Chapter 8

Polarity and intramolecular forces

Polarity of the bond

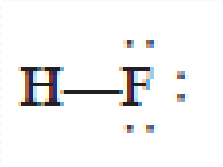
- The electronegativity is one of the factors that contributes to the polarity of the bond.
- Atoms of elements with ***widely*** different electronegativities tend to form ionic bonds. Ionic bonds involve atoms of a metal (low electronegativity) and a non-metal (high electronegativity) elements.
- **Ionic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

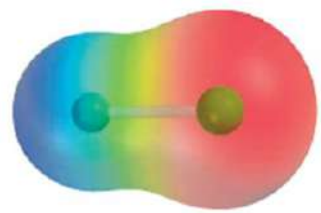
Polarity of the bond

- Most covalent bonds involve atoms of nonmetallic elements.
- Only atoms of the same element, which have the same electronegativity can be joined by a pure covalent bond (no shift in electrons) as the sharing of an electron pair by two atoms is equal that is, the electrons spend the same amount of time in the vicinity of each atom. This results in **non-polar covalent bond.**

Polarity of the bond

- However, in the covalently bonded HF molecule, the H and F atoms do not share the bonding electrons equally because H and F are different atoms and hence have different electronegativities. That means, the electrons spend more time in the vicinity of the more electronegative atom than the other. This results in a **polar covalent bond.**
- We can think of this unequal sharing of electrons as a partial electron transfer or a shift in electron density from H to F.





- Whenever two electrical charges of equal magnitude but opposite sign are separated by a distance, a **dipole** is established. Thus, the HF molecule has a dipole. The size of a dipole is measured by its **dipole moment**.

Polarity of the bond

(a)

Nonpolar covalent bond

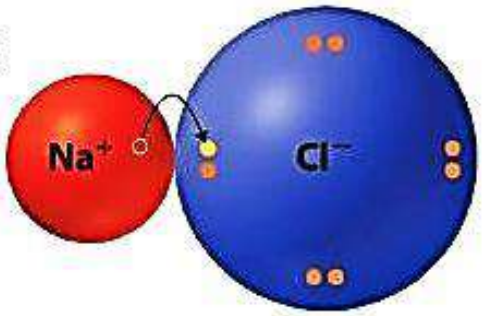
Bonding electrons shared equally between two atoms.
No charges on atoms.

(b)

Polar covalent bond

Bonding electrons shared unequally between two atoms.
Partial charges on atoms.

(c)

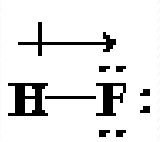


Ionic bond

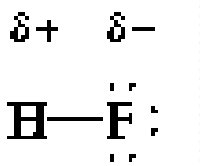
Complete transfer of one or more valence electrons.
Full charges on resulting ions.

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:

$$\mu = Q \times r$$

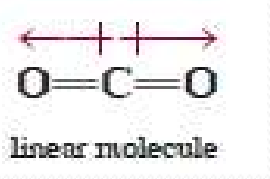
Dipole Moments of diatomic molecules

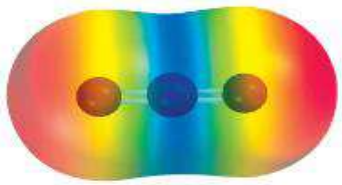
- The following table presents dipole moments of the hydrogen halides. As we proceed from HF to HI, the electronegativity difference decreases. This decreases the amount of charge separated and causes the dipole moment to decrease from HF to HI. For these molecules the change in the difference in electronegativity 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.
- Carbon dioxide (CO_2), for example, is a linear triatomic molecule shown in the figure:

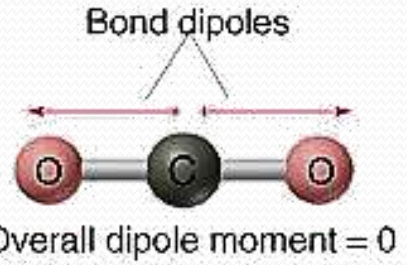




- The dipole moment of the entire molecule is made up of two bond moments, that is, individual dipole moments in the polar C=O bonds.

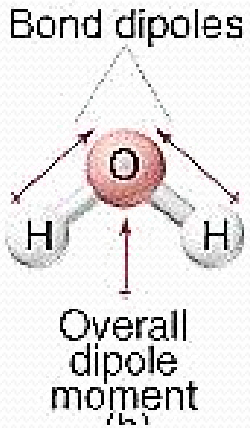
Dipole Moments of polyatomic molecules

- Does the fact that both CO bonds are polar mean that the CO_2 molecule is polar? Not necessarily, why?
- 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.
- The two bond moments in CO2 are equal in magnitude but they point in opposite directions in a linear CO2 molecule, so the resultant dipole moment would be zero. So the two bond moments cancel each other.



Dipole Moments of polyatomic molecules

- Now let's consider H_2O, which is a bent molecule with two polar bonds. The oxygen atom carries a partial negative charge, and the hydrogen atoms each have a partial positive charge. Both the bonds are identical, so the bond dipoles are equal in magnitude.
- Because the molecule is bent, however, the bond dipoles do not directly oppose each other and therefore do not cancel each other. Hence, the water molecule has an overall dipole moment.

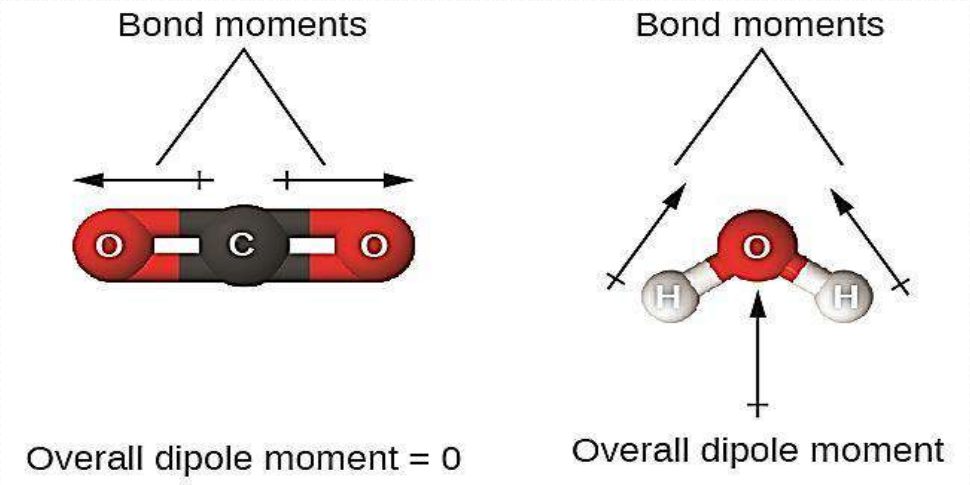


Molecular Dipole Moments

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

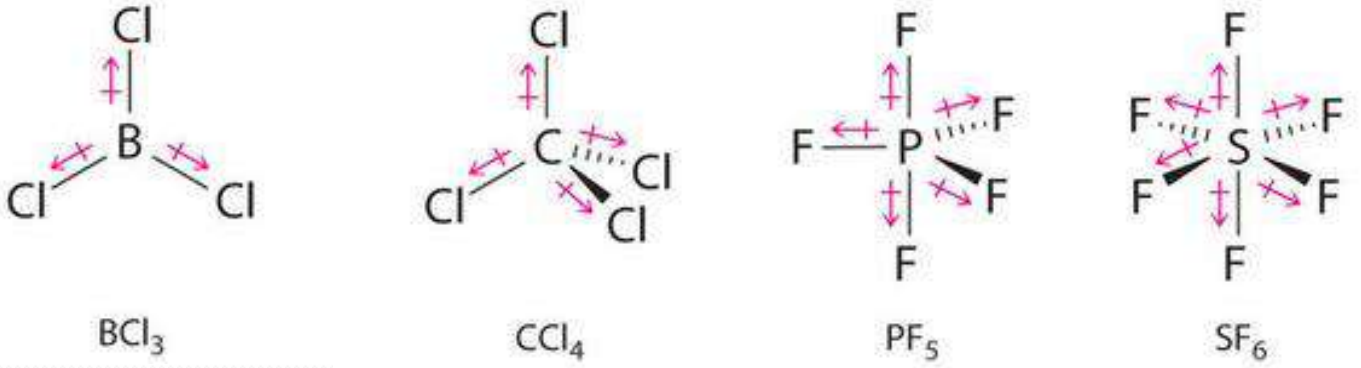
I. Contain at least one polar covalent bond.

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

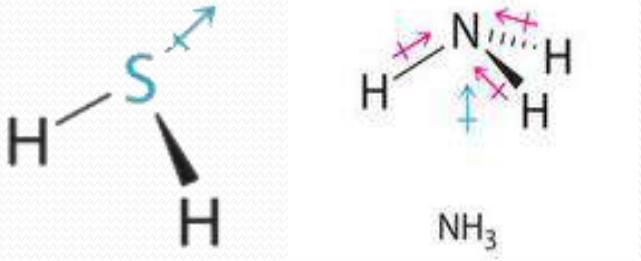


Molecular Dipole Moments

- 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.

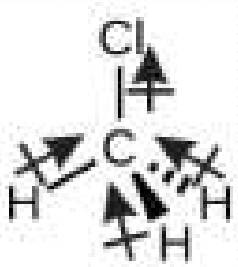


- However, molecules that have identical bonds and lone pairs on the central atoms have bond dipoles that do not cancel as H_2S, H_2O and NH_3.



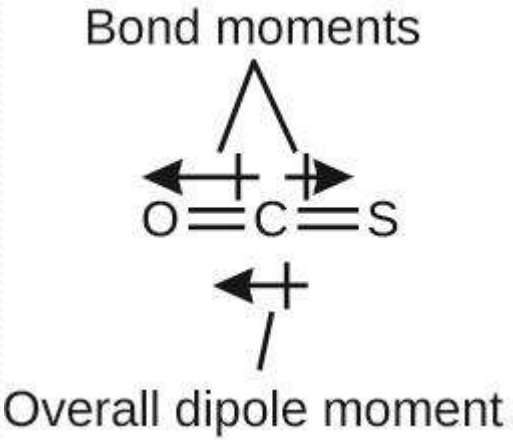
Molecular Dipole Moments

- 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.



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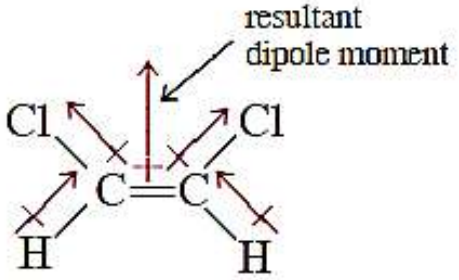
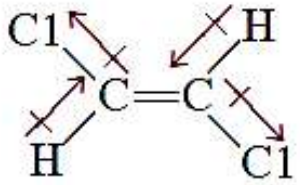
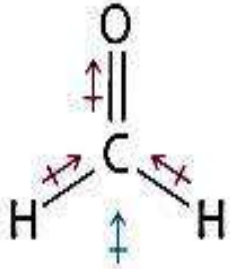
Examples



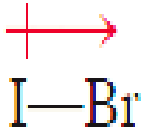
cis-dichloroethylene
$\mu = 1.89$ D

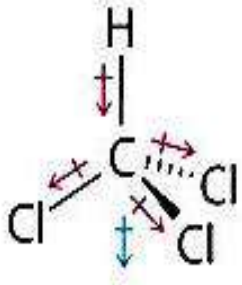


trans-dichloroethylene
$\mu = 0$

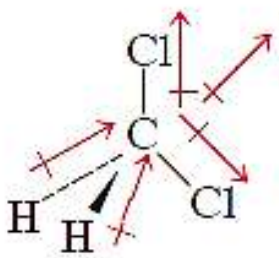


CH_2O





$CHCl_3$



Intramolecular forces

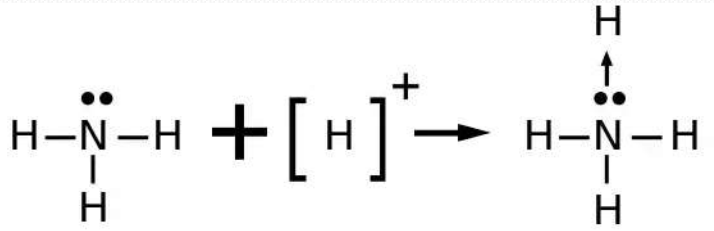
Intramolecular forces are the forces that hold atoms together within a molecule or a unit of the compound. These include mainly bonds.

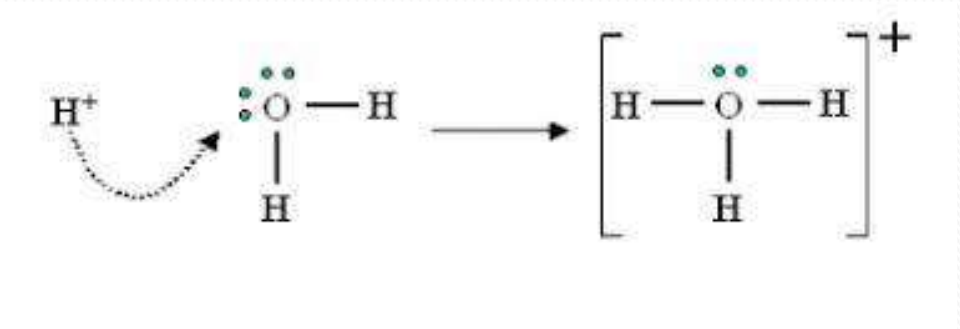
Types of intramolecular forces of attraction:

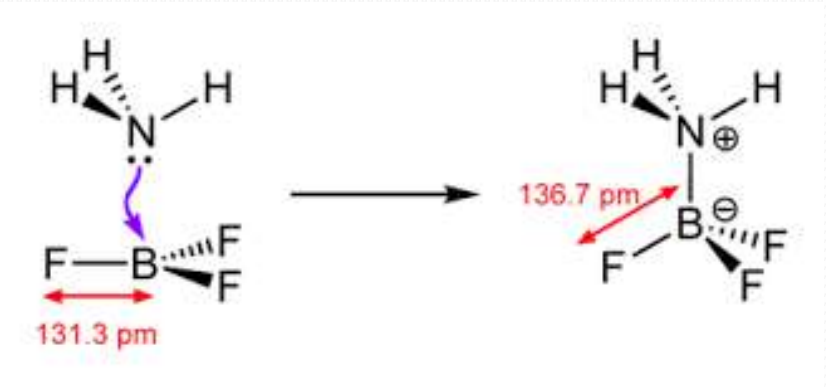
1. **Ionic bond.**
2. **Covalent bond:** including polar and nonpolar covalent bond, in addition **coordinate covalent bond**.
3. **Metallic bonding.**

Coordinate covalent bond

- A bond in which the pair of electrons is supplied by one of the two bonded atoms (also called dative bond).

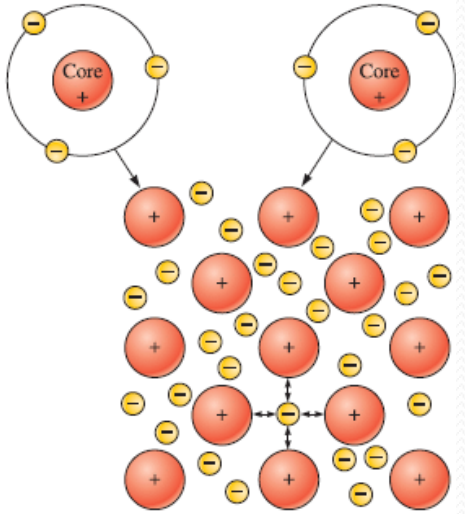






Metallic bonding

- This type of covalent bonding specifically occurs between atoms of metals, in which the valence electrons are free to move through the lattice. This bond is formed via the attraction of the mobile electrons—referred to as sea of electrons—and the fixed positively charged metal ions. Metallic bonds are present in samples of pure elemental metals, such as gold or aluminum, or alloys, like brass or bronze.



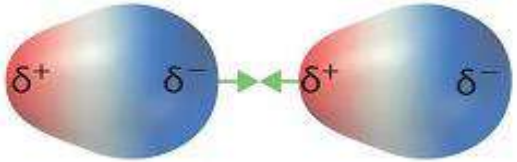
Intermolecular forces

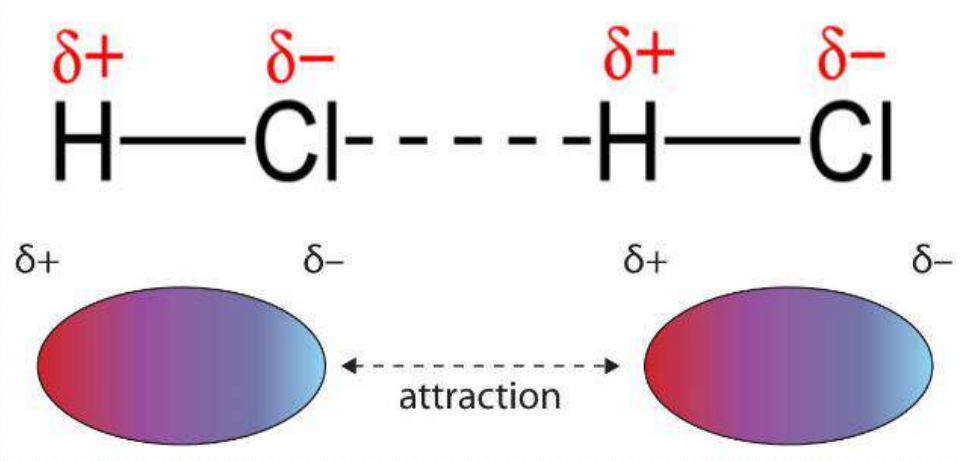
- Intermolecular forces are attractive forces between molecules or units.
- Intermolecular forces are much weaker than the intramolecular forces of attraction but are important because they determine the physical properties of molecules like their boiling point, melting point.
- The boiling and melting 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

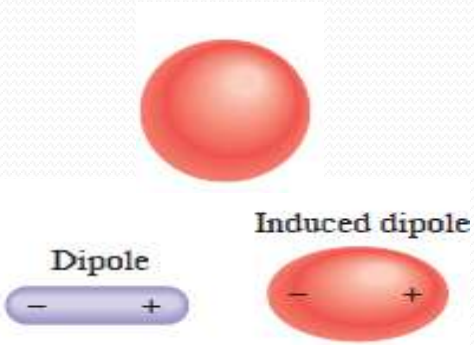
1- Van der waals forces:

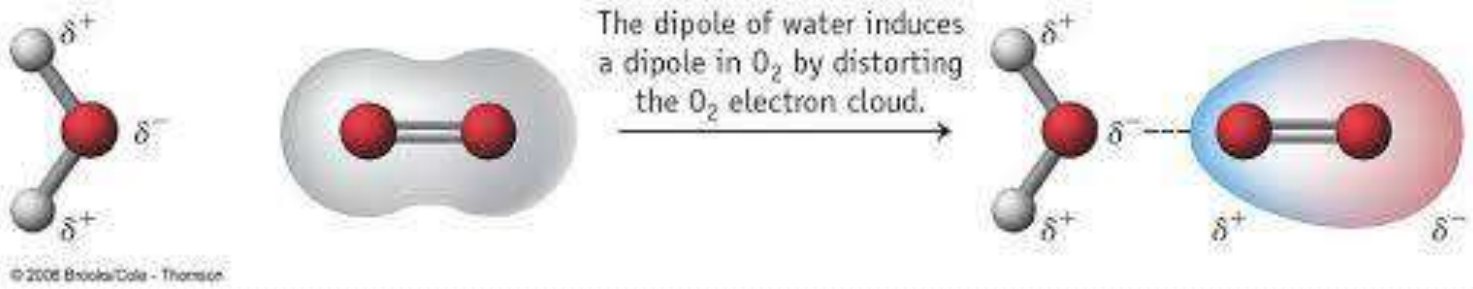
a- Dipole-dipole: are electrostatic attractive forces between polar molecules, that is, between molecules that possess permanent dipole moments. The larger the dipole moment, the greater the force (e.g. the forces between HF molecules)





- **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.

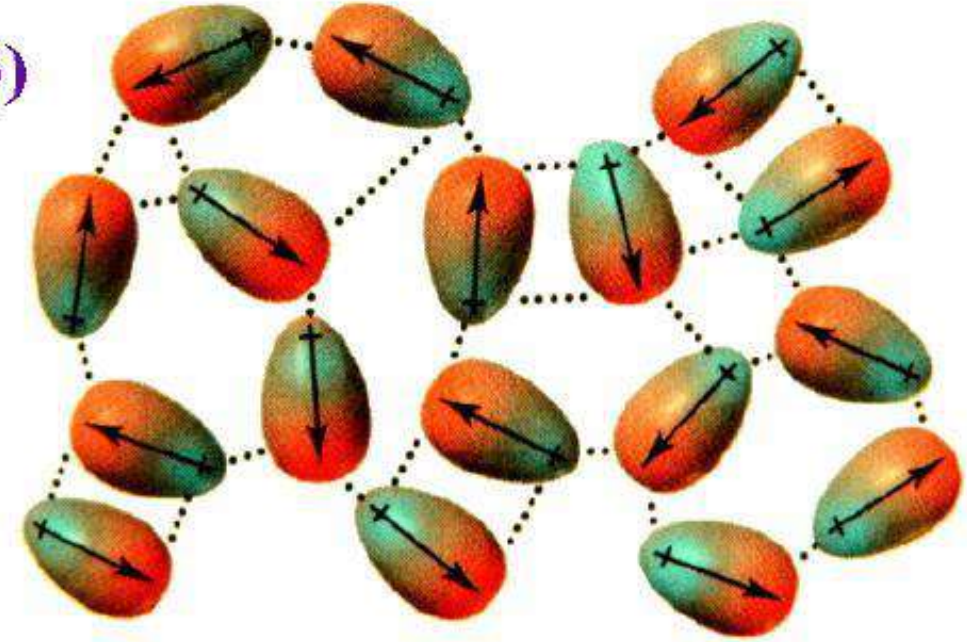
Dispersion forces usually increase with molar mass because molecules with larger molar mass tend to have more electrons, and dispersion forces increase in strength with the number of electrons that are less tightly held by the nuclei.

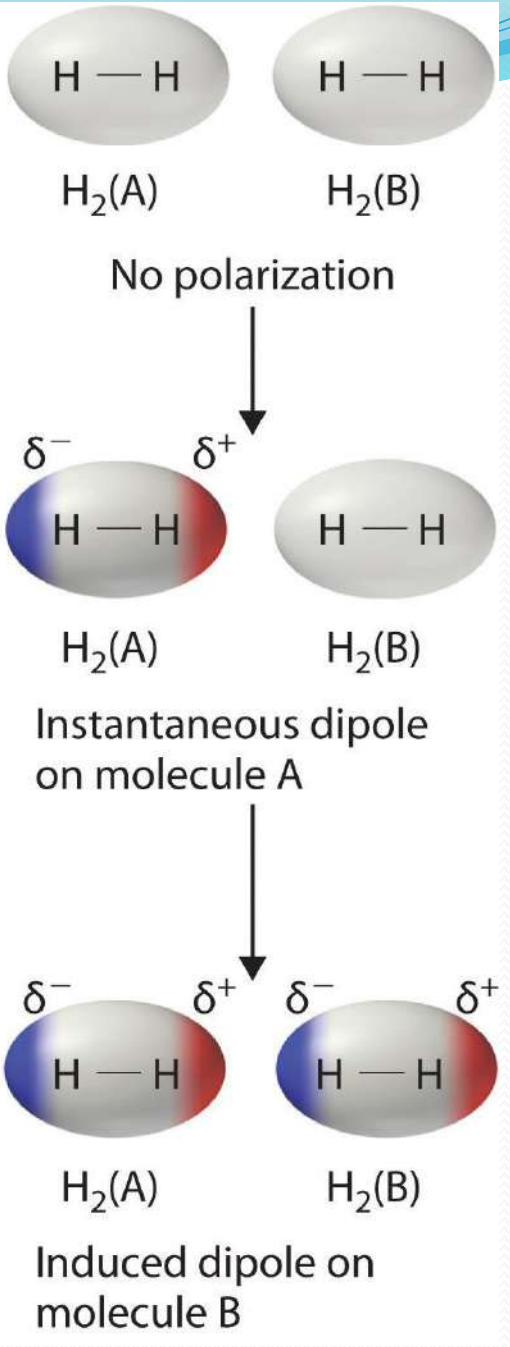
As expected, the melting point or boiling points increases as the molar mass increases.

1)

2)

3)




H — H
H — H
H_2(A)
H_2(B)
No polarization
δ^-
δ^+
H — H
H — H
H_2(A)
H_2(B)
Instantaneous dipole on molecule A
δ^-
δ^+
δ^-
δ^+
H — H
H — H
H_2(A)
H_2(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

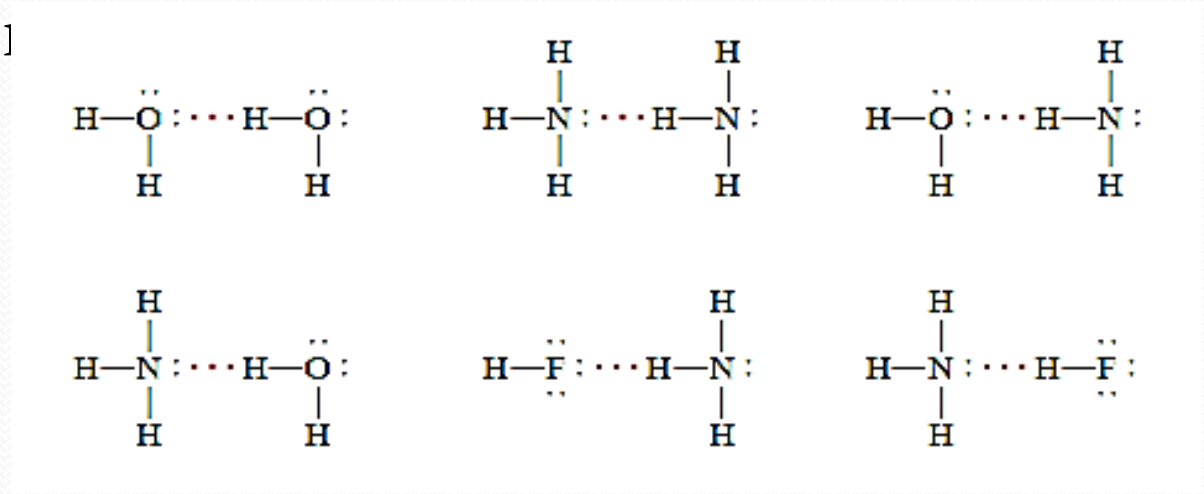
Example 2

The boiling points of CH_3F (-78.4C) and CCl_4 (76.5C). Although CH_3F has a dipole moment of 1.8 D, it boils at a much lower temperature than CCl_4, a nonpolar molecule. CCl_4 boils at a higher temperature simply because it contains more electrons.

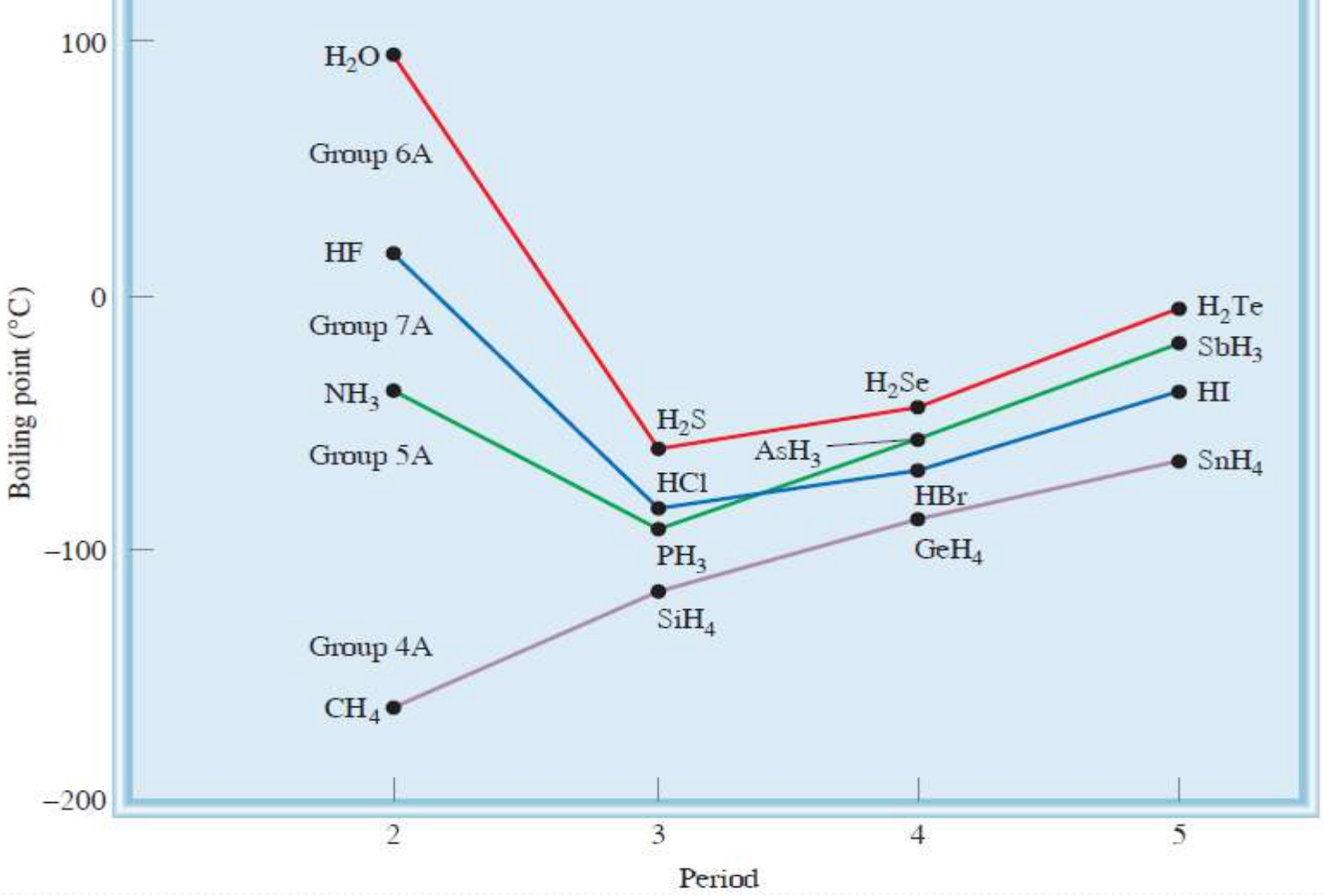
As a result, the dispersion forces between CCl_4 molecules are stronger than the dispersion forces plus the dipole-dipole forces between CH_3F molecules.

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 bo



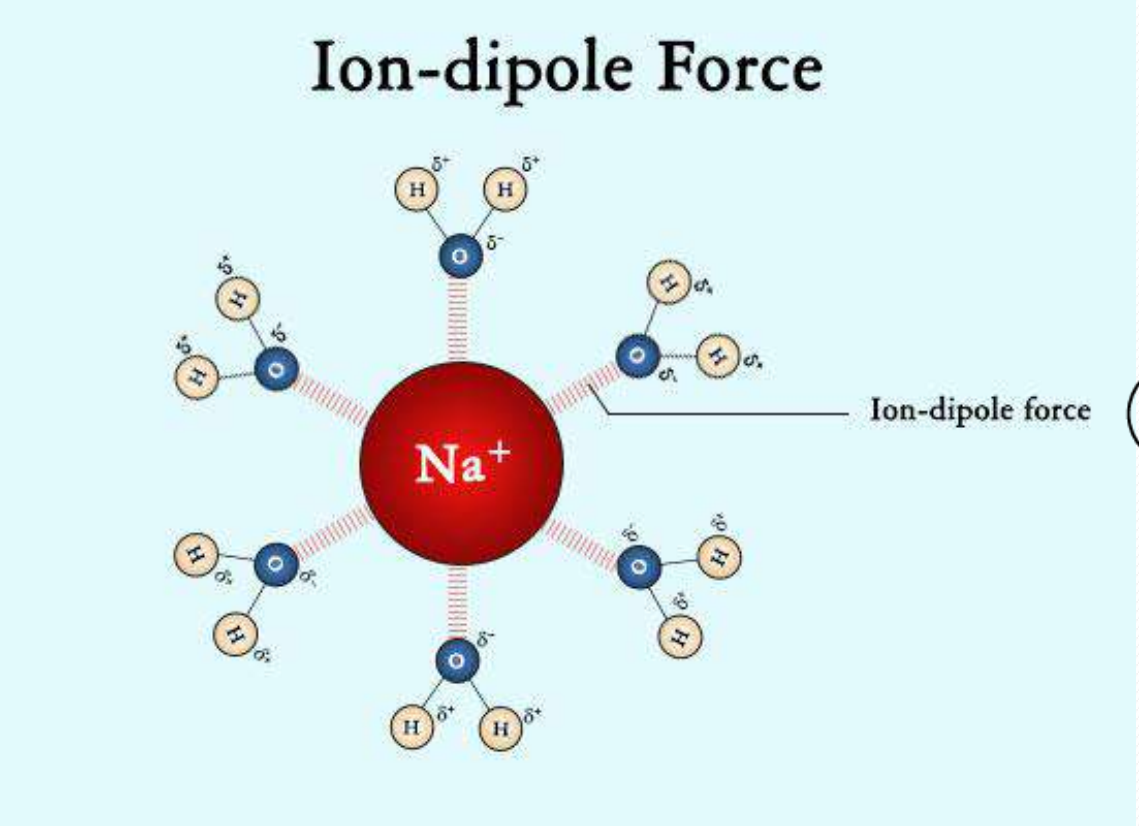
Hydrogen bonding in water, ammonia, and hydrogen fluoride. Solid lines represent covalent bonds, and dotted lines represent hydrogen bonds.

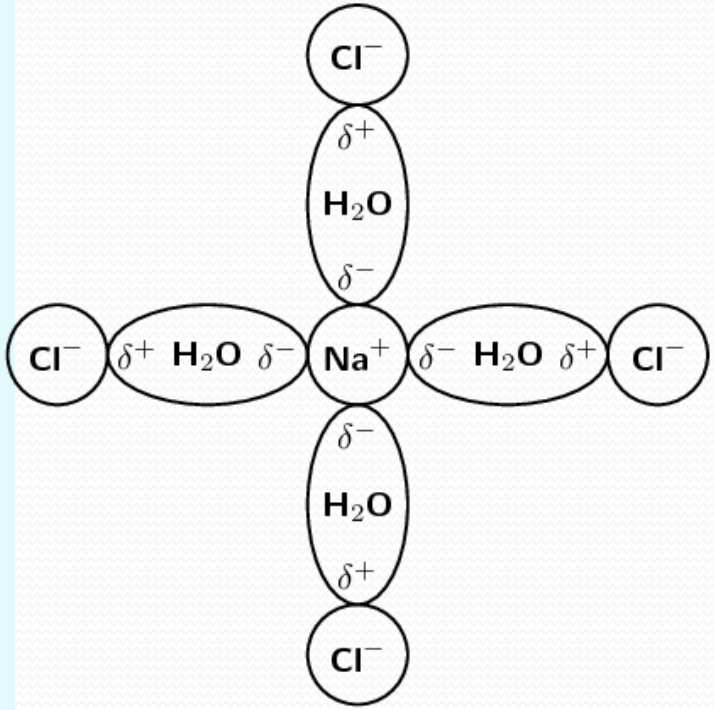


Boiling points of the hydrogen compounds of Groups 4A, 5A, 6A, and 7A elements. Although normally we expect the boiling point to increase as we move down a group with increasing molar mass, we see that three compounds (NH3, H2O, and HF) behave differently. The anomaly can be explained in terms of intermolecular hydrogen bonding.

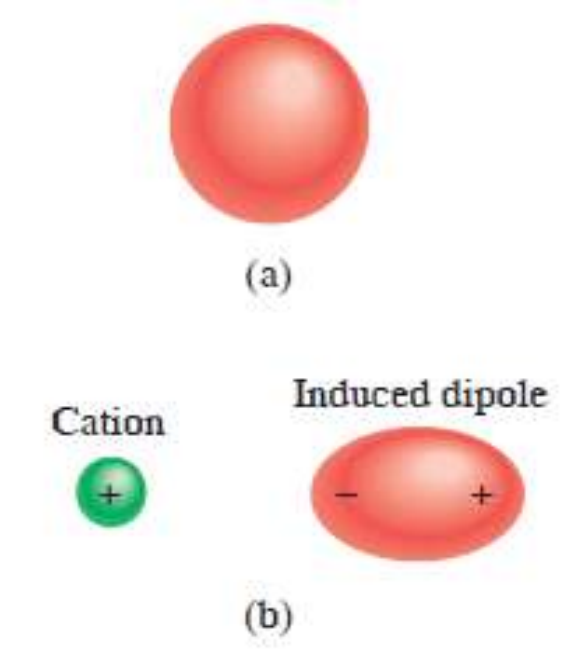
3- Ions-dipoles forces: these are electrostatic forces between ions and polar molecules.

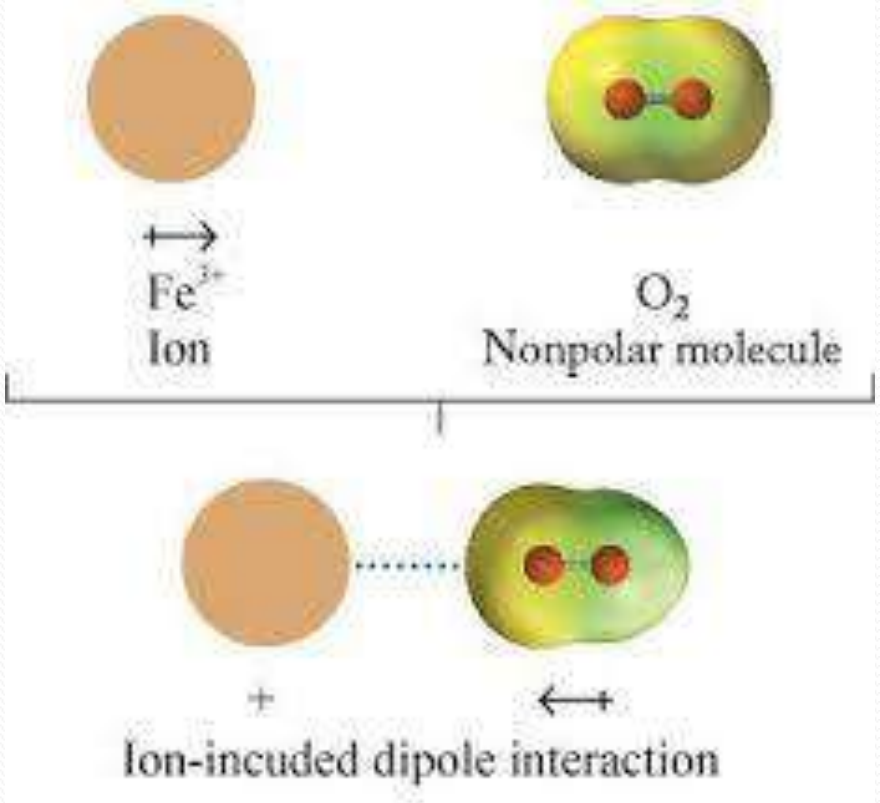
Hydration is one example of ion-dipole interactions.

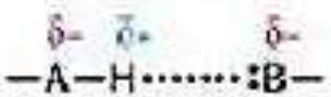




4- Ions-induced dipoles forces: these are electrostatic forces between ions and non polar molecules.





Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Ion-dipole		Ion charge–dipole charge	40–600	$Na^+ \cdots O(H)H$
H bond		Polar bond to H–dipole charge (high EN of N, O, F)	10–40	$H_2O \cdots H_2O$
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