15.4: Internal Energy

When matter absorbs or releases heat energy, we cannot always explain this energy change on the microscopic level in terms of a speeding up or a slowing down of molecular motion as we do for heat capacities. This is particularly true when the heat change accompanies a chemical change. Here we must consider changes in the kinetic and potential energies of electrons in the atoms and molecules involved, that is, changes in the **electronic energy**.

As a simple example of a chemical change, let us consider an exothermic reaction involving only one kind of atom, the decomposition of ozone, O_3:

$$2\,O_3(g) \rightarrow 3\,O_2(g) \;\; 25\,^\circ C \tag{15.4.1}$$
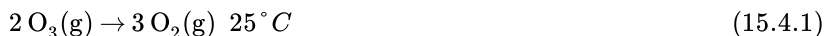
O_3 is a gas which occurs in very low but very important concentrations in the upper atmosphere. It can be produced in somewhat higher concentrations in the laboratory by using an electric spark discharge and can then be concentrated and purified. The result is a blue gas which is dangerously unstable and liable to explode without warning. Let us now suppose that we have a pure sample of 2 mol $O_3(g)$ in a closed container at 25°C and are able to measure the quantity of heat evolved when it subsequently explodes to form O_2 gas according to Eq. 15.4.1 (see Figure 15.4.1). It is found that 287.9 kJ is released. This energy heats up the surroundings.

Where do these 287.9 kJ come from? Certainly not entirely from the translational kinetic energy of the molecules. To begin with we had 2 mol O_3 at 25°C and at the end 3 mol O_2 at 25°C. Since the translational kinetic energy of any gas is $^3/_2\,nRT$, this corresponds to an increase of $^3/_2$ (3 mol − 2 mol)$RT = ^3/_2 \times 1$ mol × 8.314 J K^{-1} mol^{-1} × 298 K = 3.72 kJ. After the reaction the translational energy of the molecules is higher, and so heat should have been absorbed, not given off. In any case 3.73 kJ is only 1.3 percent of the total heat change. The changes in rotational and vibrational energy are even smaller, accounting for a decrease in energy of the substance in the container by only 0.88 kJ.
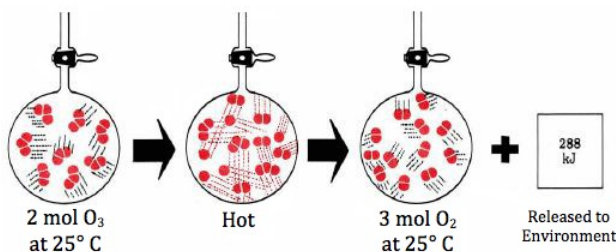

Figure 15.4.1 The reaction 2O₃(g) → 3O₂(g) (25°C). When the atoms in the O₃ molecules rearrange to form O₂ molecules, the result is a lowering in the electronic energy and a consequent release of 288 kJ of heat energy to the surroundings.

From the standpoint of energy, the most important thing that happens as 2 mol O_3 is converted into 3 mol O_2 is rearrangement of the valence electrons so that they are closer to positively charged O nuclei. We see in other sections that the closer electrons are to nuclei, the lower their total energy. Thus three O_2 molecules have less electronic energy than the two O_3 molecules from which they were formed. The remaining energy first appears as kinetic energy of the O_2 molecules. Immediately after the reaction the O_2 is at a very high temperature. Eventually this energy finds its way to the surroundings, and the O_2 cools to room temperature.

A detailed summary of the various energy changes which occur when O_3 reacts to form O_2 is given in Table 15.4.1. The important message of this table is that 99 percent of the energy change is attributable to the change in electronic energy. This is a typical figure for gaseous reactions. What makes a gaseous reaction exothermic or endothermic is the *change in the bonding*. Changes in the energies of molecular motion can usually be neglected by comparison.

TABLE 15.4.1 Detailed Balance Sheet of the Energy Changes Occurring in the Reaction $2O_3(g) \rightarrow 3O_2(g)$ 25°C, constant volume

Type of Energy	Initial Value/kJ	Final Value/kJ	Change*in Energy/kJ
Electronic	x†	$x - 290.70$	−290.70
Translational	7.43	11.15	+3.72
Rotational and vibrational	8.32	7.44	− 0.88
Total	**x + 15.75**	**x − 272.11**	**−287.86**

* Final value – initial value.

† There is no experimental means of determining the initial or final value of the electronic energy—only the change in electronic energy can be measured. Highly accurate calculations of electronic energy from wave-mechanical theory require complicated mathematics end a great deal of computer power. Therefore we have represented the initial electronic energy by x.

The sum of all the different kinds of energy which the molecules of a substance can possess is called the **internal energy** and given the symbol U. (The symbol E also widely used.) In a gas we can regard the internal energy as the sum of the electronic, translational, rotational, and vibrational energies. In the case of liquids and solids the molecules are closer together, and we must include the potential energy due to their interactions with each other. Noncovalent interactions (intermolecular forces) attract one molecule to others. In addition, the motion of one molecule now affects its neighbors, and we can no longer subdivide the energy into neat categories as in the case of a gas.

Measurement of Internal Energy

Equation 15.4.2 tells us how to detect and measure changes in the internal energy of a system. If we carry out any process in a closed container the volume remains constant), the quantity of heat absorbed by the system equals the increase in internal energy.

$$q_V = \triangle U \tag{15.4.2}$$

A convenient device for making such measurements is a bomb calorimeter (Figure 15.4.2), which contains a steel-walled vessel (bomb) with a screw-on gas-tight lid. In the bomb can be placed a weighed sample of a combustible substance together with $O_2(g)$ at about 3 MPa (30 atm) pressure. When the substance is ignited by momentarily passing electrical current through a heating wire, the heat energy released by its combustion raises the temperature of water surrounding the bomb. Measurement of the change in temperature of the water permits calculation of q_V (and thus ΔU), provided the heat capacity of the calorimeter is known.

The heat capacity can be determined as in Example 1 from Heat Capacities or by igniting a substance for which ΔU is already known.
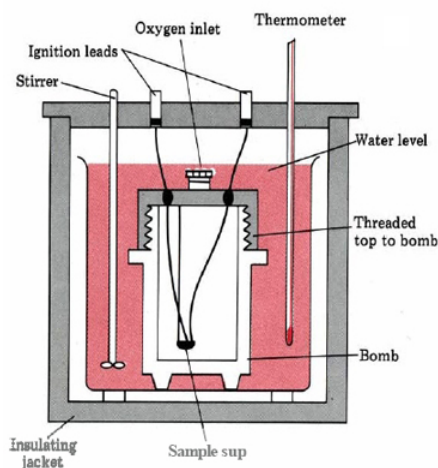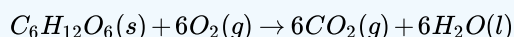

Figure 15.4.2 A schematic of a bomb calorimeter.

> ✔ Example 15.4.1: Energy
>
> When 0.7943g of glucose, $C_6H_{12}O_6$, is ignited in a bomb calorimeter, the temperature rise is found to be 1.841 K. The heat capacity of the calorimeter is 6.746 kJ K^{-1}. Find ΔU_m for the reaction
>
> $$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$
>
> under the prevailing conditions.
>
> **Solution**
>
> The heat energy absorbed by the calorimeter in increasing its temperature by 1.841 K is given by
>
> $$q = C \triangle T = 6.745 \text{kJ K}\hat{\ }\{-1\} * 1.841\text{K} = 12.42\text{kJ}\backslash)$$

Since this heat energy was released by the reaction system, we must regard it as negative. Accordingly,

$$q_V = -12.42\text{kJ} = \triangle U$$

We need now only to calculate the change in internal energy per mole, that is, ΔU_m. Now

$$n_{\text{glucose}} = 0.7953 \text{ g } \times \frac{1 \text{ mol}}{180.16 \text{ g}} = 4.409 \times 10^{-3} \text{ mol}$$

Thus

$$\triangle U_m = \frac{-12.42 kJ}{4.409} \times 10^{-3} \text{mol} = -2817\text{kJ mol}^{-1}$$

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