section. The latent heat of vaporization L_v is defined as the difference in enthalpy between a fixed mass of vapor and the same mass of liquid. That is $L_v = H_{vap} - H_{liq}$. Similarly, the latent heat of fusion is given by $L_f = H_{liq} - H_{sol}$, and the latent heat of sublimations is given by $L_s = H_{vap} - H_{sol}$. These enthalpy differences are related through $L_s = L_f + L_v$. We shall explore these relationships further when we study phase transitions and the Clausius-Clapeyron equation later.