Intermolecular forces

Several type of forces act between atoms and molecules. Some of these tend to pull these particles closer together, i.e. they are attractive forces. Other forces prevent them from coming too close to each other, i.e. they are repulsive forces.

London or Dispersion Forces

- These are short-range attractive forces that act between molecules of all types.
- Such forces are responsible for cohesion between molecules of liquid in absence of any electrostatic charges.
- Their magnitude is inversely proportional to distance raised to the power six, which means they diminish quickly as the distance increases.

Repulsive Forces

- When the distance between molecules becomes very small, their electron fields start overlapping.
- Very strong repulsive forces are generated due to repulsion between similar charges of overlapping electron fields.

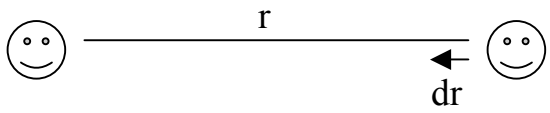
Balance of intermolecular forces

- The sum of these attractive and repulsive forces changes with the distance of separation between the particles.
- If the net sum is attractive the particles will move to come closer and if the net sum of forces happened to be repulsive, the particles will move further apart.
- At some distance the sum will be zero, and at that distance there would be no tendency to move.

Potential Energy:

Potential energy of two molecules separated by a distance 'r' is equal to the work done in bringing these molecules to this distance of separation starting from a very large distance. By large distance, we mean so large that the force between the two molecules is zero. Mathematically, it means infinity.

Now imagine two molecules that are sitting at a distance 'r' between them. There is a repulsive force 'F' acting between them. Now you push these molecules closer together a short distance 'dr'



The work done on the system in moving them a small distance Δr would be force multiplied by the distance, i.e.

Work = (Force) x (Distance travelled) = $F \cdot \Delta r$

In general the force is not constant, it varies with the distance 'r'. We can include this information in the above expression by writing it as

$W = F(r) \cdot \Delta r$

The work done in moving the molecules over a distance that comprises several short steps can be written as:

$$W = \sum F(r)\Delta r$$

When the steps are vanishingly small, the summation becomes integration. The work done in bringing the molecules to their current separation distance r from an infinite distance can be written as:

$$W = \int_{\infty}^{r} F(r)\, dr$$

This work done is equal to the potential energy that becomes stored in the pair of molecules.

$$\phi(r) = \int_{\infty}^{r} F(r)\, dr$$

We denote the potential energy with Greek letter ϕ. It is clearly a function of the separation distance r and depends on the type of force involved.

<u>Relationship between the Potential and The force</u>

- Potential is the integral of force over the distance travelled starting from a reference position.
- Force is the derivative of the potential function, i.e.

$$F = \frac{d\phi}{dr}$$

We will now look at a simple model for the dependence of force on distance.

Lennard-Jones Potential Function

This form of potential energy function was originally suggested by Mie in 1903.

$$\phi(r) = \alpha\left[\left(\frac{\sigma}{r}\right)^{d} - \left(\frac{\sigma}{r}\right)^{c}\right]$$

In this expression, α, σ, d and c are constants that would depend on the nature of molecules involved; r is the distance between the molecules and ϕ is the potential.

In 1931 Lennard and Jones came up with an explicit form that also attaches some physical meaning to the constants.

$$\phi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{3.11}$$

The parameter ε has the dimension of energy while the other parameter, σ has the dimension of length. We will examine the physical significance of these parameters shortly. First let us look at the expression for the net force resulting from this potential function, which is obtained by differentiating this equation with respect to r.

$$F = \frac{d\phi(r)}{dr} = \frac{d}{dr}\left\{4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]\right\} = -\frac{48\varepsilon\sigma^{12}}{r^{13}} + \frac{24\varepsilon\sigma^{6}}{r^{7}}$$

Note that the force expression includes a positive term and a negative term. The positive term represents the attractive force.

$$F_a = \frac{24\varepsilon\sigma^{6}}{r^{7}} \tag{3.13}$$

The negative term represents the repulsive force.

$$F_r = -\frac{48\varepsilon\sigma^{12}}{r^{13}} \tag{3.14}$$

<u>Equilibrium Separation Distance</u>

The equilibrium distance of separation between two molecules is given by zero net force. The equilibrium distance also corresponds to the minimum potential energy.

The zero force separation distance can be obtained by equating the net force expression to zero.

$$F = -\frac{48\varepsilon\sigma^{12}}{r^{13}} + \frac{24\varepsilon\sigma^{6}}{r^{7}} = 0$$

$$-\frac{2\sigma^6}{r^6} + 1 = 0$$

$$r^6 = 2\sigma^6, \text{ or } r = 2^{(1/6)}\sigma$$

The equilibrium distance is given by:

$$r_o = 1.122\ \sigma \tag{3.15}$$

When this value of r is substitute into Eq. 3.11, the potentical energy at the point of zero force, which would be the minimum potential energy,

$$\phi(r_o) = -\varepsilon \tag{3.16}$$

The parameter ε, therefore, represents the minimum potential energy between the two molecules.

<u>Points to remember:</u>

- The potential energy is zero at r = σ.
- The potential energy is minimum at the equilibrium distance.
- Net force is zero at the equilibrium distance.
- The equilibrium distance is given by $r_o = 1.122\ \sigma$
- The value of potential at the equilibrium distance is -ε.

<u>Values of ε and σ</u>

The values of these two parameters for various non-polar substances have been determined, In listing these parameters, we rely on the following basis.

For ε

We list the values a ε/k, where k is the Bolttzmann constant.

$k = R/N_a$

R = Universal gas constant = 8.314 J/mol K

$N_a = 6.023 \times 10^{23}$ molecules per mol.

Using these values, $k = 1.3805 \times 10^{-23}$ J/K
Therefore the units of ε/k become, J/(J/K) or K.

For σ

We define

$$b_o = \frac{2\pi}{3}\sigma^3 N_a \tag{3.17}$$

Which is in units of m^3/kmol. b_o represents a volume that is four times the volume of Avogadro's number of spherical molecules of diameter σ. Note that if you know b_o, you can calculate σ.

Typical values of these parameters for simple non-polar molecules are listed in Table 3-6.

Note: the Lennard-Jones function is not valid for polar or more complicated molecules.

<u>Example Problem:</u>

The Lennard-Jones parameters for a non-polar substance are given as:

$$\frac{\varepsilon}{k} = 145K$$

and

$$b_o = 0.13 \; {}^{m^3}\!/_{kmol}$$

Calculate the potential energy between two molecules of this substance when they are separated by a centre-to-centre distance of 4.5×10^{-10} m.

<u>Solution</u>

$\varepsilon/k = 145$ K; $\varepsilon = 145 \times 1.3805 \times 10^{-23} = 2.00 \times 10^{-21}$ J

$$\sigma = \left[\frac{3b_o}{2\pi N_A}\right]^{\frac{1}{3}} = \left[\frac{3x0.13}{2x\pi\, x6.023x10^{26}}\right]^{\frac{1}{3}} = 4.69x10^{-10}\ m$$

$$\phi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

$$\left(\phi(r)\right)_{r=4.5A} = 4x2.00x10^{-21}\left[\left(\frac{4.69x10^{-10}}{4.5x10^{-10}}\right)^{12} - \left(\frac{4.69x10^{-10}}{4.5x10^{-10}}\right)^{6}\right]$$

$= 2.89 \text{ x}10^{-21}$ J