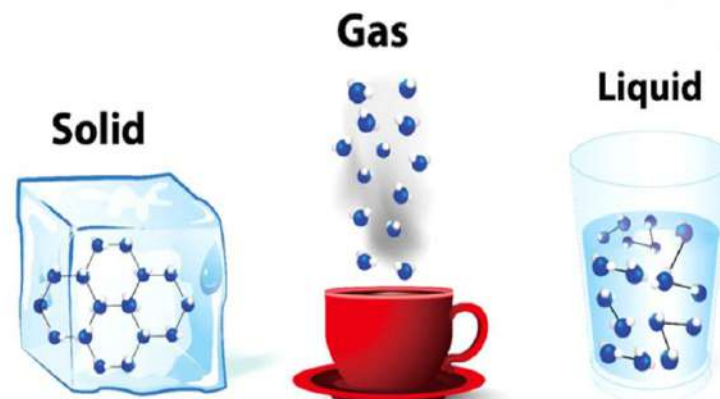


Intermolecular Forces and Potential Energy Surfaces

UNIT-III



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Intermolecular
Forces

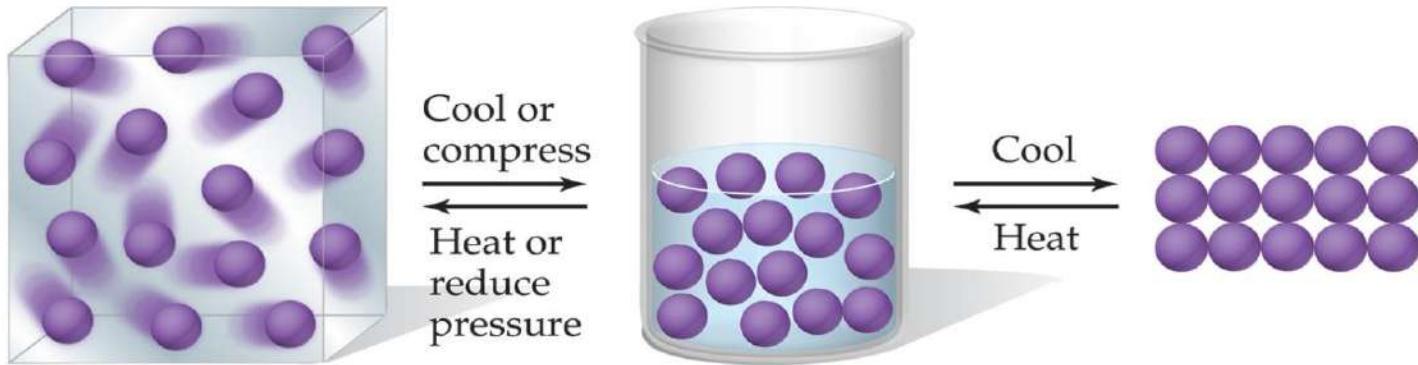
PTU-SYLLABUS

- Unit III Intermolecular forces and potential energy surfaces
Ionic, dipolar and van Der Waals interactions. Deviations of real gases from ideal behavior, equations of state of real gases (van der Waals equation of state), and critical phenomena (critical constants and their relation with van der Waals constant). Potential energy surfaces of H₃, H₂F and HCN and trajectories on these surfaces



States of Matter

The fundamental difference between states of matter is the distance between particles.



Gas

Total disorder; much empty space; particles have complete freedom of motion; particles far apart

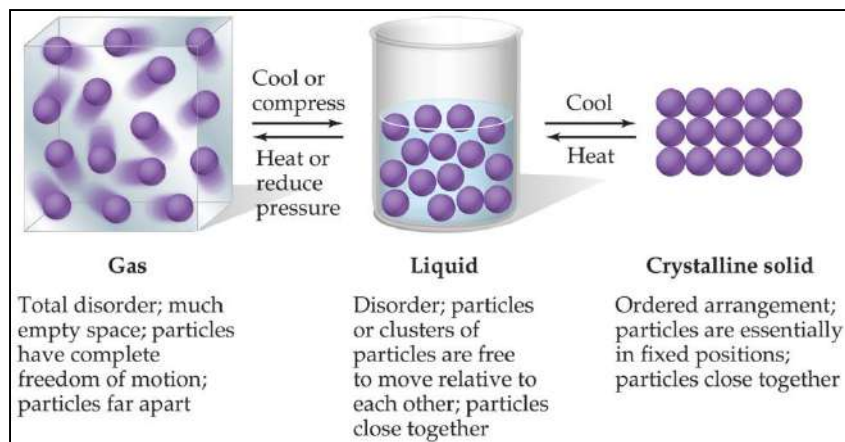
Liquid

Disorder; particles or clusters of particles are free to move relative to each other; particles close together

Crystalline solid

Ordered arrangement; particles are essentially in fixed positions; particles close together

The States of Matter

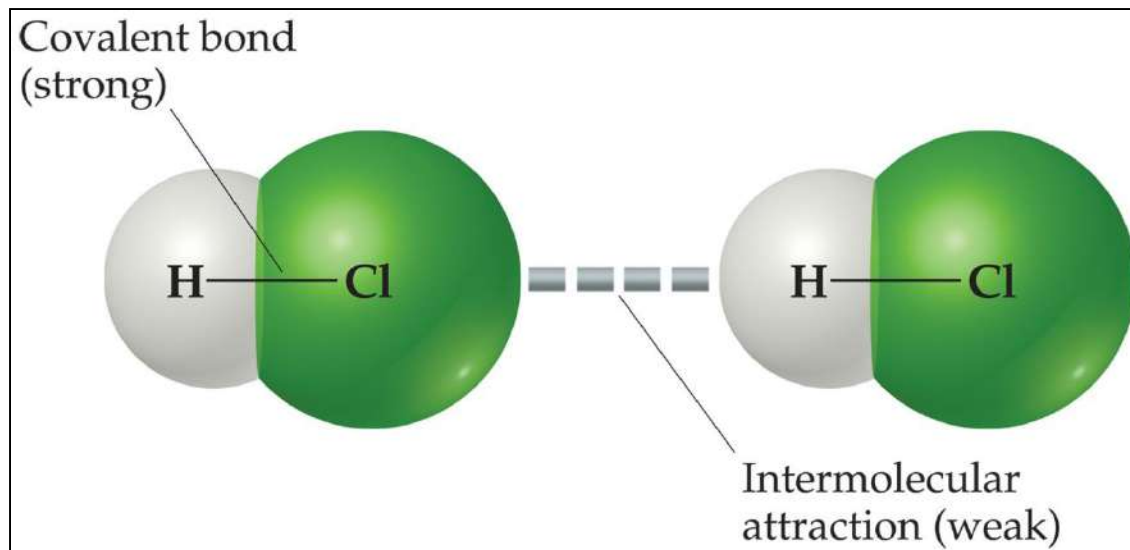


- The state a substance is in at a particular temperature and pressure depends on two antagonistic entities:

- The kinetic energy of the particles
- The strength of the attractions between the particles

Gas	Assumes both the volume and shape of its container Is compressible Flows readily Diffusion within a gas occurs rapidly
Liquid	Assumes the shape of the portion of the container it occupies Does not expand to fill container Is virtually incompressible Flows readily Diffusion within a liquid occurs slowly
Solid	Retains its own shape and volume Is virtually incompressible Does not flow Diffusion within a solid occurs extremely slowly

Intermolecular Forces



The attractions between molecules are not nearly as strong as the intramolecular attractions that hold compounds together. They are, however, strong enough to control physical properties such as boiling and melting points, vapor pressures, and viscosities.



Characteristics of Intermolecular Forces

Van der Waals forces are driven by induced electrical interactions between two or more atoms or molecules that are very close to each other. Van der Waals interaction is the weakest of all intermolecular attractions between molecules. However, with a lot of Van der Waals forces interacting between two objects, the interaction can be very strong.

- The main characteristics of van der Waals forces are:-
- They are weaker than normal covalent ionic bonds.
- Van der Waals forces are additive and cannot be saturated.
- They have no directional characteristic.
- They are all short - range forces and hence only interactions between nearest need to be considered instead of all the particles. The greater is the attraction if the molecules are closer due to Van der Waals forces.
- Van der Waals forces are independent of temperature except dipole - dipole interactions.



Types of Intermolecular Forces

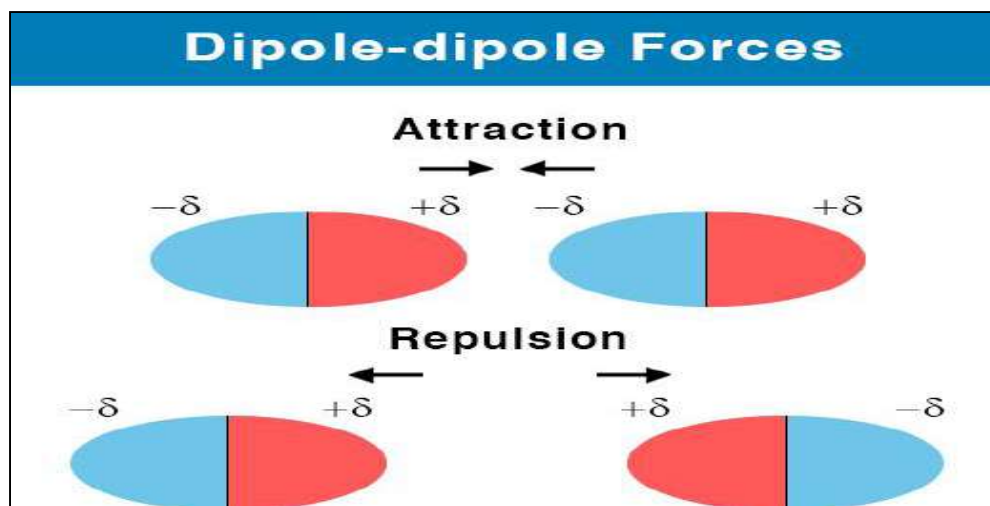
Intermolecular forces as a group are referred to as van der Waals forces these are classified as :

- Dipole-Dipole Interactions.
- Ion-Dipole Interactions.
- Ion Induced Dipole Interactions.
- Dipole Induced Dipole Interaction.
- London Forces or Dispersion Forces



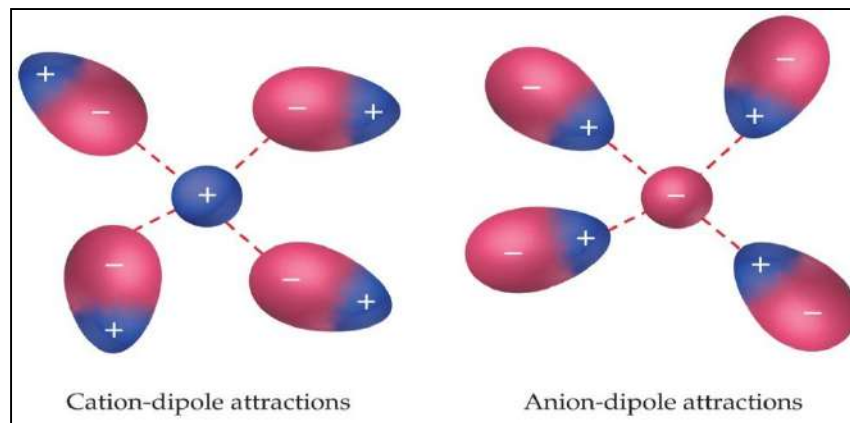
Dipole-Dipole Interactions

Dipole-dipole interactions are weak interactions that arise from the close association of permanent or induced dipoles. Collectively these forces are known as Van der Waals interactions.



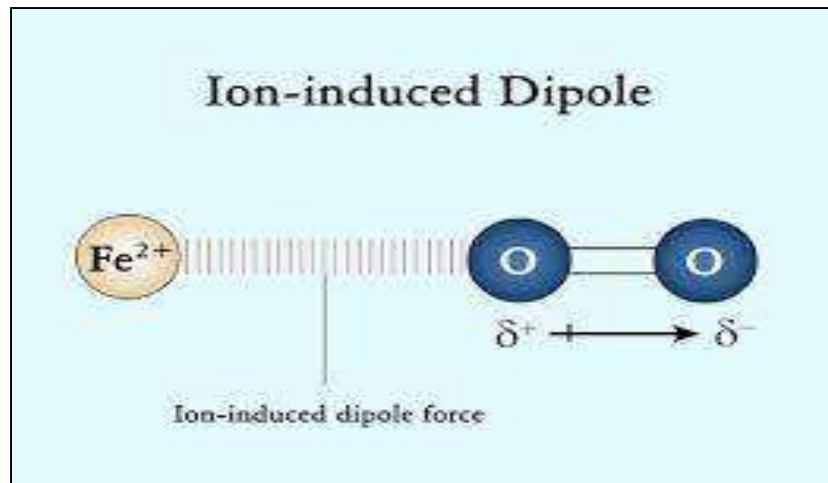
Ion-Dipole Interactions

- A fourth type of force, ion-dipole interactions are an important force in solutions of ions.
- The strength of these forces are what make it possible for ionic substances to dissolve in polar solvents.

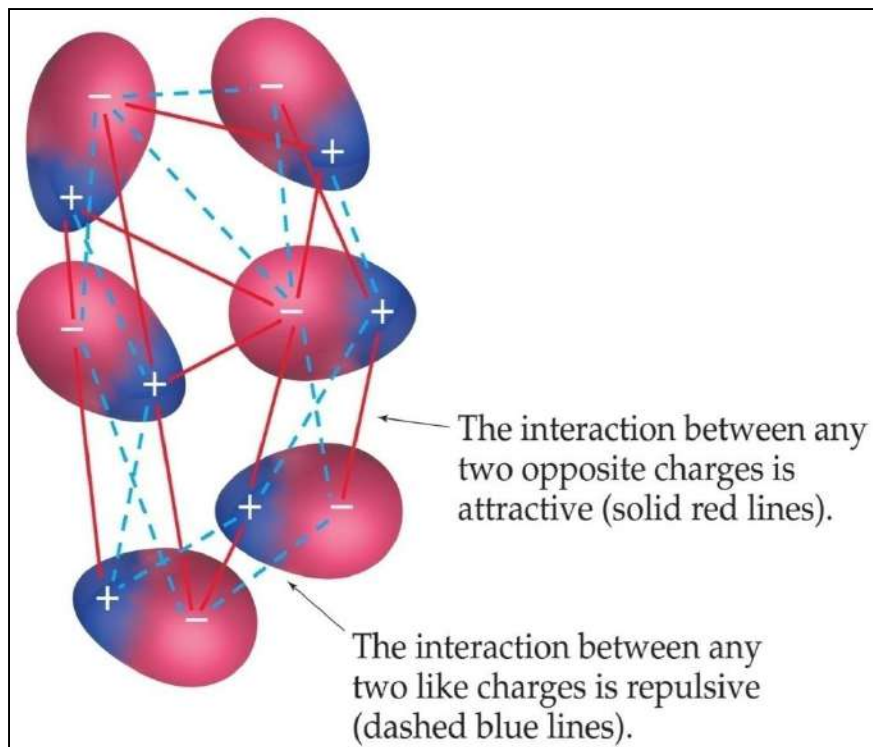


Ion induced-Dipole Interactions

- An ion-induced dipole attraction is a weak attraction that results when the approach of an ion induces a dipole in an atom or in a non polar molecule by disturbing the arrangement of electrons in the nonpolar species.



Dipole-Dipole Interactions



- Molecules that have permanent dipoles are attracted to each other.
 - The positive end of one is attracted to the negative end of the other and vice-versa.
 - These forces are only important when the molecules are close to each other.

Dipole-Dipole Interactions

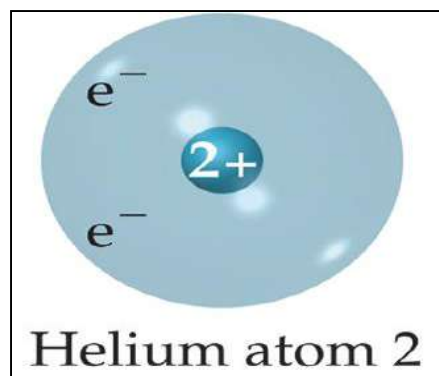
Substance	Molecular Weight (amu)	Dipole Moment μ (D)	Boiling Point (K)
Propane, CH ₃ CH ₂ CH ₃	44	0.1	231
Dimethyl ether, CH ₃ OCH ₃	46	1.3	248
Methyl chloride, CH ₃ Cl	50	1.9	249
Acetaldehyde, CH ₃ CHO	44	2.7	294
Acetonitrile, CH ₃ CN	41	3.9	355

The more polar the molecule, the higher is its boiling point.



London Dispersion Forces

London dispersion forces, or dispersion forces, are attractions between an instantaneous dipole and an induced dipole



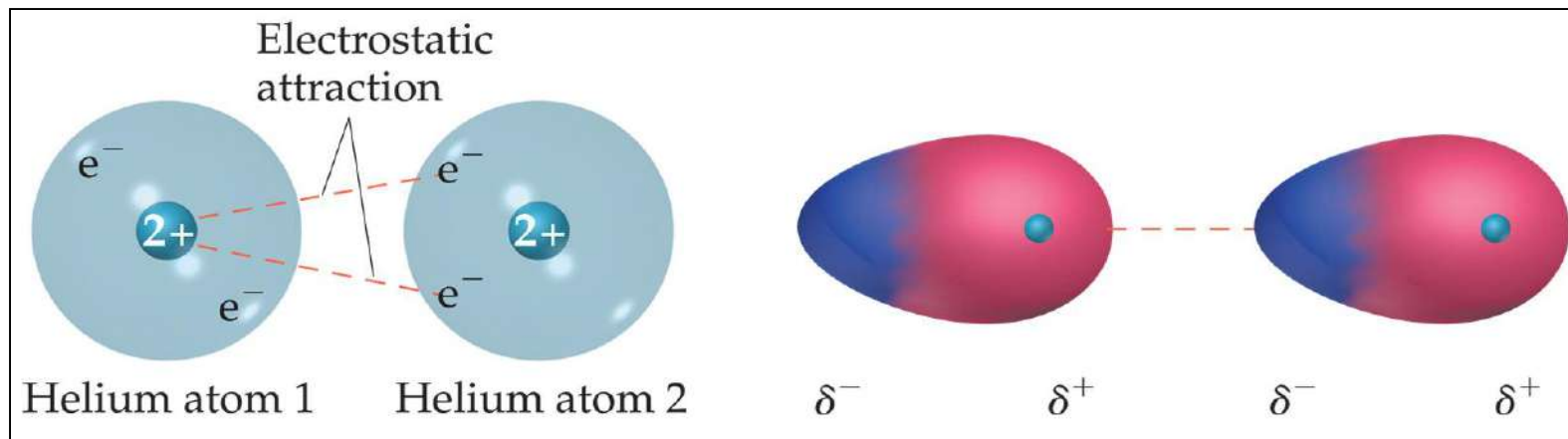
The electrons in the $1s$ orbital of helium would repel each other (and, therefore, tend to stay far away from each other), it does happen that they occasionally wind up on the same side of the atom.

London Dispersion Forces



At that instant, then, the helium atom is polar, with an excess of electrons on the left side and a shortage on the right side.

London Dispersion Forces



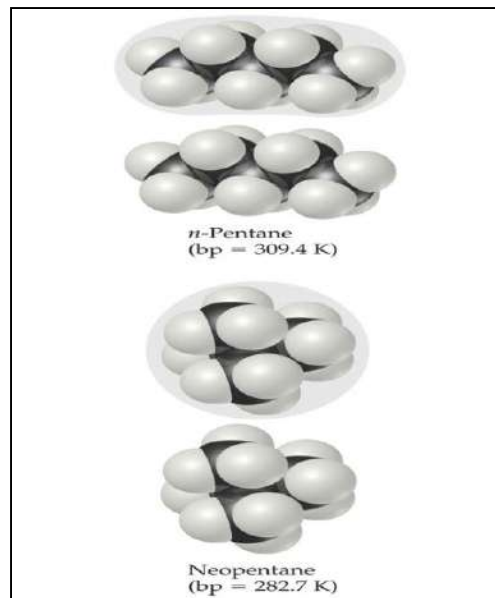
Another helium nearby, then, would have a dipole induced in it, as the electrons on the left side of helium atom 2 repel the electrons in the cloud on helium atom 1.

London Dispersion Forces

- These forces are present in *all* molecules, whether they are polar or nonpolar.
- The tendency of an electron cloud to distort in this way is called polarizability.

Factors Affecting London Forces

- The shape of the molecule affects the strength of dispersion forces: long, skinny molecules (like *n*-pentane) tend to have stronger dispersion forces than short, fat ones (like neopentane).
- This is due to the increased surface area in *n*-pentane.



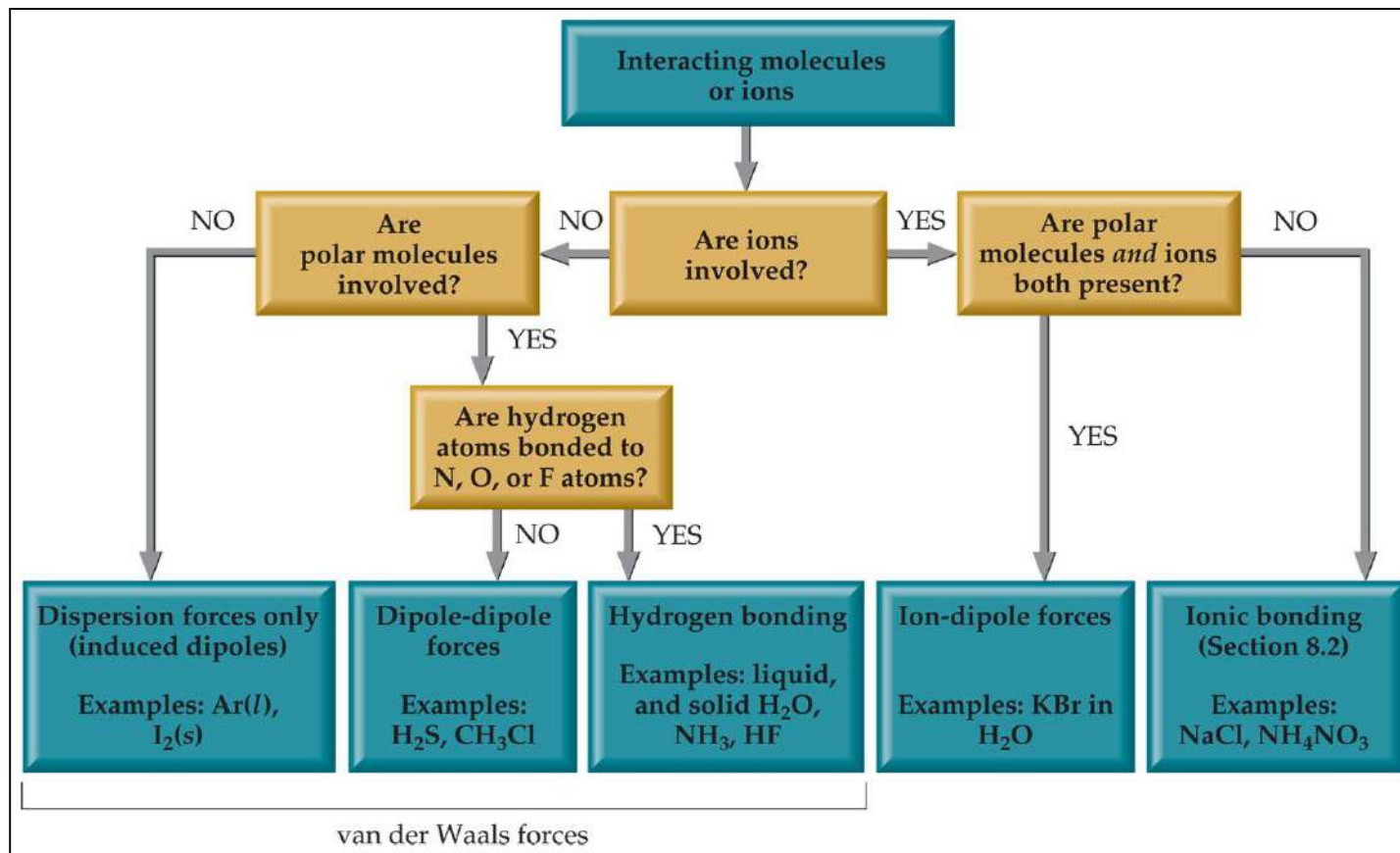
Factors Affecting London Forces

Halogen	Molecular Weight (amu)	Boiling Point (K)	Noble Gas	Molecular Weight (amu)	Boiling Point (K)
F ₂	38.0	85.1	He	4.0	4.6
Cl ₂	71.0	238.6	Ne	20.2	27.3
Br ₂	159.8	332.0	Ar	39.9	87.5
I ₂	253.8	457.6	Kr	83.8	120.9
			Xe	131.3	166.1

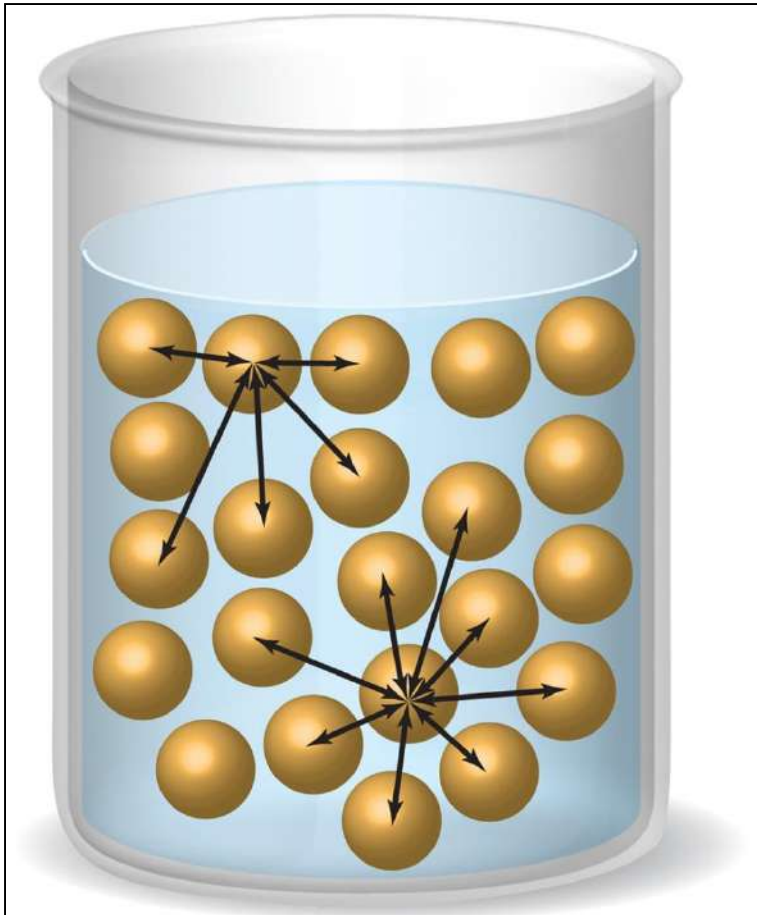
- The strength of dispersion forces tends to increase with increased molecular weight.
- Larger atoms have larger electron clouds, which are easier to polarize.



Summarizing Intermolecular Forces



Intermolecular Forces Affect Many Physical Properties



The strength of the attractions between particles can greatly affect the properties of a substance or solution.

SAMPLE EXERCISE 1 Identifying Substances that Can Form Hydrogen Bonds

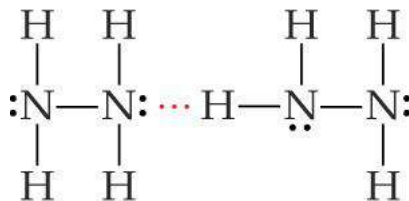
In which of the following substances is hydrogen bonding likely to play an important role in determining physical properties: methane (CH_4), hydrazine (H_2NNH_2), methyl fluoride (CH_3F), or hydrogen sulfide (H_2S)?

Solution

Analyze: We are given the chemical formulas of four substances and asked to predict whether they can participate in hydrogen bonding. All of these compounds contain H, but hydrogen bonding usually occurs only when the hydrogen is covalently bonded to N, O, or F.

Plan: We can analyze each formula to see if it contains N, O, or F directly bonded to H. There also needs to be an unshared pair of electrons on an electronegative atom (usually N, O, or F) in a nearby molecule, which can be revealed by drawing the Lewis structure for the molecule.

Solve: The criteria listed above eliminate CH_4 and H_2S , which do not contain H bonded to N, O, or F. They also eliminate CH_3F , whose Lewis structure shows a central C atom surrounded by three H atoms and an F atom. (Carbon always forms four bonds, whereas hydrogen and fluorine form one each.) Because the molecule contains a C—F bond and not an H—F bond, it does not form hydrogen bonds. In H_2NNH_2 , however, we find N—H bonds. If we draw the Lewis structure for the molecule, we see that there is a nonbonding pair of electrons on each N atom. Therefore, hydrogen bonds can exist between the molecules as depicted below.



SAMPLE EXERCISE 2 Predicting the Types and Relative Strengths of Intermolecular Forces

List the substances BaCl_2 , H_2 , CO , HF , and Ne in order of increasing boiling points.

Solution

Analyze: We need to relate the properties of the listed substances to boiling point.

Plan: The boiling point depends in part on the attractive forces in the liquid. We need to order these according to the relative strengths of the different kinds of forces.

Solve: The attractive forces are stronger for ionic substances than for molecular ones, so BaCl_2 should have the highest boiling point. The intermolecular forces of the remaining substances depend on molecular weight, polarity, and hydrogen bonding. The molecular weights are H_2 (2), CO (28), HF (20), and Ne (20). The boiling point of H_2 should be the lowest because it is nonpolar and has the lowest molecular weight. The molecular weights of CO , HF , and Ne are roughly the same. Because HF can hydrogen bond, however, it should have the highest boiling point of the three. Next is CO , which is slightly polar and has the highest molecular weight. Finally, Ne , which is nonpolar, should have the lowest boiling point of these three. The predicted order of boiling points is therefore



Check: The actual normal boiling points are H_2 (20 K), Ne (27 K), CO (83 K), HF (293 K), and BaCl_2 (1813 K), in agreement with our predictions.

PRACTICE EXERCISE

(a) Identify the intermolecular forces present in the following substances, and (b) select the substance with the highest boiling point: CH_3CH_3 , CH_3OH , and $\text{CH}_3\text{CH}_2\text{OH}$.

Answers: (a) CH_3CH_3 has only dispersion forces, whereas the other two substances have both dispersion forces and hydrogen bonds; (b) $\text{CH}_3\text{CH}_2\text{OH}$

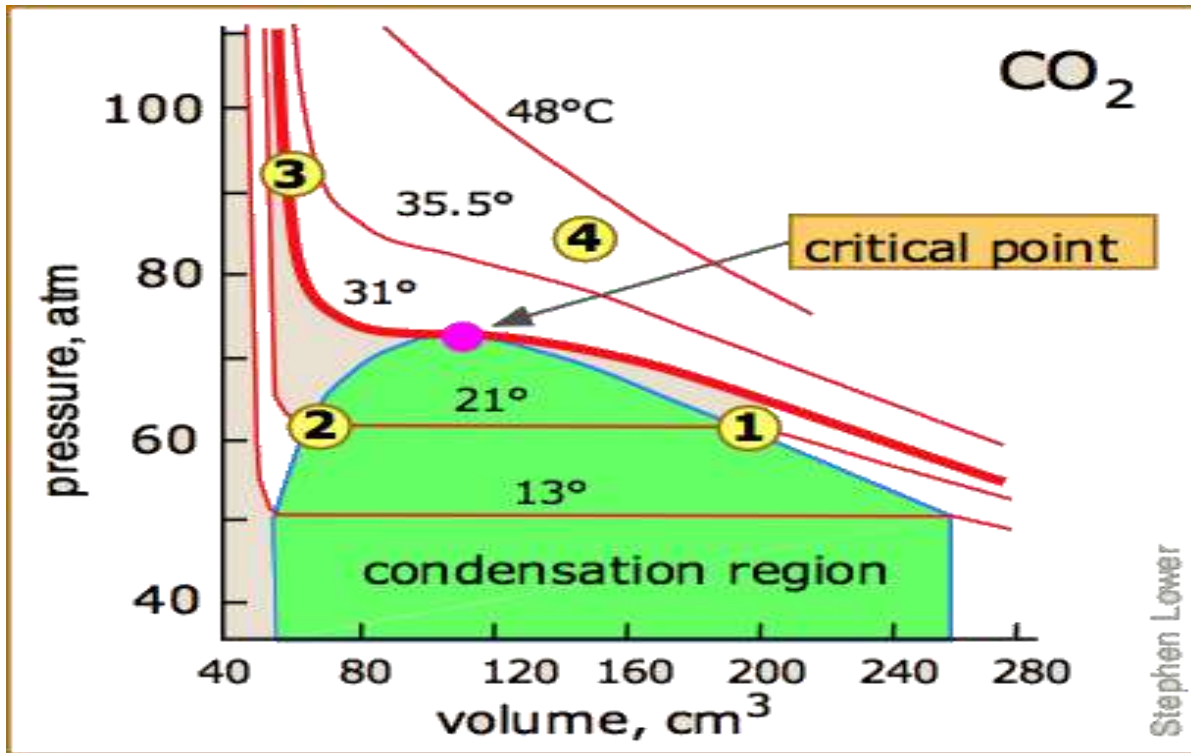


The Critical Point and isotherm for Carbon Dioxide:

Liquid and gas can coexist only within the regions indicated by the green-shaded area in the diagram above. As the temperature and pressure rise, this region becomes more narrow, finally reaching zero width at the *critical point*. The values of P , T , and V at this juncture are known as the *critical constants* P_c , T_c , and V_c .

The isotherm that passes through the critical point is called the *critical isotherm*. Beyond this isotherm, the gas and liquids become indistinguishable; there is only a single fluid phase, sometimes referred to as a *supercritical liquid*





At temperatures below 31° C (the *critical temperature*), CO₂ acts somewhat like an ideal gas even at a rather high pressure . Below 31° , an attempt to compress the gas to a smaller volume eventually causes condensation to begin. Thus at 21° C, at a pressure of about 62 atm, the volume can be reduced from 200 cm³ to about 55 cm³ without any further rise in the pressure. Instead of the gas being compressed, it is replaced with the far more compact liquid as the gas is essentially being "squeezed" into its liquid phase. After all of the gas has disappeared , the pressure rises very rapidly because now all that remains is an almost incompressible liquid. Above this isotherm , CO₂ exists only as a *supercritical fluid*.



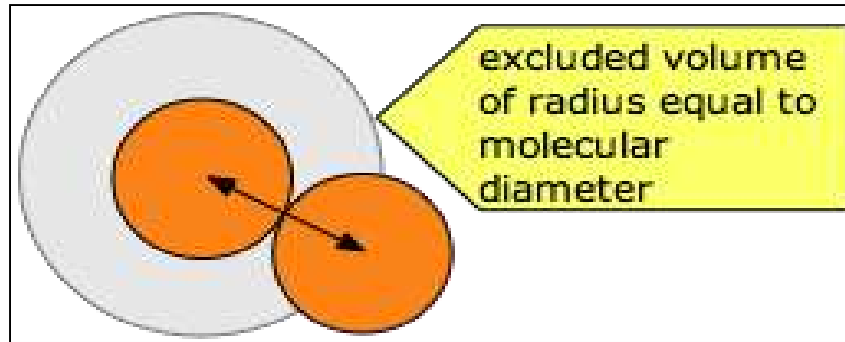
Equation of State for real gases

The van der Waals Equation of State:

How might we modify the ideal gas equation of state to take into account the effects of intermolecular interactions? The first and most well known answer to this question was offered by the Dutch scientist J.D. van der Waals (1837-1923) in 1873. The ideal gas model assumes that the gas molecules are merely points that occupy no volume; the "V" term in the equation is the volume of the container and is independent of the nature of the gas.



Equation of State for real gases



Van der Waals recognized that the molecules themselves take up space that subtracts from the volume of the container (Figure) so that the “volume of the gas” V in the ideal gas equation should be replaced by the term $(V-b)$, in which b relates to the *excluded volume*, typically of the order of $20\text{-}100\text{ cm}^3\text{ mol}^{-1}$.

The excluded volume surrounding any molecule defines the closest possible approach of any two molecules during collision. The excluded volume is greater than the volume of the molecule, its radius being half again as great as that of a spherical molecule.

The other effect that van der Waals needed to correct for are the intermolecular attractive forces. These are ignored in the ideal gas model, but in real gases they exert a small cohesive force between the molecules, thus helping to hold the gas together and reducing the pressure it exerts on the walls of the container.

Because this pressure depends on both the frequency *and* the intensity of collisions with the walls, the reduction in pressure is proportional to the *square* of the number of molecules per volume of space, and thus for a fixed number of molecules such as one mole, the reduction in pressure is inversely proportional to the square of the volume of the gas.



The smaller the volume, the closer are the molecules and the greater will be the effect. The van der Waals equation replaces the P term in the ideal gas equation with $P + \frac{a}{V^2}$ in which the magnitude of the constant a increases with the strength of the intermolecular attractive forces. The complete van der Waals equation of state can be written as

$$\underbrace{P + a \left(\frac{n}{V} \right)^2}_{\text{ideal gas pressure}} \times \underbrace{(V - nb)}_{\text{ideal gas volume}} = nRT$$

Diagram illustrating the van der Waals equation of state. The equation is shown as $P + a \left(\frac{n}{V} \right)^2 \times (V - nb) = nRT$. The term $P + a \left(\frac{n}{V} \right)^2$ is labeled as "actual pressure" (with a downward arrow) and "ideal gas pressure" (with a bracket underneath). The term $(V - nb)$ is labeled as "actual volume" (with a downward arrow) and "ideal gas volume" (with a bracket underneath).



Potential Energy Surfaces of H₃, H₂F & HCN

A potential energy surface is a graphical representation of the potential energy of a molecule as a function of its nuclear coordinates. The potential energy surfaces of molecules can provide insight into their chemical behavior and reactivity.

H₂F:

The H₂F molecule, also known as difluorine monohydride, consists of two fluorine atoms and one hydrogen atom. The potential energy surface of H₂F is relatively flat, with a broad minimum at a bent geometry. This indicates that H₂F is a stable molecule, with a low-energy transition state for rotation about the H-F bond.

HCN:

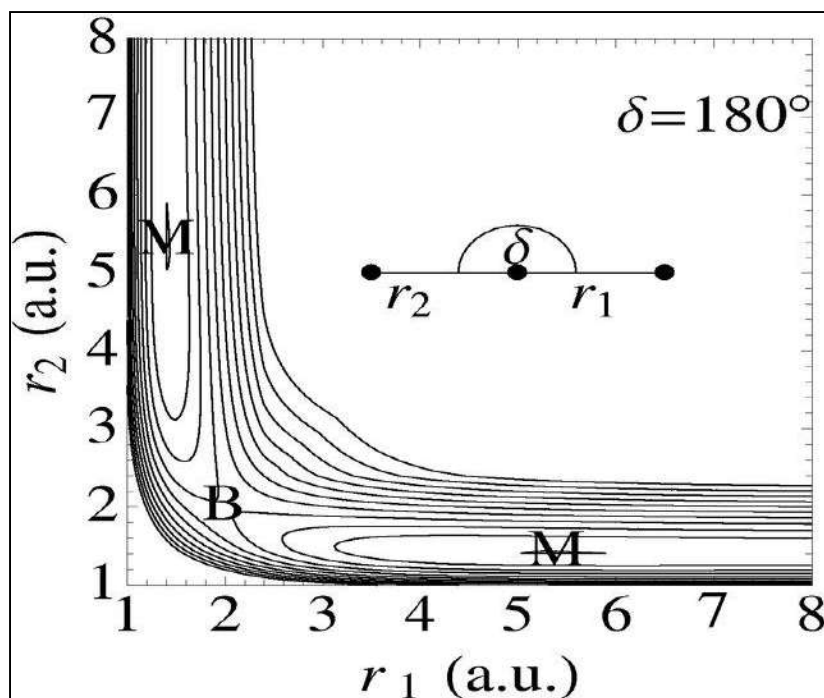
The HCN molecule, also known as hydrogen cyanide, consists of a hydrogen atom, a carbon atom, and a nitrogen atom. The potential energy surface of HCN has a deep minimum at a linear geometry, where the carbon and nitrogen atoms are bonded by a triple bond. The potential energy surface rises rapidly as the molecule is distorted from this equilibrium geometry, indicating that HCN is a very rigid molecule.



Potential Energy Surface for H₃

H₃:

The H₃ molecule, also known as triatomic hydrogen, consists of three hydrogen atoms. The potential energy surface of H₃ has a shallow minimum at equilateral triangle geometry, where all three hydrogen atoms are equidistant from each other. The potential energy surface rises rapidly as the hydrogen atoms are displaced from this equilibrium geometry, indicating that H₃ is a very reactive molecule.



Energy contour plots of the H – 3 electronic ground state PES in the space of the two internuclear distances (r_1 and r_2) for two values of the bonding angle δ defined in each plot. Successive contours differ by 0.006 a.u. The dissociation energy D as $= -1.7016828$ a.u. of the PES corresponds to the infinite separation

Application of Potential Energy Surfaces

A PES is a conceptual the analysis of molecular geometry and chemical reaction dynamics.

Once the necessary points are evaluated on a PES, the points can be classified according to the first and second derivatives of the energy with respect to position, which respectively are the gradient and the curvature.

Stationary points (or points with a zero gradient) have physical meaning: energy minima correspond to physically stable chemical species and saddle points correspond to transition states, the highest energy point on the reaction coordinate (which is the lowest energy pathway connecting a chemical reactant to a chemical product).

- PES does not show kinetic energy, only potential energy.
- At $T = 0$ K (no KE), species will want to be at the lowest possible potential energy, (i.e., at a minimum on the PES).
- Between any two minima (valley bottoms) the lowest energy path will pass through a maximum at a **saddle point**.



Thank You

