

3 Molecular Interactions

Intermolecular forces that operate between the molecules of a pure substance determine the thermodynamic properties of that substance. In the case of a mixture, however, consideration must be given not only to interactions between like molecules, but also to interaction between unlike molecules.¹⁸⁶ The purpose of this section is to give a brief introduction to the nature and variety of forces acting between molecules.

When a molecule is in the proximity of another, forces of attraction and repulsion strongly influence its behavior. For example, if there are no forces of attraction, gases would not condense to form liquids and solids, and in the absence of repulsive forces, condensed matter would not show resistance to compression. The net energy of interaction, or potential energy, E , of non-bonded atoms or molecules is the result of both these attractive ($-E_A$) and repulsive effects (E_R). There is one major repulsive interaction, the tendency of two molecules to avoid occupying the same space (known as the occluded space). There are several components to the overall attractive interaction energy (including induced dipole-induced dipole, dipole-induced dipole, dipole-dipole and quadrupole), collectively known as *van der Waals'* forces, as well as specific forces (including Lewis acid-base interactions and hydrogen bonding).

To determine the magnitude of interaction between a solute and a given solvent, it is necessary to consider the balance of the intermolecular forces between solvent-solvent, solute-solute, and solvent-solute pairs of molecules in solution. These intermolecular

forces are considered in terms of the electrical properties of the molecules. The electrical behavior of individual molecules may be classified as (a) electrically neutral and symmetric, usually giving rise to nonpolar molecules; (b) electrically neutral but asymmetric, that is, possessing permanent dipole moments, giving rise to polar molecules; and (c) those having residual valences, giving rise to specific interactions such as Lewis acid/base interactions and hydrogen bonding.¹⁸⁷

3.1 Dispersion Interactions

Every molecule possess an instantaneous electric dipole due to electron oscillations that induce dipoles in neighboring molecules. The result is a net attractive interaction that determines the solubility of a non-polar solute in a non-polar solvent. For non-polar molecules, such as CO₂, these instantaneous dipoles average to zero over time due to their rapidly changing direction and magnitude. A simplified expression can be used to describe the potential energy of this induced dipole-induced dipole interaction, known as dispersion or *van der Waals-London* energy,¹⁸⁸

$$-E_d = \frac{3I_i I_j \alpha_i^p \alpha_j^p}{2(I_i + I_j)r^6} \quad (3-1)$$

Where E_d is the dispersion energy between molecules “*i*” and “*j*”, α^p is the *polarizability* (the ease with which the molecule’s electron “cloud” can be deformed by an electric field), r is the distance between the two molecules, and I is the ionization potential. From eqn. (3-1), it is the *polarizability* which is the key molecular property of the solute and solvent molecules that provides an indication of the strength of their interaction.

London's equation, eqn. (3-1), does not hold at very small separations where the electron clouds overlap and the forces between molecules are repulsive rather than attractive.¹⁸⁹ Figure 3-1 is a representation of Mie's potential energy function, of which the Lennard-Jones potential function (E_{LJ}) is a special case,¹⁹⁰ commonly used to describe the repulsive and attractive potential energies as a function of intermolecular distance r .

$$E_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (3-2)$$

As seen in the figure, the component of repulsive interaction rises very steeply to high positive values (E_R) when the intermolecular separation falls below a certain distance ($r < \sigma$) but otherwise has little effect on the net energy, which is seen to be attractive ($-E_A$).

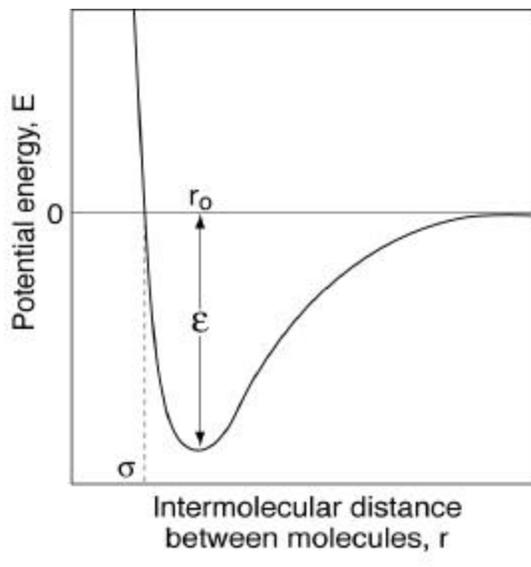


Figure 3-1. Mie's potential, where σ is the collision diameter, at which the potential energy is zero, and the maximum depth of the potential is ϵ and occurs at an equilibrium separation r_0 .

3.2 Polar Interactions

In addition to van der Waals-London dispersion forces, which are always present for all molecules, there can be additional forces of attraction between two molecules if one or both of these has a permanent dipole moment. A permanent dipole moment, $\boldsymbol{\mu}$ is a result of an unsymmetrical charge distribution present in some electrically neutral molecules. If the magnitude of the two equal and opposite charges of this molecular dipole is denoted by q , and the distance of separation l , the dipole moment is given by

$$\boldsymbol{\mu} = q \cdot l \quad (3-3)$$

Apart from hydrocarbons (such as n-hexane, cyclohexane, benzene, etc.) and some symmetrical compounds (such as carbon disulfide, tetrachloromethane, and tetrachloroethene) all common organic solvents possess a permanent dipole moment between 0 and 5.4 Debye (D).¹⁹¹ (1 D is equal to 1.0×10^{-18} electrostatic units or 3.336×10^{-30} coulomb meters).

3.2.1 Dipole-Induced Dipole Interactions

If one of the molecules possesses a permanent dipole moment, $\boldsymbol{\mu}$ it can induce a dipole in the second, neighboring molecule. This induced moment always lies in the direction of the inducing dipole. Thus, attraction always exists between the two molecules, which is independent of temperature.¹⁹² The resulting permanent dipole-induced dipole, or *van der Waals-Debye* interaction energy, can be described by

$$-E_i = \frac{\alpha_i^p \mu_j^2 + \alpha_j^p \mu_i^2}{r^6} \quad (3-4)$$

where E_i is the dipole-induced dipole energy between molecules “ i ” and “ j ”. For *van der Waals-Debye* interactions, it is the strength of the *dipole moment* in D which defines the strength of the molecular interaction.¹⁹³

3.2.2 Dipole- Dipole Interactions

Finally, if both molecules have permanent dipole moments, there will be a force of attraction between the molecules whose strength and direction are fixed as a result of their molecular structure. This situation only exists, however, when the attractive energy is larger than the thermal energy which can prevent the dipoles from optimal orientation, leading to a net attraction which is strongly temperature dependent. The simplified expression that accounts for permanent dipole-permanent dipole, or *van der Waals-Keesom*, potential energy is

$$-E_p \approx \frac{2\mathbf{m}_i \mathbf{m}_j}{3r^6 kT} \quad (3-5)$$

where E_p is the dipole energy between molecules “ i ” and “ j ”, \mathbf{m} is the strength of the *dipole moment* in D, T is the absolute temperature, and k is Boltzmann’s constant. As with the *van der Waals-Debye* energy, the key parameter which determines the strength of the interaction is the *dipole moment*. It is observed that *van der Waals-Debye* and *van der Waals-Keesom* forces can be significant if the magnitude of either molecular dipole is greater than about ≈ 1.0 Debye. Such large values of \mathbf{m} are commonly associated with functional groups of atoms, such as -OH, -CN, -NH₂, -COOH, and -NO.

Substances that are highly polar at ambient conditions, such as acetone, ammonia, and water, typically have high critical temperatures, as shown in Table 3-1. However, while a polar solvent such as acetone will always have a permanent dipole moment due to its molecular structure, regardless of its physical state, it will exhibit interactions more like those of a non-polar solvent at the elevated temperatures and pressures needed to make it supercritical. This is because as the temperature increases, the attractive interaction energies decrease in magnitude until, at some higher temperature, all dipole orientations are equally populated and the net interaction energy is zero. In fact, it is these high critical temperatures and the inverse temperature-interaction energy relationship that precludes the possibility of finding a highly polar liquid solvent that is also a polar SCF solvent.

Table 3-1. Critical temperature and pressure of some common fluids.

Fluid	Critical Temperature (°C)	Critical Pressure (psi)
Neon, Ne	-229	400
Nitrogen, N ₂	-147	492
Argon, Ar	-122	706
Xenon, Xe	17	858
Carbon dioxide, CO ₂	31	1072
Sulfur hexafluoride, SF ₆	46	545
Propane, C ₃ H ₈	97	617
Ammonia, NH ₃	133	1654
Acetone, C ₃ H ₆ O	235	682
Water, H ₂ O	374	3209

3.2.3 Quadrupolar Interactions

Molecules can also have higher-order polar moments such as a quadrupole moment. CO₂, perhaps the most commonly used SCF, has a rather large quadrupole

moment (-4.3×10^{-26} esu, the sign indicating that the oxygen atoms are negative with respect to the carbon atom¹⁹⁴). In this instance, the simplified formula for the intermolecular quadrupole-quadrupole potential energy is¹⁹⁵

$$-E_Q \approx C_1 \frac{Q_i^2 Q_j^2}{r^{10} kT} \quad (3-6)$$

where E_Q is the quadrupole energy between molecules “ i ” and “ j ”, C_1 is a constant, and Q is the *quadrupole moment*. For this type of interaction, Q , is the important parameter in determining interaction strength. Like dipolar forces of attraction, quadrupolar forces of attraction are inversely proportional to temperature, but decrease in magnitude with intermolecular distance much faster than dipolar forces. Therefore, the effect of a quadrupole moment on thermodynamic properties is expected to be much less significant than a dipole moment.

Quadrupoles and dipoles can also interact according to the simplified expression,¹⁹⁶

$$-E_{Qp} \approx C_2 \frac{\mathbf{m}_i^2 Q_j^2}{r^8 kT} + C_3 \frac{\mathbf{m}_j^2 Q_i^2}{r^8 kT} \quad (3-7)$$

where all variables are as described previously.

3.3 Donor-acceptor Interactions

In addition to dispersion and polar interactions, specific donor-acceptor interactions may exist between pairs of molecules. Lewis acid-base interactions are completely

independent of the dipole moment and are operative when a basic (electron donating) site interacts with an acidic (electron accepting) site. A subset of the Lewis acid-base interactions are hydrogen bonds, where the strength of hydrogen bonding is a function of the acid strength of the hydrogen-bond donor and the base strength of the hydrogen-bond acceptor. Atoms of higher electronegativity than hydrogen (i.e. C, N, P, O, S, F, Cl, Br, I), are capable of forming bonds with hydrogen. The strength of these interactions increases with increasing separation of the electronegative series. From Figure 3-2, it can be seen then that the strongest hydrogen bonds would therefore occur between hydrogen and oxygen, nitrogen, or fluorine. Other elements are either too electropositive or too large to approach sufficiently close to the hydrogen atom.¹⁹⁷ It should be noted that hydrogen bonds can be either *intermolecular* or *intramolecular*.

H																
2.20																
Li	Be											B	C	N	O	F
0.98	1.57											2.04	2.55	3.04	3.44	3.90
Na	Mg											Al	Si	P	S	Cl
0.93	1.31											1.61	1.90	2.19	2.58	3.16
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
0.82	1.00	1.36	1.54	1.63	1.66	1.55	1.83	1.88	1.91	1.90	1.65	1.81	2.01	2.18	2.55	2.96
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
0.82	0.95	1.22	1.33	1.6	2.16	2.10	2.2	2.28	2.20	1.93	1.69	1.78	1.96	2.05	2.1	2.66
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
0.79	0.89	1.10	1.3	1.5	1.7	1.9	2.2	2.2	2.2	2.4	1.9	1.8	1.8	1.9	2.0	2.2
Fr	Ra	Ac														
0.7	0.9	1.1														

Figure 3-2. Electronegativities of the elements.¹⁹⁸

Specific interactions typically decrease with increasing temperature, in the same way as van der Waals-Keesom forces, since they depend on the alignment of the molecules in solution.

3.4 Strengths of Intermolecular Interactions

Dispersion (van der Waals-London) forces are universal for all atoms and molecules, and it is they that are responsible for the aggregation of molecules which possess neither free charges nor permanent electrical dipole moments. Even for many molecules possessing permanent dipole moments, the major part of the cohesion may be due to dispersion forces. For example, the calculated cohesion energy of methyl ethyl ketone ($m = 3.3D$) at 40°C consists of 22% polar energy, and 78% dispersion energy.¹⁹⁹ In addition, typically, induced intermolecular potentials are negligibly small in comparison with potentials caused by permanent moments. Table 3-2 and 3-3 gives examples of the relative magnitude of van der Waal forces between identical and different molecules, respectively.

Table 3-2. Relative magnitude of van der Waals forces between two identical molecules.²⁰⁰

Molecule	Dipole Moment (D)	VDW Forces between Two Identical Molecules at 0°C (erg cm ⁶ x 10 ⁶⁰)		
		Dipole Eqn. (3-5)	Induction Eqn. (3-4)	Dispersion Eqn. (3-1)
Carbon Tetrachloride, CCl ₄	0	0	0	1460
Cyclohexane, C ₆ H ₁₂	0	0	0	1560
Carbon Monoxide, CO	0.10	0.0018	0.0390	64.3
Hydrogen bromide, HBr	0.80	7.24	4.62	188
Hydrogen chloride, HCl	1.08	24.1	6.14	107
Ammonia, NH ₃	1.47	82.6	9.77	70.5
Water, H ₂ O	1.84	203	10.8	38.1
Acetone, C ₃ H ₆ O	2.87	1200	104	486

The computed values in Table 3-2 indicate that the contribution of induction forces is small and that even for strongly polar substances, like ammonia, water, or acetone, the contribution of dispersion forces is far from negligible.

Table 3-3. Relative magnitude of van der Waals forces between two different molecules.²⁰¹

Molecules		Dipole Moment (D)		VDW Forces between Two Different Molecules at 0°C (erg cm ⁶ x 10 ⁶⁰)		
(1)	(2)	(1)	(2)	Dipole Eqn. (3-5)	Induction Eqn. (3-4)	Dispersion Eqn. (3-1)
Carbon Tetrachloride, CCl ₄	Cyclohexane, C ₆ H ₁₂	0	0	0	0	1510
Carbon Tetrachloride, CCl ₄	Ammonia, NH ₃	0	1.47	0	22.7	320
Acetone, C ₃ H ₆ O	Cyclohexane, C ₆ H ₁₂	2.87	0	0	89.5	870
Carbon Monoxide, CO	Hydrogen chloride, HCl	0.10	1.08	0.206	2.30	82.7
Water, H ₂ O	Hydrogen chloride, HCl	1.84	1.08	69.8	10.8	63.7
Acetone, C ₃ H ₆ O	Ammonia, NH ₃	2.87	1.47	315	32.3	185
Acetone, C ₃ H ₆ O	Water, H ₂ O	2.87	1.84	493	34.5	135

Again, it is noticed that polar forces are not important when the dipole moment is less than about 1 D and induction forces always tend to be smaller than dispersion forces.

Donor-acceptor interactions between solute and solvent molecules generally have a greater influence than the combined van der Waals forces, due to their greater bond energies. Strong Lewis acid-base bond energies lie between -42 and -188 kJ/mol, and weaker complexes, while less than approximately -42 kJ/mol, are usually still larger than van der Waals forces, which range from -4 to -40 kJ/mol.²⁰² The bond dissociation

energy for normal hydrogen bonds is from -13 to -42 kJ/mol,²⁰³ while the strongest hydrogen bonds, those formed with the most electronegative elements (i.e. fluorine), are as large as -155 kJ/mol. The greater strength of hydrogen bonds as compared with van der Waals forces is due to the much smaller size of the hydrogen atom relative to any other atom, which allows it to approach another atom more closely. Table 3-4 gives a summary of the strengths of the various intermolecular interactions.

Table 3-4. Interaction strengths.

Interaction Type	Interaction Strength
Van der Waals	- 4 to - 40 kJ/mol
Hydrogen bonds (normal - large)	- 13 to - 42 kJ/mol (up to - 155 kJ/mol)
Weak Lewis acid/base	< - 42 kJ/mol but generally larger than van der Waals
Strong Lewis acid/base	- 42 to - 188 kJ/mol