**Chem 331 Phases of Substances and solutions**

1. **Kinetic theory**

The kinetic particle theory explains the properties of the different states of matter. The particles in solids, liquids and gases have different amounts of energy. They are arranged differently and move in different ways.

This table summarizes the arrangement and movement of the particles in solids, liquids and gases, and shows simple diagrams of the arrangement of the particles that you should be able to recognize.

**Diagram of particle arrangement and movement**

|  | **Solid** | **Liquid** | **Gas** |
| --- | --- | --- | --- |
| **Arrangement of particles** | close together  regular pattern | close together random | far apart  random |
| **movement of particles** | vibrate about a fixed position | move around each other | move quickly in any direction |
| **diagram** | http://www.bbc.co.uk/schools/gcsebitesize/science/images/solids.gif | http://www.bbc.co.uk/schools/gcsebitesize/science/images/liquids.gif | http://www.bbc.co.uk/schools/gcsebitesize/science/images/gases.gif |

**Solids**

**The table shows some of the properties of solids and why they are like this.**

| **Property of solids** | **Why they are like this** |
| --- | --- |
| They have a fixed shape and cannot flow | The particles cannot move from place to place |
| They cannot be compressed or squashed | The particles are close together and have no space to move into |

**Liquids**

**Some of the properties of liquids and why they are like this**

| **Property of liquids** | **Why they are like this** |
| --- | --- |
| They flow and take the shape of their container | The particles can move around each other |
| They cannot be compressed or squashed | The particles are close together and have no space to move into |

**Gases**

**Some of the properties of gases and why they are like this**

| **Property of gases** | **Why they are like this** |
| --- | --- |
| They flow and completely fill their container | The particles can move quickly in all directions |
| They can be compressed or squashed | The particles are far apart and have space to move into |

1. **Interactions between Atoms and Molecules**

There are three aspects that are of particular importance for any interaction: Its strength, the distance over which it acts, and the environment through which it acts. Short range interactions, as summarized in Table 1, can be of following nature: ionic, covalent, metallic, or dipolar origin. Ionic, covalent, metallic and hydrogen bonds are so-called atomic forces that are important for forming strongly bonded condensed matter. These short range forces arise from the overlap of electron wave functions. Interactions of dipolar nature are classified further into strong hydrogen bonds and weak Van der Waals (VdW) interactions. They arise from dipole-dipole interactions. Both, hydrogen and VdW interactions can be responsible for cooperation and structuring in fluidic systems, but are also strong enough to build up condensed phases. Following is a description of these short range forces:

1. ***Ionic Bonds*:**

These are simple Coulombic forces, which are a result of electron transfer.

For example in lithium fluoride, lithium transfers its 2s electron to the fluorine 2p state.

Consequently the shells of the atoms are filled up, but the lithium has a net positive charge and the Flourine has a net negative charge. These ions attract each other by Coulombic interaction which stabilizes the ionic crystal in the rock-salt structure.

1. ***Covalent Bond*:**

The standard example for a covalent bond is the hydrogen molecule.

When the wave-function overlap is considerable, the electrons of the hydrogen atoms will be indistinguishable. The total energy will be decreased by the “exchange energy”, which causes the attractive force. The characteristic property of covalent bonds is a concentration of the electron charge density between two nuclei. The force is strongly directed and falls off within a few Ǻngstroms.

1. ***Metallic Bonds and Interaction*:**

The strong metallic bonds are only observed when the atoms are condensed in a crystal. They originate from the free valency electron sea which holds together the ionic core. A similar effect is observed when two metallic surfaces approach each other. The electron clouds have the tendency to spread out in order to minimize the surface energy. Thus a strong exponentially decreasing, attractive interaction is observed.

**D. *Dipole Interactions*:**

**D.1. Hydrogen Bond Interaction:** Strong type of directional dipole-dipole interaction

**D.2. Van der Waals Interaction:** The relevance of VdW interactions goes beyond of building up matter (e.g., Van der Waals organic crystals (Naphthalene)). Because of their “medium” range interaction length of a few Ǻngstroms to hundreds of Ǻngstroms, VdW forces are significant in fluidic systems (e.g, colloidal fluids), and for adhesion between microscopic bodies. VdW forces can be divided into three groups:

o *Dipole-dipole force*: Molecules having permanent dipoles will interact by dipole-dipole interaction.

o *Dipole-induced dipole forces:* The field of a permanent dipole induces a dipole in a non-polar atom or molecule.

o *Dispersion force:* Due to charge fluctuations of the atoms there is an instantaneous displacement of the center of positive charge against the center of the negative charge. Thus at a certain moment a dipole exists and induces a dipole in another atom.

Therefore non-polar atoms (e.g. neon) or molecules attract each other.

**Table 1:** Short Range Interaction Forces

|  |  |  |  |
| --- | --- | --- | --- |
| **Nature of Bond** | **Type of Force** | **Energy (kcal/mol)** | **Distance** |
| ***Ionic bond*** | Coulombic force | 180 (NaCl)  240 (LiF) | 2.8 Å  2.0 Å |
| ***Covalent bond*** | Electrostatic force  (wave function overlap) | 170 (Diamond)  283 (SiC) N/A | N/A |
| ***Metallic bond*** | free valency electron sea  interaction  (sometimes also partially  covalent (e.g., Fe and W) | 26 (Na)  96 (Fe)  210 (W) | 4.3 Å  2.9 Å  3.1 Å |
| ***Hydrogen Bond*** | a strong type of directional  dipole-dipole interaction | 7 (HF) |  |
| ***Van der Waals*** | (i) dipole-dipole force  (ii) dipole-induced dipole force  (iii) dispersion forces  (charge fluctuation) | 2.4 (CH4) | significant in the  range of a few Å to  hundreds of Å |

***Types of intermolecular forces***

The nature of the phases and their changes are due primarily to forces among the molecules. Both bonding (intramolecular) forces and intermolecular forces arise from electrostatic attractions between opposite charges. Bonding forces are due to the attraction between cations and anions (ionic bonding), nuclei and electron pairs (covalent bonding), or metal cations and delocalized valence electrons (metallic bonding). Intermolecular forces, on the other hand, are due to the attraction between molecules as a result of partial charges, or the attraction between ions molecules. The two types of forces differ in magnitude, and Coulomb's law explains why:

* Bonding forces are relatively strong because they involve larger changes that are closer together.
* Intermolecular forces are relatively weak because they typically involve smaller charges that are farther apart.

There are several types of intermolecular forces: ion-dipole, dipole-dipole, hydrogen bonding, dipole-induced dipole, and dispersion forces. The intermolecular forces also called the Van der Waals forces.

1. ***Ion-dipole Forces***

An ion-dipole force (IDF) results from an ion and a nearby polar molecule (dipole) attract each other.

Example: When an ionic compound (salt) dissolves in water.

**IDF**

1. ***Dipole-Dipole Forces (DDF)***

When polar molecules lie near one another, as in liquids and solids, their partial charges act as tiny electric fields that orient them and give rise to dipole-dipole forces (DDF): the positive pole of one molecule attracts the negative pole of another.

**DDF**

1. ***The hydrogen bond***

A special type of dipole-dipole force arises between molecules that have an H atom bound to a small, highly electronegative atom with lone electron pairs. The most important atoms that fit this description are N, O and F. The H-N, H-O, and H-F bonds are very polar, so electron density is withdrawn from. As a result, the partially positive H of one molecule is attracted to the partially negative lone pair on the N, O, or F of another molecule, and a hydrogen bond (H-bond) forms.

R-O-H R-N-H N-H F

H-O-R H-O-R

***The dipolar moment calculation***

For a molecule as, A - B the general equation of is expressed as follow:

******

Where, δ, is the partial charge and d the distance between A and B

d

1. *For a molecule as, H2O*

μ

O 2δ-

+δ H

H δ+

θ

******

*b*) *For a linear molecule as CO2*

-δ O C O δ-

******

*c)For a aromatic molecule as benzene (C6H6)*

H H

H H ******

H H

***The ionic character of a bond (CB)***

A-B bond

******

Where *q* is the total charge of A or B in a.m.u (atomic mass unit) unit

***Example***

What the character of HCl bond if δ = 0.70 u.m.a and dHC = 0.34 Ao.

***Solution***

The absolute charge of Cl ion is one electron = 1.0 u.m.a

****** this bond is at 70% ionic

1. ***Polarizability and charge-induced Dipole Forces***

The ease with a particle's electron cloud can be distorted is called its polarizability. Smaller atoms (or ions) are less polarizable than larger ones because their electrons are closer to the nucleus and held more tightly. Thus,

* Polarizability increases down a group of atoms (or ions) because size increases and larger electron clouds are more easily distorted.
* Polarizability decreases from left to right across a period because the increasing effective nuclear charge holds the electrons more tightly.
* Cations are less polarizable than their parent atom because they are smaller. Whereas anions are more polarizable because they are larger.

Ion-induced dipole and dipole-induced dipole forces are the two types of charge-induced dipole forces.

1. ***Dispersion (London) forces (DLF)***

The intermolecular force primarily responsible for the condensed states of nonpolar substances is the dispersion force or London force.

Dispersion forces are caused by momentary oscillations of electron charge. Over time, the electron charge within an atom is distributed uniformly around the nucleus, and the atom is nonpolar. But at any instant, this may not be the case, and the atom has an instantaneous dipole that can influence nearby atoms. The instantaneous dipole in each atom induces a dipole in its neighbor.

***Problems***

1. Which of the following substances exhibits H-bonding? For those that do, draw two molecules of substance with the H-bonds between them.
2. C2H6 ; b) CH3OH; c) CH3(CO)NH2; d) CH3COOH
3. Which of these substances exhibits H- bonding? Draw the H-bonds between two molecules of the substances where appropriate.
4. ClCH2COOH; b) CH3CH2OH; c) CH3COCH3
5. For each pair of chemicals, identify the dominant intermolecular forces in each chemical compound and select the substance with the higher boiling point:
6. MgCl2 or PCl3
7. CH3NH2 or CH3F
8. CH3OH or CH3CH2OH
9. Hexane or 2,2-dimethylbutane
10. **Ideal and non ideal gas**

Equation of ideal gas:



This law is the combination of tree laws:

1. Boyle law : V = k1/P
2. Gay-Lussac law: V = k2 xT
3. Avogadro law: V =k3 x n





1 atm is the pressure exerted by a column of 760 mm of mercury (density 13595.1 kg.m-3) under the acceleration of gravity (g= 9.80665 m.s-2). Since P = m.g/area = m.g.h/V=ρ.g.h (h, height; ρ, density)

**R = 8.314 J/K.mol ; R = 0.082 L.atm/K.mol**

1 L.atm = (0.76 m)(135951 kg.m-3)(9.80665 m.s-2) =

= 101.325 kg.m-1.s-2 = 101325 N.m-2 = 101325 Pa

***Example 1***

3.50 L of a gas at 500 mmHg pressure and 21.0oC weights 1.53g. What is its molar mass?

***Solution***

PV = nRT P = (n/V)RT = (m/M.V)RT = (ρ/M)RT



***Example 2***

Calculate the number of molecules inside a soap bubble 1.0 cm in diameter at atmospheric pressure and 25oC.

***Solution***

The volume of the bubble is:





The number of molecules N is obtained from this and the Avogadro number

N = (2.2 x 10-5 mol)(6.022x1023 mol-1) = 1.3 x 1019 molecules

***Example 3***

The vapor pressure of solid I2 at 25oC is 0.35 mmHg. Calculate the concentration of I2 in the vapor phase. Answer (1.9 x10-5 M)

**Dalton's Law of partial pressures**

If we have a mixture of gases A/B in a container at a pressure (*P*) and temperature (*T*) where the intermolecular interaction were negligible, the partial pressure of each component is calculated from:

  where *V* is the volume of the container.

The total pressure is given by *P = pA + pB*

The molar fraction ( *xi*) of each component in the mixture is given by:

 where *nA* and nB are the mole number of the component *A* and *B* respectively.

 and *pA = x A P*

***Example 4***

Nitrogen tetroxide is known to dissociate according to the equation N2O4(g)  2NO(g)

A sample of 250 mL of this gas mixture weights 0.181 g and has a total pressure of 0.257 bar. Calculate the partial pressures of the two oxides.

Let *pi* be the pressure before dissociation. Then

 = (0.181 g)(0.08314 L.bar K-1mol-1)(298K)/(92 g mol-1)(0.250 L) = 0.195 bar

*The total pressure P = P(N2O4) +P(NO2) = (Pi - x) + 2x = 0.257 bar*

From this and *pi* = 0.195 bar, we get

P(N2O4)= 0.133 bar and p(NO2)= 0.124 bar

**Molecular speeds and translational energies**

According to the kinetic molecular model

1. A sample of gas consists of rigid molecules with negligible volume.
2. The molecules move according to Newton's laws, without any preferred direction.
3. The interaction between molecules is negligible.

From these premises we can derive the relation between molecular speeds and temperature, as will shown:



 with k (J/K) = R/*NA*

*k* is the Boltzman constant, *NA* the Avogadro number

The root mean squared speed (*vrms*) is expressed as follow



Example

Calculate the rms speed of nitrogen molecules at 25.0oC



*Note: 1 J = 1 kg.m2.s-2*

The translational kinetic energy E of a molecule is calculated from this relationship:



The kinetic energy of a mole of noninteracting gas molecules *Em* is given by



**Equation of state for non ideal gases**

*Compressibility Factors (z)*

The nonideal gases deviate from ideality under a given set of conditions as the intermolecular interactions. This is best assessed by computing the compressibility factor z defined by the equation:



where *Vm* is the molar volume. Since z =1 for an ideal gas, deviation of z from unity is a quantitative measure of non ideality.

*The Van der Waals equation*

For an non ideal gas 

***Example 5***

The molar volume for methane is 0.528L at 273 K and 40 bars. How does the calculated pressure from (a) the ideal gas law and (b) the Van der Waals equation compare the measured pressure? a = 2.283 L2.bar.mol-2, b = 0.04278L.mol-1.

**Solution**

1. From the ideal gas law: *PVm = nRT*



1. From the non ideal gas law (Van der Waals),





*P = 38.6 bar*

The compressibility factor for the Van der Waals gas is obtained from:





**Exercices**

***Gas Laws: Ideal Gases***

1. The volume of a gas increases by a factor of 2 while the pressure decreases by a factor of 3. Given that the number of moles is unaffected, calculate the factor by which the temperature changes.
2. The pressure is 1.5x10-10 bar in a certain high-vacuum system. What is the number of molecules in a sample of 10 cm3 at 21oC?
3. Calculate the mass of 1.56 L of SF6 at 557 mmHg and 240oC.
4. A 350 mL sample of ammonia at 1.00 bar and 27oC is absorbed by water to form 500 mL of solution at that temperature and pressure. Calculate the molar concentration of ammonia.
5. A 1.5 L sample of helium from a tank at 100 atm and 3.5 L of neon from a tank at 125 atm are introduced into a 5.0 L vessel. What are the partial pressures in the vessel given that the temperature remained constant during the process?

***Ideal gases: Molecular speeds and Transformation Energies***

a) Calculate the average and rms speeds of He, CO2, and anthracene at 25oC.

b) Calculate their kinetic energies at this temperature.

c) By what factor does the average speed increase if the temperature is increased from 25 to 50oC?

***Equations of state for Non-ideal Gases***

1. The compressibility factor for CO2 at 400K and 71.0 bars is 0.8697. Calculate the molar volume of CO2 under these conditions. How does this volume compare with the ideal gas gas volume?
2. The compressibility factor for CO2 at 400K and 100 atm is 0.8155. Caculate the volume of 10.0 g of CO2 under these conditions.
3. From the volume in exercice b) and Van der waals equation, calculate the pressure.

**VI. Proprieties of the liquid state**

1. ***Surface tension***

The intermolecular forces exert different effects on a molecule at the surface than on one in the interior. Interior molecules are attracted by others on all sides whereas molecules at the surface have others only below and to the sides. The surface tension is the energy required to increase the surface area by a unit amount.

Drop of water

Drop of water

oily surface

Paper surface

Tension surface

θ

**Table 1. Surface tension and forces between particles**

|  |  |  |  |
| --- | --- | --- | --- |
| **Substance** | **Formula** | **Surface Tension**  **(J/m2) at 20oC** | **Major Force(s)** |
| Diethylether | CH3CH2OCH2CH3 | 1.7x10-2 | Dipole-dipole; dispersion |
| Ethanol | CH3CH2OH | 2.3x10-2 | H-bonding |
| Butanol | CH3CH2CH2CH2OH | 2.5x10-2 | H bonding; dispersion |
| Water | H2O | 7.3x10-2 | H bonding |
| Mercury | Hg | 48x10-2 | Metallic bonding |

**V. Proprieties of the solid state**

***The solid state is characterized by the following criterions:***

1. Weak cohesion forces
2. Weak vibration
3. Conservation of form
4. The density is affected weakly by the variation of temperature

***The crystallization and crystallinity***

***1-The non ionic crystal***

The centered cubic structure

Each atom has 8 neighbors

The density is inferior

Example of atoms characterized by a centered cubic structure is:

Mn, Cr, V, Fe, Ta, W .

***2-The ionic cristal***

*Example* : NaCl, NaBr, KCl, KBr, RbCl

Each Cl- ion has 6 Na+ ions around

1. **Calculation of crystal's dimensions**

***4-1 Cubic system (CS)***

R

d

**d = 2 R**

***4-2 Cubic centered faces(CCF)***

d

R

****

d

R

***4-3 Cubic centered***

****

1. **Density of crystal**

****

nA: atom/cell

A: Atomic weight

Vc: crystal volum

NA: Avogadro number

1. **Energy of crystallization**



Z1 and Z2 are the anion number of cation and anion respectively.

e: is the electronic charge = 1.6x10-19 C

re: is the distance between anion and cation

μ: is a constant depends to the crystal structure.

For NaCl , μ = 1.74756 cubic faces centered

For the centered cubic μ= 1.76267

n varies from 9 to 12 according to the ionic structure n = 9 for NaCl.

*Example:*

For NaCl:

N= 9, re = 0.281 nm

Z1 = Z2 = 1

E= 1.6 x10-19 C

μ = 1.74756

E crist = -183.3 Kcal/mol

***Exercices***

1. Calculate the crystal dimension of iron if the atomic radian of iron is 0.124 nm.
2. Calculate the density of iron if its atomic weight is 55.85 and the radian is 0.124 nm.

3.14 *Below are listed the atomic weight, density, and atomic radius for three hypothetical alloys.*

*For each determine whether its crystal structure is FCC, BCC, or simple cubic and then justify your determination.*

*Alloy Atomic Weight Density Atomic Radius* (*g/mol*) (*g/cm3*) (*nm*)

|  |  |  |  |
| --- | --- | --- | --- |
| *Alloy* | *Atomic weight* | *Density* | *Atom Radius* |
| *A* | *77.4* | *8.22* | *0.125* |
| *B* | *107.6* | *6.13* | *0.133* |
| *C* | *127.3* | *9.23* | *0.142* |

***Solution***

For each of these three alloys we need, by trial and error, to calculate the density using Equation

3.5, and compare it to the value cited in the problem. For SC, BCC, and FCC crystal structures, the respective values of *n* are 1, 2, and 4, whereas the expressions for *a* (since *VC* = *a*3) are 2*R*, 2*R* and .

For alloy A, let us calculate ρ assuming a simple cubic crystal structure.

****

****

**** = 8.22 g/cm3

Therefore, its crystal structure is simple cubic.

For alloy B, let us calculate ρ assuming an FCC crystal structure.

****

****

****

Therefore, its crystal structure is FCC.

For alloy C, let us calculate ρ assuming a simple cubic crystal structure.

****

****

****

1. Therefore, its crystal structure is simple cubic.
2. **The phase equilibrium**

*Equilibrium*

Thermodynamic definition: a system is in equilibrium if its free energy is at the minimum.

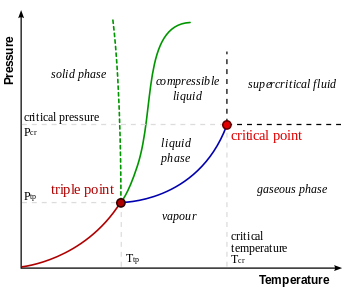
* The characteristics of the system do not change with time, i.e., the system is stable
* If you change the temperature, pressure, or composition, the free energy will change the specific phase(s) present may (or may not) change but the phase assemblage

*Definition*: Transformation = state change

1. The transformation of matter from solid state to liquid state = **fusion**
2. Transformation of matter from liquid state to solid state = **solidification**
3. Transformation of matter from liquid state to vapor state = **vaporization**
4. Transformation of matter from vapor state to liquid state = **condensation**
5. Transformation of matter directly from solid state to vapor state = **sublimation**

## Triple points of substance

### Gas–liquid–solid triple point

[](http://en.wikipedia.org/wiki/File:Phase-diag2.svg)

[http://bits.wikimedia.org/static-1.23wmf19/skins/common/images/magnify-clip.png](http://en.wikipedia.org/wiki/File:Phase-diag2.svg)

A typical phase diagram. The solid green line applies to most substances;

the dotted green line gives the anomalous behaviour of water

The single combination of pressure and temperature at which liquid as water, solid as ice and  water vapor can coexist in a stable equilibrium occurs at exactly 273.16 K (0.01 [°C](http://en.wikipedia.org/wiki/%C2%B0C)) and a partial vapor pressure of 611.73 pa  (0.0060373 atm). At that point, it is possible to change all of the substance to ice, water, or vapor by making arbitrarily small changes in pressure and temperature. Even if the total pressure of a system is well above triple point of water, provided the partial pressure of the water vapor is 611.73 pa then the system can still be brought to the triple point of water. Strictly speaking, the surfaces separating the different phases should also be perfectly flat, to negate the effects of surface tensions.

The gas–liquid–solid triple point of water corresponds to the minimum pressure at which liquid water can exist. At pressures below the triple point, solid ice when heated at constant pressure is converted directly into water vapor in a process known as sublimation. Above the triple point, solid ice when heated at constant pressure first melts to form liquid water, and then evaporates or boils to form vapor at a higher temperature.

For most substances the gas–liquid–solid triple point is also the minimum temperature at which the liquid can exist. For water, however, this is not true because the melting point of ordinary ice decreases as a function of pressure, as shown by the dotted green line in the phase diagram. At temperatures just below the triple point, compression at constant temperature transforms water vapor first to solid and then to liquid (water ice has lower density than liquid water, so increasing pressure leads to a liquefaction).

**The Clapeyron relationship**

The slopes of the lines on a one-component pressure-temperature phase diagram may be derived from the Clapeyron equation.

For any two phases we can write:

For state α dGα = VαdP -SαdT

For state β dGβ = VβdP -SβdT

Where Vα is the molar volume of phase α and Sβ is the molar entropy of phase.

At equilibrium dGα = dGβ and VαdP -SαdT = VβdP -SβdT

If Vα-Vβ = ΔV and Sα-Sβ =ΔS we can write ΔVdP=ΔSdT

or 

but also at equilibrium ΔG = ΔH-TΔS = 0 and ΔG = Gα-Gβ

and therefore 

by this way we have  this expression, the Clapeyron equation, is entirely general and applies to any phase change in a one-component system.

We can write  P2 –P1=

In case of vaporization of sublimation we can assume that since the volume of the gas formed is so much greather than that of the solid or liquid, respectively

For sublimation ΔV= Vg-Vs≈ Vg and for vaporization ΔV = Vg- VL ≈ Vg

Furthermore, if we assume that the vapor is considered as ideal and work only with molar quantities, we can write

 so that  and 

Which is the differential form of the Clausius-Clapeyron equation. Rearranging gives  which, in its integrated form is



The equation relates the values of any pair of points (*p*1, *T*1) and (*p*2, *T*2) on the vaporisation or sublimation line. By measuring experimentally the gradient of a pressure-temperature line we may therefore determine an average value for the enthalpy of vaporisation or sublimation over that temperature range.

Example 1 The densities of ice and of liquid water vary little with temperature and pressure. We can therefore use these values to calculate the change in volume Δfus*V* on melting and, with a value for the enthalpy of fusion Δfus*H*o, determine the melting temperature of ice at different pressures from a rearranged form the integrated form of the Clapeyron equation

http://www.chm.bris.ac.uk/~chdms/Teaching/Chemical_Interactions/images/pic082.gif

|  |
| --- |
| Given the density of a substance ρ, we can calculate its molar volume *V*  *http://www.chm.bris.ac.uk/~chdms/Teaching/Chemical_Interactions/images/pic083.gif*  where *M* is the molar mass. The densities of ice and liquid water are 0.917 g dm-3 and 1.000 g dm-3 and the molar mass, *M* = 18.02 g, so that the molar volumes of ice and liquid water are  *V*ice= 18.02 g / 0.917 g dm-3 = 19.58 dm3  and  *V*water= 18.02 g / 1.000 g dm-3 = 18.02 cm3  respectively. The volume change on melting is therefore  Δfus*V* = *V*water - *V*ice =18.02 - 19.58 = -1.56 cm3.  We must remember to convert this value into units of m3  Δfus*V* = -1.56 cm3 = -1.56 × 10-6 m3  before substituting it into the Clapeyron equation.  We already know one point on the solid-liquid equilibrium line since we know that ice melts at a temperature of *T*1 = 273.15 K and pressure of *p*1 = 101325 Pa. The enthalpy of fusion of ice Δfus*H*o = 6.030 kJ mol-1.  Thus at a pressure of 70 bar ( 7093000 Pa, which is typical of the pressure exerted by an ice skater  http://www.chm.bris.ac.uk/~chdms/Teaching/Chemical_Interactions/images/pic084.gif  and so  http://www.chm.bris.ac.uk/~chdms/Teaching/Chemical_Interactions/images/pic085.gif  http://www.chm.bris.ac.uk/~chdms/Teaching/Chemical_Interactions/images/pic086.gif  Thus at a pressure of 70 bar, the melting point of ice is *T*2 = 272.66 K, a decrease of 0.49 K.  The melting temperature of ice is therefore lowered by the effect of increased pressure. The application of pressure to a block of ice held at a constant temperature may therefore cause melting. This is unusual; for most substances, the melting point increases with pressure. The peculiar behaviour of water arises because the density of liquid water is greater than that of ice. The contraction on melting causes results in a negative value for Δfus*V* and so the solid-liquid line on the pressure-temperature phase diagram of water has a negative gradient.  **Example 2**  Given the normal boiling temperature and enthalpy of vaporisation of a substance, we can use the Clausius-Clapeyron equation to predict the vapour pressure at a range of different temperatures.  For example, the normal boiling temperature of benzene is 353.25 K, with a standard enthalpy of vaporisation Δvap*H*o = 30.8 kJ mol-1. If we assume that the enthalpy of vaporisation varies little with temperature and pressure, we may use the integrated form of the Clausius-Clapeyron equation  http://www.chm.bris.ac.uk/~chdms/Teaching/Chemical_Interactions/images/pic087.gif  to determine the vapour pressure of benzene at another temperature, such as 298.15 K.  The normal boiling temperature is the temperature at which the vapour pressure of benzene is 101325 Pa. We may therefore take *T*1 = 353.25 K and*p*1 = 101325 Pa and substitute into the Clausius-Clapeyron equation. This will allow us to determine a value for the vapour pressure *p*2 at a temperature of *T*2 = 298.15.  http://www.chm.bris.ac.uk/~chdms/Teaching/Chemical_Interactions/images/pic088.gif  giving *p*2 = 14600 Pa.  Note that we must assume that the enthalpy of vaporisation remains constant over the entire temperature and pressure range. In theory, the value quoted is only appropriate for a temperature of 353.25 K and a pressure of 105 Pa. Significant variation in the enthalpy of vaporisation with temperature and pressure would be observed as a curve in the liquid-vapour equilibrium line on the benzene phase diagram. |

**VII- The simple mixtures**

**The thermodynamic description of mixtures**

**5.1 Partial molar quantities**

*a)**The partial molar volume of a substance is the contribution to the volume that a substance makes when it is part of a mixture.*

*b) The chemical potential is the partial molar Gibbs energy and enables us to express the dependence of the Gibbs energy on the composition of a mixture.*

*c) The chemical potential also shows how, under a variety of different conditions, the thermodynamic functions vary with composition.*

*d) The Gibbs-Duhem equation shows how the changes in chemical potential of the components of a mixture are related.*

***A- Partial molar volume Vp***

The partial molar volumes of the components of a mixture vary with composition because the environnement of each type of molecule changes as the composition changes from pure A to pure B.

 (5.1)

Where n is the amounts of all other substances present are constant.

The definition in equation 5.1 implies that, when the composition of the mixture is changed by the addition of nA of A and nB of B, then the total volume of the mixture changes by

 (5.2)

0 0.2 0.4 0.6 0.8 1

Mole fraction of ethanol, x(C2H5OH)

Partial molar volume of water, V(H2O)/cm3 mol-1)

16

14

18

20

Water

Ethanol

Partial molar volume of ethanol, V(C2H5OH)/cm3mol-1

54

56

58

1. ***The partial molar volumes of water and ethanol at 25oC.***

****

**** (5.3)

***Illustration***

A polynomial fit to measurements of the total volume of water /ethanol mixture at 25oC that contains 1.000 kg of water is:



Where v= V/cm3, x = nE/mol, and nE is the amount of C2H5OH present.

***Solution***

The partial molar volume of ethanol, VE, is therefore



Then, because



we can conclude that



0 2 4 6 8 10

Mole fraction of ethanol, x(C2H5OH)=nE/mol

Partial molar volume of water, VE/(cm3 mol-1)

54

53

55

58

Water

Ethanol

**The partial molar volumes of ethanol as expressed by the polynomial.**

**b) *Partial molar Gibbs energies***

The concept of a partial molar quantity can be extended to any extensive state function. For a substance in a mixture, the chemical potential is defined as the partial molar Gibbs energy:

 (5,4)

The total Gibbs energy of a binary mixture constituted of A and B components is

 (5.5)

where μA and μB are the chemical potentials at the composition of the mixture.

The Gibbs energy of a mixture may change when these variables change, and, for a system of components A, B, etc.,

the equation dG = Vdp –SdT becomes

dG= Vdp-SdT + μAdnA + μBdnB + …. (5.6)

This expression is the fundamental equation of chemical thermodynamics. Its implication and consequences are explored and developed in this and the next chapters.

At constant pressure and temperature equation 5.6 simplifies to

dG = μAdnA + μBdnB + … (5.7)

We saw in section 3.5e that under the same conditions dG = dwadd,max . Therefore, at constant temperature and pressure,

dw add,max = μAdnA + μBdnB + … (5.8)

That is, additional (non-expansion) work can arise from the changing composition of a system.

**(c) *The wider significance of the chemical potential***

The chemical potential does not more than show G varies with composition. Because G = U + PV-TS, and therefore U = -PV + TS + G, we can write a general infinitesimal change in U for a system of variable composition as

dU = -PdV – VdP + SdT +TdS + dG

dU = -PdV-VdP +SdT + TdS + (VdP –SdT +μAdnA +μBdnB +…)

dU = -PdV + SdT + μAdnA +μBdnB +…

This expression is the generalization of equation 3.46 (that dU = TdS –PdV) to systems in which the composition may change. It follows that, at constant volume and entropy,

dU = μAdnA + μBdnB + … (5.9)

and hence that  (5.10)

Therefore, not only does the chemical potential show G changes when the composition changes, it also shows how the internal energy changes too ( but under a different set of conditions). In the same way it is easy to deduce that

1.  ; (b) 

Thus we see that the μj shows how all the extensive thermodynamic properties U, H, A, and G depend on the composition. This is why the chemical potential is so central to chemistry.

***d) The Gibbs Duhem equation***

**dG = μAdnA + μBdnB + nAdμA + nBdμB**

at constant temperature and pressure

*nAdμA + nBdμB = 0*

*Σ njdμj = 0*

This equation is special case of the Gibbs-Duhem equation

The significance of the Gibbs-Duhem equation is that the chemical potential of one component of a mixture cannot change independently of the chemical potentials of the other components.

If one partial molar quantity increases, then the other must decrease, with the two changes related by:



***Example***

The experimental values of the partial molar volume of K2SO4(aq) at 298 K are found to fit the expression

*vB = 32.280 + 18.216 x1/2*

where *vB = VK2SO4/(cm3.mol-1)* and *x* is the numerical value of the molality of K2SO4 (*x=b/bφ*, we write cφ = 1 moldm-3. The term, *b,* is the molality (*mol.kg-1*). We write *bφ* = *1 mol.kg-1*.). Use the Gibbs-Duhem equation to derive an equation for the molar volume of water in the solution. The molar volume of pure water at 298K is 18.079 cm3.mol-1.

***Solution***

*Method*

Let A denote H2O the solvent, and B denote K2SO4, the solute.

The Gibbs-Duhem equation for the partial molar volumes of two components is:

*nAdvA + nBdvB = 0*. This relation implies that *dvA =- (nB/nA)dvB*, and therefore that  *vA* can be found by integration:



Where = *VA*/(cm3.mol-1) is the numerical value of the molar volume of pure A. The first step is to change the variable *vB* to *x = b/bφ* and then to integrate the right-hand side between *x = 0* (pure B) and the molality of onterest.

***Answer***

*With*  B = K2SO4, *dvB/dx = 9.108 x-1/2*. Therefore, the integration required is:



However, the ratio of amounts of A(H2O) and B(K2SO4) is related to the molality of B, *b =nB*/(1kg water) and *nA* = (1 kg water)/*MA* where *MA* is the molar mass of water, by :



and hence



It then follows, by substituting the data (including *MA* = 1.802.10-2 kg.mol-1, the molar mass of water), that

VA/(cm3.mol-1) = 18.079 – 0.1094 (b/bφ)3/2

***Exercise***

Repeat the calculation for a salt B for which:

*VB/(cm3.mol-1) = 6.218 + 5.146 b -7.147b2*

**The thermodynamics of mixing**

a) The Gibbs energy of mixing is calculated by forming the difference of the Gibbs energies before and after mixing: the quantity is negative for perfect gases at the same pressure.

b) The entropy of mixing of perfect gases initially at the same pressure is positive and the enthalpy of mixing is zero.

(A) The Gibbs energy of mixing of perfect gases

Two perfect gases in two containers be *nA* and *nB*; both are at a temperature T and a pressure p. At this stage, the chemical potentials *μA* and *μB* have their pure values, which are obtained by applying the definition μ = Gm to:



where μo is the standard chemical potential, the chemical potential of the pure gas at 1 bar. It will be much simpler notationally if we agree to let *p* denote the pressure relative to *po*; that is, to replace *p/po* by *p*, for then we can write:



We can write the Gi by:

*Gi = nAμA + nBμB* = nA() + nB(

After mixing



The difference *Gf - Gi* , the Gibbs energy of mixing, ∆mixG, is therefore:



At this point we may replace *nj* by *xj*, where n is the total amount of A and B, and use the relation between partial pressure and mole fraction to write *pj/p = xj* for each component, which gives:



Because mole fractions are never greater than 1, the logarithms in this equation are negative, and .

***Example***

Calculating a Gibbs energy of mixing

A container is divided into two equal compartments. One contains 3.0 mol of H2(g) at 25oC; the other contains 1.0 mol of N2(g) at 25oC. Calculate the Gibbs energy of mixing when the partition is removed. Assume perfect behaviour.

***Answer***

3.0 mol H2, 3p

1.0 mol N2, p

3.0 mol H2, 1.0 mol N2 , 2p

P(H2)=3/2p , p(N2) =1/2p

Given that the pressure of N2 is *p*, the pressure of H2 is *3p*; therefore, the initial Gibbs energy is:



When the partition is removed and each gas occupies twice the original volume, the partial pressure of N2 falls to *1/2p* and that H2 falls to *3/2p*. Therefore, the Gibbs energy changes to:



The Gibbs energy of mixing is the difference of these two quantities:





**= -6.9kJ**

**b) Other thermodynamic mixing functions**

**Because , for a mixture of perfect gas initially at the same pressure, the entropy of mixing,**

****

Because *lnx ˂ 0, it follows that ∆Smix˃ 0*

We can calculate the isothermal (constant temperature), isobaric (constant pressure) enthalpy of mixing, ∆Hmix, the enthalpy change accompanying mixing, of two perfect gases from ∆G = ∆H-T∆S

∆Hmix = 0

**The Chemical potential of liquids**

a) Raoult's law provides a relation between the vapour pressure of a substance and its mole fraction in a mixture; it is the basis of the definition of an ideal solution.

b) Henry's law provides a relation between the vapour pressure of a solute and its mole fraction in a mixture; it is the basis of the definition of an ideal-dilute solution.

To discuss the equilibrium properties of liquid mixtures we need to know how the Gibbs energy of a liquid varies with composition. To calculate its value, we use the fact that, at equilibrium, the chemical potential of a substance present as a vapour must be equal to its chemical potential in the liquid.

1. ***Ideal solutions***

We shall denote quantities relating to pure substances by a superscript \*, so the chemical potential of pure A is written  and as (l) when we need to emphasizs that A is a liquid. Because the vapour pressure of the pure liquid is it follows from  that the chemical potential of A in the vapour ( perfect gas) is . These two chemical potentials are equal at equilibrium, so we can write:



Next, we combine these two equations to eliminate the standard chemical potential of the gas.



According to the Raoult's law



When we write equations that are valid only for ideal solutions, we shall label them with a superscript \*

For an ideal solution



0 1

Mole fraction of toluene x(C6H5CH3)

Pressure, p(torr)

Benzene

Toluene

**Fig. 1** Two similar liquids, in this case benzene and methylbenzene (toluene), behave almost ideally, and the variation of their vapour pressures with composition resembles that for an ideal solution.

Total pressure

0 1

Mole fraction of Carbon disulfide, x(CS2)

Pressure, p(torr)

Carbon disulfide

Acetone

**Fig. 2** Strong positive deviations from ideality are shown by dissimilar liquids.

Total pressure

0 1

Mole fraction of Carbon disulfide, x(A)

Pressure, p(torr)

A

B

**Fig. 2** Strong negative deviations from ideality are shown by dissimilar liquids.

Total pressure

A deviation from the ideality is observed in this previous diagram due to the interaction between CS2 and Acetone. This interaction can be attraction or repulsion:

* A positive deviation indicating a repulsion between the different molecules
* A negative deviation indicating an attraction between the different molecules

In this case, the partial pressure of acetone becomes:

 and 

where ai is called activity of the constituent (i ) in solution with 

 and 

0 1

Mole fraction of B, xB

Pressure, p(torr)

Real

solution

Ideal solution (Raoult)

**Fig. 3** When a component (the solvent) is nearly pure, it has a vapour pressure that is proportional to its mole fraction with a slope pB\* (raoult's law). When it is the minor component (the solute) its vapour pressure fraction, but the constant of proportionality is now KB (Henry's law).

Ideal-dilute solution (Henry)

KB

P\*A

This important equation can be used as the definition of an ideal solution (so that it implies Raoult's law rather than stemming from it).

The molecular origin of Raoult's law is the effect of the solute on the entropy of the solution. In the pure solvent, the molecules have a certain disorder and corresponding entropy; the vapour pressure then represents the tendency of the system and its surroundings to reach a higher entropy. When a solute is present, the solution has a greater disorder than the pure solvent because we cannot be sure that a molecule chosen at random will be a solvent molecule. Because the entropy of the solution is higher than that of the pure solvent, the solution has a lower tendency to acquire an even higher entropy by the solvent vaporizing. In other words, the vapour pressure of the solvent in the solution is lower than that of the pure solvent.

1. **Ideal-dilute solutions**

In ideal solutions the solute, as well as the solvent, obeys Raoult's law. However, Henry found experimentally that, for real solutions at low concentrations, although the vapour pressure of the solute is proportional to its mole fraction, the constant of proportionality is not the vapour pressure of the pure substance (Fig.3).

Henry's law is:

*pB = xb KB*

In this expression *xB* is the mole fraction of the solute and *KB* is an empirical constant chosen so that the plot of the vapour pressure of B against its mole fraction is tangent to the experimental curve at *xB = 0.*

Table 1 Henry's law constants for gases in water at 298K

|  |  |
| --- | --- |
| Substance (gas) | K/kPa.kg.mol-1 |
| CO2 | 3.01x103 |
| H2 | 1.28x105 |
| N2 | 1.56x105 |
| O2 | 7.92x104 |

***Example***

The vapour pressures of each compound in a mixture of propanone (acetone, A) and trichloromethane (chloroforme, C) were measured at 35oC with the following results:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| *xC* | 0 | 0.20 | 0.40 | 0.60 | 0.80 | 1.00 |
| *pC/kPa* | 0 | 4.7 | 11 | 18.9 | 26.7 | 36.4 |
| *pA/kPA* | 46.3 | 33.3 | 23.3 | 12.3 | 4.9 | 0 |

Confirm that the mixture conforms to Raoult's law for the component in large excess and to Henry's law for the minor component. Find the Henry's law constants.

***Answer***

0 0.2 0.4 0.6 0.8 1.0

Mole fraction of chloroform, x(CHCl3)

Pressure, p(kPa)

**Fig. 4** The experimental partial vapour pressures of a mixture of chloroform and acetone. The values of K are obtained by extrapolating the dilute solution vapour pressures.

K(acetone)

K(chloroform)

p\*(acetone)

p\*(chloroform)

Raoult's law

Henry's law

10

20

30

40

50

The data are plotted in Fig 4 toghether with the Raoult's law lines Henry's law requires K = 23.3 kPa for propanone and K = 22.0 kPa for trichloromethane.

**The properties of solutions**

In this section we consider the thermodynamics of mixing of liquids. First, we consider the simple case of mixtures of liquids that mix to form an ideal solution.

***5.4 Liquid mixtures***

a) The Gibbs energy of mixting of two liquids to form an ideal solution is calculated in the same way as for two perfect gases. The enthalpy of mixing is zero and the Gibbs energy is due entirely to the entropy of mixing.

b) A regular solution is one in which the entropy of mixing is the same as for an ideal solution but the enthalpy of mixing is non-zero.

(a) Ideal solutions

The Gibbs energy of mixing of two liquids to form an ideal solution is calculated in exactly the same way as for two gases. The total Gibbs energy before liquids are mixed is:



When they are mixed, the individual chemical potentials are given by  and the total Gibbs energy of mixing, the difference of these two quantities, is:





Where *n = nA + nB* . As for gases, it follows that the ideal entropy of mixing of two liquids is:



Because , the ideal enthalpy of mixing is zero.

The ideal volume of mixing, the change in volume on mixing, is also zero because it follows from  that  but ∆Gmix in  is independent of pressure, so the derivative with respect to pressure is zero.

1. ***Excess functions and regular solutions***

The thermodynamic properties of real solutions are expressed in terms of the excess functions, XE, the difference between the observed thermodynamic function of mixing and the function for an ideal solution. The excess entropy, SE, for example, is defined as:

SE = ∆Smix - ∆Smix (ideal)

The deviation of the excess energies from zero indicates the extent to which the solutions are nonideal. In this connection a useful model system is regular solution, a solution for which HE ≠ 0, but SE = 0. We can think of a regular solution as one in which the two kinds of molecules are distributed randomly (an in an ideal solution) but have different energies of interactions with each other. To express this concept more quantitatively we can suppose that the excess enthalpy depends on composition as:



where ξ (xi) is a dimentionless parameter that is a measure of the energy of AB interactions relative to that of the AA and BB interactions. If ξ ˂ 0, mixing is exothermic and the solute-solvent interactions are more favorable than the solvent-solvent and solute-solute interactions. If ξ ˃ 0, then the mixing is endothermic. Because the entropy of mixing has its ideal value for a regular solution, the excess Gibbs energy is equal to the excess enthalpy, and the Gibbs energy of mixing is:



**HE/nRT**

0

+0.5

0 0.5 1

*xA*

2

1

0

-1

-2

-0.2

-0.1

-0.3

-0.4

0.0

+0.1

0 0.5 1

*xA*

3

2.5

2

1.5

1

**Fig. 5** The excess enthalpy according to a model in which it is proportional to ξ*xAxB*, for different values f the parameter ξ.

**Fig. 6** The Gibbs energy of mixing for different values f the parameter ξ.

**(a)The elevation of boiling point**

The heterogeneous equilibrium of interest when considering boiling is between the solvent vapour and the solvent in solution at 1 atm. We denote the solvent by A and the solute by B. The equilibrium is established at a temperature for which

****

We show in the following justification that this equation implies that the presence of a solute at a mole fraction xB causes an increase in normal boiling point from T\* to T\* + ∆T, where

**(b)The depression of freezing point**

The heterogeneous equilibrium of interest is between pure solid solvent A and the solution with solute present at a mole fraction *xB*. At the freezing point, the chemical potentials of A in the two phases are equal:

****

The only difference between this calculation and the last is the appearance of the solid's chemical potential in place of the vapour's. Therefore we can write the result directly from equation

Where ∆T is the freezing point depression, T\*-T, ∆Hfus is the enthalpy of fusion of the solvent. When the solution is diluted, the mole fraction is proportional to the molality of the solute, b, and it is common to write the last equation as

∆T = Kf x b

1. **The solubility**

In a saturated solution the chemical potential of pure solid solute, μB\*(s), and the chemical potential of B in solution, μB, are equal. Because the latter is  we can write 

This expression is the same as the starting equation of the last section, except that the quantities refer to the solute B, not the solvent A. We now show in the following justification that:



1. **The Osmosis**

The thermodynamic treatment of osmosis depends on noting that, at equilibrium, the chemical potential of the solvent must be the same on each side of the membrane. The chemical potential of the solvent is lowered by the solute, but is restored to its pure value by the application of pressure. This equality implies that for dilute solutions the osmotic pressure is given by the Van't'Hoff equation:



Where *[B] = nB/V* is the molar concentration of the solute.

**Example**

The osmotic pressures of solutions of poly(vinylchloride), PVC, in cyclohexanone at 298K are given below. The pressures are expressed in terms of the heights of solution (of mass density ῥ = 0.980 g.cm-3) in balance with the osmotic pressure.

Determine the molar mass of the polymer.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| c/(g.dm-3) | 1.00 | 2.00 | 4.00 | 7.00 | 9.00 |
| h/cm | 0.28 | 0.71 | 2.01 | 5.10 | 8.00 |

***Answer***

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| c/(g.dm-3) | 1.00 | 2.00 | 4.00 | 7.00 | 9.00 |
| h/cm | 0.28 | 0.71 | 2.01 | 5.10 | 8.00 |
| (h/c)/(cm.g-1.dm3 | 0.28 | 0.36 | 0.503 | 0.729 | 0.889 |

**(h/c)/(cm.g-1.dm3)**

0 2 4 6 8 10

**c/(g.dm-3)**

**Fig. 7** The plot involved in the determination of molar mass by osmometry. The molar mass is calculated from the intercept at c = 0.

0.2

0.4

0.6

0.8

The points are plotted in figure 7. The intercept is at 0.21. Therefore,





M = 1200000 g/mol

**X. Phase diagrams of binary systems**

***Vapour pressure diagrams***

Raoult's law is used to calculate the total vapour pressure of a binary system of two volatile liquids.

1. The composition of the vapor in equilibrium with a binary mixture is calculated by using Dalton's law.
2. The compositions of the vapour and the liquid phase in equilibrium are located at each end of a tie line.
3. The lever rule is used to deduce the relative abundances of each phase in equilibrium.

The partial pressures of the components of an ideal solution of two volatile liquids are related to the composition of the liquid mixture by Raoult's law

 and  (5.6.1)

where  is the vapour pressure of pure A and  that of pure B. The total vapor pressure p of the mixture is therefore

 (5.6.2)

This expression shows that the total vapour pressure (at some fixed temperature) changes linearly with the composition from  to as *xA* changes from 0 to 1.

***The composition of the vapor***

The composition of the liquid and vapour that are in mutual equilibrium are not necessarily the same. Common sense suggests that the vapour should be richer in the more volatile component. This expectation can be confirmed as follows. The partial pressures of the components are given by the Daton's equation.

 ;  (5.6.3)

*yA* and *yB* are the mole fractions in the gas.

Provided the mixture is ideal, the partial pressures and the total pressure may be expressed in terms of the mole fractions in the liquid by using:  and  and  which gives:

 and  (5.6.4)

0 0.2 0.4 0.6 0.8 1.0

Mole fraction of A in the liquid, *xA*

0.2

0.4

0.6

0.8

1.0

Mole fraction of A in the vapour*, yA*

1

4

10

50

1000

0 0.2 0.4 0.6 0.8 1.0

Mole fraction of A in the vapor, *yA*

Total vapour pressure, p/p\*A

0.2

0.4

0.6

0.8

1.0

1

2

4

10

30

1000

The dependence of the vapour pressure of the same system as in the side figure, but expressed in terms of the mole fraction of A in the vapour by using eqn (5.6.5). Individual curves are labeled with the value of PA\*/PB\*

The mole fraction of A in the vapour of binary ideal solution expressed in terms of its mole fraction in the liquid, calculated using eqn (5.6.4) for various values of PA\*/pB\* with A more volatile than B. In all cases tha vapour is richer than the liquid in A.

0 xA yA 1

Mole fraction of A, *zA*

Pressure, p

a

b

pA\*

pB\*

Vapour

Liquid

The dependence of the total vapour pressure of an ideal solution on the mole fraction of A in the entire system.

A point between the two lines corresponds to both liquid and vapour being present; outside that region there is only one phase present. The mole fraction of A is denoted *zA*, as explained below.

We can also relate the total vapour pressure to the composition of the vapour:

 (5.6.5)

This expression is plotted in the middle figure.

**Temperature-composition diagrams**

a) a phase diagram can be used to discuss the process of fractional distillation.

b) Depending on the relative strengths of the intermolecular forces, high- or low-boiling azeotropes may be formed.

c) The vapour pressure of a system composed of immiscible liquids is the sum of the vapour pressures of the pure liquids.

d) A phase diagram may be used to discuss the distillation of partially miscible liquids.

To discuss distillation we need a temperature-composition diagram, a phase diagram in which the boundaries show the composition of the phases that are in equilibrium at various temperatures (and a given pressure, typically 1 atm). An exemple is shown in this figure.

Mole fraction of A, *zA*

Temperature, T

Vapour composition

Boiling temperature of liquid

The temperature-composition diagram corresponding to an ideal mixture with the component A more volatilethan component B. Successive boiling and condensations of a liquid originally of composition a1 lead to a condensate that is pure A. the separation-technique is called fractional distillation.

a1

T2

T3

a2

a'2

a'3

a3

a4

1. ***Azeotropes***

Although many liquids have temperature-composition phase diagrams resembling the ideal version in the precedent figure, in a number of important cases there are marked deviations. A maximum in the phase diagram (figure below) may occur when the favourable interactions between A and B molecules reduce the vapour pressure of the mixture below the ideal value: in effect, the A-B interactions stabilize the liquid. In such cases the excess Gibbs energy, GE, is negative (more favourable to mixing than ideal). Examples of this behaviuor include trichloromethane/propanone and nitric acid/water mixtures. Phase diagrams showing a minimum (figure) indicate that the mixture is destabilized relative to the ideal solution, A-B interactions then being unfavourable. For such mixtures GE is positive (less favourable to mixing than ideal), and there may be contributions from both enthalpy and entropy effects. Examples include dioxane/water and ethanol/water mixtures.

Temperature, T

Vapour composition

Boiling temperature

of liquid

A high-boiling azeotrope. When the liquid of composition *a* is distilled, the composition of the remaining liquid changes towards *b* but no further.

a3

a4

a'4

a'2

a'3

a2

a

b

The system shown in the figure below is also azeotropic, but shows its azeotropy in a different way. Suppose we start with a mixture of composition *a1*, and follow the changes in the composition of the vapour that raises trough a fractionatimg column.

The mixture boils at *a2* to give a vapour of composition *a'2*. This vapour condenses in the column to a liquid of the same composition (*a3*). That liquid reaches equilibrium with its vapour at *a3'*, which condenses higher up the tube to give a liquid of the same composition, which we now call *a4*. The fractionation therefore shifts the vapour towards the azeotropic composition at *b*, but not beyond, and the azeotropic vapour emerges from the top of the column. An example is ethanol/water, which boils unchanged when the water content is 4 per cent by mass and the temperature is 78oC.

Mole fraction of A, *zA*

Temperature, T

Vapour composition

Boiling temperature

of liquid

A low-boiling azeotrope. When the mixture at *a* is fractionally distilled, the vapour in equilibrium in the fractionating column moves towards b and then remains unchanged

a3

a4

a1

a'2

a'3

a2

a

b

**Liquid-liquid phase diagrams**

1. Phase separation of partially miscible liquids may occurs when the temperature is below the upper critical solution temperature or above the lower critical solution temperature.
2. The upper critical solution temperature is the highest temperature at which phase separation occurs.
3. The outcome of a distillation of a low-boiling azeotrope depends on whether the liquids become fully miscible before they boil or boiling occurs before mixing is complete.
4. *Phase separation*

Suppose a small amount of a liquid B is added to a sample of another liquid A at a temperature T'. Liquid B dissolves completely, and the binary system remains a single phase. As more B is added, a stage comes at which no more dissolves. The sample now consists of two phases in equilibrium with each other, the most abundant one consisting of A saturated with B, the minor one a trace of B saturated with A. In the temperature-composition diagram drawn below, the composition of the former is represented by the point a' and that of the latter by the point a". The relatives abundances of the two phases are given by the level rule.

Temperature

Mole fraction of A, xA

0

1

T

a'

a"

a

Heterogeneous zone

homogeneous zone

**Liquid-Solid phase diagrams**

1. A phase diagram summarizes the temperature-composition properties of a binary system with solid and liquid phases; at the eutectic composition the liquid phase solidifies without change of composition.
2. The phase equilibria of binary systems in which the components react may also be summarized by a phase diagram.
3. In some cases, a solid compound does not survive melting.

Temperature, T

Solid A + Solid B

Liquid A + Liquid B

Liquid + B

Liquid + A

Mole fraction of B, XB

1

0

TmB

TmA

Eutectic

*Eutectics*

At certain temperature called eutectic temperature the two components in certain composition called also euthectic composition in the mixture has the same melting temperature.

A ternary mixture A, B and C can also contain two euthectic points in which at certain composition the three component have the same melting temperature.

Liquid A + Liquid B + liquid C

Liquid + C

Liquid + A

Solid A + Solid B + Solid C

Eutectic

B

Composition

Eutectic

TmA

TmB

A

C

Temperature, T

# IX. Colloids

A colloid is one of the three main types of mixtures, with the other two being a [solution](http://chemwiki.ucdavis.edu/Physical_Chemistry/Physical_Properties_of_Matter/Solutions)or suspension. A colloid is a solution that has particles ranging between 1 and 1000 nanometers in diameter, yet is still able to remain evenly distributed throughout the solution. These are also known as colloidal dispersions because the substances remain dispersed and don't settle to the bottom. In a colloid one substance is evenly dispersed in another. The substance being dispersed is referred to as being in the dispersed phase, while the substance in which it is dispersed is in the continuous phase.

### Properties of Colloids

In order to be classified as a colloid, the substance in the dispersed phase must be larger than the size of a molecule but smaller than what can be  seen with the naked eye. This can be more precisely quantified as one or more of the substance's dimensions must be between 1 and 1000 nanometers. If the dimensions are smaller than this the substance is considered a solution and if they are larger than the substance is a suspension.

A common method of classifying colloids is based on the phase of the dispersed substance and what phase it is dispersed in. The types of colloids include sol, emulsion, foam, and aerosol.

1. **Sol**is a colloidal suspension with solid particles in a liquid.
2. **Emulsion** is between two liquids.
3. **Foam**is formed when many gas particles are trapped in a liquid or solid.
4. **Aerosol**contains small particles of liquid or solid dispersed in a gas.

When the dispersion medium is water, the collodial system is referred to as a hydrocolloid. The particles in the dispersed phase can take place in different phases depending on how much water is available. For example, Jello powder mixed in with water creates a hydrocolloid. A common use for hydrocolloids is in the creation of medical dressings.

| **Dispersion Medium** | **Dispersed Phase** | **Type of Colloid** | **Example** |
| --- | --- | --- | --- |
| Solid | Solid | Solid sol | Ruby glass |
| Solid | Liquid | Solid emulsion/gel | Pearl, cheese |
| Solid | Gas | Solid foam | Lava, pumice |
| Liquid | Solid | Sol | Paints, cell fluids |
| Liquid | Liquid | Emulsion | Milk, oil in water |
| Liquid | Gas | Foam | Soap suds, whipped cream |
| Gas | Solid | Aerosol | Smoke |
| Gas | Liquid | Aerosol | Fog, mist |

### Problems

1. Is dust a colloid? If so, what type is it?
2. Is whipped cream a colloid? if so, what type is it?
3. What does Sol mean?
4. When hit by light what happens to a colloidal mixture?
5. What is the mixture considered if the particles are larger than the particles of a colloidal substance

### Answers

1. Dust is a colloid. It consists of a solid in a gas, so it is a aerosol.
2. Whipped cream is a colloid. It consists of a gas in a liquid, so it is a foam.
3. Sol is a colloidal suspension with solid particles in a liquid.
4. The light is reflected off the large particles and spread out.
5. It's considered a suspension if the particles are larger than 1000 nanometers.
   1. **Emulsion**

An **emulsion** is a [mixture](http://en.wikipedia.org/wiki/Mixture) of two or more [liquids](http://en.wikipedia.org/wiki/Liquid) that are normally [immiscible](http://en.wikipedia.org/wiki/Immiscible) (non mixable or unblendable). Emulsions are part of a more general class of two-phase systems of [matter](http://en.wikipedia.org/wiki/Matter) called [colloids](http://en.wikipedia.org/wiki/Colloid). Although the terms *colloid* and *emulsion* are sometimes used interchangeably, *emulsion* should be used when both the dispersed and the continuous phase are liquids. In an emulsion, one liquid (the dispersed [phase](http://en.wikipedia.org/wiki/Phase_(matter))) is [dispersed](http://en.wikipedia.org/wiki/Dispersion_(chemistry)) in the other (the continuous phase). Examples of emulsions include [vinaigrettes](http://en.wikipedia.org/wiki/Vinaigrette), [milk](http://en.wikipedia.org/wiki/Milk), [mayonnaise](http://en.wikipedia.org/wiki/Mayonnaise), and some [cutting fluids](http://en.wikipedia.org/wiki/Cutting_fluid) for [metal working](http://en.wikipedia.org/wiki/Metal_working). The photo-sensitive side of [photographic film](http://en.wikipedia.org/wiki/Photographic_film) is an example of a colloid.

The word "emulsion" comes from the Latin word for "to milk", as milk is an emulsion of milk fat and water, among other components.

Two liquids can form different types of emulsions. As an example, oil and water can form, first, an oil-in-water emulsion, wherein the oil is the dispersed phase, and water is the dispersion medium. Second, they can form a water-in-oil emulsion, wherein water is the dispersed phase and oil is the external phase. Multiple emulsions are also possible, including a "water-in-oil-in-water" emulsion and an "oil-in-water-in-oil" emulsion.

Emulsions, being liquids, do not exhibit a static internal structure. The droplets dispersed in the liquid matrix (called the “dispersion medium”) are usually assumed to be [statistically distributed](http://en.wikipedia.org/wiki/Probability_distribution).

**Electrolyte Solutions**

An electrolyte solution is a solution that generally contains ions, atoms or molecules that have lost or gained electrons, and is electrically conductive. For this reason they are often called ionic solutions, however there are some cases where the electrolytes are not ions. For this discussion we will only consider solutions of ions. A basic principle of electrostatics is that opposite charges attract and like charges repel. It also takes a great deal of force to overcome this electrostatic attraction.

**Introduction**

The general form of Coulomb's law describes the force of attraction between charges:

*F*=*kq*1*mq*2*/r*2

However, we must make some changes to this physics formula to be able to use it for a solution of oppositely charged ions. In Coulomb's Law, the constant *k*=1/4*πε*0, where *ε*0is the permittivity of free space, such as in a vacuum. However, since we are looking at a solution, we must consider the effect that the medium (the solvent in this case) has on the electrostatic force, which is represented by the dielectric constant *ε*:

*F*=*q*1*q*2/4*πε*0*εr*2

Polar substances such as water have a relatively high dielectric constant.

**Standard Definitions of Enthalpy, Entropy, and Gibbs Energy for Ions**

Ions are not stable on their own, and thus no ions can ever be studied seperately. Particularly in biology, all ions in a certain cell or tissue have a counterion that balances this charge. Therefore, we cannot measure the enthalpy or entropy of a single ion as we can atoms of a pure element. So we define a reference point. The Δ*fH*∘ of a hydrogen ion *H*+ is equal to zero, as are the other thermodynamic quantities.

Δ*H*of [*H*+(*aq*)]=0

Δ*G*∘f[*H*+(*aq*)]=0

*S*∘[*H*+(*aq*)]=0

**Chemical Potential**

When studying the formation of ionic solutions, the most useful quantity to describe is chemical potential *μ*, defined as the partial molar Gibbs energy of the i th component in a substance:



where *xi* can be any unit of concentration of the component: mole fraction, molality, or for gases, the partial pressure divided by the pressure of pure component.

**Ionic Solutions**

To express the chemical potential of an electrolyte in solution in terms of molality, let us use the example of a dissolved salt such as magnesium chloride, *MgCl*2.

*MgCl*2 ⇌*Mg*2+ +2*Cl*− (1)

We can now write a more general equation for a dissociated salt:

*Mν*+*Xν*− ⇌ *ν*+*Mz*+ + *ν*−*Xz*− (2)

where *ν*+ and *ν*- represent the stoichiometric coefficient of the cation and anion, respectively and z represents the charge, and M and X are the metal and halide, respectively.

The total chemical potential for these anion-cation pair would be the sum of their individual potentials multiplied by their stoichiometric coefficients:

*μ* = *ν*+*(μ*+) + *ν*−*(μ*−) (3)

The chemical potentials of the individual ions are:

*μ*+ =** + *RTln(m*+) (4)

*μ*− =**+*RTln(m*−) (5)

and the molalities of the individual ions are related to the original molality of the salt m by their stoichiometric coefficients

*m*(+)=*ν*+*(m*)

Substituting equations (4) and (5) into equation (3),

*μ*=(*ν*+*m*+*ν*−*m*)+*RTln*(*mν*+++*mν*−-) (6)

since the total number of moles  *ν* = *ν*+ + *ν*−, we can define the mean ionic molality as the geometric average of the molarity of the two ions:

*m*± = (*mν*++ +*mν*−−)1*/ν*

then equation (6) becomes

*μ* = (*ν*+**+*ν*−**)+ *νRTln(m*± ) (7)

We have derived this equation for an ideal solution, but ions in solution exert electrostatic forces on one another to deviate from ideal behavior, so instead of molarities we must use the activity (a) to represent how the ion is behaving in solution. Therefore the mean ionic activity is defined as

*a*±=(*aν*+++*aν*−−)1*/ν* where *a*± = *γ m*±

and *γ*± is the mean ionic activity coefficient, which is dependent on the substance.  
  
Substituting the mean ionic activity into (6),

*μ*=(*ν*+*μ*∘++*ν*−*μ*∘−) +*νRTlna*± =(*ν*+**+*ν*−**) +*RTlnaν*±=(*ν*+**+*ν*−**) +*RTln(a)*

when *a* = *aν*±. Equation (11) then represents the chemical potential of a nonideal electrolyte solutions. To calculate the mean ionic activity coefficient requires the use of the Debye-Hückel limiting law, part of the [Debye-Hückel theory of electrolytes](http://chemwiki.ucdavis.edu/Physical_Chemistry/Physical_Properties_of_Matter/Solutions/Nonideal_Ssolutions/Debye-H%C3%BCckel/Debye-H%C3%BCckel_Theory_of_Electrolytes) .

**Sample Problem**

Let us now write out the chemical potential in terms of molality of the salt in our first example, *MgCl*2. First from equation (1), the stoichiometric coefficients of the ions are:

*ν*+ =1, *ν*− = 2, *ν* =3

The mean ionic molality is

*m*±=(*m*1+ *m*2−)1/3=(*ν*+*m*×*ν*−*2m*2)1/3=*m*(1122)1/3=1.6*m*

The expression for the chemical potential of *MgCl*2 is

*μMgCl*2=*μ*∘*MgCl*2+3*RTln*1.6*m*

# Debye-Hückel Theory of Electrolytes

The properties of electrolyte solutions can significantly deviate from the laws used to derive chemical potential of solutions. In nonelectrolyte solutions, the intermolecular forces are mostly comprised of weak Van der Waals interactions, which have a 1/*r*7 dependence, and for practical purposes this can be considered ideal. In ionic solutions, however, there are significant electrostatic interactions between solute-solvent as well as solute-solute molecules. These electrostatic forces are governed by Coulomb's law, which has a 1/*r*2 dependence. Consequently, the behavior of an electrolyte solution deviates considerably from that an ideal solution. Indeed, this is why we utilize the activity of the individual components and not the concentration to calculate deviations from ideal behavior. In 1923, Peter Debye and Erich Hückel developed a theory that would allow us to calculate the mean ionic activity coefficient of the solution, *γ*±, and could explain how the behavior of ions in solution contribute to this constant.

### Assumptions

The Debye-Hückel theory is based on three assumptions of how ions act in solution:

1. Electrolytes completely dissociate into ions in solution.
2. Solutions of Electrolytes are very dilute, on the order of 0.01 M.
3. Each ion is surrounded by ions of the opposite charge, on average.

### The Theory

Debye and Hückel developed the following equation to calculate the mean ionic activity coefficient *γ*±:



where

* *ε* is the dielectric constant,
* *z*+ and *z*− are the charges of the cation and anion, respectively, and
* *I* is a quantity called the ionic strength of the solution.

The above equation is known as the **Debye-Hückel Limiting Law**. The ionic strength is calculated by the following relation:

*I*=1/2∑*I mi z*2*i*

where *mi* and *zi* are the molality and the charge of the ith ion in the electrolyte. Since most of the electrolyte solutions we study are aqueous (*ε* = 78.54) and have a temperature of 298 K, the Limiting Law reduces to

*logγ*± = − 0.509∣*z*+*z*−∣**

|  |
| --- |
| **Example 1** |
| To use the information we have now learned, let's calculate ionic strength, mean ionic activity coefficient *γ*±, and the mean ionic molality *m*± for a 0.02 molal solution of zinc chloride, *ZnCl*2.  **SOLUTION**  Zinc chloride will dissolve as *ZnCl*2⟶*Zn*2+(*aq*)+2*Cl*−(*aq*). The concentrations of the zinc and chloride ions will then be 0.02 and 0.04 molal, respectively. First let's calculate the mean ionic molality. From reading [Electrolyte Solutions](http://chemwiki.ucdavis.edu/Physical_Chemistry/Physical_Properties_of_Matter/Solutions_and_Mixtures/Solution_Basics/Electrolyte_Solutions), the mean ionic molality is defined as the average molality of the two ions:  *m*±=(*mν*+++*mν*−−)1*/ν*,  where *ν* is the stoichiometric coefficient of the ions, and the total of the coefficients in the exponent. In our case, the mean ionic molality is      To calculate the mean ionic activity coefficient, we first need the ionic strength of the solution from Equation (2):  *I*=1/2[(0.02)(+2)2+(0.04)(−1)2]=1/2(0.08+0.04)=0.06.  Now we can use Equation (3) to calculate the activity coefficient:  *logγ*±=−0.509∣(+2)(−1)∣ =(−0.509)(2)(0.245)=−0.250.  *γ*± = 10−0.25 = 0.1627 |