

# Heat Capacity, Specific Heat, and Enthalpy

Stephen R. Addison

January 22, 2001

## Introduction

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

## 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  $q = \Delta E + p\Delta V$ , and inserting this into  $C = \frac{q}{\Delta T}$ , we arrive at

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

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

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

For an infinitesimal process we write this as

$$C_v = \left( \frac{q}{dT} \right)_v = \left( \frac{dq}{dT} \right)_v$$

or

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

In the above “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

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

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.

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

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

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

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

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

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

Our author prefers 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

$$H = E + pV.$$

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  $q = \Delta E + p\Delta V$  (Let's call this the first law for hydrostatic processes) and the definition  $C_p = \left(\frac{\partial E}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p$ , 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

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

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 in chapter 12.