

## 2.4: Internal Energy (U) and the Equipartition Theorem

As we progress in this course, you will learn that there are four equations for energy. They are the Internal (U), Enthalpy (H), Helmholtz (H) and Gibbs (G) energies. The reason we have four different types of energy is that each is useful under a different set of conditions. To illustrate, if we want to perform a chemical reaction at constant pressure then we must allow the volume of the system's container to change. This is because the reaction might generate a gaseous product, and the pressure would increase if held in a rigid, fixed volume container. As a result, the volume expansion needed to keep pressure constant simultaneously causes a loss of energy due to negative work out of the system. Contrast this to performing the reaction under constant volume conditions, in which there would be no expansion work and thus no loss of energy. This example reveals that the energetics of the reaction are fundamentally different depending on whether it is conducted under constant pressure or constant volume conditions. This in turn requires us to analyze the energy for this chemical process using different equations; this is discussed further in later chapters.

Of the four equations for energy, we will start with the internal energy (U). **Internal energy is the energy of a single molecule**; this includes the energy that it uses to translate, to rotate and vibrate, and to interact with other molecules. Internal energy is a state function, and its differential  $\partial U$  is exact. Since  $\partial U$  is exact then there must be an equation for U, and there is:  $U = \frac{1}{2} k_B T \cdot (\text{degrees of freedom})$

where  $k_B = \frac{R}{N_A}$ , which you can think of as the perfect gas constant for a single molecule. Equation ??? is the Equipartition theorem, which defines internal energy as a function of the molecule's degrees of freedom and temperature. We can determine what are degrees of freedom by logically dissecting what a molecule can "do" and then giving it the thermal energy to do it. We will limit the discussion to gas phase molecules for now to simplify the situation; also, if we discuss the internal energy of a mole of gas molecules then the Equipartition equation is:  $U_m = \frac{1}{2} RT \cdot (\text{degrees of freedom})$ , where  $U_m$  is the internal energy per mole.

Every atom in every molecule has three degrees of freedom (i.e., ways it can move) because we live in a three-dimensional universe. Furthermore, the number of degrees of freedom for the N atoms adds together; thus, every molecule has a total of 3N degrees of freedom. The Equipartition theorem states that thermal energy flows into and out of these motions equally by an amount  $\frac{1}{2} k_B T$ . Thus, every molecule ought to have  $3N \cdot \frac{1}{2} k_B T$  of internal energy by virtue of the fact it has N atoms at a finite temperature. For example, monatomic argon gas (N=1) has three degrees of translational freedom. Heating a vessel of argon gas causes the atoms to move faster, raising the energy of each individual Ar atom. And if the vessel is cooled, the atoms slow down which lowers their U; in either case the internal energy per mole of argon is  $U_m = \frac{3}{2} RT$ . The degrees of freedom of an actual molecule like O<sub>2</sub> include rotation and vibration on top of the three translations. Thus, heating a mole of gaseous O<sub>2</sub> results in the molecules translating, rotating, and vibrating more such that there *should be* 3RT of internal energy.

However, there is a catch. If  $U = 3N \cdot \frac{1}{2} k_B T$  to be true every single degree of freedom must be able to absorb and/or release thermal energy. Experimental measurements demonstrate that the internal energy of a mole of O<sub>2</sub> near room temperature is  $\sim \frac{5}{2} RT$ , not 3RT as expected, which means that one degree of freedom is not contributing to  $U_m$ . To discover which one, let's first think about what the degrees of freedom are and then count them. Since we live in a 3-dimensional world, everything has at least three translational degrees of freedom (x, y, and z). For an N-atom molecule, the translational degrees of freedom are for all the atoms moving together in the same direction. Aside translation, the atoms may be moving in such a way that the molecule is rotating. For linear O<sub>2</sub> there are two ways to rotate, one is like a forward flip and the other is a sideways somersault as shown in Figure 2.7. For a non-linear molecule like methane, there are three ways to rotate including the flip, somersault, and a pirouette (Google "pirouette" if you don't know what that is or look at Figure 2.7). Now we need to count the number of vibrations. To do this, we note that all molecules have a total of 3N degrees of freedom. We subtract from this the 3 translations+2 rotations for a linear molecule like O<sub>2</sub>, leaving us with 3N-5 vibrations. Consequently, O<sub>2</sub> has one vibrational degree of freedom. Similarly, there are 3N-6 vibrations for non-linear molecules like CH<sub>4</sub>.

Concerning O<sub>2</sub>, it must be true that the single vibration is not contributing to  $U_m$ . To explain, we have to use some quantum mechanics which dictates how molecules vibrate. Quantum mechanics works with an "all or nothing" principle when it comes to changes of energy, meaning that you cannot simply add a small amount of heat to make a bond vibrate a little more. You must add a specific amount of energy (a "quantum") to excite a vibration, and this tends to be much larger than  $\frac{1}{2} k_B T$  at room temperature. Thus, vibrations do not *practically* count towards a molecule's internal energy. This is equivalent to stating you cannot "store" heat energy in vibrations. To summarize, Table 1.1 provides a list of molecules, their degrees of freedom,  $U_m$ , and the same at terrestrial temperatures where vibrations are "frozen out".

Molecule	Degrees of Freedom	$U_m$	Terrestrial $U_m$
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	Molecule	Degrees of Freedom	$U_m$	Terrestrial $U_m$	
	Ar	3 translational	$3/2 RT 12.471 \text{ J/mol}$	$3/2 RT 12.471 \text{ J/mol}$	
	O <sub>2</sub>	3 translational, 2 rotational, $3 \times 2 - 5 = 1$ vibrational	$3 RT 24.942 \text{ J/mol}$	$5/2 RT 20.785 \text{ J/mol}$	
	CO <sub>2</sub>	3 translational, 2 rotational, $3 \times 3 - 5 = 4$ vibrational	$9/2 RT 37.413 \text{ J/mol}$	$5/2 RT 20.785 \text{ J/mol}$	
	CH <sub>4</sub>	3 translational, 3 rotational, $3 \times 5 - 6 = 9$ vibrational	$15/2 RT 62.355 \text{ J/mol}$	$3 RT 24.942 \text{ J/mol}$	

**2.5.1 Internal energy change due to work.** As we make progress in our understanding of thermodynamics, we will continuously introduce new thermodynamic variables and ways to calculate their change under various conditions. For example, in the previous section we discussed how to calculate reversible and irreversible work at constant temperature. Now we are requesting you to calculate the changes in  $U$ . Fortunately, under isothermal conditions this is incredibly easy because  $\Delta U = 0 \text{ J}$ . This is the result of the fact that, if the temperature doesn't change, nor does the number of atoms in the molecule nor the gas constant (that's a joke fy), then the  $U$  of the gas molecule also doesn't change. This is evident from the differential of the equipartition theorem:  $\partial U = \frac{1}{2} k_B \cdot (\text{degrees of freedom}) \cdot \partial T$ . Hence, if  $\partial T = 0 \text{ K}$ , then  $\partial U = 0 \text{ J}$ !

We can raise the bar further- what are the heat transactions associated with performing isothermal reversible and irreversible work? First, we must specify that heat is rather narrowly defined as an exchange of energy between the exterior and the system. Furthermore, since  $\int \partial U = 0 \text{ J} = \Delta w + \Delta q$ , then  $\Delta q = -\Delta w$ . Basically, the change in work energy is counterbalanced by an exchange of heat energy, which is why the temperature doesn't change. This also keeps  $U$  constant. Example problem 2.5 below illustrates this and several other principles. It also demonstrates an important point, that being that the individual heat transactions can be added to determine the net heat transaction. This is a manifestation of the 1<sup>st</sup> law of thermodynamics:

#### ***Energy cannot be created nor destroyed***

Rather, it just gets shuffled around. Also, the example problem shows that the work resulted in a net release of heat to the environment because  $\Delta q$  is negative. As we will see in Chapter 4, this results in an increase in the entropy of the Universe, which is why we call this process irreversible. And did you notice that the reversible process presented in example problem 2.3 and 2.4 has a  $\Delta q_{tot} = \Delta q_1 + \Delta q_2 = 0 \text{ J}$ ? This is one reason why we call this process reversible.

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