

## Heat capacity and the Degrees of Freedom (DoF):

Figure 2.5 is an important diagram. It is important to have a basic understanding that the magnitude of the values of the heat capacity. The example in 2.5 is for the substance  $Cl_2$ .

The heat capacity  $C_{v,m}$  is related to the number of degrees of freedom of the system.

Consider the ideal gas. We know that (from previous supplemental notes) the energy (as kinetic energy) of the gas is proportional to  $PV$ , which is, in turn, related to the temperature by the I.G. EoS (Equation of State).

$$U = \frac{3}{2}PV = \frac{3}{2}nRT$$

From here, we defined the molar heat capacity at constant volume as:

$$C_v = \frac{q}{\Delta T}$$

In a constant volume process  $w = 0$  (no work is done). Therefore, the first law is:

$U = q_v$  and so the heat capacity is related to the change in internal energy upon warming:

$$C_v = \frac{\Delta U}{\Delta T} = \left. \frac{\partial U}{\partial T} \right|_V$$

Here we have written the changes as derivatives and the part where we hold  $V$  fixed is shown by a subscript: Now from the I.G. EoS we can take the derivative to find:

$$C_v = \left. \frac{\partial U}{\partial T} \right|_V = \left. \frac{\partial \left( \frac{3}{2}nRT \right)}{\partial T} \right|_V = \frac{3}{2}nR$$

$$C_{v,m} = \frac{C_v}{n} = \frac{3}{2}R$$

So now we ask: Why the  $(3/2)$ ? The answer is that for each translational degree of freedom we get  $\frac{1}{2}R$  contributing to the heat capacity. The molecule can move in  $x$ ,  $y$  or  $z$ ; and in each direction. As heat enters the system, the molecule's average speed increases. The increase in speed of the molecule means that the temperature increased.

Let's generalize to more complex systems and consider solids and liquids. The idea, which is called the Equipartition of Energy, is that  $\frac{1}{2}R$  will go into each mode that can access the energy (more about that later).

For gaseous He then the heat capacity should be  $C_{v,m} = \frac{3}{2}R = 12.5 J / mol - K$ . And the heat capacity at constant pressure for a gas is always:  $C_{p,m} = C_{v,m} + R = 20.8 J / mol - K$

For a diatomic molecule, like  $H_2$  or  $Cl_2$ , each atom has 3 degrees of freedom. So the diatomic has 6 degrees of freedom. In the gas phase these degrees of freedom are partitioned as 3 translational, 2 rotational, and 1 vibrational DoF. The total number of

DoFs is then 6, as we had to start with. However one of these is vibration. Vibration is special because it really encompasses two ways to store energy. The first way is that the motion of the two atoms relative to each other can change and the second way is that the internal motion (or momentum) of the two atoms can change and thereby absorb heat. Therefore we multiply that by 2, so the total contributing modes is:  $3 + 3 + 1 \cdot 2 = 7$ . The

$$C_{V,m} = \frac{7}{2}R = 29.0J / mol - K$$

expected heat capacity

$$C_{P,m} = \frac{9}{2}R = 37.5J / mol - K$$

An examination of figure 2.5 in your text shows that the heat capacity  $C_{P,m}$  for gaseous  $Cl_2$  is around 30 J/mol-K. What went wrong? The vibrational mode is hard to access. This is because it is a vibration in the infra-red region. Without going into the details, which you will do in statistical mechanics (next in the series), the temperature must be on the order of the oscillation energy in order to have much impact on it. Low temperature is like a soft blow to a hard object, not much happens. The infrared region for the vibration of  $Cl_2$  is comparable to a temperature around 800K. Therefore this mode is not appreciably excited. A closer look at the diagram, figure 2.5, does show that the heat capacity of the gas is up a bit at the higher temperatures (400K) indicating partial use of this mode. At 400K one expects an additional contribution from the vibronic mode of about  $\frac{1}{2}R$ , which is on the order of the change shown in Fig. 2.5. So this method gives an idea of what sort of heat capacity to expect, and generally can be used to bound the experimental heat capacity.

Now let's consider the same  $Cl_2$  but as a solid. For each Cl atom we have 3 degrees of freedom. Because solids and liquids are nearly incompressible it doesn't matter whether the materials are allowed to expand or not, therefore  $C_{V,m} \approx C_{P,m}$ . The atoms can only

vibrate, so the heat capacity should be  $C_{P,m} = \frac{1}{2} \cdot (3 \cdot 2)R = 25.0J / molCl - K$ . This

expression is the law of Dulong and Petit. The law is that all simple substances (metals in particular) have the same molar heat capacity at high temperatures, which is  $C_{V,m} = 3R$ . For the case of  $Cl_2$ , however, we want the molar heat capacity per mole of diatomic molecule. Therefore we must double the value:

$$C_{P,m} = 2 \cdot \frac{6}{2} \cdot R = 50.0J / molCl_2 - K$$

Essentially all of the modes are vibrational for a solid. Therefore for  $Cl_2$  the maximum possible heat capacity should be  $C_{V,m} = 6R$ . If the heat capacity is lower than this it is because some of the vibrational frequencies are too high to be used. This parallels what we saw for the gaseous  $Cl_2$ , in which the one vibronic mode was not fully accessed. In a solid, the frequencies of the vibronic modes span a range that runs from low to high frequencies. At the lower temperatures only the low frequency modes are available to take up heat. When the experimental heat capacity approaches the limit (in our case  $6R$ ), then we can infer that nearly all of the vibrational modes of the solid are actively taking

up energy. Figure 2.5 illustrates well that the heat capacity drops as the temperature drops. This shows that some of the modes of vibration of the solid are at sufficiently high frequencies that they cannot be accessed at low temperatures. At the lowest temperatures the heat capacity is generally proportional to  $T^3$  and goes to zero as the temperature goes to zero.

When the material changes phase, (solid to liquid to gas), the heat capacity is not well defined and is technically infinite because the heat goes into the material but the temperature does not change. So we restrict the meaning of the heat capacity to a substance in a single phase.

As the solid approaches the liquid phase, the solid begins to soften and the frequencies of the modes begin to drop, and so the heat capacity increases. The heat capacity of the liquid is more complex, because there are local clusters that have low energy vibrational modes that can be thermally excited, and individual molecules now can begin to access rotational and translational degrees of freedom as well as the local cluster vibrational modes. The conversion of frequency modes to translation and rotation is not straightforward: A vibrational mode contributes twice as much to the heat capacity as a translational mode, but only if it is accessible. If inaccessible vibrational modes are converted to translational modes then the heat capacity will increase in the liquid relative to the solid. However, if the vibrational modes are already in use then the heat capacity of the liquid could be lower than that of the solid. Moreover the liquid, especially halogens, are somewhat compressible, and this will contribute to (increase)  $C_p$  but not  $C_v$  for the liquid. The theoretical maximum heat capacity for  $Cl_2$  is  $7R$ . Figure 2.5 shows that the liquid phase has a heat capacity of  $8R$ . I do not understand that discrepancy.

Another example is water. Water, maximally can have a constant pressure molar heat capacity of  $(3 \cdot 3 + 1)R$ . Liquid water, experimentally, has a molar heat capacity of  $C_{p,m} = 9.05 \cdot R = 75.3 \text{ J/mol} \cdot \text{K}$ .