29.3: Internal Energy of a Gas

The internal energy of a gas is defined to be the total energy of the gas when the center of mass of the gas is at rest. The internal energy consists of the kinetic energy, K , of the center-of-mass motions of the molecules; the potential energy U_{inter} associated with the intermolecular interactions, U_{inter}; and the potential energy U_{inter} associated with the intramolecular interactions such as vibrational motion;

$$E_{\text{intermal}} = K + U_{\text{inter}} + U_{\text{intra}}$$

Generally, the intermolecular force associated with the potential energy is repulsive for small r and attractive for large r , where r is the separation between molecules. At low temperatures, when the average kinetic energy is small, the molecules can form bound states with negative energy $E_{\text{internal}} < 0$ and condense into liquids or solids. The internal intermolecular forces act like restoring forces about an equilibrium distance between atoms, a distance at which the potential energy is a minimum. For energies near the potential minimum, the atoms vibrate like springs. For larger (but still negative) energies, the atoms still vibrate but no longer like springs and with larger amplitudes, undergoing thermal expansion. At higher temperatures, due to larger average kinetic energies, the internal energy becomes positive, $E_{\text{internal}} < 0$. In this case, molecules have enough energy to escape intermolecular forces and become a gas.

Degrees of Freedom

Each individual gas molecule can translate in any spatial direction. In addition, the individual atoms can rotate about any axis. Multi-atomic gas molecules may undergo rotational motions associated with the structure of the molecule. Additionally, there may be intermolecular vibrational motion between nearby gas particles, and vibrational motion arising from intramolecular forces between atoms that form the molecules. Further, there may be more contributions to the internal energy due to the internal structure of the individual atoms. Any type of motion that contributes a quadratic term in some generalized coordinate to the internal energy is called a degree of freedom. Examples include the displacement x of a particle undergoing one-dimensional simple harmonic motion position with a corresponding contribution of $(1/2)kx^2$ to the potential energy, the x -component of the velocity v_x for translational motion with a corresponding contribution of $(1/2)mv_x^2$ to the kinetic energy, and z -component of angular velocity ω_z for rotational motion with a corresponding contribution of $(1/2)I_z\omega_z^2$ to the rotational kinetic energy where I_z is the moment of inertia about the z-axis. A single atom can have three translational degrees of freedom and three rotational degrees of freedom, as well as internal degrees of freedom associated with its atomic structure.

Equipartition of Energy

We shall make our first assumption about how the internal energy distributes itself among N gas molecules, as follows:

Each independent degree of freedom has an equal amount of energy equal to $(1/2)kT$,

where the constant k is called the Boltzmann constant and is equal to

$$k = 1.3806505 \times 10^{-23} \mathrm{J} \cdot \mathrm{K}^{-1}$$

The total internal energy of the ideal gas is then

$$E_{\text{internal}} = N(\# of degrees of freedom)\frac{1}{2}kT$$

This equal division of the energy is called the equipartition of the energy. The Boltzmann constant is an arbitrary constant and fixes a choice of temperature scale. Its value is chosen such that the temperature scale in Equation (29.3.2) closely agrees with the temperature scales discussed in Section 29.2.

According to our classical theory of the gas, all of these modes (translational, rotational, vibrational) should be equally occupied at all temperatures but in fact they are not. This important deviation from classical physics was historically the first instance where a more detailed model of the atom was needed to correctly describe the experimental observations.

Not all of the three rotational degrees of freedom contribute to the energy at all temperatures. As an example, a nitrogen molecule, N_2, has three translational degrees of freedom but only two rotational degrees of freedom at temperatures lower than the temperature at which the diatomic molecule would dissociate (the theory of quantum mechanics in necessary to understand this phenomenon). Diatomic nitrogen also has an intramolecular vibrational degree of freedom that does not contribute to the internal energy at room temperatures. As discussed in Section 29.6, N_2 constitutes most of the earth's atmosphere (\sim 78%).

Example 29.1 Diatomic Nitrogen Gas

What is the internal energy of the diatomic N_2 gas?

Solution

At room temperature, the internal energy is due to only the five degrees of freedom associated with the three translational and two rotational degrees of freedom,

$$E_{\text{intemal }}=N \frac{5}{2} k T$$

As discussed above, at temperatures well above room temperature, but low enough for nitrogen to form diatomic molecules, there is an additional vibrational degree of freedom. Therefore there are six degrees of freedom and so the internal energy is

$$E_{\text{intemal }}=N(\# of degrees of freedom) \frac{1}{2} k T=3 N k T$$

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