

Intermolecular Forces and Ideal Behaviour of Gases

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Introduction:

Intermolecular forces are the attractive forces between molecules. They are responsible for the non-ideal behaviour of gases. They exert even more influence in the condensed phases of matter liquids and solids. As the temperature of a gas drops, the average kinetic energy of its molecules decreases. Eventually, at a sufficiently low temperature, the molecules no longer have enough energy to break away from the attraction of neighbouring molecules. At this point, the molecules aggregate to form small drops of liquid. This transition from the gaseous to the liquid phase is known as condensation. In contrast to intermolecular forces, intramolecular forces hold atoms together in a molecule. Intramolecular forces stabilize individual molecules, whereas intermolecular forces are primarily responsible for the bulk properties of matter.

Intermolecular forces are much weaker than intramolecular forces. Much less energy is usually required to evaporate a liquid than to break the bonds in the molecules of the liquid. For example, it takes about 41 kJ of energy to vaporize 1 mole of water at its boiling point; but about 930 kJ of energy are necessary to break the two O–H bonds in 1 mole of water molecules. The boiling points of substances often reflect the strength of the intermolecular forces operating among the molecules. At the boiling point, enough energy must be supplied to overcome the attractive forces among molecules before they can enter the vapour phase. If it takes more energy to separate molecules of substance A than of substance B because A molecules are held together by stronger intermolecular forces, then the boiling point of A is higher than that of B. The same principle applies also to the melting points of the substances.

Melting points of substances increase with the strength of the intermolecular forces. In order to discuss the properties of condensed matter, we must understand the different types of intermolecular forces. Dipole-dipole, dipole-induced dipole, and dispersion forces make up what chemists commonly refer to as van der Waals forces, after the Dutch physicist Johannes van der Waals. Ions and dipoles are attracted to one another by electrostatic forces called ion-dipole forces, which are not van der Waals forces. Hydrogen bonding is a particularly strong type of dipole-dipole interaction. Depending on the phase of a substance, the nature of chemical bonds, and the types of elements present, more than one type of interaction may contribute to the total attraction between molecules. Let us discuss in detail.

Dipole-Dipole Forces:

Dipole-dipole forces are attractive forces between polar molecules, that is, between molecules that possess dipole moments. Their origin is electrostatic, and they can be understood in terms of Coulomb's law. The larger the dipole moment, the greater the force.

Ion-Dipole Forces:

Coulomb's law also explains ion-dipole forces, which attract an ion and a polar molecule to each other. The strength of this interaction depends on the charge and size of the ion and on the magnitude of the dipole moment and size of the molecule. The charges on cations are generally more concentrated, because cations are usually smaller than anions. Therefore, a cation interacts more strongly with dipoles than does an anion having a charge of the same magnitude.

Dispersion Forces:

If we place an ion or a polar molecule near an atom, the electron distribution of the atom (or molecule) is distorted by the force exerted by the ion or the polar molecule, resulting in a kind of dipole. The dipole in the atom is said to be an induced dipole because the separation of positive and negative charges in the atom is due to the proximity of an ion or a polar molecule. The attractive interaction between an ion and the induced dipole is called ion-induced dipole interaction, and the attractive interaction between a polar molecule and the induced dipole is called dipole-induced dipole interaction. The likelihood of a dipole moment being induced depends not only on the charge on the ion or the strength of the dipole but also on the polarizability of the atom or molecule that is, the ease with which the electron distribution in the atom (or molecule) can be distorted. Generally, the larger the number of electrons and the more diffuse the electron cloud in the atom or molecule, the greater its polarizability. By diffuse cloud we mean an electron cloud that is spread over an appreciable volume, so that the electrons are not held tightly by the nucleus.

Polarizability allows gases containing atoms or nonpolar molecules to condense. In a helium atom, the electrons are moving at some distance from the nucleus. At any instant it is likely that the atom has a dipole moment created by the specific positions of the electrons. This dipole moment is called an instantaneous dipole because it lasts for just a tiny fraction of a second. In the next instant, the electrons are in different locations and the atom has a new

instantaneous dipole, and so on. Averaged over time however, the atom has no dipole moment because the instantaneous dipoles all cancel one another. In a collection of He atoms, an instantaneous dipole of one He atom can induce a dipole in each of its nearest neighbours. At the next moment, a different instantaneous dipole can create temporary dipoles in the surrounding He atoms. The important point is that this kind of interaction produces dispersion forces, attractive forces that arise as a result of temporary dipoles induced in atoms or molecules. At very low temperatures, dispersion forces are strong enough to hold He atoms together, causing the gas to condense. The attraction between nonpolar molecules can be explained similarly. A quantum mechanical interpretation of temporary dipoles was provided by the German physicist Fritz London in 1930. London showed that the magnitude of this attractive interaction is directly proportional to the polarizability of the atom or molecule. As we might expect, dispersion forces may be quite weak.

Dispersion forces, which are also called London forces, usually increase with molar mass because molecules with larger molar mass tend to have more electrons, and dispersion forces increase in strength with the number of electrons. Furthermore, larger molar mass often means a bigger atom whose electron distribution is more easily disturbed because the outer electrons are less tightly held by the nuclei. The melting point increases as the number of electrons in the molecule increases. Because these are all nonpolar molecules, the only attractive intermolecular forces present are the dispersion forces. In many cases, dispersion forces are comparable to or even greater than the dipole-dipole forces between polar molecules.

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