15.3: Heat Capacity and Microscopic Changes

Let us turn our attention from the macroscopic to the microscopic level. According to the first law of thermodynamics, the heat energy absorbed as we raise the temperature of a substance cannot be destroyed. But where does it go? In the case of a monatomic gas, like neon, this question is easy to answer. All the energy absorbed is converted into the kinetic energy of the neon molecules (atoms). In other sections, we found that the kinetic energy of the molecules in a sample of gas is given by the expression

$$E_k = \tfrac{3}{2} nRT$$

Thus if the temperature of a sample of neon gas is raised from T_1 to T_2, the kinetic energy of the molecules increases from $^3/_2 \, nRT_1$ to $^3/_2 \, nRT_2$, a total change of

$$\tfrac{3}{2} nR \left(T_2 - T_1 \right) = \left(\tfrac{3}{2} R \right) n \left(T_2 - T_1 \right)$$

Inserting the value of R in appropriate units, we obtain

$$\tfrac{3}{2} \left(8.314 \tfrac{\text{J}}{\text{K mol}} \right) n \left(T_2 - T_1 \right) = \left(12.47 \tfrac{\text{J}}{\text{K mol}} \right) n \left(T_2 - T_1 \right) \tag{15.3.1}$$

This is the same quantity that is obtained by substituting the experimental value of C_V for neon (calculated in Example 2 from Heat Capacities) into Eq. (4) from Heat Capacities. In other words the quantity of heat found experimentally exactly matches the increase in kinetic energy of the molecules required by the kinetic theory of gases.

Table 15.3.1 lists the C_V values not only for neon but for some other gases as well. We immediately notice that only the noble gases and other mon-atomic gases such as Hg and Na have molar heat capacities equal to $^3/_2 R$, or 12.47 J K^{-1} mol^{-1}. All other gases have higher molar heat capacities than this. Moreover, as the table shows, the more complex the molecule, the higher the molar heat capacity of the gas. There is a simple reason for this behavior.

Table 15.3.1: Molar Heat Capacities at Constant Volume (CV) for Various Gases (Values at 298 K Unless Otherwise Stated).

Gas	C_v /J K^{-1} mol^{-1}	Gas	C_v /J K^{-1} mol^{-1}
Monoatomic Gases		**Triatomic Gases**	
Ne	12.47	CO_2	28.81
Ar	12.47	N_2O	30.50
Hg	12.47 (700K)	SO_2	31.56
Na	12.47 (1200K)		
Diatomic Gases		**Alkanes**	
N_2	20.81	CH_4	27.42
O_2	21.06	C_2H_6	44.32
Cl_2	25.62	C_3H_8	65.20
		C_4H_{10}	89.94

A molecule which has two or more atoms is not only capable of moving from one place to another (**translational motion**), it can also *rotate* about itself, and it can change its shape by *vibrating*. When we heat a mole of Cl_2 molecules, for example, we not only need to supply them with enough energy to make them move around faster (increase their translational kinetic energy), we must also supply an additional quantity of energy to make them rotate and vibrate more strongly than before. For a mole of more complex molecules like *n*-butane even more energy is required since the molecule is capable of changing its shape in all sorts of ways. In the butane molecule there are three C—C bonds around which segments of the molecule can rotate freely. All the bonds can bend or stretch, and the whole molecule can rotate as well. Such a molecule is constantly flexing and writhing at room temperature. As we raise the temperature, this kind of movement occurs more rapidly and extra energy must be absorbed in order to make this possible.

When we heat solids and liquids, the situation is somewhat different than for gases. The rapid increase of vapor pressure with temperature makes it virtually impossible to heat a solid or liquid in a closed container, and so heat capacities are always measured at constant pressure rather than at constant volume. Some C_p values for selected simple liquids and solids at the melting point are shown in Table 15.3.2. In general the heat capacities of solids and liquids are higher than those of gases. This is because of the intermolecular forces operating in solids and liquids. When we heat solids and liquids, we need to supply them with potential energy as well as kinetic energy. Among the solids, the heat capacities of the metals are easiest to explain since the solid consists of individual atoms. Each atom can only vibrate in three dimensions. According to a theory first suggested by Einstein, this vibrational energy has the value $3RT$, while the heat capacity is given by $3R$ = 24.9 J K^{-1} mol^{-1}.

Table 15.3.2: Molar Heat Capacities at Constant Pressure Cp for Various Solids and Liquids at the Melting Point.

Substance	C_p (solid)/J K^{-1} mol^{-1}	C_p (liquid)/J K^{-1} mol^{-1}
Monoatomic Substances		
Hg	27.28	27.98
Pb	29.40	30.33
Na	28.20	31.51
Diatomic Substances		
Br$_2$	53.8	75.7
I$_2$	54.5	80.7
HCl	50.5	62.2
HI	47.5	68.6
Polyatomic Substances		
H$_2$O	37.9	76.0
NH$_3$	49.0	77.0
Benzene	129.0	131.0
n-Heptane	146.0	203.1

As can be seen from the table, most monatomic solids have C_p values slightly larger than this. This is because solids expand slightly on heating. The atoms get farther apart and thus increase in potential as well as vibrational energy.

Solids which contain molecules rather than atoms have much higher heat capacities than $3R$. In addition to the vibration of the whole molecule about its site in the crystal lattice, the individual atoms can also vibrate with respect to each other. Occasionally molecules can rotate in the crystal, but usually rotation is only possible when the solid melts. As can be seen from the values for molecular liquids in Table 15.3.2, this sudden ability to rotate causes a sharp increase in the heat capacity. For monatomic substances, where there is no motion corresponding to the rotation of atoms around each other, the heat capacity of the liquid is only very slightly higher than that of the solid.