

Fundamentals of Distribution Separations (II)

(01/12/15)

1. Principles of distribution equilibria

$$dG = -S^* dT + V^* dP + \sum (\mu_i^{\text{int}} + \mu_i^{\text{ext}}) dn_i \quad (\text{open systems under external field})$$

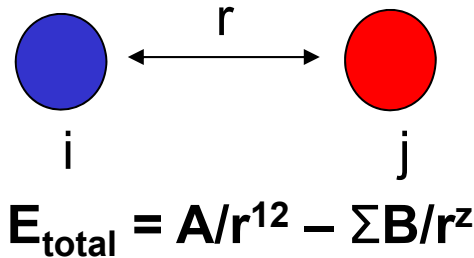
$$K = \exp\left[\frac{-\Delta\mu_i^0 - \Delta\mu_i^{\text{ext}}}{RT}\right] \quad \text{distribution coefficient}$$

$$\Delta\mu_i^0 = \Delta\bar{H}_i^0 - T\Delta\bar{S}_i^0 \quad \text{A} \rightleftharpoons \text{B} \xrightarrow{q} \text{A} + \text{B}$$

2. Intermolecular interactions

Intermolecular Interactions

The intermolecular interactions can either be attractive or repulsive in nature.



Where: E_{total} = net total energy of interactions

A = constant describing repulsive forces between i and j

B = constant describing attractive forces between i and j

z = constant for a given type of attractive force

┆ Lennard-Jones potential: $z=6$

1. Dipole-dipole interaction

2. Induction interaction

3. Dispersion interaction (London forces)

4. Hydrogen bond

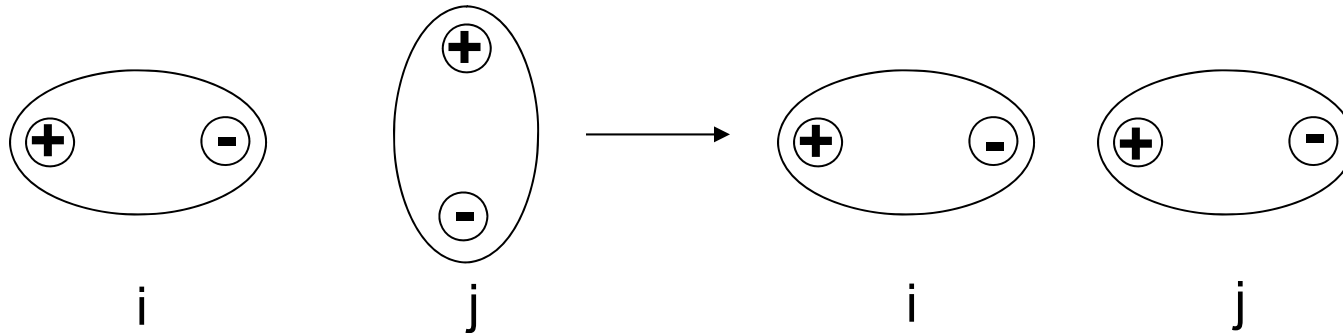
5. Lewis acid-base interactions

Electrostatic interaction (Coulombic)
(hard interactions)

Electron transfer (sharing electron)
(soft interactions)

van der Waals forces

1. Dipole-dipole interaction



$$E_D = - \frac{\mu_i^2 \mu_j^2}{3 (4 \pi \epsilon_0)^2 k T r^6}$$

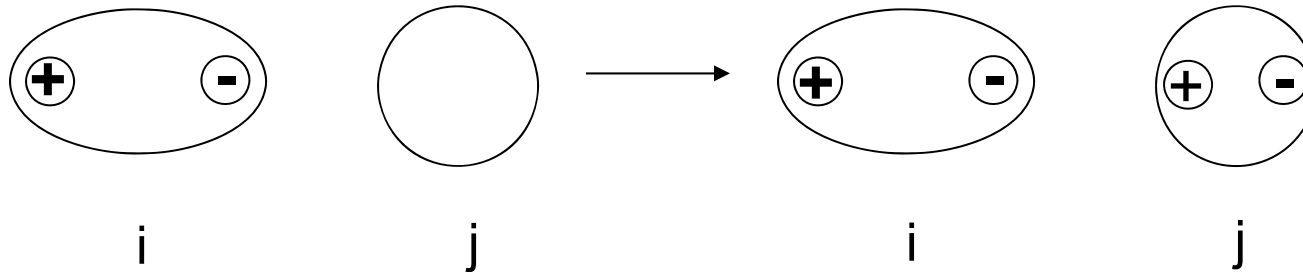
μ_i, μ_j = dipole moments of i and j

T = Temperature

k = Boltzmann's constant

Note: Temperature dependent

2. Induction interaction



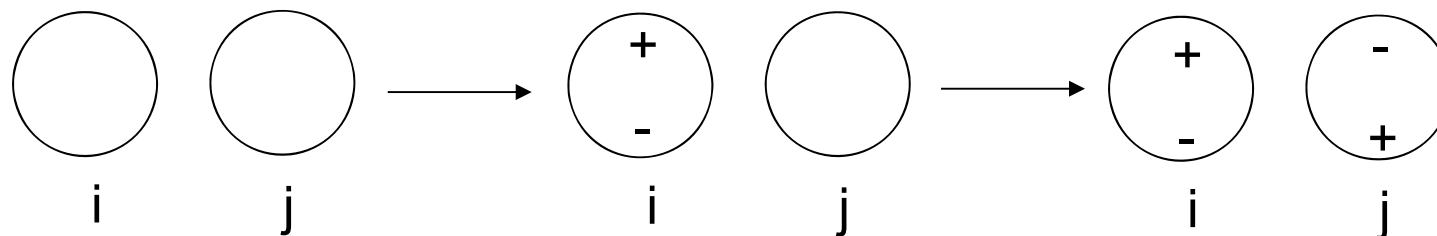
$$E_i = - \frac{\mu_i^2 \alpha_j}{(4 \pi \epsilon_0)^2 r^6}$$

μ_i = dipole moments of i

α_j = polarizability of j

Note: independent of temperature

3. Dispersion interactions (London Force)



$$E_L = - \frac{3 h\nu\alpha_i \alpha_j}{4 (4 \pi \epsilon_0)^2 r^6} \quad \text{two atoms}$$

α_i, α_j = polarizability of i and j

r = distance

h = Plank' s constant

ν = Frequency of light required for ionization of each species

ϵ_0 = dielectric permittivity of the medium

$$E_L = -C_L \bar{V}_i (\alpha_i)_v (\alpha_j)_v \quad \text{two molecules}$$

$(\alpha_i)_v (\alpha_j)_v$ = polarizability of i (solute) and j (solvent) per unit volume

C_L : Dispersion constant (uniform for most compounds)

V_i = Molar volume of i (MW/density)

4. Hydrogen bonds

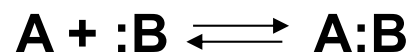
Non-covalent bond forms between a molecule with a proton donor group
And proton acceptor group.

(a) Common proton donors are –OH, –NH, and –SH

(b) Common proton acceptor are –O-, =N-, -F, -S-, -Cl, C=C.....

(c) $E \sim 1/r^6$

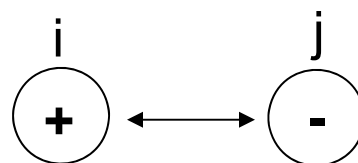
(d) Hydrogen bond is one example of a more general class of Lewis acid-base interactions.



5. Lewis acid-base interactions

(A) Electrostatic interaction (Coulombic) (hard interactions)

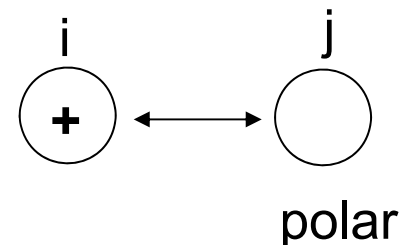
(1) Coulombic interaction



$$E_{AB} = \frac{Q_i Q_j}{4 \pi \epsilon_0 r}$$

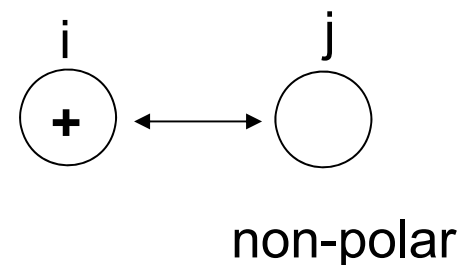
(2) Interactions with polar and non-ionic compounds (E_D)

$$E_D = - \frac{Q_i^2 \mu_j^2}{6 (4 \pi \epsilon_0)^2 k T r^4}$$

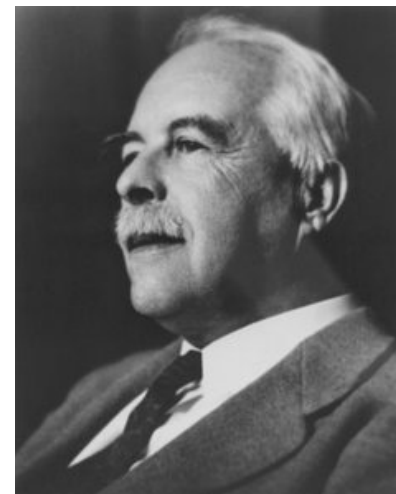


(3) Interactions with non-polar compounds (E_L)

$$E_L = - \frac{Q_i^2 \alpha_j^2}{2 (4 \pi \epsilon_0)^2 r^4}$$



(B) Electron transfer (sharing electron) (soft interactions)



Gilbert N. Lewis

5. Lewis acid-base interactions

$$E_{AB} = - [E_A * E_B + C_A * C_B], \text{ Approximation for A-B interaction}$$

Where: $E_A * E_B$ = Measures of acid (A) and base (B)' s ability to undergo *hard* acid-base interaction

$C_A * C_B$ = Measures of acid (A) and base (B)' s ability to undergo *soft* acid-base interaction

The values of E_A , E_B , C_A , C_B :

	Rel. Acidity		Rel. Basicity		
	E_A	C_A	E_B	C_B	
HF	17.0	0.0	Ammonia	1.3	0.3
Alcohols	3.6	0.8	Ketones	0.7	0.1
Phenols	4.7	1.7	1' Amines	1.2	0.6
SO ₂	1.1	7.2	2' Amines	0,9	0,9
Iodine	1.0	10.0	3' Amines	0,6	1.2
			Esters	0.6	0.4
			Sulfides	0.0	0.8

Strong interactions: hard-hard interactions, and soft-soft interactions

Weak interactions: hard-soft interactions.

Distribution equilibria and Solubility

$$K = \exp\left(\frac{-\Delta\mu_i^0 - \Delta\mu_i^{\text{ext}}}{RT}\right) \text{ distribution coefficient}$$

Solubility: i dissolved in j

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta H = \Delta\mu^0 \quad - T\Delta S = RT \ln(C_i)$$

$$\Delta G = \Delta\mu^0 + RT \ln(C_i)$$

At soluble equilibrium: $\Delta G = \Delta\mu^0 + RT \ln(C_i) = 0$

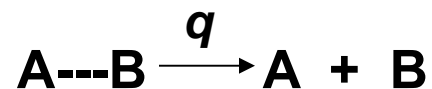
$$C_i = \exp\left(\frac{-\Delta\mu^0}{RT}\right)$$

$$\Delta\mu_i^0 = \Delta\bar{H}_i^0 - T\Delta\bar{S}_i^0 \quad \text{A} \cdots \text{B} \xrightarrow{q} \text{A} + \text{B}$$

$$\Delta H = E_L + E_I + E_D + E_{AB}$$

Distribution equilibrium and Solubility

$$\Delta\mu_i^0 = \Delta\bar{H}_i^0 - T\Delta\bar{S}_i^0$$



$$\Delta H = E_L + E_I + E_D + E_{AB}$$

Type of Compounds	Possible interactions	Relative strength
Acid-base compounds	E_L, E_I, E_D, E_{AB}	Strong
Non Acid-base Permanent dipole moment Polar compounds	E_L, E_I, E_D	↑ Weak
Non-Polar compounds	E_L	

For all of the above interactions are present in one compounds

$$E_L < E_I < E_D < E_{AB}$$

Quantitative Approach for the Strength of Molecular Interactions

A more quantitative approach in estimating the strength of molecular interactions is to use various scales that describe molecular polarity.

- (a) Polarizability
- (b) Dipole Moments
- (c) Solubility parameters

(a) Polarizability

- (1) The polarizability (α) of a compound is a measure of how easily the electron clouds of a compound may be distorted
- (2) The value of α for any atom or molecules can be calculated from spectroscopic properties, such as its refractive index.

$$(\alpha_i)_v = [3 \pi N/4][(n^2-1)/(n^2+2)]$$

Where, $(\alpha_i)_v$ = polarizability of the compound per unit volume

N = Avogadro's number

n = refractive index of the compounds

Dispersion interaction (London forces)

$$E_L = - C_L \bar{V}_i (\alpha_i)_v (\alpha_j)_v \text{ between two molecules}$$

Where: $(\alpha_i)_v$ $(\alpha_j)_v$ = polarizability of i (solute) and j (solvent) per unit volume

C_L : Dispersion constant (uniform for most compounds)

\bar{V}_i = Molar volume of i (MW/density)

Note: it is useful in predicting boiling points and solubility of non-polar compounds, such as saturated aliphatics.

Compound	MW (g/mol)	Density (g/mL)	Refractive Index	Boiling Points (°C)
Ethane	30.07	0.572	1.0377	-88.6
Octane	114.23	0.7025	1.3974	125.7