The General Characteristic of Weak Intermolecular Interactions in Liquids and Crystals

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ABSTRACT

A characteristic feature of weak interactions is the relative insensitivity of the bond energy on interatomic distance. The point is that in studying weak interactions one should not adopt a too stringent distance criterion in deciding what constitutes any given type of interaction. The types of weak interaction can arise from dipole-dipole interactions, quadrupole-quadrupole interactions, halogen-halogen interactions. We have seen that in crystals weak intermolecular interactions are strongly directional and that the mutual orientation of neighboring groups is important in achieving stable packing arrangements. Information about weak interactions in crystals is obtained from packing patterns which provide tests for the quality of atom-atom force fields. Whether a particular group of bonded molecules takes the form of a solid, liquid, or gas depends not only on the bonds that exist within each individual molecule, but also on the presence and type of bonds between molecules. Molecular substances are often soluble in organic solvents which are themselves molecular.

Keywords – **Hydrogen bonding, Interactions, Molecular crystals, Van der Waals, Weak intermolecular**

I. INTRODUCTION

Weak intermolecular interactions are not only important in supramolecular chemistry. Those hold the organic world together and are responsible for the very existence of liquids and crystals. For liquids, reliable structural information is hard to come by, but also extensive thermodynamic data are available for certain classes of compounds. Molecular substances are often soluble in organic solvents by molecular. Both the solute, the substance which is dissolving and the solvent are likely to have molecules attracted to each other by van der Waals forces. Although these attractions will be disrupted when they mix, they are replaced by similar ones between the two different sorts of molecules. Molecular substances will not conduct electricity. Even in cases where electrons may be delocalized within a particular molecule, there is not sufficient contact between the molecules to allow the electrons to move through the whole liquid or crystal.

Condensed media in which the distance between molecules is smaller than in gases, invariably show substantial interaction between molecules with saturated chemical bonds. The features of the intermolecular interaction determine the thermodynamic properties of liquids and the kinetics and mechanisms of the elementary chemical acts. The intermolecular interaction also control the formation of donor or acceptor complexes, and are responsible for the formation of colloidal systems. In biological systems intermolecular forces control the stability of all the compounds which are essential to life.

A phenomenon which has long been of interest and use to the coordination or acid-base chemist is the alteration of donor and acceptor vibrational frequencies upon formation of the coordinate bond. In addition to the structural applications of these shifts, qualitative, and in selected instances quantitative, estimates of interaction strengths have been determined from the magnitudes of the frequency shifts of normal vibrations involving the donor or acceptor atom. A few acids, those in which the acceptor site is a hydrogen atom, would seem to allow a quantitative and linear relationship between hydrogen stretching frequency shifts and enthalpy of adduct formation or base strength [1-3].

A molecular parameter more meaningful than frequency shifts as a criterion of the strength of a coordinate bond is the force constant for stretching of that bond. An alternative is to study the change in force constant of a bond adjacent to the coordinate bond. In the case of a donor frequency shifts, this potential constant is anticipated to be sensitive to the acidity of the acid and the nature of the bond which it forms with the donor [4]. A rough estimate of this sensitivity is indicated by the magnitude of the frequency change upon coordination as noted above. The typical interaction induced modification of a vibrational spectrum upon solution of a probe molecule in a solvent consists of vibrational frequency shifts appropriate to the selected vibrational mode and the interaction partners. Hydrogen bonded or weakly bound van der Waals complexes, being perturbed by a relatively inert environment, are known to exhibit in some cases pronounced intramolecular vibrational shifts which might enable one to derive information on the nature of the intermolecular perturbation. In recent years, a wealth of information has been collected on vibrational effects caused in monomeric units by the formation of weakly

bound dimmers in the gas phase. An even wider body of data exists which has been obtained by measuring vibrational frequency shifts of individual molecules or van der Waals and hydrogen bonded complexes trapped in low temperature matrices. Recently, the spectra of individual molecules and weakly bound complexes deposited on rare gas host clusters in molecular beams have become available.

Hydrogen bonding has emerged as the most important organizing principle not only for the structures of biologically important molecules but also for crystal engineering [5]. The hydrogen bonding forces a rather open structure on the ice; if you made a model of it, you would find a significant amount of wasted space. When ice melts, the structure breaks down and the molecules tend to fill up this wasted space. This means that the water formed takes up less space than the original ice. Ice is a very unusual solid in this respect most solids show an increase in volume on melting. When water freezes the opposite happens, there is an expansion as the hydrogen bonded structure establishes. Most liquids contract on freezing. Remnants of the rigid hydrogen bonded structure are still present in very cold liquid water, and don't finally disappear until 4 °C. From 0 °C to 4 °C, the density of water increases as the molecules free themselves from the open structure and take up less space. After 4 °C, the thermal motion of the molecules causes them to move apart and the density falls. That is the normal behaviour with liquids on heating. The conversion of a solid to a liquid is called either fusion or melting; the temperature at which this change occurs is the melting point. The quantity of heat required to melt a given amount of a solid is the enthalpy (heat) of fusion. A plot of temperature versus time as a solid is slowly heated is known as a heating curve; a similar plot for a liquid that is slowly cooled is known as a cooling curve. In some cases, it is possible to cool a liquid below its freezing point without having a solid form, a process known as super cooling. The conversion of a solid directly to a gas (vapor) is called sublimation. A plot of the vapor pressure of a solid versus temperature is known as a sublimation curve. The quantity of heat required to convert a given amount of solid directly to a gas is the enthalpy (heat) of sublimation.

The fluctuations in electron charge density in a molecule produce an instantaneous dipole, which in turn creates induced dipoles in neighboring molecules. The ease with which this occurs in a substance is known as its polarizability. Attractions between instantaneous and induced dipoles, called dispersion forces, are found in all substances. Polar molecules also have dipole-dipole and dipole-induced dipole intermolecular forces, arising from permanent dipoles in the molecules. Collectively known as van der Waals forces, dispersion forces, dipole-dipole forces, and dipole-induced dipole forces affect such physical properties as melting points and boiling points. A series of compounds with regularly varying structures

and formulas also has regularly varying properties; this is the principle of homology [6].

When a substance is in the liquid state, its molecules or atoms are held together by mutual attraction; without these forces, the molecules or atoms would expand to fill all the space available, becoming a gas. However, these forces are not as strong as those holding solids together, giving liquid molecules or atoms freedom to move about. We can measure the strength of the intermolecular or interatomic forces in liquids through the boiling point: the more tightly the units are held together, the more heat energy will be needed to separate them into a gas. Conversely, if intermolecular attractions are weak, the boiling point will be low. There are four main types of intermolecular forces, from strongest to weakest: ion-dipole, dipole-dipole, dipole-induced dipole, and induced dipole-induced dipole. Collectively, they are referred to as van der Waals' forces, after the scientist who also investigated their effects on gases. When we refer to dipoles, we mean an electrically asymmetrical molecule. If a molecule is not electrically symmetrical, a positive charge will accumulate on one side, and a negative will build up on the other. Molecules with dipoles are said to be polar, nonpolar molecules do not have dipoles. Water is a polar molecule because the oxygen atom wants electrons more than the hydrogen, pulling the molecule's electrons towards the oxygen and creating a charge imbalance. Since electrical charges can attract or repel each other, dipoles are important in intermolecular forces.

The first type of attraction is ion-dipole. In these situations, a charged ion is attracted to the dipole of a polar molecule. These are by far the most powerful types of attraction. Examples include the dissolution of salt in water; the negatively charged Cl ions will be attracted to the positive dipole near the hydrogens, while the positively charged Na ions will seek the negative dipole of the oxygen atom. These attractions are powerful enough to tear apart the NaCl crystal when it enters water, meaning that salt dissolves. If the crystal structure is too strong to be broken by attractions between a solvent and the ionic solid, then the solid will not dissolve. The next type of attraction is dipole-dipole, in which the dipoles of two molecules are mutually attracted. For example, the molecule FI has a permanent dipole because fluorine wants electrons more than iodine, which leads to a positive charge on the iodine and a negative charge on the fluorine. These molecules will attract each other, because the negatively charged fluorine will be drawn to the positive iodine atom of another molecule. A subtype of dipole-dipole interactions is hydrogen bonding, which occurs when a nitrogen, oxygen, or fluorine atom is bonded with one or more hydrogens. Since each of these atoms wants electrons more than hydrogen, a dipole will result. These dipoles result in strong attractions between molecules. The intermolecular attractions in water (H_2O), methanol (CH_3OH), ammonia (NH_3), and hydrogen fluoride (HF) are all examples of hydrogen bonding. All

of these substances have conspicuously high boiling points, due to the unusual strength of hydrogen bonding. Another type of intermolecular attraction is dipole-induced dipole. This occurs when a polar molecule, such as water, is attracted to a nonpolar molecule, such as pentane (C_5H_{12}). This type of attraction occurs because the charge on the water molecule distorts the electron clouds of pentane's component atoms, causing them to be either attracted to the positive dipole or repelled by the negative dipole. These interactions are very weak, but explain the solubility of nonpolar compounds in polar solvents, such as oxygen dissolved in water. Note that the first three types of forces generally decrease with size; the larger the atoms or molecules, the less attractive the intermolecular forces will be. The final type of interaction, the induced dipole-induced dipole forces, is also known as dispersion forces or London forces. Since the electron clouds whirling about an atom are not always perfectly symmetrical, there will be occasional attractions between nonpolar molecules because of the anomalies in their electron clouds. These forces are usually weak, but increase with the atom's or molecule's sizes, and can become fairly strong in large molecules or atoms (because there are more opportunities for electron cloud distortion). Therefore, dispersion forces occur between all molecules, but are most evident in nonpolar molecules, because they are the only attractions holding the molecules together. Ion-ion attractive forces also occur when ionic solids are melted, and are even stronger than ion-dipole interactions. These forces only occur at very high temperatures; trying to melt an ionic solid requires a lot of energy. These interactions lead us to postulate a solubility law for liquids, like dissolves like. For example, polar liquids will dissolve other polar liquids because of dipole-dipole interactions, and nonpolar liquids will also usually dissolve nonpolar liquids due to dispersion forces. However, nonpolar liquids are not sufficiently attracted to polar liquids to break the strong dipole-dipole interactions between solvent molecules. Therefore, liquids with like polarities will dissolve, whereas a nonpolar liquid will not dissolve in a polar liquid. Intermolecular attractions have some other effects on liquids. Viscosity is a measure of how fluid, or runny, a liquid is. For example, water has low viscosity and runs easily. Cold maple syrup flows slowly, so it has high viscosity. Intermolecular forces play some role in viscosity, because stronger attractions between molecules cause them to resist flow more strongly. Molecule size is also an important factor in viscosity; longer molecules can become tangled and flow slowly. Surface tension is also a result of intermolecular forces. Molecules at the surface of a liquid are attracted to the molecules beneath and beside them, leading to an inward force on the liquid and a kind of skin on the surface. This tension also causes drops of water to contract into spheres, minimizing surface area [7].

All the different types of intermolecular interaction can be classified into two main groups: physical (determined by the physical characteristics of the interacting molecules) and chemical (responsible for the formation of directional chemical or quasi chemical bonds between molecules. Other workers classify the intermolecular interaction into volume interactions (in which each molecule is bound to surrounding molecules by a force inversely related to distance) and local interactions (in which two or more molecules are held together fairly strongly but the bonds between these groups of molecules have only secondary importance). Other distinguish between short range and long range order when classifying intermolecular forces. The former involves interactions described in terms of the physical parameters of the molecules, whereas the latter involves valency or chemical forces arising from overlap of the electron clouds of the interacting molecules [8-11].

Electrostatic interactions are dominant in ionic crystals, but are also very important in molecular crystals. The magnitudes of any localized charges in the latter are small, but the electrostatic energy is often still large relative to the energies of the van der Waals interactions. To a first approximation electrostatic interactions can be optimized by avoiding like-like interactions in favor of like-unlike interactions, variously depicted as bumps against hollows, donors against acceptors, positive ends of bond dipoles against negative ends. Favorable interactions among overall molecular dipoles are usually much less important than local interactions among bond dipoles [7]. In any case, the dimensions of most molecules are much larger than the shortest distances between molecules so that inferences based on the dipole-dipole approximation are invalid [12].

II. INTERMOLECULAR FORCES

Potential energy is stored whenever work must be done to change the distance between two objects. The attraction between the two objects may be gravitational, electrostatic, magnetic, or strong force. Chemical potential energy is the result of electrostatic attractions between atoms. Differences in the physical and chemical properties of substances are explained by the arrangement of the atoms, ions, or molecules of the substances and by the strength of the forces of attraction between the atoms, ions, or molecules. Atoms within a molecule are attracted to one another by the sharing of electrons, this is called an intramolecular force. The electrostatic forces that held molecules together are called intermolecular forces, and are in general much weaker than the intramolecular forces. Intermolecular forces are electrostatics in nature. It can be divided into: (permanent) dipole-(permanent) dipole interaction, dipole-induced dipole interaction (induction forces), instantaneous dipole-induced dipole interaction (London forces or dispersion forces), and hydrogen bonding. Typically, the first three forces are grouped together and called van der Waals' forces. Van

der Waals' forces exist between all molecules. Most of the intermolecular forces are identical to bonding between atoms in a single molecule. Intermolecular forces just extend the thinking to forces between molecules and follow the patterns already set by the bonding within molecules.

•   **Ionic forces:** The forces holding ions together in ionic solids are electrostatic forces. Opposite charges attract each other. These are the strongest intermolecular forces. Ionic forces hold many ions in a crystal lattice structure.
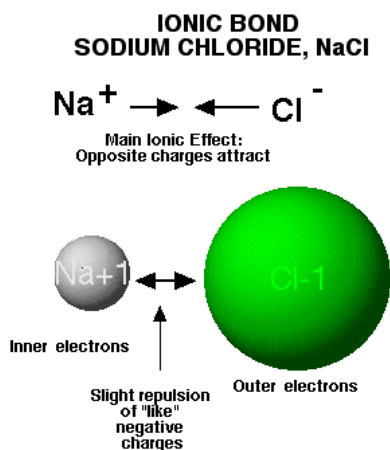
Figure 1. Ionic forces

•   **Dipole forces:** Polar covalent molecules are sometimes described as dipoles, meaning that the molecule has two poles. One end (pole) of the molecule has a partial positive charge while the other end has a partial negative charge. The molecules will orientate themselves so that the opposite charges attract principle operates effectively. At the example in Fig. 2, hydrochloric acid is a polar molecule with the partial positive charge on the hydrogen and the partial negative charge on the chlorine. A network of partial + and − charges attract molecules to each other.
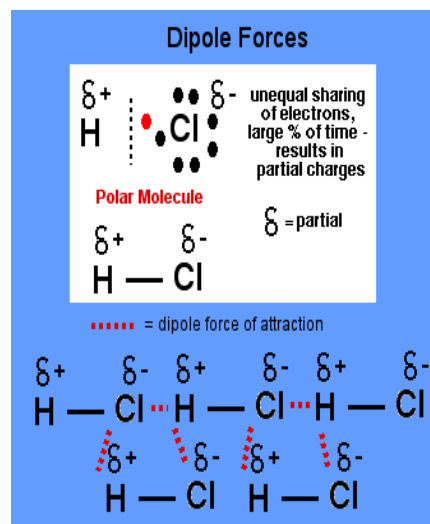

Figure 2. Dipole forces

•   **Hydrogen bonding:** The hydrogen bond is really a special case of dipole forces. A hydrogen bond is the attractive force between the hydrogen attached to an electronegative atom of one molecule and an electronegative atom of a different molecule. Usually the electronegative atom is oxygen, nitrogen, or fluorine. In other words, the hydrogen on one molecule attached to O or N that is attracted to an O or N of a different molecule. In Fig. 3, the hydrogen is partially positive and attracted to the partially negative charge on the oxygen or nitrogen. Because oxygen has two lone pairs, two different hydrogen bonds can be made to each oxygen. This is a very specific bond as indicated. Some combinations which are not hydrogen bonds include: hydrogen to another hydrogen or hydrogen to a carbon.
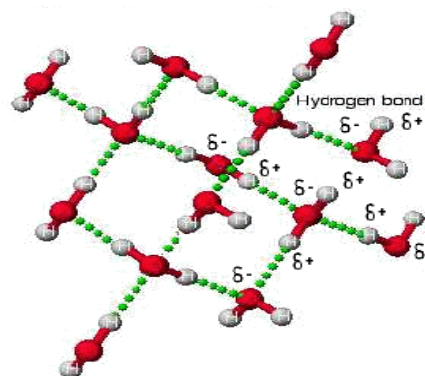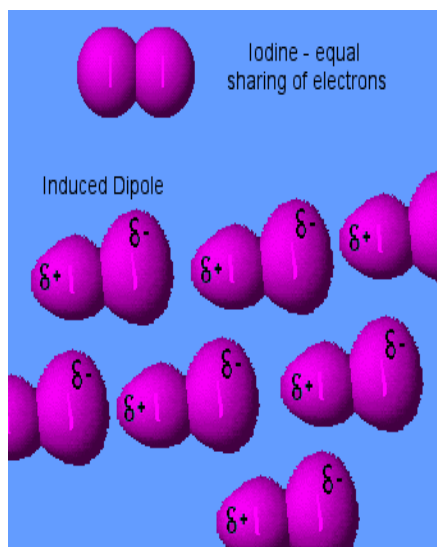

Figure 3. Hydrogen bonding

Figure 4. Induced dipole forces

- **Induced dipole forces:** Forces between essentially nonpolar molecules are the weakest of all intermolecular forces. "Temporary dipoles" are formed by the shifting of electron clouds within molecules. These temporary dipoles attract or repel the electron clouds of nearby nonpolar molecules. The temporary dipoles may exist for only a fraction of a second but a force of attraction also exists for that fraction of time. The strength of induced dipole forces depends on how easily electron clouds can be distorted. Large atoms or molecules with many electrons far removed from the nucleus are more easily distorted.

II.1. CLASSIFYING INTERMOLECULAR FORCES

In general, intermolecular forces can be divided into several categories:

1. Strong ionic attraction: Recall lattice energy and its relations to properties of solid. The more ionic, the higher the lattice energy. Ionic bonds are the result of electrostatic attraction between positive and negative ions. Ionic bonding is directly proportional to ionic charge and inversely proportional to ionic size.

2. Intermediate dipole-dipole forces: Substances whose molecules have dipole moment have higher melting point or boiling point than those of similar molecular mass, but their molecules have no dipole moment. Dipole-dipole interaction is the attraction between a partially negative portion of one molecule and a partially positive portion of a nearby molecule. Dipole-dipole interaction occurs in any polar molecule as determined by molecular geometry.

3. Weak London dispersion forces or van der Waal's force: These forces always operate in any substance. The force arisen from induced dipole and the interaction is weaker than the dipole-dipole interaction. In general, the heavier the molecule, the stronger the van der Waal's force or interaction. For example, the boiling points of inert gases increase as their atomic masses increases due to stronger London dispersion interactions. London dispersion forces result from instantaneous non permanent dipoles created by random electron motion. London dispersion forces are present in all molecules and are directly proportional to molecular size.

4. Hydrogen bond: Certain substances such as H_2O, HF, and NH_3 form hydrogen bonds, and the formation of which affects properties (melting point, boiling point, solubility) of substance. Other compounds containing OH and NH_2 groups also form hydrogen bonds. Molecules of many organic compounds such as alcohols, acids, amines, and amino acids contain these groups, and thus hydrogen bonding plays an important role in biological science [13]. Hydrogen bonding is significantly stronger than the dipole-dipole interactions which are in turn stronger than London dispersion forces. Hydrogen bonding exists only in molecules with an N-H, O-H, or F-H bond.

5. Covalent bonding: Covalent is really intramolecular force rather than intermolecular force. It is mentioned here, because some solids are formed due to covalent bonding. For example, in diamond, silicon, quartz etc., the all atoms in the entire crystal are linked together by covalent bonding. These solids are hard, brittle, and have high melting points. Covalent bonding holds atoms tighter than ionic attraction.

6. Metallic bonding: Forces between atoms in metallic solids belong to another category. Valence electrons in metals are rampant. They are not restricted to certain atoms or bonds. Rather they run freely in the entire solid, providing good conductivity for heat and electric energy. These behaviors of electrons give special properties such as ductility and mechanical strength to metals.

The division into types is for convenience in their discussion. All types can be present simultaneously for many substances. Intermolecular forces also play important roles in solutions, a discussion of which is given in hydration, solvation in water. A summary of the interactions is illustrated in the following Fig. 5.
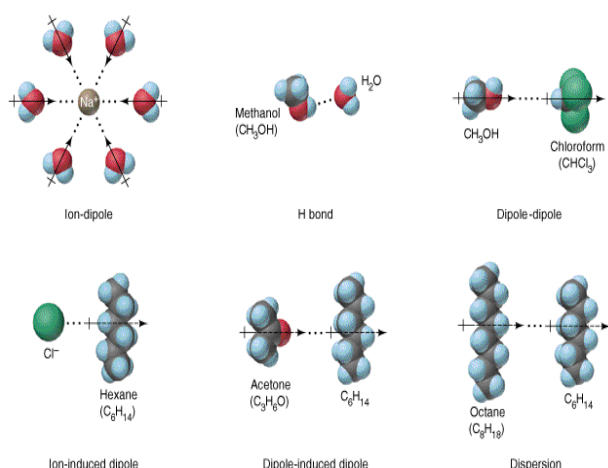
Figure 5. The classifying intermolecular forces
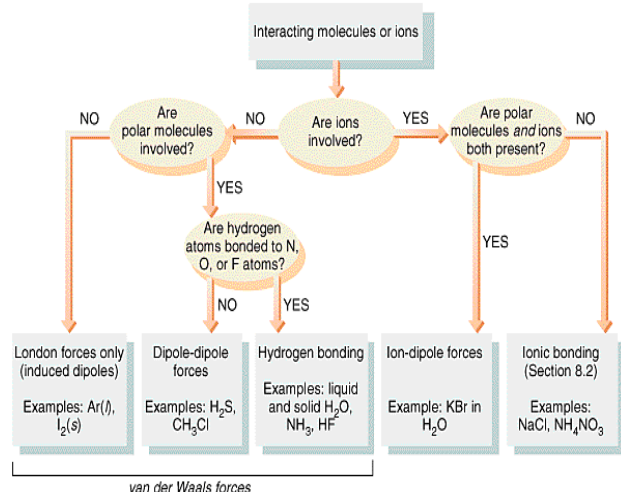
II.2. SUMMARY OF TYPES OF INTERMOLECULAR FORCES

Figure 6. The types of intermolecular forces

The physical properties of melting point, boiling point, vapor pressure, evaporation, viscosity, surface tension, and solubility are related to the strength of attractive forces between molecules. These attractive forces are called intermolecular forces (Fig. 6). The strength of intermolecular forces present in a substance is related to the boiling point and melting point of the substance. Stronger intermolecular forces cause higher melting and boiling points.

Three types of force can operate between covalent molecules: dispersion forces also known as London forces (named after Fritz London who first described these forces theoretically 1930) or as weak intermolecular forces or as van der Waal's forces (named after the person who contributed to our understanding of non ideal

gas behavior), dipole-dipole interactions, and hydrogen bonds.

Figure 7. Relative strength of intermolecular forces

Relative strength of intermolecular forces: intermolecular forces (dispersion forces, dipole-dipole interactions and hydrogen bonds) are much weaker than intramolecular forces (covalent bonds, ionic bonds or metallic bonds), dispersion forces are the weakest intermolecular force (one hundredth-one thousandth the strength of a covalent bond); hydrogen bonds are the strongest intermolecular force (about one-tenth the strength of a covalent bond), dispersion forces < dipole-dipole interactions < hydrogen bonds. Since van der Waals' forces are much weaker than covalent bond, ionic bond and metallic bond, only small amount of energy is needed to break the intermolecular forces of molecular substances. Molecular crystals or liquids are volatile, molecular crystals are soft and non conductors since there is no delocalized electrons.

The earth's crust may be held together mainly by ionic forces, molecules by covalent bonds, but it is weak intermolecular interactions which hold us along with the rest of the organic world together. The hydrogen bond is the best known example: because of its small bond

energy and the small activation energy involved in its formation and rupture, the hydrogen bond is especially suited to play a part in reactions occurring at normal temperatures. It has been recognized that hydrogen bonds restrain protein molecules to their native configurations. That as the methods of structural chemistry are further applied to physiological problems it will be found that the significance of the hydrogen bond for physiology is grater than that of any other single structural feature [14].

II.3. EFFECT OF INTERMOLECULAR FORCES ON SOLUBILITY

Solute is soluble in a solvent when there is a strong solute-solvent interactions (a force large enough to pull the solute particles away from each other). The following substances are soluble in water: ammonium, nitrate and sulphate salts, alkanols, carbonhydrates with low relative molecular mass since they form hydrogen bonds with water molecules. Most of the molecular substances are insoluble (or only very sparingly soluble) in water. Those which do dissolve often react with the water. Molecular substances are often soluble in organic solvents which are themselves molecular. Both the solute and the solvent are likely to have molecules attracted to each other by van der Waals' forces. In general like dissolves like:

- nonpolar solutes dissolve in nonpolar solvents paraffin wax $(C_{30}H_{62})$ is a nonpolar solute that will dissolve in nonpolar solvents like oil, hexane (C_6H_{14}) or carbon tetrachloride (CCl_4). Paraffin wax will not dissolve in polar solvents such as water (H_2O) or ethanol (ethyl alcohol, C_2H_5OH).

- polar solutes such as glucose $(C_6H_{12}O_6)$ will dissolve in polar solvents such as water (H_2O) or ethanol (ethyl alcohol, C_2H_5OH) as the partially positively charged atom of the solute molecule is attracted to the partially negatively charged atom of the solvent molecule, and the partially negatively charged atom of the solute molecule is attracted to the partially positively charged atom of the solvent molecule. Glucose will not dissolve in nonpolar solvents such as oil, hexane (C_6H_{14}) or carbon tetrachloride (CCl_4).

- Ionic solutes such as sodium chloride (NaCl) will generally dissolve in polar solvents but not in nonpolar solvents, since the positive ion is attracted the partially negatively charged atom in the polar solvent molecule, and the negative ion of the solute is attracted to the partially positively charged atom on the solvent molecule.
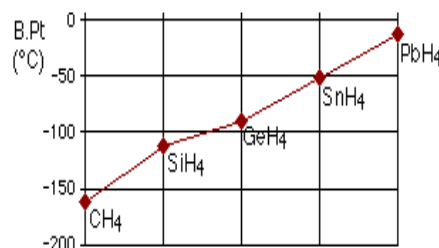

Figure 8. Plot the boiling points of the compounds with hydrogen

Since melting or boiling result from a progressive weakening of the attractive forces between the covalent molecules, the stronger the intermolecular force is, the more energy is required to melt the solid or boil the liquid. If only dispersion forces are present, then the more electrons the molecule has (and consequently the more mass it has) the stronger the dispersion forces will be, so the higher the melting and boiling points will be. Consider the hydrides of Group IV, all of which are nonpolar molecules, so only dispersion forces act between the molecules. CH_4 (molecular mass ~16), SiH_4 (molecular mass ~32), GeH_4 (molecular mass ~77) and SnH_4 (molecular mass ~123) can all be considered nonpolar covalent molecules. As the mass of the molecules increases, so does the strength of the dispersion force acting between the molecules, so more energy is required to weaken the attraction between the molecules resulting in higher boiling point [15]. The increase in boiling point happens because the molecules are getting larger with more electrons, and so van der Waals dispersion forces become greater (Fig. 8). Although for the most part the trend is exactly the same as in Group IV (for exactly the same reasons), the boiling point of the compound of hydrogen with the first element in each group is abnormally high (Fig. 9).

If a covalent molecule has a permanent net dipole then the force of attraction between these molecules will be stronger than if only dispersion forces were present between the molecules. As a consequence, this substance will have a higher melting or boiling point than similar molecules that are nonpolar in nature. Consider the boiling points of the hydrides of Group VII elements. All of the molecules HF (molecular mass ~20), HCl (molecular mass ~37), HBr (molecular mass ~81) and HI (molecular mass ~128) are polar, the hydrogen atom having a partial positive charge (H^+) and the halogen atom having a partial negative charge (F^-, Cl^-, Br^-, I^-) [8].
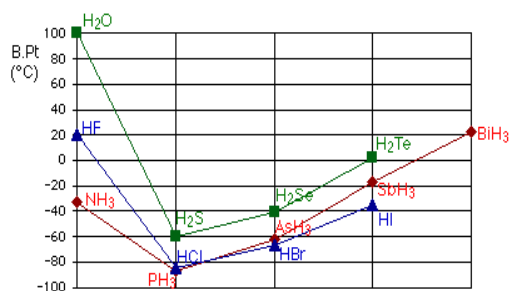
Figure 9. Boiling point of the compound of hydrogen with the first element

As a consequence, the stronger dipole interactions acting between the hydride molecules of Group VII elements results in higher boiling points than for the hydrides of Group IV elements. With the exception of HF, as the molecular mass increases, the boiling points of the hydrides increase. HF is an exception because of the stronger force of attraction between HF molecules resulting from hydrogen bonds acting between the HF molecules. Weaker dipole-dipole interactions act between the molecules of HCl, HBr and HI. So HF has a higher boiling point than the other molecules in this series. In the cases of NH_3, H_2O and HF there must be some additional intermolecular forces of attraction, requiring significantly more heat energy to break (Fig. 9). These relatively powerful intermolecular forces are described as hydrogen bonds.

II.4. ASPECTS OF WEAK INTERACTIONS

Until fairly recently, the term hydrogen bonding was more or less restricted to interactions involving F-H, O-H, and N-H as proton donors, O and N as proton acceptors with typical bond energies in the range 5 to 20 kcal/mol for F···H···F. However, it is now generally recognized that C-H···O interactions also play an important role in determining molecular packing arrangements [6]. They are admittedly weaker with energies typically less than 1 kcal/mol, but they are of common occurrence in molecular crystals containing C, H, and O atoms. Sometimes they have remarkable consequences. For example, eclipsed conformation of a $C(sp^3)$-CH_3 grouping in a crystalline trihydrate has been attributed to the presence of such C-H···O interactions in a cooperative system of O-H···O, O-H···N, and C-H···O hydrogen bond [6, 15].

Hydrogen bonding even the weak C-H···O interactions mentioned above can be described in good approximation as an essentially electrostatic phenomenon, i.e., as a first order coulomb interaction. Other kinds of weak interaction involve mutual polarization of molecules and dispersion forces. A characteristic of weak interactions is the relative insensitivity of the bond energy on interatomic distance. Elongation of a covalent bond by say 0.2 A˚ reduces the binding energy by something of

the order of 50 kcal/mol (roughly half the standard bond energy). The same elongation of a typical hydrogen bond reduces the binding energy only by about 1.2 kcal/mol (roughly 25% of the standard binding energy, taken here as 5 kcal/mol). Typical potential energy curves for a OH···O(alcohol) hydrogen bonded interaction with well depth 5 kcal/mol and equilibrium distance 1.8 A˚ and for a non hydrogen bonded H···O interaction with well depth 0.12 kcal/mol and equilibrium distance 2.8 A˚, based on atom-atom potential parameters listed by Gavezzotti [15].

III.   TYPES OF WEAK INTERACTION
Hydrogen bonding is undoubtedly the best studied and most important type of weak interaction. We interpret it here in its most general sense, as including all types of X-H···Y interactions. The types of weak interaction can arise from:

- **Dipole-dipole interactions:** The example is the structure of dimethylsulfoxide which is virtually determined by such interactions among the S=O bonds [16]. Interactions among overall molecular dipoles are usually much less important than local interactions among bond dipoles. Indeed, inferences based on interactions among molecular dipoles are not to be trusted. The repulsive nature of local dipole-dipole interactions across rotation axes and mirror planes helps to explain the low frequency of occurrence of these symmetry elements in molecular crystals [4, 7].

- **Quadrupole-quadrupole interactions:** The cubic crystal structures of carbon dioxide and acetylene [17] illustrate the favorable arrangement of like quadrupolar molecules in three dimensions. The molecules sit on the threefold axes of space group Pa3, such that each terminal atom in one molecule is equidistant from the centers of three surrounding molecules.

Benzene and hexafluorobenzene have almost the same molecular quadrupole moments but of opposite sign (around 30×10^{-40} Cm^2, negative for C_6H_6, positive for C_6F_6). The molecules are roughly the same shape and size, and since the interaction energy should not depend on the sign of the quadrupole moment, the quadrupole-quadrupole interaction alone should lead to the same stable packing arrangement for both [14]. Even for such small molecules, the packing optimizes local interactions at the expense of the global quadrupole-quadrupole interaction.

- **Halogen-halogen interactions:** The crystal structures of the halogens make an interesting series. They have the same space group and essentially the same layer packing arrangement as low temperature acetylene. In the halogen crystals the interlayer contact distances are roughly equal to the van der Waals diameters, but within the layers there is an increasingly strong tendency towards a specific, highly halogen-halogen interaction. For example, iodine has gone so far that the shortest

intermolecular I···I distance 3.50 A°, or about 0.8 A° less than the van der Waals diameter. The iodine structure does not fit simple electrostatic models with charges on the atoms or interactions between molecular quadrupoles [18]. It looks as if the molecule is acting as an electron acceptor along the direction of the I-I bond and as electron donor perpendicular to the bond or vice versa, from the halogen crystal structures alone one can not decide.

Most organic molecules crystallize in low symmetry space groups and most elemental metals and many inorganic salts crystallize in high symmetry groups, but this difference is a consequence of the shapes of the packing units and of the presence or absence of strong electrostatic interactions rather than of any fundamental difference in the packing rules followed by organic and inorganic materials [7].

Highly directional interactions, the first such complex to be studied was 1:1 complex formed by molecular bromine and 1,4-dioxane. The remarkably short O···Br distance of 2.71 A° (compared with 3.35 A°, sum of van der Waals radii) is along the direction of the Br-Br bond (at 2.31 A°, slightly longer than the distance in gaseous bromine) and roughly in the direction expected for a tetrahedral lone pair on the oxygen atom. Clearly the bromine molecule is acting as an electron acceptor along the direction of the Br-Br bond [14]. From the extensive list of complexes studied, the same conclusion applies to the other halogens and also to halogen-C bonds.

The directionality of nonbonded contacts has been examined for several C-X systems and interpreted in terms of orientation dependent van der Waals surfaces, rotation ellipsoids with the short radius along the C-X bond [19]. However, such a picture would be complicated by the need to construct a different surface for different types of contact atoms, depending on their electron donor abilities. From recent work at the Cambridge Crystallographic Data Centre, C-Cl···O contact distances tend to be shorter in the C-Cl bond direction and longer perpendicular to it, but C-Cl···H distances show practically no orientation dependence. Similarly, electron donors as nucleophiles tend to approach divalent sulfur along one of the X-S directions whereas electron acceptors as electrophiles tend to approach nearly perpendicular to the X-S-Y plane [20].

Allowance for the highly directional nature of weak intermolecular interactions has hardly begun to be made in force fields for atom-atom potential calculations, which adhere, for the most part, to spherical atom models as far as the nonbonded atoms are concerned. Further information about such interactions should be important not only for crystal engineering but also for chemistry. Just as hydrogen bonding can tell us about acid-base relationships, so the wider study of how molecules approach one another in crystals can inform us about the incipient stages of chemical reactions in general.

III.1. THE EXAMPLES TO EXISTENCE OF INTERMOLECULAR FORCES
Examples to show that existence of intermolecular forces are very important.

- **Example 1. Hot pressing hair:** A metal pressing comb is heated and is passed quickly through the hair. The high temperature breaks the biochemical disulfide bonds between and within the keratin proteins and allows the hair to be straightened through the tension applied to the hair during the combing procedure. After the comb has passed through the hair the temperature drops rapidly and this allows the broken biochemical bonds in the hair to reconnect and fix their new position. This reformation of the bonds holds the hair in its new, straightened shape.

In the helical protein of hair, hydrogen bonds within individual helices of keratin and disulfide bridges between adjacent helices, impart strength and elasticity to individual hairs. Also, water can disrupt the hydrogen bonds making the hair limp. When the hair dries, new hydrogen bonding allows it to take on the shape of a curler. Permanent wave solutions induce new disulfide bridges between the helices. Genetically determined, natural curly hair also has a different arrangement of disulfide bridges compared with straight hair.

- **Example 2. Protein:** The primary structure of a protein is a polypeptide which is a polymer of amino acids. Polypeptide chains form a helical structure owing to the hydrogen bonds formed between the N-H and C=O groups. This creates the secondary structure of proteins. In many proteins, including those in hair wool and nails. Hydrogen bonding causes the polypeptide chains to become twisted into tightly coiled helices.

- **Example 3. DNA:** DNA is present in the nuclei of living cells and carries genetic information. The DNA molecule consists of two helical nucleic acid chains which is very stable. Each nucleic acid is made up of three components: a sugar, a phosphoric acid unit and a nitrogen containing heterocyclic base: adenine, cytosine, guanine or thymine. The two nucleic acid chains are held together by hydrogen bonds. These hydrogen bonds are formed between specific pairs or bases on the chains. The two strands coil tightly around each other.

Protein and DNA is very important to our lives: Enzyme controls the metabolic reaction. Proteins also act as a cytoskeleton, membrane proteins, a raw materials for growth, for movement myosin form the basic structure of muscles, osmotic balance and buffering and energy source. The hydrogen bonds between the base pairs tend to drive double helix to reform spontaneously after uncoiling in replication and transcription.

- **Example 4. Plant:** In a narrow capillary of e.g. cellulose there are many oxygen atoms on the surface for hydrogen bonding to the water.

- **Example 5. Calcium sulfate (CaSO₄):** Gypsum (hydrated $CaSO_4$, $CaSO_4.H_2O$). Layer of ions are attracted by hydrogen bonds, it is soft and can be cleaved easily. Anhydrite (anhydrous $CaSO_4$) no hydrogen bonds, there are only ionic bonds between ions. It is very hard and very difficult to cleave. Plaster of Paris, a fine white powder is produced by heating gypsum to expel the water. If this powder is moistened and then allowed to dry, it becomes hard or sets. Its major use is in statuary, ceramics, dental plates, fine metal parts for precision instruments and surgical splints.

- **Example 6. Soap and detergent:** Molecules liquid state experience strong intermolecular attractive forces. When those forces are between like molecules, they are referred to as cohesive forces. The molecules of water droplet are held together by cohesive forces and the especially strong cohesive forces at the surface to form surface tension. So, surface tension is a type of intermolecular forces. Soap and detergents help the cleaning of clothes by lowering the surface tension of the water so that it more readily soaks into pores and soiled areas.

IV. LIQUIDS AND CRYSTALS

Walking on water small insects such as the water strider can walk on water because their weight is not enough to penetrate the surface due to the surface tension presented. Washing with cold water the major reason for using hot water for washing is that its surface tension is lower and it is a better wetting agent. But if the detergent lowers the surface tension, the heating may be unnecessary. Example in depth to show the significance of existence of intermolecular forces is water and ice. There are lots of different ways that the water molecules can be arranged in ice. The one below is known as cubic ice or "ice Ic". It is based on the water molecules arranged in a diamond structure. Cubic ice is only stable at temperatures below -80 ºC. The ice you are familiar with has a different, hexagonal structure. It is called "ice Ih".

The hydrogen bonding forces a rather open structure on the ice. When ice melts, the structure breaks down and the molecules tend to fill up this wasted space. This means that the water formed takes up less space than the original ice. Ice is a very unusual solid in this respect most solids show an increase in volume on melting [6, 7].

Why does ice float on water? Hydrogen bonding as a water molecule is composed of two hydrogen atoms and one oxygen atom. The atoms of hydrogen and oxygen are bound by sharing their electrons with one another. This bond is called a "covalent bond". However, since oxygen atoms pull electrons more strongly than hydrogen atoms, the oxygen atom in a water molecule has a slightly negative charge and the hydrogen atoms have a slightly positive charge. So adjacent water molecules are attracted to one another through the slightly negatively charged oxygen atoms and the slightly positively charged

hydrogen atoms. This interaction is called "hydrogen bonding". Hydrogen bonding is much weaker than covalent bonding, however, this type of bonding has a large total effect because there are so many hydrogen bonds. The bonds in water molecules are inclined at a tetrahedral angle of 109º [9]. The lone pairs occupy the other corners of the tetrahedron. Liquid water contains associations of water molecules. In ice the arrangement of water molecules is similar, but the regularity extends throughout the whole structure. The structure spaces the molecules further apart than they are in the liquid. This is why when water freezes, it expands (by 9%), and ice is less dense than water.

Table 1. Types of crystals and general properties.

Type of Crystal	Force(s) Holding the Units Together	General Properties	Examples
Ionic	Electrostatic attraction	Hard, brittle, high melting point, poor conductor of heat and electricity	NaCl, LiF, MgO, CaCO₃
Covalent	Covalent bond	Hard, high melting point, poor conductor of heat and electricity	C (diamond), SiO₂ (quartz)
Molecular	Dispersion forces, dipole-dipole forces, hydrogen bonds	Soft, low melting, poor conductor of heat and electricity	Ar, CO₂, I₂, H₂O, C₁₂H₂₂O₁₁
Metallic	Metallic bond	Soft to hard, low to high melting point, good conductor of heat and electricity	All metallic elements (Na, Mg, Fe, Cu)

A crystalline solid possesses rigid and long range order. In a crystalline solid, atoms, molecules or ions occupy specific (predictable) positions. An amorphous solid does not possess a well defined arrangement and long range molecular order. A glass is an optically transparent fusion product of inorganic materials that has cooled to a rigid state without crystallizing (Table 1). A unit cell is the basic repeating structural unit of a crystalline solid. We have seen that in crystals weak intermolecular interactions are strongly directional and that the mutual orientation of neighboring groups is important in achieving stable packing arrangements. On melting to a liquid, there is usually only a slight change in packing density but the breakdown of periodicity means that the regular, favorable orientation neighboring molecules is partly lost.

Molecular crystals are bound by intermolecular (van der Waals) forces, and knowledge of such force fields should be sufficient to predict crystal structures. In principle, accurate force fields can be obtained using electronic structure methods, but for reasons discussed below. This has not yet been achievable in practice. Thus, theoretical investigations of crystal structures typically rely on empirical force fields that are parametrized using

experimental information. Unfortunately, the predictive capability of such fields is limited, since a given field can describe well only the system used for its parametrization and thus is often not transferable even to polymorphs of this system. As a result, prediction of crystal structures has been considered an impossible task. This opinion was echoed first by Ball [21] and more recently by Desiraju [22], who wrote that the issue eluded scientists for more than 50 years and emphasized the low success rate of crystal structure predictions in the blind tests conducted by the Cambridge Crystallographic Data Center [23]. One of the key issues in predicting crystal structures is the accuracy of the force fields. This accuracy is also critical for calculations of lattice energies at experimental crystal structures [24]. The force fields can be computed ab initio using wave function based methods, but until recently the accuracy achievable for molecules containing more than a few atoms was far from quantitative and was insufficient for determination of crystal structures. One might have hoped that the problem could be resolved by the development of density functional theory, which can be applied to systems containing hundreds of atoms [25]. Unfortunately, conventional density functional theory methods fail badly in describing intermolecular interactions for which dispersion is the dominant component; such systems include molecular organic crystals.

V. CONCLUSION

The hydrogen is attached directly to one of the most electronegative elements, causing the hydrogen to acquire a significant amount of positive charge. Each of the elements to which the hydrogen is attached is not only significantly negative, but also has at least one active lone pair. An alcohol is an organic molecule containing an O-H group. Any molecule which has a hydrogen atom attached directly to an oxygen or a nitrogen is capable of hydrogen bonding. Such molecules will always have higher boiling points than similarly sized molecules which don't have an O-H or an N-H group. The hydrogen bonding makes the molecules stickier, and more heat is necessary to separate them.

Hydrogen bonding also occurs in organic molecules containing N-H groups in the same sort of way that it occurs in ammonia. Examples range from simple molecules like CH_3NH_2 (methylamine) to large molecules like proteins and DNA. The two strands of the famous double helix in DNA are held together by hydrogen bonds between hydrogen atoms attached to nitrogen on one strand, and lone pairs on another nitrogen or an oxygen on the other one.

Intermolecular forces are forces between molecules that determine the physical properties of liquids and crystals. Molecular substances are often soluble in organic solvents which are themselves molecular. Both the solute and the solvent are likely to have molecules attracted to each other by van der Waals' forces.

For liquids, we have a wealth of thermodynamic data from which averaged interaction energies can be estimated but we lack structural information about the relative orientations of neighboring molecules. The equilibrium vapor pressure is the vapor pressure measured when a dynamic equilibrium exists between condensation and evaporation. The boiling point is the temperature at which the (equilibrium) vapor pressure of a liquid is equal to the external pressure.

For crystals, we need better atom-atom potential energy functions. We have a wealth of information about the directional properties of weak interactions but very little thermodynamic data with which to test packing energy estimates. The phenomenon of polymorphism shows that the crystal form stable at room temperature is not necessarily that with the best packing energy, the entropy cannot be neglected.

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