

## MOLECULAR INTERACTIONS NOTES

### Summary of Fundamental Molecular Interactions

<b>Ion-Ion</b>	$U(r) = \frac{Q_1 Q_2}{4\pi\epsilon\epsilon_0 r^2}$
<b>Ion-Dipole</b>	$U(r) = \frac{-\mu Q \cos\theta}{4\pi\epsilon\epsilon_0 r^2}$
<b>Dipole-Dipole (fixed)</b>	$U(r) \propto \frac{\mu_1 \mu_2}{r^3}$
<b>Dipole-Rotating Dipole</b>	$U(r) \propto -\frac{\mu_1^2 \mu_2^2}{r^6}$
<b>Dipole-Induced Dipole</b>	$U(r) \propto -\frac{\mu_1^2 \alpha_2}{r^6}$
<b>Dispersion</b>	$U(r) = -\frac{3\alpha_o^2 E_I}{4(4\pi\epsilon\epsilon_o)^2 r^6}$ $U(r) = -\frac{3\alpha_{o1}\alpha_{o2}}{2(4\pi\epsilon\epsilon_o)^2 r^6} \left( \frac{E_{I1}E_{I2}}{E_{I1} + E_{I2}} \right)$
<b>Quadrupolar</b>	Short range
<b>Van der Waals Repulsion</b>	$U(r) \propto e^{-r/\sigma_o}$ [ Buckingham ] $U(r) \propto r^{-12}$ [ Lennard-Jones ]
<b>H-bonding</b>	Short range

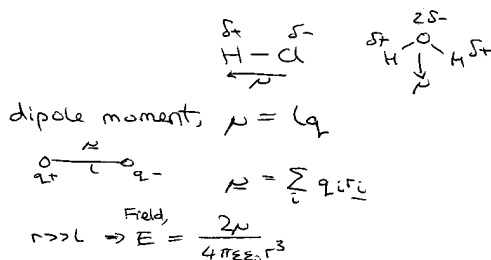
### Microscopic Interactions

Coulombic Force –

$$\text{Potential, } \phi = \frac{Q}{4\pi\epsilon\epsilon_0 r} \quad \text{Field, } E = \frac{Q\hat{r}}{4\pi\epsilon\epsilon_0 r^2}$$

$$F(r) = \frac{-Q_1 Q_2}{4\pi\epsilon\epsilon_0 r^2} \quad U(r) = \int F(r) dr = \frac{Q_1 Q_2}{4\pi\epsilon\epsilon_0 r}$$

**Polar Molecules**

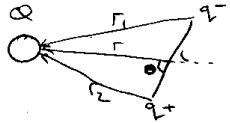


In the limit  $r^2 \gg l^2$ , treat molecule as point dipole.

### Inductive Interactions

There are several types of dipole interaction.

**Charge-Dipole Interactions -**

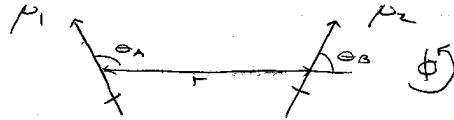


$$U(r) = \frac{-Qq}{4\pi\epsilon_0} \left[ \frac{1}{r - \frac{l}{2}\cos\theta} - \frac{1}{r + \frac{l}{2}\cos\theta} \right]$$

$$= \frac{-Qq}{4\pi\epsilon_0 l} \left[ \frac{l\cos\theta}{r^2 - \frac{l^2\cos^2\theta}{4}} \right]$$

$$U(r) = \frac{-\mu Q \cos\theta}{4\pi\epsilon_0 r^2} \quad (\mu = ql)$$

**2 Fixed Dipoles -**



$$U(r) = -\mu_2 E_1 = \frac{1}{4\pi\epsilon_0 r^3} (\mu_1 \cdot \mu_2 - 3(\mu_1 \cdot \hat{r})(\mu_2 \cdot \hat{r}))$$

2 point dipole,  $r \gg l$ :

$$U(r, \theta_1, \theta_2, \phi) = \frac{-\mu_1 \mu_2}{4\pi\epsilon_0 r^3} (2\cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos\phi)$$

**Rotating Dipoles -**

Dipole-dipole: generally  $\ll kT$ .  
 Free rotation, but Boltzmann Weight,  $e^{-U/kT}$ , favour orientations of lower energy.  
 Thus, average over all possible orientations:

$$\langle U(r) \rangle = \frac{-2\mu_1^2 \mu_2^2}{3(4\pi\epsilon_0)^2 kT r^6} \quad [r^6 \text{ \& } kT \text{ dependence}]$$

Must be entropically unfavourable to align dipole ( $\Delta S$  larger when aligned).

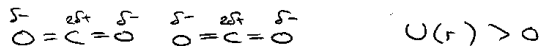
$$U = A + TS = A - T \left( \frac{dA}{dT} \right)_N = -T^2 \left( \frac{d}{dT} \right) \left( \frac{A}{T} \right)$$

$$A = \frac{-\mu_1^2 \mu_2^2}{3(4\pi\epsilon_0)^2 kT r^6} = \frac{U}{2}$$

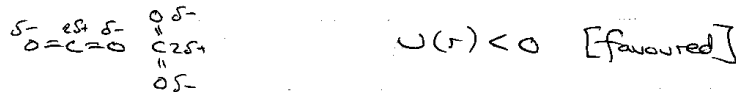
**Quadrupolar Interactions -**

Some molecules have no  $\mu$ , but quadrupole moment ( $H$ ) =  $\sum_i q_i r_i^2$  (for linear charge distribution)

e.g. CO<sub>2</sub>, benzene.



vs.



Compare values:

**QUADRUPOLE:**

$$U(r) \propto r^{-5} \text{ (fixed)}$$

$$U(r) \propto r^{-10} \text{ (rotating)}$$

**DIPOLE:**

$$U(r) \propto r^{-3} \text{ (fixed)}$$

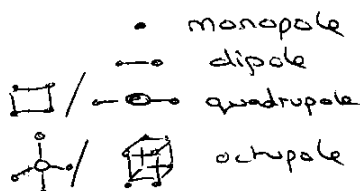
$$U(r) \propto r^{-6} \text{ (rotating)}$$

Also, some molecules neither, e.g. CH<sub>4</sub>.

Multipoles –

An n-pole is an array of charges with an n-pole moment but no lower moment.  
Higher order → weaker.

$$V(r) \propto 1/r^{n+m-1} \text{ (n-pole to m-pole interaction).}$$



**Dipole-Induced Dipole –**

Field due to one dipole ( $\sim \mu/r^3$ ) induces dipole in 2<sup>nd</sup> molecule – 2 dipoles then interact →  $U \sim \alpha \mu^2/r^6$ .

Induced dipole,  $\mu^{ind} = e l$  (i.e. electron's charge).

$$F_{ext} = eE = \frac{e}{4\pi\epsilon_r\epsilon_0 r^3} \mu^{ind}$$

$$\mu^{ind} = 4\pi\epsilon_r\epsilon_0 r^3 E = \alpha_0 E$$

$$\alpha_0 = \text{polarisability, } = \frac{\alpha_0}{4\pi\epsilon_r\epsilon_0} \text{ (m}^3\text{)}$$

$$\alpha_0 E \propto \frac{\alpha_0 \mu_1}{r^3}$$

$$U(r) \propto \frac{-\mu_1 \mu^{ind}}{r^3} \propto \frac{-\mu_1^2 \alpha_0}{r^6}$$

$$\therefore U(r) = \frac{-\mu_1^2 \alpha_0}{(4\pi\epsilon_r\epsilon_0)^2 r^6}$$

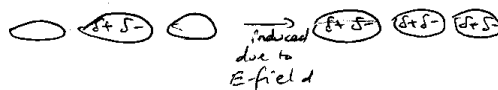
**Dispersive Interactions**

Instantaneous dipole due to asymmetry in electron distribution, therefore exists even in non-polar molecules →  $U \sim \alpha^2/r^6$ .

**Induced-Induced Dipole –**

- ⚡ Acts between all atoms and molecules. Always present.
- ⚡ Long range.
- ⚡ Quantum Origin.
- ⚡ Not a simple power law.

Consider an instance where a finite dipole moment exists because of instantaneous position of electrons.



London Expression for identical molecules:

$$U(r) = \frac{-3\alpha_0 E_I}{4(4\pi\epsilon_r\epsilon_0)^2 r^6} \rightarrow \text{Ionisation Potential}$$

London Expression for dissimilar molecules:

$$U(r) = \left( \frac{-3\alpha_0 \alpha_2}{2(4\pi\epsilon_r\epsilon_0)^2 r^6} \right) \left( \frac{E_{I1} E_{I2}}{(E_{I1} + E_{I2})} \right)$$

These forces are **Van der Waals** –

Dipole-rotating Dipole | Dipole-Induced | Dispersion

$$U \propto \frac{1}{r^6}$$

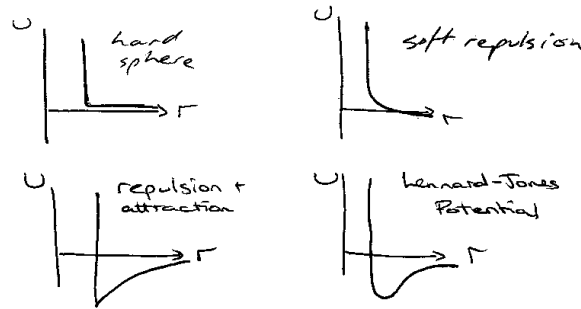
$$U_{VDW} = \frac{-C}{r^6} = \frac{-(C_{orient} + C_{ind} + C_{disp})}{r^6}$$

**Hydrogen Bonds** –

Strong, highly directional (linear favoured).

**Repulsive Interactions**

Overlap electron clouds. For closed shell molecules / atoms, net interaction is antibonding and hence repulsive, e.g. H cations.



**Interactions b/w Particles, Surfaces & Particles + Surfaces**

Physisorption –

$$\Delta H_{ads} \approx -\Delta H_{vap} \approx -10 \dots -40 \text{ kJ mol}^{-1}$$

Bound by Van der Waals or dipolar forces (weak, but long range).

Physisorbed molecule retains identity.

e.g. noble gas on any solid, stable gases on salts, oxides, silicates (some exceptions).

Molecules diffuse and rotate rapidly at rtp.

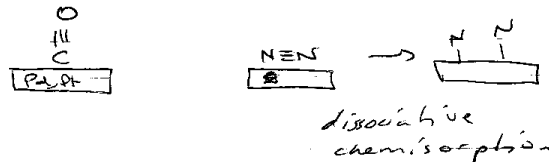
Chemisorption –

$$\Delta H_{ads} \approx -100 \dots -400 \text{ kJ mol}^{-1}$$

Strong interactions between adsorbate and solid, normally leads to some kind of chemical bond formation.

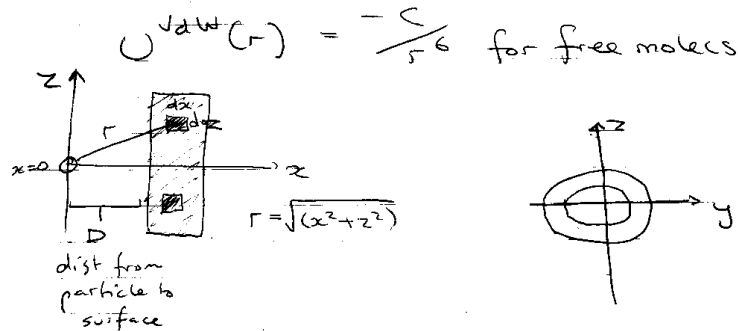
- ⚡ Chemically selective.
- ⚡ Surface catalysts.
- ⚡ Adsorption essentially irreversible at rtp.

e.g.



**Molecule-Surface Interactions**

Assume purely attractive, and additive.



Total interaction:

$$U(D) = \int_{x=D}^{\infty} \int_{z=0}^{\infty} 2\pi \rho z dx dz \frac{C}{(x^2+z^2)^3}$$

$\hookrightarrow r^6$

Total interaction between Molecule and Solid:

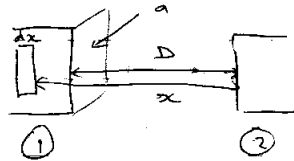
$$U(D) = \frac{-\pi C \rho}{6D^3}$$

# moles per unit vol in solid

distance of particle from surface

Inverse cube dependence on separation

### Surface-Surface Interactions



Molecule in slab 1 interacts with all of slab 2 as:

$$U(D) = \frac{-\pi C \rho_2}{6x^3}$$

Interaction between sheet of thickness dx in slab 1:

$$U(D) = \frac{-\pi C \rho_1 \rho_2 a dx}{6x^3}$$

(area)

Therefore total interaction between slabs:

$$U(D) = \int_{x=D}^{\infty} \frac{-\pi C \rho_1 \rho_2 a dx}{6x^3}$$

Total Interaction Energy per unit area between 2 flat surfaces:

$$U(D) = \frac{-\pi C \rho_1 \rho_2}{12D^2}$$

Surface & Sphere:

$$U(D) = \frac{-\pi^2 C \rho_1 \rho_2 R}{6D}$$

Sphere-Sphere:

$$U(D) = \left( \frac{-\pi^2 C \rho_1 \rho_2}{6D} \right) \left( \frac{R_1 R_2}{R_1 + R_2} \right)$$

**The Hamaker Constant**

$$A_{12} = \pi^2 C \rho_1 \rho_2$$

NOTE:  $A > 0$  means attractive force.

Hamaker Constants usually fall in the range  $(0.4-4) \times 10^{-19}$  J.

Interaction between 2 dissimilar particles related to interaction between identical particles:

$$A_{12} \approx \sqrt{(A_{11}A_{22})}$$

**Particle-Particle Interactions**

Important in Colloids – “a dispersed phase distributed uniformly in a finely divided state (1nm – 1µm) in a dispersion medium”.

- fog, smoke, foam, milk, ink, stained glass.

Interaction between 2 particles in a dielectric medium:

$$\boxed{1} \quad \boxed{2} \quad A_{132} \approx A_{12} + A_{33} - A_{13} - A_{32}$$

*provided dispersion forces dominate*

Interaction between identical particles always attractive:

$$A_{131} \approx A_{11} + A_{33} - 2A_{13} \approx A_{11} + A_{33} - 2\sqrt{A_{11}A_{33}}$$

$$= (\sqrt{A_{11}} - \sqrt{A_{33}})^2 > 0$$

$A_{131} \approx A_{313}$ , i.e. 2 droplets of water in fog = 2 air bubbles in foam.

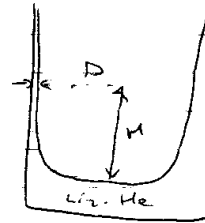
**Summary:**

- interaction between identical molecules always attractive ( $A > 0$ ).
- If medium 2 has same properties as 1 & 3 then  $A_{123}$  effectively zero (no interaction).
- For dissimilar particles  $A_{123}$  may be attractive (positive) or repulsion (negative) → dispersion forces can lead to repulsion.

**Consequences of Repulsive Interactions –**

$$A_{123} + A_{He,g / He,l / glass} < 0.$$

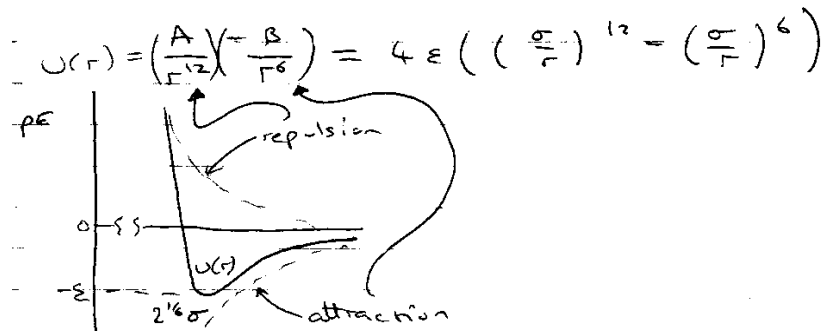
- Repulsive van der Waals across adsorbed liquid He film.
- Lower energy by thickening film.
- Counteracts gravity.



$$U = -\frac{A_{123}}{12\pi D^2} + \rho g H D$$

At equilibrium,  $dU/dD = 0$ , → climbs up container.

**Lennard-Jones Potential –**



How measure – van der Waals complexes very weak.

Use *Molecular Beam Experiments* –

- Transfer momentum in direction of beam.
- Molecules travel at similar speeds, very low translational temperature (supersonic).

Even better → supersonic nozzle – skims off some molecules off jet and results in better defined velocity.

- Trap Van der Waals molecules, few Energy Levels populated.
- Virtually collision-free – no break up of complexes.

*Other information* –

- Gas imperfections.

$$\frac{pV_m}{RT} = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \dots$$

B(T) → pairs, C(T) → threes, etc...

*Gas Transport Properties* –

- Momentum, mass, energy – depends on intermolecular forces.

Shear velocity, diffusion coefficient (pair potential for dilute gas) and thermal conductivity can also be used.

**Pair Distribution Function, g(r)**

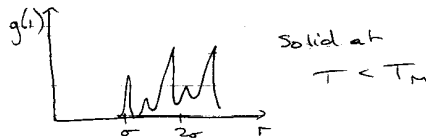
Measures probability of finding another molecule at distance r from reference,  $\rho(r) = \rho_0 g(r)$

How measure – diffraction methods.

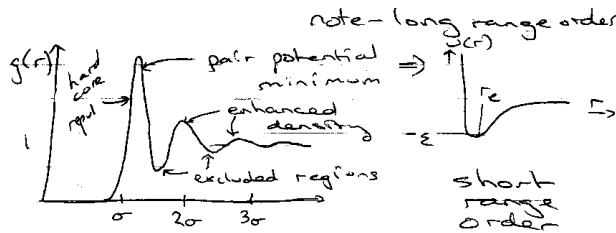
X-ray Scattering – electrons, increase scattering with atomic number, to locate heavy atoms.

Neutron Scattering – strong Nuclear force scattering by nuclei. Don't vary much with atomic number, therefore good for locating light atoms.

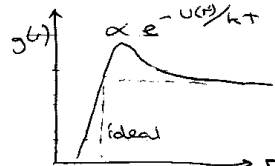
**Solid:**



**Liquid:**



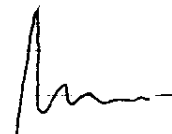
**Gas:**



**Examples –**

Ar(l) –

Model as hard spheres. Dispersion forces hold molecules together:



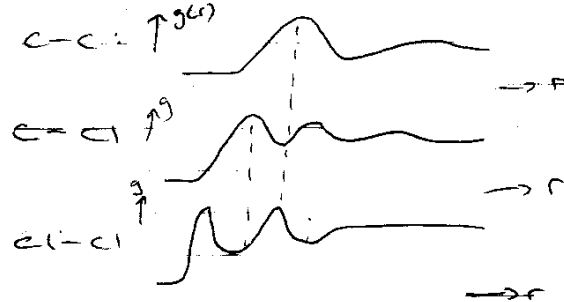
Structure dominated by repulsion between atoms.

$CCl_4(l)$  –

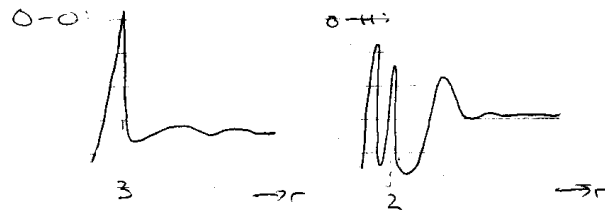
Cannot treat as soft sphere. Very high density.

Molecules interlock with neighbours, increasing viscosity and decreasing the diffusion constant.

Atom-Atom Pair Distribution Functions:



$H_2O(l)$  –



Hydrophobic Effect – in non-polar medium, need one or more (partial)  $H_2O$  charges to point to inert solute, i.e. lost to H-bond formation.

→ arrange so that least number of tetrahedral charge point towards non-polar molecule but towards water phase, i.e. H-bond formation.

All H-bond sites can be active if non-polar molecule is not too big. Reorientation of water molecules in cages. But this orders water molecules, so process is entropically unfavourable.

Presence of non-polar molecules makes neighbouring molecules more ice-like (increased H-bonding, decrease entropy).

Consequences:

- Detergents congregate around dirt particles.
- Membranes (polar heads, hydrophobic tails).
- Protein folding (hydrophobic side chains buried inside folded protein).

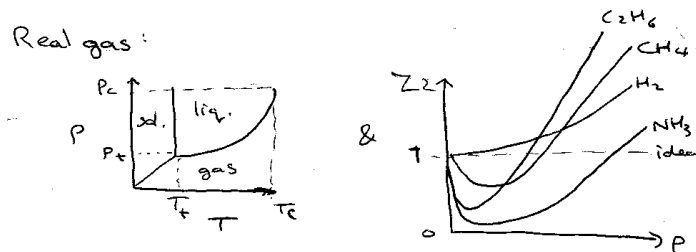
**Macroscopic Interactions**

Gas Imperfections –

Ideal,  $pV = nRT$

Z, compression factor,  $= pV_m/RT = 1$ .

Real Gas:





Virial Equation:

$$\frac{p\bar{V}}{RT} = 1 + \frac{B(T)}{\bar{V}} + \frac{C(T)}{\bar{V}^2} + \dots$$

At Boyle Temperature,  $T_B$ ,  $B = 0$

Van der Waals Equation:

$$\left(p + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT$$

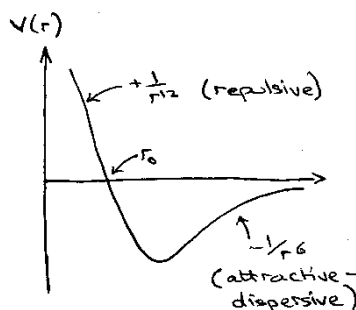
$$B = b - \frac{a}{RT}$$

Principle of Corresponding States –

Molecules that interact through a pair potential of the same form will have the same equation of state in “reduced” variables. Such systems are said to be “conformal”.

**Potential Well –**

$$V(r) = 4\epsilon \left[ \left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^6 \right]$$



$$F(r) = -\frac{dV(r)}{dr} = -4\epsilon \left[ \left(\frac{-12r_0^{12}}{r^{13}}\right) + \left(\frac{6r_0^6}{r^7}\right) \right]$$

At the minimum,

$$\frac{dV(r)}{dr} = 0,$$

$$\therefore 4\epsilon \left[ \left(\frac{-12r_0^{12}}{r^6}\right) + 6 \right] = 0$$

$$\Rightarrow \frac{r_0^6}{r^6} = \frac{1}{2}$$

Well depth at  $r = r_0$ :

$$V(2^{1/6}r_0) = 4\epsilon \left[ \left(\frac{r_0}{2^{1/6}r_0}\right)^{12} - \left(\frac{r_0}{2^{1/6}r_0}\right)^6 \right] = \epsilon$$

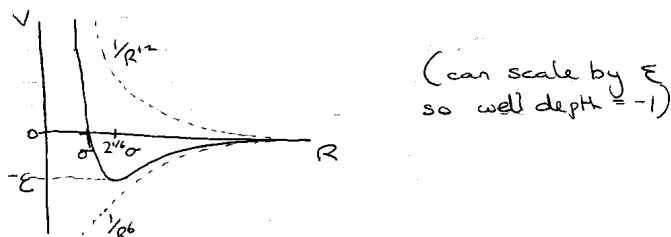
Assumptions –

- Ignore interactions beyond inner layer.
- Ignore 3 body interactions.
- Ignore interactions in gas phase.
- Inadequacy cf. Lennard-Jones.
- Close packing assumed.

**Lennard-Jones Potential (again!) –**

$$U(r) = \underbrace{\frac{A}{r^{12}}}_{\text{repel}} - \underbrace{\frac{C}{r^6}}_{\text{Van der Waals}} = 4\epsilon \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$

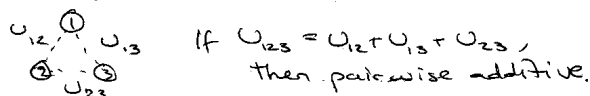
$\epsilon = \text{well depth}, \sigma = \text{collision diameter}.$



Principle of Corresponding States works well at near critical temperature, where dispersion dominates (low  $\rho$ , high thermal  $E$ ).

At triple point, short-range interactions are important. For liquid,  $V_{m,c} \sim 3 \times V_{m,t}$

Also, some interactions are not pairwise additive. This means,



- This applies to fixed charges (crystals).
- Dipole/induced are non-additive.
- Dispersions are weakly non-additive.
- H-bonding is highly non-additive, cf.  $H_2O(l)$  and  $H_2O(g)$ .

**Condensed Phases –**

**Gas → Liquid** via  $T_b$  – attractive, Van der Waals. Boiling Point of simple Van der Waals liquid:

$$V_{m,g}/V_{m,l} \sim 300.$$

$$\Delta S_{vap} \approx R \ln 1000 \approx 7R.$$

$$\Delta H_{vap} = \Delta U_{vap} + p \Delta V_{vap} \approx \Delta U_{vap} + RT_b.$$

In simple liquids, max nearest neighbours is 12. Minimum in pair potential is  $U = -\epsilon$ , then:

$$\Delta U_{vap} \sim 6\epsilon$$

At normal boiling point:

$$\Delta G_{vap} = \Delta H_{vap} - T_b \Delta S_{vap} = \Delta U_{vap} - T_b (\Delta S_{vap} - R) = 0$$

$$\Rightarrow T_b = \frac{\Delta U_{vap}}{\Delta S_{vap} - R} \approx \frac{6\epsilon}{6R} = \frac{\epsilon}{R}$$

**Liquid → Solid** via  $T_m$  – short-range interactions. Repulsive forces. Specific interactions become important.

**Mixtures of Non-Electrolytes**

Reminder:

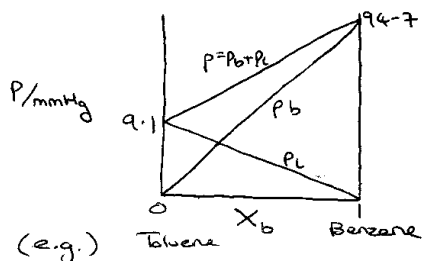
$$\mu_A(l) = \mu_A^*(l) + RT \ln x_A(l) \quad (\text{IDEAL})$$

$$\mu_A(l) = \mu_A^*(l) + RT \ln \left(\frac{P_A}{P_A^*}\right) \quad (\text{REAL})$$

$$= \mu_A^*(l) + RT \ln x_A(l) + RT \ln f_A(l)$$

i.e. Ideal  $\Rightarrow x_A(l) = \left(\frac{P_A}{P_A^*}\right)$  (Raoult's Law) ...

**Ideal Behaviour –**



Molar Free Energy:

$$G^i = \sum_j x_j(l) \mu_j(l)$$

$$= \sum_j x_j(l) \mu_j^*(l) + RT \sum_j x_j(l) \ln x_j(l)$$

Separate components,

$$G^i = \sum_j x_j(l) \mu_j^*(l)$$

Mixing,

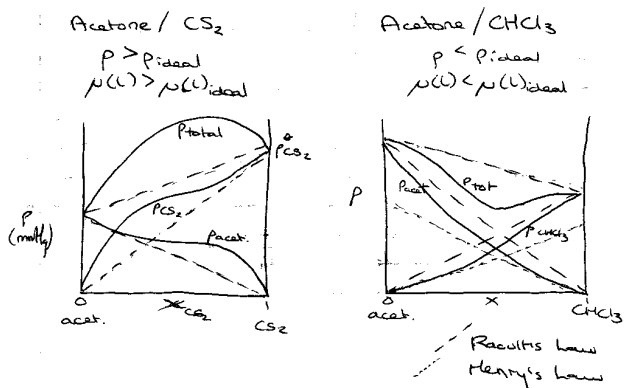
$$\Delta G_{mix}^i = RT \sum_j x_j(l) \ln x_j(l)$$

$$\Delta S_{mix}^i = \left. \frac{\partial \Delta G_{mix}^i}{\partial T} \right|_p = -R \sum_j x_j(l) \ln x_j(l)$$

$$\Delta H_{mix}^i = \Delta G_{mix}^i + T \Delta S_{mix}^i = 0.$$

Also for ideal,  $\Delta V_{mix}^i = 0$ .

**Non-ideal Mixtures**



As  $x \rightarrow 1$ , solvent obeys Raoult's Law.  
 As  $x \rightarrow 0$ , solute obeys Henry's Law,  $p_B = K_B x_B(l)$

**Gibbs-Duhem Equation**

Chemical Potentials of the components in a mixture cannot vary independently.  
 Open system,

$$dG(T, p, n_j) = V dp - S dT + \sum_j \mu_j dn_j$$

$$= \sum_j \mu_j dn_j \quad \text{at constant } T, p. \quad (1)$$

Integrate at constant  $\mu_j$ :

$$G = \sum_j n_j \mu_j$$

$$dG(n_j, \mu_j) = \sum_j \mu_j dn_j + \sum_j n_j d\mu_j \quad (2)$$

Compare (1) and (2):

$$\sum_j n_j d\mu_j = 0 \quad \text{GIBBS-DUHEM}$$

Example -

Binary Mixture. Component 1 obeys Raoult's Law over certain range of composition. Show that component 2 obeys Henry's Law over this range.

Gibbs-Duhem:

$$x_1 d\mu_1 + x_2 d\mu_2 = 0$$

Vary  $x_1$  at constant T and  $p_{\text{rot}}$ :

$$x_1 \left. \frac{d\mu_1}{dx_1} \right|_T + x_2 \left. \frac{d\mu_2}{dx_1} \right|_T = 0 \quad (1)$$

Assume vapour ideal:

$$\mu_1 = \mu_1^* + RT \ln \left( \frac{p_1}{p_1^*} \right)$$

$$\Rightarrow \left. \frac{d\mu_1}{dx_1} \right|_T = RT \left. \frac{d \ln p_1}{dx_1} \right|_T \quad (2)$$

$$x_2 = 1 - x_1 \quad \therefore dx_1 = -dx_2$$

$$\left. \frac{d\mu_2}{dx_1} \right|_T = - \left. \frac{d\mu_2}{dx_2} \right|_T = -RT \left. \frac{d \ln p_2}{dx_2} \right|_T \quad (3)$$

Sub (2) and (3) into (1):

$$x_1 \left. \frac{d \ln p_1}{dx_1} \right|_T = x_2 \left. \frac{d \ln p_2}{dx_2} \right|_T \quad (4)$$

$$\text{Raoult's Law} \Rightarrow x_1 = \frac{p_1}{p_1^*} \Rightarrow \ln p_1 = \ln p_1^* + \ln x_1$$

$$\therefore x_1 \left. \frac{d \ln p_1}{dx_1} \right|_T = x_1 \cdot \frac{1}{x_1} = 1$$

$$(4) \Rightarrow x_2 \left. \frac{d \ln p_2}{dx_2} \right|_T = 1$$

$$\left. \frac{d \ln p_2}{d \ln x_2} \right|_T = 1$$

$$\Rightarrow \ln p_2 = \ln x_2 + \text{constant},$$

$$\therefore p_2 = k_2 x_2 \quad (\text{Henry's law})$$

Simple Non-ideal Mixture -

2 components, A and B.  $\Delta S_{\text{mix}}$  ideal - no association or preferred orientation.

Each molecule interacts with Z neighbours through pair potential with average E ( $\Delta V_{\text{mix}}=0$ ). Each A surrounded by, on average:

$Zx_A$  molecules of A

$Zx_B$  molecules of B

$$\Delta H_{mix} = \left[ \begin{aligned} & -x_A N (Z_{xA} H_{AA} + Z_{xB} H_{AB}) / 2 \\ & -x_B N (Z_{xB} H_{BB} + Z_{xA} H_{AB}) / 2 \\ & + (N x_A Z_{HA} + N x_B Z_{HB}) / 2 \end{aligned} \right]$$

$$x_A = (1 - x_B) \Rightarrow$$

$$\Delta H_{mix} = \frac{NZ}{2} (H_{AA} + H_{BB} - 2H_{AB}) x_A x_B$$

$$\therefore \Delta H_{mix} = \beta x_A x_B$$

$$\Delta S_{mix} = -R (x_A \ln x_A + x_B \ln x_B)$$

$$\Delta G_{mix} = \beta x_A x_B + RT (x_A \ln x_A + x_B \ln x_B)$$

If  $\beta < 0$  - mixing exothermic. Liquid miscible in all proportions.

If  $\beta > 0$  - mixing endothermic. Behaviour depends on  $\beta$ .

For dispersions,

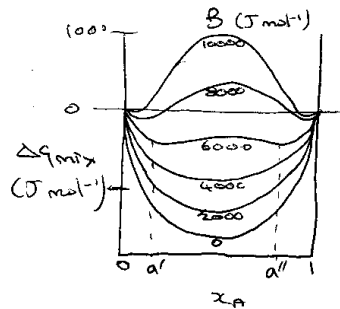
$$U_{AA} \sim x_A^2 I_A \quad U_{BB} \sim x_B^2 I_B$$

$$U_{AB} \sim 2x_A x_B \frac{I_A I_B}{I_A + I_B} \approx \sqrt{U_{AA} U_{BB}}$$

$$H_{AA} + H_{BB} - 2H_{AB} \approx H_{AA} + H_{BB} - 2\sqrt{H_{AA} H_{BB}}$$

$$= (H_{AA}^{1/2} - H_{BB}^{1/2})^2 > 0$$

Effect of  $\beta$  on Phase Behaviour:



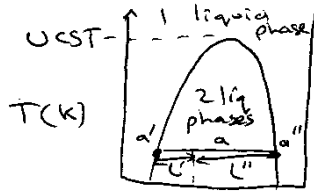
- $\beta = 0, 2000, 4000$  - miscible in all prop.
- $\beta = 6000$  - miscible for  $x_A < a'$  &  $x_A > a''$  - two phases for  $a' < x_A < a''$  with compositions  $a'$  &  $a''$
- $\beta > 6000$  - miscible only near  $x_A = 0, x_A = 1$ .

T-dependence -

The minimum temperature at which the mixture is miscible in all proportions is the Upper Critical Solution Temperature,  $T_c$ .

$$\beta = 2RT_c$$

**Temperature-Composition Diagram -**



Tie-lines (join phases in equilibrium).  
Allow calculation of relative proportions of the 2 phases:

$$\frac{L''}{L'} = \frac{x_A}{\text{amt. of phase } a'} = \frac{\text{amt. of phase } a''}{\text{amt. of phase } a''} \quad (\text{Lever Rule})$$

**Phase Rule -**

$$P + F = C + 2$$

P = number of phases.

C = number of independent components.

F = number of degrees of freedom, i.e. number of variables (T, p,  $\mu_j$  ...) that can be varied independently.

e.g.

- 1 component & 3 phases, F = 0. Therefore triplet point (T, p fixed).
- 1 component & 2 phases, F = 1. Therefore solid-liquid and liquid-gas equilibria are lines in phase diagram ( p = f(T) ).
- 2 components & 1 phase, F = 3. Therefore at constant T and p,  $\mu_A$  can vary.
- 2 components & 2 phases, F = 2. Therefore at constant T and p,  $\mu_A$  and  $\mu_B$  are fixed (and so are  $x_A$  and  $x_B$  as a result).

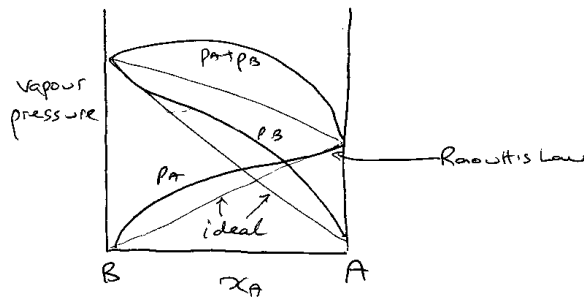
Vapour Pressures –

$$\mu_j = \left( \frac{\partial G}{\partial n_j} \right)_{T, p, n_i \neq j}$$

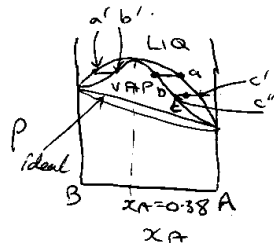
$$\left. \begin{aligned} \mu_A &= \mu_A^* + RT \ln x_A + \beta x_B^2 \\ \mu_B &= \mu_B^* + RT \ln x_B + \beta x_A^2 \end{aligned} \right\} \text{in liquid}$$

$$\frac{\beta x_B^2}{RT \ln y_B}$$

Ideal vapour,



**Pressure-Composition Diagram**



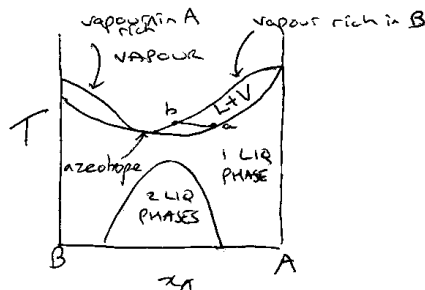
X = 0.38 → liquid and vapour have same composition, this is AZEOTROPIC.

Liquid at a is in equilibrium with gas at b.

System at c consists of liquid with composition c' in equilibrium with vapour of composition c''.

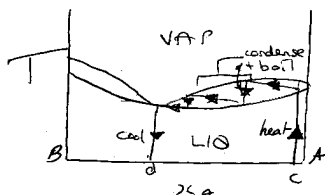
Lever Rule gives relative amounts.

**Temperature-Composition Diagram**



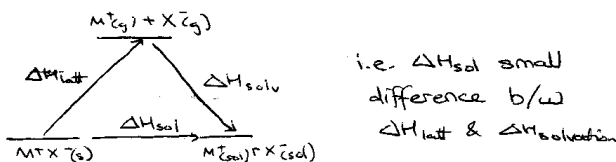
- Minimum boiling point occurs at azeotropic composition.
- Liquid at a is in equilibrium with vapour of composition b.

**Fractional Distillation**



From c, cannot generate pure B (get azeotropic composition "d").  
Eutectic Point – temperature at which solid/liquid equivalent of azeotropic (vapour/liquid).

**Ions in Solution**



**Born Equation:**

Ion is a sphere, radius a. Charge sphere from q = 0 to q = Ze (self-energy of ion).

$$G(\text{vacuum}) = \int_0^{Ze} \frac{q}{4\pi\epsilon_0 a} dq = \frac{Z^2 e^2}{8\pi\epsilon_0 a}$$

$$G(\text{solvent}) = \int_0^{Ze} \frac{q}{4\pi\epsilon\epsilon_0 a} dq = \frac{Z^2 e^2}{8\pi\epsilon\epsilon_0 a}$$

$$\therefore \Delta G_{\text{solw}} = \frac{-N_A Z^2 e^2}{8\pi\epsilon_0 a} \left(1 - \frac{1}{\epsilon}\right) \quad \left[\Delta S = \frac{d\Delta G}{dT} < 0\right]$$

Therefore salts dissolve in media of high dielectric constant, ε, but not in media of low ε.

Ions are stabilised by charge-dipole and charge-induced dipole interactions.

Born used a continuum model → not correct in detail for aqueous solution.

Consider structure of water nearest the ions – neutron scattering.

If the water molecules are strongly coordinated to the ions (e.g. Al<sup>3+</sup>, Ni<sup>2+</sup>) there are sharp, well-resolved peaks in the pair distribution function and the hydration number is well-defined (e.g. 4 for Be<sup>2+</sup>, 6 for Al<sup>3+</sup>).

If water molecules are weakly bound, peaks in g(r) are broader and weaker.

In water, H<sup>+</sup> is always found as H<sub>3</sub>O<sup>+</sup>, never as a free proton. The predominant species is believed to be planar H<sub>9</sub>O<sub>4</sub><sup>+</sup>.

Conductivity – very, very high. Relay mechanism – it is INCORRECT that there are concerted proton “hops”, in fact a series of uncorrelated single proton hops is more likely.

Extent of hydration increases with increasing charge and increasing ionic radius. As a consequence, cations are more strongly solvated than anions.

**Debye-Huckel Theory**

Treatment of interactions between ions in solution directly analogous to diffuse double layer.

**ASSUMPTIONS:**

- Central ion of radius a. Other ions point charges (no allowance for finite counterions).
- Ions move in average potential due to all other ions (no ion correlation).
- Purely electrostatic (no ion pairing).

- Weak interaction:  $Ze\phi / kT \ll 1$  (best for univalent ions).
- Continuous, structure-less solvent with uniform dielectric constant (ignores solvation shells, dielectric saturation).

METHOD:

Solve Poisson-Boltzmann equation in spherical polar coordinates.

SOLUTION:

Screened Coulomb Potential

$$\phi \approx \frac{Ze}{4\pi\epsilon_0 r} e^{-kr}$$

$k^{-1}$  = Debye length

$$k \propto \sqrt{I}, \therefore \text{Debye length } r_D \propto \frac{1}{\sqrt{I}}$$

Average distance to counterion =  $r_D$ .

Debye Length  $\rightarrow$  "thickness" of ionic atmosphere.

Self-energy absent of ionic interactions:

$$\frac{Z^2 e^2}{8\pi\epsilon_0 a}, \text{ where } a = \text{radius of ion.}$$

With ionic interactions,

$$\int_0^{\infty} \frac{Ze}{4\pi\epsilon_0 a} e^{-a/r_0} dq \approx \frac{Z^2 e^2}{8\pi\epsilon_0 \epsilon a} \left(1 - \frac{a}{r_0}\right)$$

Lowering of energy due to ionic interactions -

$$-\frac{Z^2 e^2}{8\pi\epsilon_0 r_D}$$

Assuming deviations from ideality are purely electrostatic:

$$RT \ln \gamma = \frac{-N_A Z^2 e^2}{8\pi\epsilon_0 \epsilon r_D}$$

$$\log \gamma_{\pm} = -AZ^2 \sqrt{I} \quad (A = 0.51 @ 298K)$$

$$(v_+ + v_-) \gamma_{\pm} = v_+ \ln \gamma_+ + v_- \ln \gamma_-$$

$\underbrace{\hspace{10em}}$   
mean ionic activity
 $\underbrace{\hspace{10em}}$   
moles of anion per mole salt

$$\Rightarrow \log \gamma_{\pm} = -A |z_+ z_-| \sqrt{I}$$

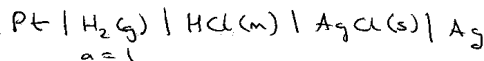
Debye-Huckel Limiting Law -

Good for  $I \ll 0.001$

Worse for  $I > 0.01$

EXAMPLE 1: Standard Electrode Potential





$$\begin{aligned} \text{Nernst: } E &= E_{\text{Ag,AgCl}}^\ominus - \frac{RT}{F} \ln(a_{\text{H}^+} a_{\text{Cl}^-}) \\ &= E_{\text{Ag,AgCl}}^\ominus - \frac{RT}{F} \ln\left(\frac{m}{m^\ominus}\right)^2 - \frac{RT}{F} \ln \gamma_{\pm}^2 \end{aligned}$$

$$\begin{aligned} \ln \gamma_{\pm}^2 &= Z \ln \gamma_{\pm} = 2 \times 2 \times 3 \log \gamma_{\pm} \\ &= 2 \times 2 \times 3 (-A |z_+ z_-| \sqrt{I}) \\ &= -2.34 I^{1/2} \end{aligned}$$

For 1:1 electrolyte,

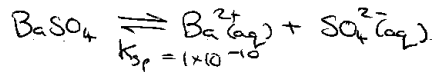
$$I = \frac{1}{2} \sum_i \frac{m_i}{m^\ominus} z_i^2 = \frac{3}{m^\ominus}$$

Nernst again:

$$E + \frac{2RT}{F} \ln\left(\frac{m}{m^\ominus}\right) = E_{\text{Ag,AgCl}}^\ominus + \frac{2.34RT}{F} \left(\frac{m}{m^\ominus}\right)^{1/2}$$

Plot LHS against  $\left(\frac{m}{m^\ominus}\right)^{1/2}$  for a range of molalities  
Intercept  $\Rightarrow E_{\text{Ag,AgCl}}^\ominus$ .

### EXAMPLE 2: Solubility Products



Solubility in water?

Assume ideal:  $\frac{m}{m^\ominus} = 1 \times 10^{-5}$

Check,

$$I = \frac{1}{2} \sum_i \frac{m_i}{m^\ominus} z_i^2 = 4 \times 10^{-5}$$

$$\log \gamma_{\pm} = -A |z_+ z_-| \sqrt{I} = -0.01$$

$$\Rightarrow \gamma_{\pm} \approx 0.97 \text{ (close to ideal)}$$

Solubility in NaCl? (0.005M)

$$I = 0.025$$

Activity coefficient of  $\text{BaSO}_4(\text{aq})$

$$\log \gamma_{\pm} = -A |z_+ z_-| \sqrt{I}$$

$$= -0.51 \times 2 \times 2 \times 0.07 = -0.14$$

$$\Rightarrow \gamma_{\pm} = 0.72$$

Solubility:  $K_{sp} = \gamma_{\pm}^2 \left(\frac{m}{m^\ominus}\right)^2 = 1 \times 10^{-10}$

$$\frac{m}{m^\ominus} = 1.4 \times 10^{-5}$$