Chapter 8

Polarity and intramolecular forces

Polarity of the bond

- The **electronegativity** is one of the factors that contributes to the polarity of the bond.
- Atoms of elements with ***widely*** different electronegativities tend to form ionic bonds. Ionic bonds involve atoms of a metal (low electronegativity) and a non-metal (high electronegativity) elements.
- **Ionic bond is highly polar (complete – or + charges) as the transfer of the electron(s) is nearly complete.**

Polarity of the bond

- Most covalent bonds involve atoms of nonmetallic elements.
- In molecules that contain atoms of the same element, the sharing of an electron pair by the two atoms is equal. This results in **non-polar covalent bond.**
- However, in molecules that have different atoms and hence have different electronegativities, the sharing of bonding electrons is unequal. This results in a **polar covalent bond** (a **dipole** is established). The size of a dipole is measured by its **dipole moment**.

Polarity of the bond

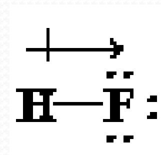
Nonpolar covalent bond
Bonding electrons shared equally between two atoms.
No charges on atoms.

Polar covalent bond
Bonding electrons shared unequally between two atoms.
Partial charges on atoms.

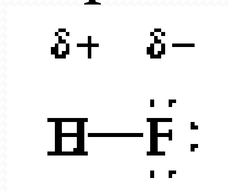
Ionic bond
Complete transfer of one or more valence electrons.
Full charges on resulting ions.

Dipole Moments

- The shift of electron density toward the most electronegative atom is symbolized by placing a crossed arrow (+⟶) above the Lewis structure to indicate the direction of the shift.
- For example,



- The consequent charge separation can be represented as:



- Where δ (delta) denotes a partial charge.
- A quantitative measure of the polarity of a bond is its dipole moment (μ) which is the product of the charge Q and the distance r between the charges:

$$\mu = Q \times r$$

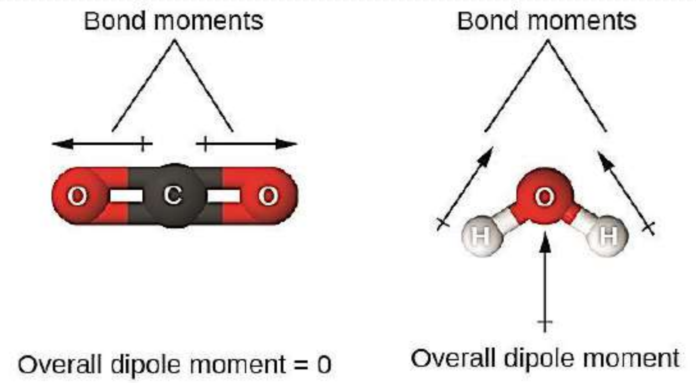
Dipole Moments of diatomic molecules

- For diatomic molecules the change in the difference in electronegativity is the more important factor on the dipole moment.
- The greater the difference between the electron-attracting ability of two atoms joined by a covalent bond, the more polar the bond, and the larger the magnitude of the partial charges.

Compound	Electronegativity Difference	Dipole Moment (D)
HF	1.9	1.82
HCl	0.9	1.08
HBr	0.7	0.82
HI	0.4	0.44

Dipole Moments of polyatomic molecules

- For a molecule made up of three or more atoms, both the polarity of the bonds (determined by difference in electronegativity) and the molecular geometry determine whether there is a dipole moment. In this case, even if polar bonds are present, the molecule will not necessarily have a dipole moment.
- The bond moment is a vector quantity, which means that it has both magnitude and direction. The measured dipole moment is equal to the vector sum of the bond moments.



Molecular Dipole Moments

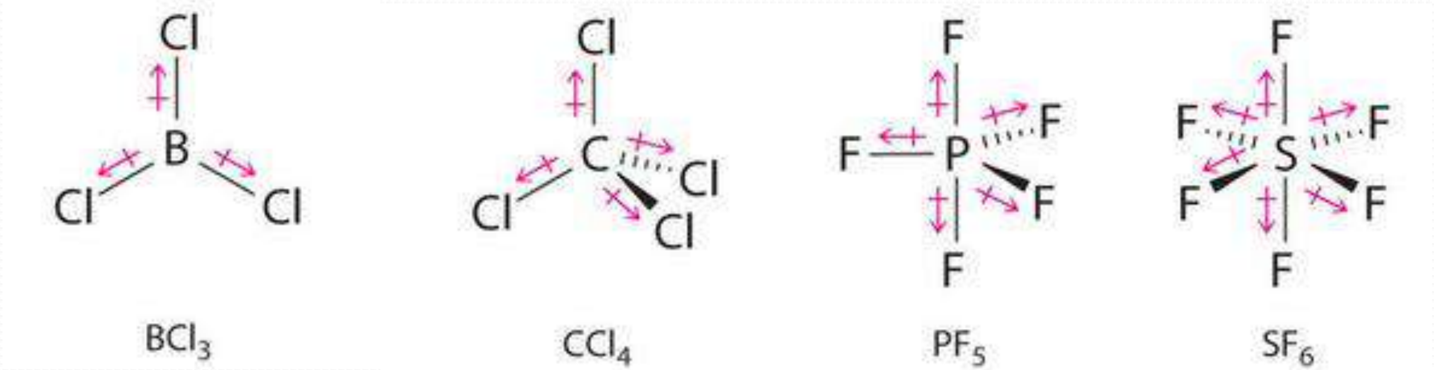
- **To summarize, to be polar, a molecule must:**

I. Contain at least one polar covalent bond.

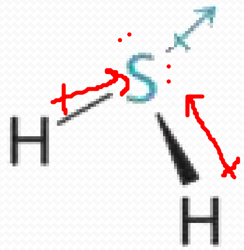
II. Have a molecular geometry such that the sum of the vectors of each bond dipole moment does not cancel.

Molecular Dipole Moments

- When we examine the highly symmetrical molecules as BF_3, CH_4, PF_5, and SF_6, in which all the polar bonds are identical, the molecules are nonpolar. The bonds in these molecules are arranged such that their dipoles cancel.

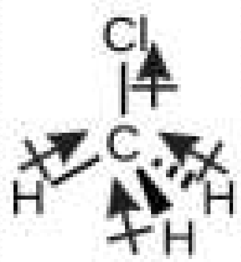


- However, molecules that have identical bonds and lone pairs on the central atoms have bond dipoles that do not cancel as H_2S, H_2O and NH_3.



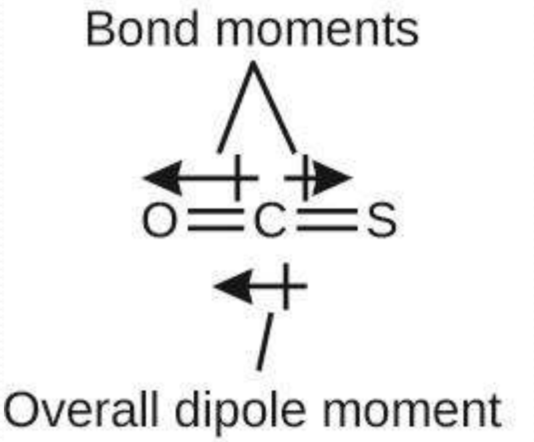
Molecular Dipole Moments

- Chloromethane, CH_3Cl, is a polar molecule.

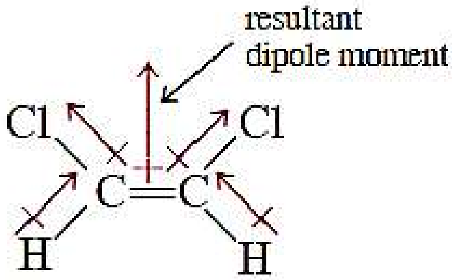


Although the polar C–Cl and C–H bonds are arranged in a tetrahedral geometry, the C–Cl bonds have a larger bond moment than the C–H bond, and the bond moments do not completely cancel each other.

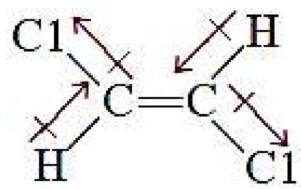
- The OCS molecule is polar, the C–O bonds have a larger bond moment than the C–S bond, and the bond moments do not completely cancel each other.



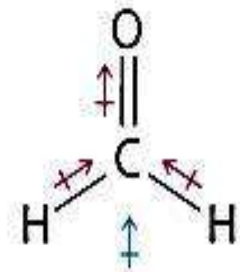
Examples



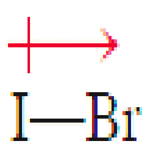
cis-dichloroethylene
$\mu = 1.89$ D

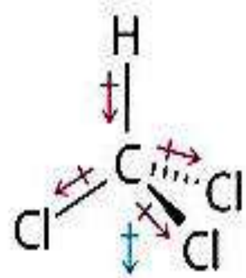


trans-dichloroethylene
$\mu = 0$

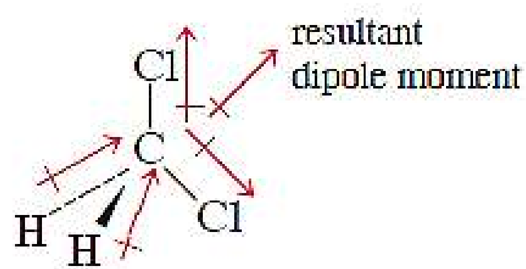


CH_2O





$CHCl_3$



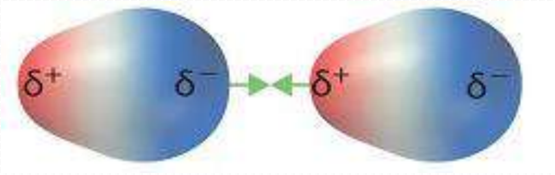
Intermolecular forces

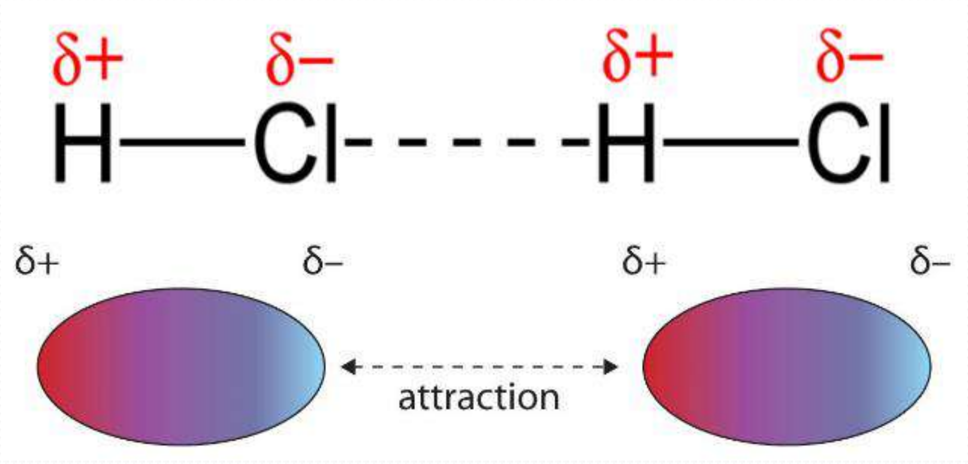
- Intermolecular forces are attractive forces between molecules or units.
- Intermolecular forces are much weaker than the intramolecular forces of attraction but are important because they determine the physical properties of molecules like their boiling point, melting point.
- The boiling and melting points of substances often reflect the strength of the intermolecular forces operating among the molecules. It takes more energy to separate molecules that are held together by stronger intermolecular forces.

Types of intermolecular forces

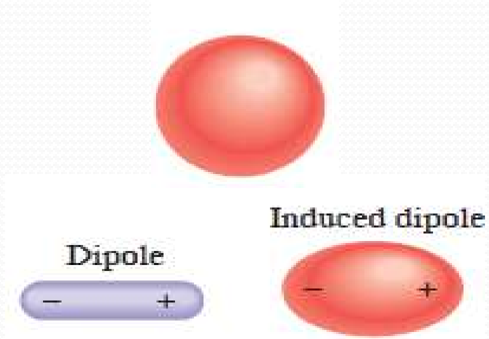
1- Van der waals forces:

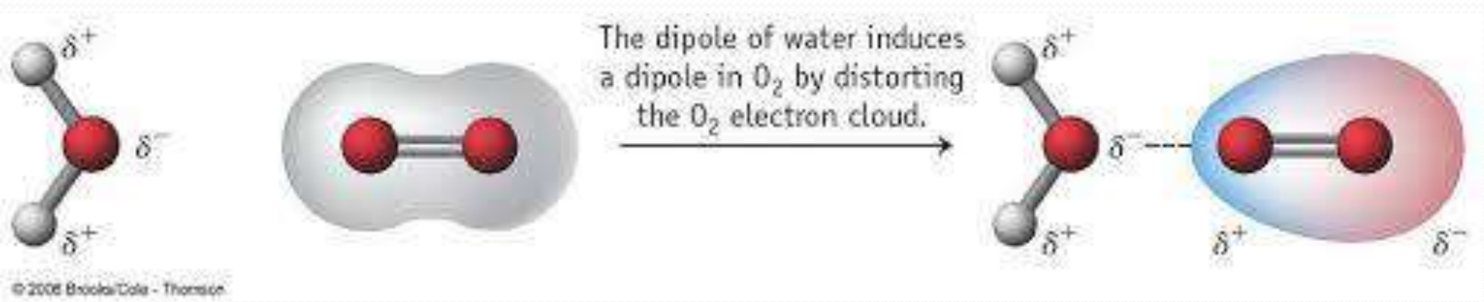
a- Dipole-dipole: are electrostatic attractive forces between polar molecules, that is, between molecules that possess permanent dipole moments. The larger the dipole moment, the greater the force (e.g. the forces between HF molecules)





- **b- Dipole-induced dipole:** are electrostatic attractive interaction between a polar and non-polar molecules. The electron distribution of the non-polar molecule is distorted by the force exerted by polar molecule.





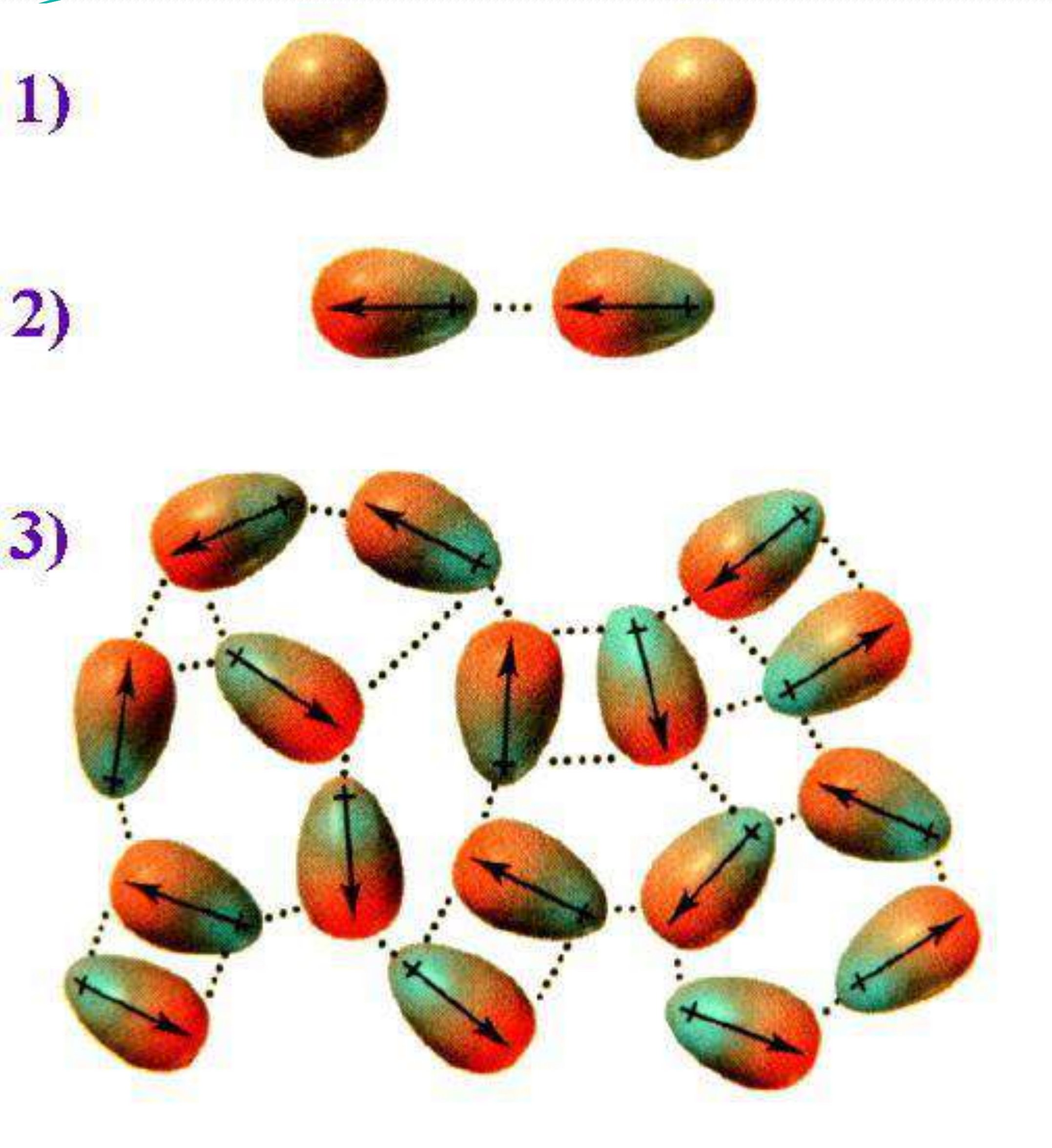
c- Dispersion forces (London): (induced dipole-induced dipole)

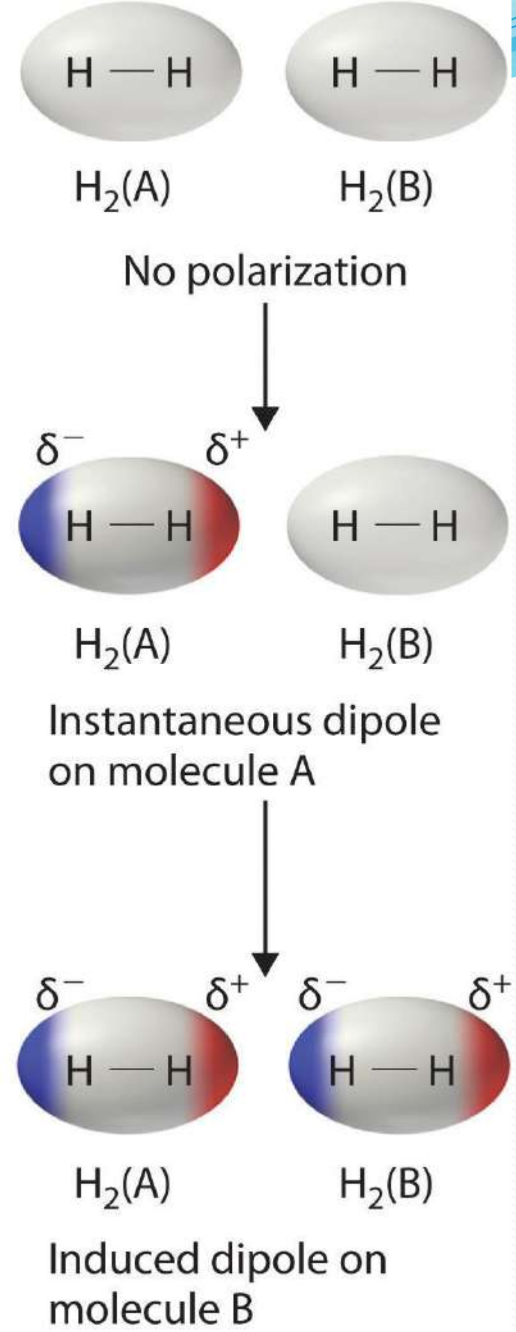
it is the main intermolecular forces between nonpolar molecules. They are electrostatic attractive forces that arise as a result of temporary dipoles induced in atoms or molecules or ions at any instant created by the specific positions of the electrons.

Dispersion forces are the weakest intermolecular forces that exist among species of all types.

Dispersion 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 that are less tightly held by the nuclei.

As expected, the melting point or boiling points increases as the molar mass increases.


1)
2)
3)


H — H
H — H
H2(A)
H2(B)
No polarization
δ−
δ+
H — H
H — H
H2(A)
H2(B)
Instantaneous dipole on molecule A
δ−
δ+
δ−
δ+
H — H
H — H
H2(A)
H2(B)
Induced dipole on molecule B

Example 1

Melting Points of Similar Nonpolar Compounds	
Compound	Melting Point (°C)
CH_4	−182.5
CF_4	−150.0
CCl_4	−23.0
CBr_4	90.0
CI_4	171.0

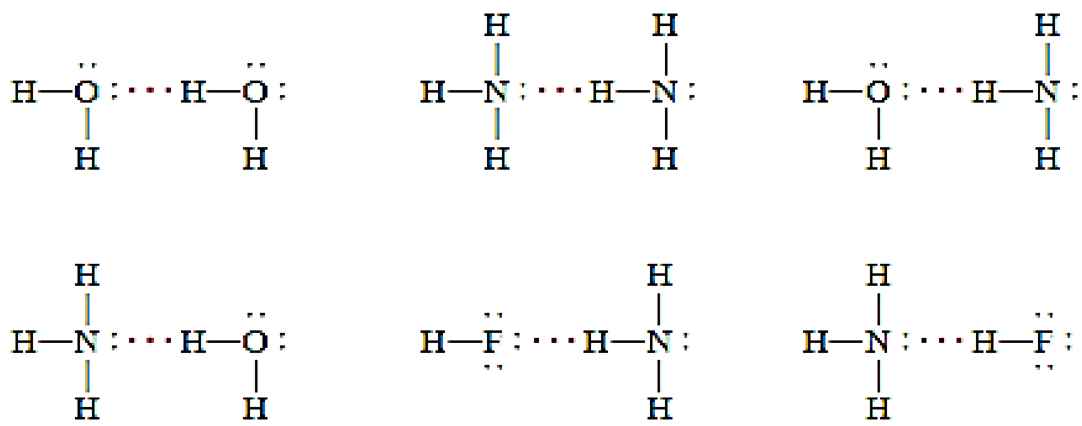
Example 2

The boiling points of CH3F (-78.4C) and CCl4 (76.5C). Although CH3F has a dipole moment of 1.8 D, it boils at a much lower temperature than CCl4, a nonpolar molecule. CCl4 boils at a higher temperature simply because it contains more electrons.

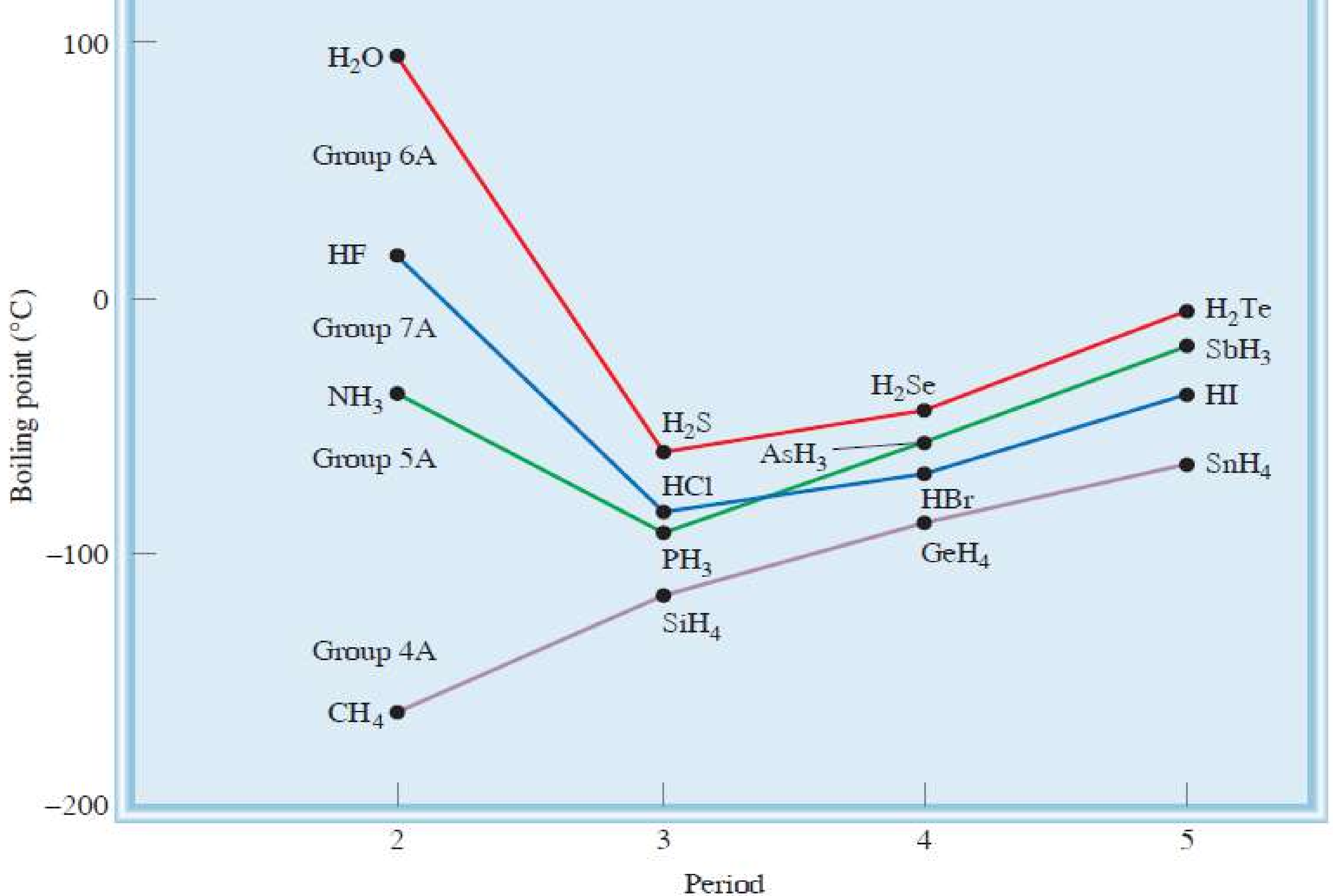
As a result, the dispersion forces between CCl4 molecules are stronger than the dispersion forces plus the dipole-dipole forces between CH3F molecules.

2- Hydrogen bonding:

It is a particularly strong type of dipole-dipole interaction between the hydrogen atom in a polar bond, such as N—H, O—H, or F—H, and an electronegative O, N, or F atom. Note that the O, N, and F atoms all possess at least one lone pair that can interact with the hydrogen atom in hydrogen bonding. Molecular compounds tend to form hydrogen bonds show higher boiling points.



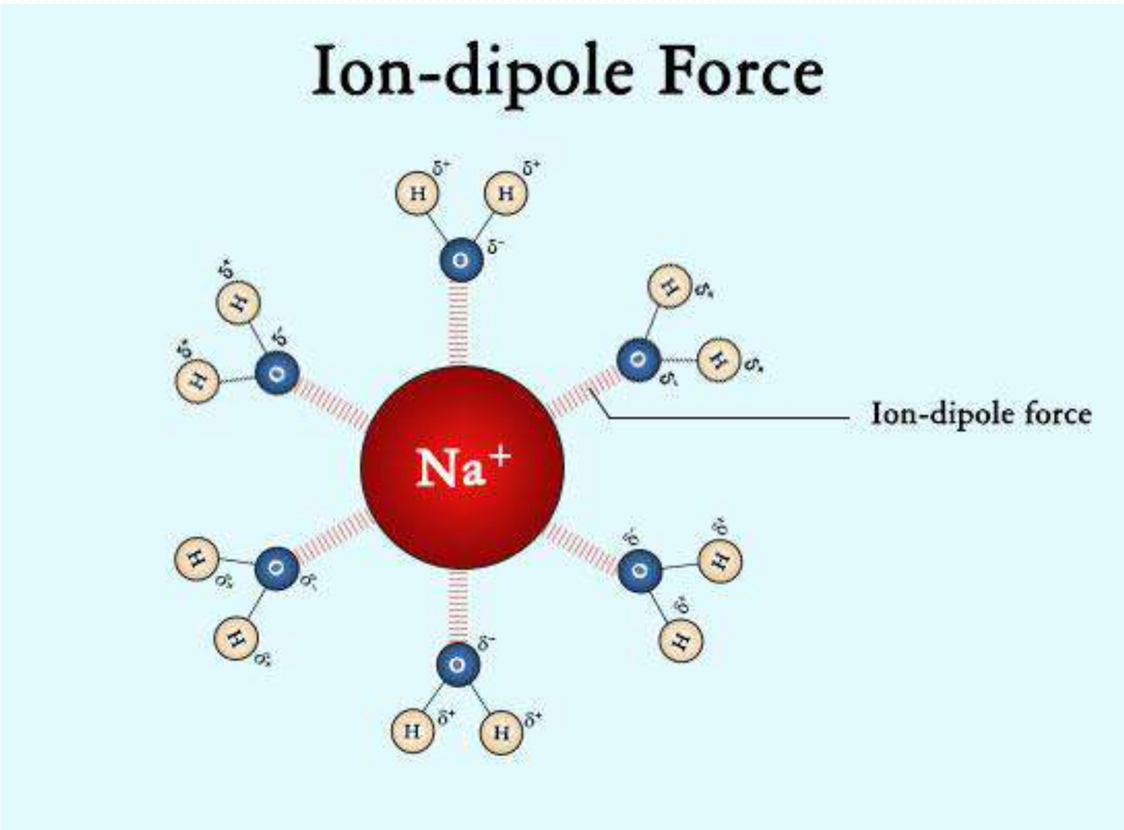
Hydrogen bonding in water, ammonia, and hydrogen fluoride. Solid lines represent covalent bonds, and dotted lines represent hydrogen bonds.

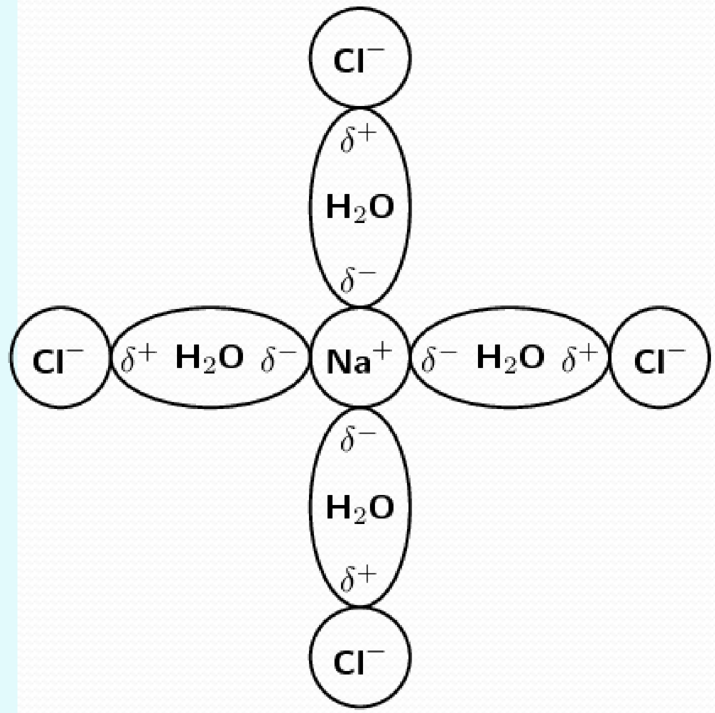


Boiling points of the hydrogen compounds of Groups 4A, 5A, 6A, and 7A elements. Although normally we expect the boiling point to increase as we move down a group with increasing molar mass, we see that three compounds (NH_3, H_2O, and HF) behave differently. The anomaly can be explained in terms of intermolecular hydrogen bonding.

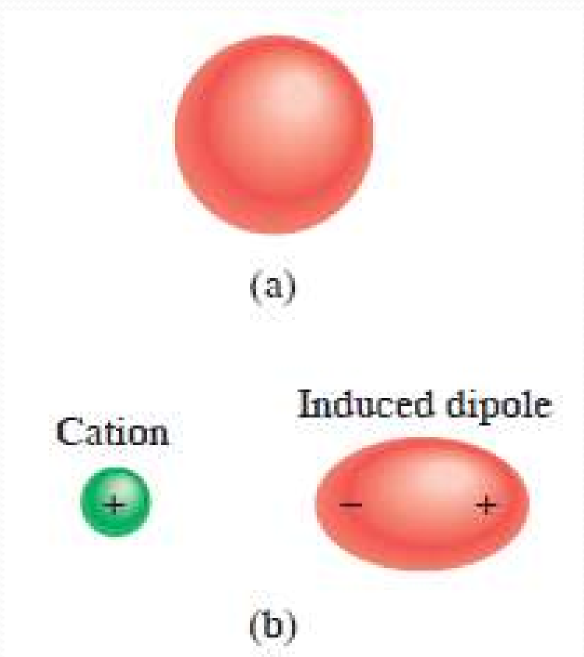
3- Ions-dipoles forces: these are electrostatic forces between ions and polar molecules.

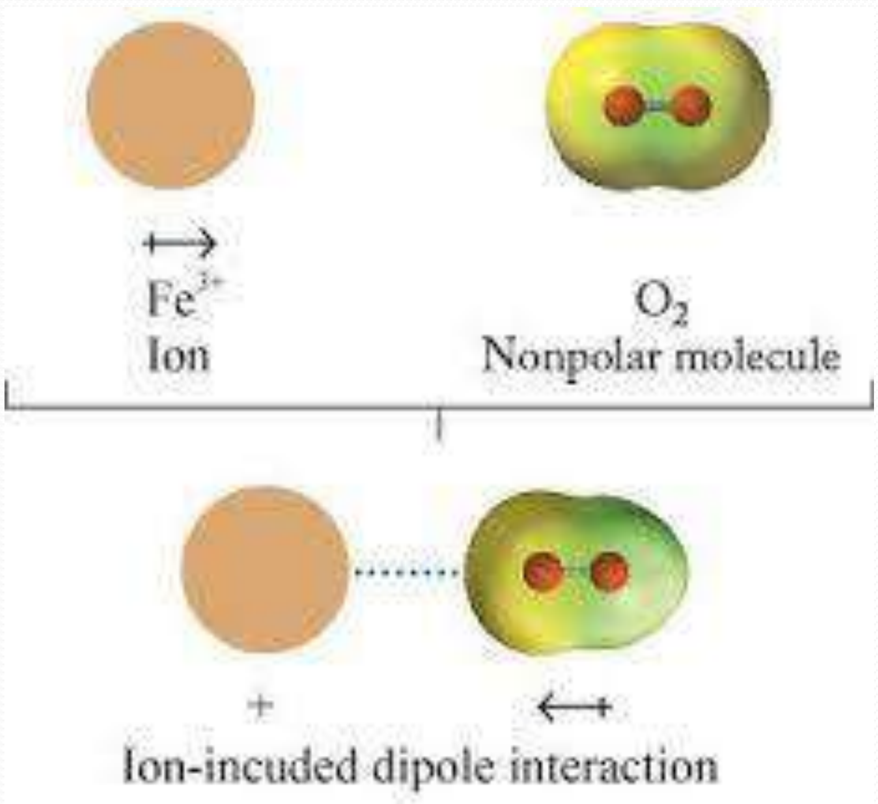
Hydration is one example of ion-dipole interactions.



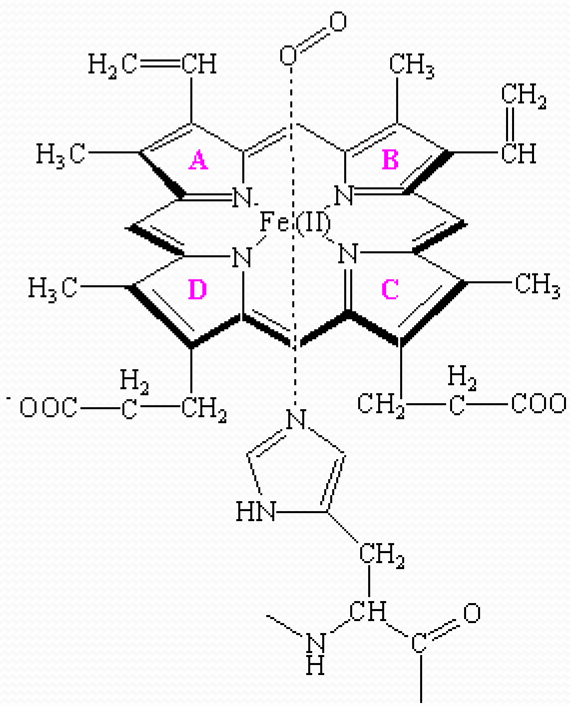


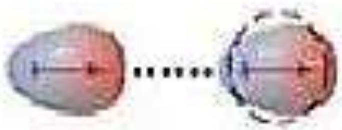
4- Ions-induced dipoles forces: these are electrostatic forces between ions and non polar molecules.





Hemoglobin molecule carrying Oxygen molecule



Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Ion-dipole		Ion charge–dipole charge	40–600	$Na^+ \cdots OH_2$
H bond	$\overset{\delta-}{-A}-\overset{\delta+}{H}\cdots\cdots:\overset{\delta-}{B}-$	Polar bond to H–dipole charge (high EN of N, O, F)	10–40	$:\ddot{O}(H)-H\cdots:\ddot{O}(H)-H$
Dipole-dipole		Dipole charges	5–25	I—Cl···I—Cl
Ion–induced dipole		Ion charge–polarizable e^- cloud	3–15	$Fe^{2+}\cdots O_2$
Dipole–induced dipole		Dipole charge–polarizable e^- cloud	2–10	H—Cl···Cl—Cl
Dispersion (London)		Polarizable e^- clouds	0.05–40	F—F···F—F