Further Solution Chemistry

CH-2016

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Learning Objectives

1) Define and use mole fraction, molality and concentration to describe composition.
2) Express equilibrium constants for solution reactions in terms of the above three composition scales.
3) Understand the idea of standard state.
4) Be able to calculate Gibbs energies from enthalpy and entropy data for a reaction.
5) Know and be able to use the relation between Gibbs energy and equilibrium constant
6) Know how variation in Gibbs energy with temperature is related to entropy change and use this to determine how equilibrium constants vary with temperature.
7) Be able to calculate equilibrium constants from enthalpy and entropy data and *vice-versa*.
8) Explain the definition and physical interpretation of the behaviour of ideal and non-ideal liquid mixtures.
9) Explain the definition and physical interpretation of ideal and non-ideal solution behaviour.
10) Derive and explain an expression for the Gibbs energy of mixing of two ideal liquids.

Learning Objectives (continued)

11) Define and use activity and activity coefficient and explain the different standard states.
12) Define and use chemical potential and relate it to concentration or activity.
13) Define the “true” or “thermodynamic” equilibrium constant for a reaction in solution.
14) Define mean ionic activity coefficient and justify its use.
15) Define and use ionic strength.
16) Understand the phenomenon of ionic atmosphere.
17) Know the Debye-Huckel Limiting Law and be able to state and discuss its assumptions and limitations.
18) Use the Limiting Law to calculate activity coefficients and “thermodynamic” equilibrium constants.
19) Outline methods of measurement of equilibrium constants in solution.
20) Define and explain solubility product and activity product, show how they are related and use them to illustrate the solubility of a salt in a strong ionic solution.

What is a Solution?

Solid dissolved in a liquid

→ Sodium chloride dissolved in water

70% of the surface of the earth

Liquid dissolved in liquid

→ Alcohol dissolved in water

Beer, wines, spirits, antifreeze, etc…

Gas dissolved in a liquid

→ Oxygen dissolved in water

Oceans, rivers, lakes, etc…

Solid dissolved in a solid

→ Steel

Solution of carbon (and other materials in iron), Bridges, heavy industry, trains, planes, cars, etc…

Gas dissolved in a gas

→ The air we breathe

Solution of oxygen, carbon dioxide (and other gases) in nitrogen, supports life on Earth

Solvent: the component present in larger quantity.
Solute: the component present in smaller quantity.

What is the Difference Between a Solution and a Mixture?

A **solution** must be **homogeneous** – its **composition** is the same throughout its bulk.

NaCl dissolved in water never settles out. Cyclohexane in water separates over time and is termed an **inhomogeneous** mixture.

Each liquid will however dissolve a small amount of the other. It is rarely, if ever, correct to claim that a solute is **insoluble** in a given solvent.

The terms **soluble** and insoluble are thus relative.

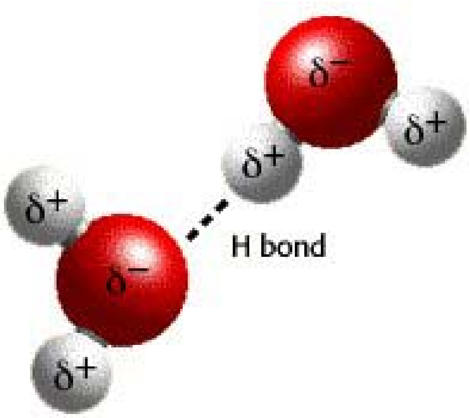
Solubility

Solubility: the mass of solute that will dissolve in a certain quantity of solvent at a given temperature.

Units: kg / dm^3, g / 100 cm^3, g / L

Experimental observation dictates that like dissolves like. Polar materials dissolve best in polar solvents and non-polar materials in non-polar solvents.

Polarity in a molecule arises as a consequence of differences in electronegativity.

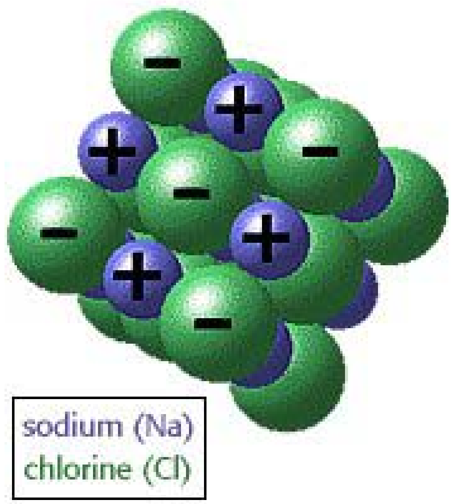


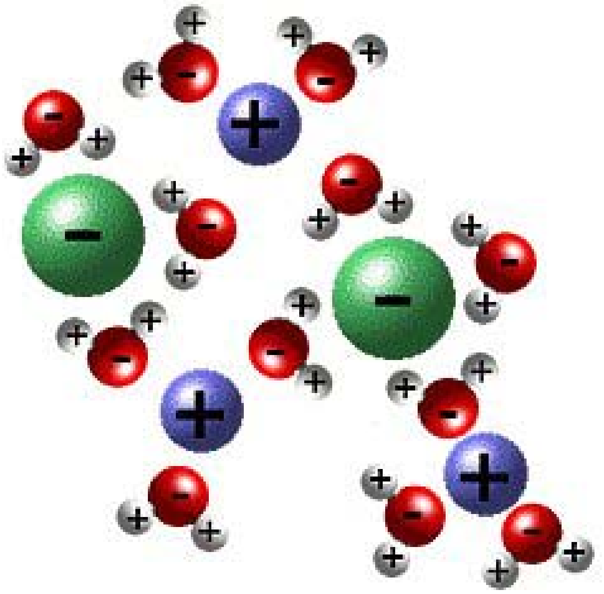
The polarity of a solvent is measured by its relative permittivity, ε_r. This dimensionless quantity is large for polar solvents and small for non-polar ones.

water $\varepsilon_r = 80$
ethanol $\varepsilon_r = 24$ all at 25°C
cyclohexane $\varepsilon_r = 2$

For the process of solution to be favourable, interactions between the solute and the solvent must be favourable.

An ionic solid will generally dissolve in water, since the electrostatic forces between ions in the crystal lattice and the hydrogen bonds between water molecules are readily replaced by electrostatic interactions between water and the ions.





A non-polar solvent such as cyclohexane cannot achieve this.

The Composition of a Solution

In order to discuss the properties of a solution we need to be able to express its composition in a meaningful way.

Composition is an intensive property – it does not depend on quantity. Properties such as volume that *do* depend on quantity are called extensive.

There are three primary ways to measure composition of a solution:

1) Mole fraction
2) Molarity / Concentration
3) Molality

Consider a solution in which n_A moles of solvent A contains n_B moles of solute B.

Mole fraction

Mole fraction is defined as the number of moles of a species over the total number of moles.

Thus:

$$x_A = \frac{n_A}{n_A + n_B} \quad ①$$

$$x_B = \frac{n_B}{n_A + n_B} \quad ②$$

Mole fractions are dimensionless numbers that do not vary with temperature. They vary from 0 to 1.

Molarity / Concentration

Molarity is defined as the number of moles of a species per unit volume of solution.

Thus:

$$c_B = \frac{n_B}{V} \quad ③$$

Units: mol dm^{-3} or mol L^{-1}

Molality

Molality is defined as the number of moles of a species per unit mass of the solvent (and NOT the solution).

Thus:

$$\text{molality}_B = \frac{n_B}{m_A} \qquad ④$$

Units: mol kg^{-1}

Q. You should be familiar with the concept of molarity. So why introduce the further concept of molality?

A. Molarity varies with temperature because solvents (liquids) expand and contract upon heating and cooling. In practice, mole fractions tend to be used for liquid mixtures, molalities for precise work with solid solutes and molarities for less precise work with solid solutes.

Thermodynamics of Solutions

In terms of chemical equations you have probably encountered three different types of chemical reaction…

(1) Reactions that go to completion.

$$\longrightarrow$$

$$C_4H_{10}(g) + 6\tfrac{1}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$$

(2) Equilibrium reactions.

$$\rightleftarrows$$

$$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$$

(3) Reactions that simply don’t go.

$$\not\longrightarrow$$

This is a very simplistic ideology. In reality, *ALL* reactions are equilibria. Equilibrium is achieved when the relative compositions of reactants and products no longer change with time.

A measurement of these compositions is given by the equilibrium constant which for the reaction

$$aA + bB \rightleftarrows cC + dD$$

Is defined as $K = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$ ⑤

The terms in square brackets represent measures of composition, however as we have three different ways of describing composition in solutions, there are three different equilibrium constants we can write.

Suppose we consider the dissociation of a weak acid in water.

$$HA\ (aq) + H_2O\ (l) \rightleftarrows H_3O^+\ (aq) + A^-\ (aq)$$

In terms of mole fraction:

$$K_x = \frac{x_{H_3O^+} x_A}{x_{HA} x_{H_2O}} \quad ⑥$$

In terms of molarity:

$$K_c = \frac{c_{H_3O^+} c_A}{c_{HA} c_{H_2O}} \quad ⑦$$

In terms of molality:

$$K_{molality} = \frac{molality_{H_3O^+}\ molality_A}{molality_{HA}\ molality_{H_2O}} \quad ⑧$$

In general, K_x, K_c and $K_{molality}$ have different values and often different units (in this example, all are actually dimensionless)

For weak ionisations and dilute solutions, x_{H_2O}, c_{H_2O} and $molality_{H_2O}$ remain unchanged and are often included in the constants.

Equilibrium constants determine the extent to which reactions 'proceed'. Reactions considered as going to completion simply have VERY large values for *K*. Reactions considered as 'not going' have VERY small values for *K*. Any reaction considered to be an equilibrium will have an intermediate value for *K*.

Q. What determines the value of *K* for a given reaction?

A. The Gibbs free energy change for the reaction according to the relationship:

$$\Delta G^\circ = -RT\ln\frac{K}{K^\circ}$$ ⑨

If ΔG° is positive then the log term is negative and *K* must be less than 1. Conversely for negative ΔG°, *K* must be greater than 1.

The change in the Gibbs free energy is related to changes in enthalpy, ΔH and entropy, ΔS.

$$\Delta G = \Delta H - T\Delta S \tag{⑩}$$

This is also true for standard molar changes

$$\Delta G_m^o = \Delta H_m^o - T\Delta S_m^o \tag{⑪}$$

The degree symbol is the modern way to indicate a quantity measured under standard conditions. The old symbol being ⦵. Standard conditions means a pressure of 1 atm and a stated temperature. It does NOT necessarily mean 25 °C or 0 °C.

For molar changes you MUST right down the equation concerned as the term means for one mole of the equation as written.

Both enthalpy and entropy are state functions and thus changes in either may be obtained by appropriate summation of the individual molar quantities for each constituent of a reaction.

For example:

$$2H_2O\ (l) \rightleftarrows H_3O^+\ (aq) + OH^-\ (aq)$$

$$\Delta H_m = H_{m\,H_3O^+(aq)} + H_{m\,OH^-(aq)} - 2H_{m\,H_2O(l)}$$

$$\Delta S_m = S_{m\,H_3O^+(aq)} + S_{m\,OH^-(aq)} - 2S_{m\,H_2O(l)}$$

Here you should note that contributions from 'products' are positive, while those from 'reactants' are negative. Moreover the contribution from each constituent is multiplied by its stoichiometric coefficient.

Manipulations of the Hess' law type are more often used for evaluation of ΔH_m from information from related reactions. It is more usual to calculate the molar enthalpy of a particular reaction from molar enthalpies of formation or from enthalpies of combustion for various related reactions, as the following example shows.

Q.

Why do we use enthalpies of combustion?

A.

Because organic materials burn they are easily measured

Q. Calculate the equilibrium constant at 298 K for the following reaction.

$$C_2H_4\,(g) + H_2\,(g) \rightarrow C_2H_6\,(g)$$ ①

given that the standard molar entropies for C_2H_4 (g), H_2 (g) and C_2H_6 (g) at 298 K are 220, 131 and 231 J K^{-1} mol^{-1} respectively and their standard molar enthalpies of combustion at 298 K are -1399, -287 and -1566 kJ mol^{-1} respectively.

A. The combustion reactions are as follows:

$$C_2H_4\,(g) + 3O_2\,(g) \rightarrow 2CO_2\,(g) + 2H_2O\,(g)$$ ②

$$H_2\,(g) + \tfrac{1}{2}O_2\,(g) \rightarrow H_2O\,(g)$$ ③

$$C_2H_6\,(g) + 3\tfrac{1}{2}O_2\,(g) \rightarrow 2CO_2\,(g) + 3H_2O\,(g)$$ ④

① = ② + ③ - ④

So ΔH^o_m ① = ΔH^o_m ② + ΔH^o_m ③ - ΔH^o_m ④

ΔH^o_m ① $= (-1399) + (-287) - (-1566)\ \text{kJ mol}^{-1}$

$= -1399 - 287 + 1566\ \text{kJ mol}^{-1}$

$= -120\ \text{kJ mol}^{-1}$

and

ΔS^o_m ① $= S_{m\,C_2H_6(g)} - S_{m\,C_2H_4(g)} - S_{m\,H_2(g)}$

$= 231 - (220) - (131)\ \text{J K}^{-1}\ \text{mol}^{-1}$

$= -120\ \text{J K}^{-1}\ \text{mol}^{-1}$

Using eqn ⑪ …

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

$$\Delta G^o_m = -120\ \text{kJ mol}^{-1} - 298\ \text{K} \,.\, -120\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$= -120\ \text{kJ mol}^{-1} + 35760\ \text{J mol}^{-1}$$

$$= -120\ \text{kJ mol}^{-1} + 35.76\ \text{kJ mol}^{-1}$$

$$= -84.24\ \text{kJ mol}^{-1}$$

Using eqn ⑨ …

$$\ln\frac{K}{K^\circ} = -\frac{\Delta G^\circ_m}{RT}$$

$$\ln\frac{K}{K^\circ} = -\frac{-84200\ \mathrm{J\,mol^{-1}}}{8.314\ \mathrm{J\,K^{-1}mol^{-1}} \times 298\ \mathrm{K}}$$

$$\ln\frac{K}{K^\circ} = 33.98$$

$$\frac{K}{K^\circ} = 5.95 \times 10^{14}$$

This is a classic example of a reaction with a negative Gibbs free energy change that we would consider as a reaction that goes to completion.

Q. How are equilibrium constants affected by temperature?

A. The relationship between equilibrium constant and temperature at constant pressure is defined by the Gibbs-Helmholtz equation:

$$\frac{d\Delta G_m^o}{dT} = -\Delta S_m^o$$

Using eqn ⑪ …

$$\Delta G^{o}_{m} = \Delta H^{o}_{m} - T\Delta S^{o}_{m}$$

Thus

$$\Delta S^{o}_{m} = \frac{\Delta H^{o}_{m} - \Delta G^{o}_{m}}{T}$$

Substituting into eqn ⑫ …

$$\frac{d\Delta G^{o}_{m}}{dT} = \frac{\Delta G^{o}_{m} - \Delta H^{o}_{m}}{T}$$

Using eqn ⑨ …

$$\Delta G^{o}_{m} = -RT \ln \frac{K}{K^{\circ}}$$

$$\frac{d(-RT \ln K/K^{\circ})}{dT} = \frac{-RT \ln K/K^{\circ} - \Delta H^{o}_{m}}{T}$$

Differentiation: the product rule

$$\frac{d(uv)}{dx} = u\frac{dv}{dx} + v\frac{du}{dx}$$

We must treat the term $\dfrac{d(-RT\ln K/K^\circ)}{dT}$ as a product since both –*RT* and $\ln K/K^\circ$ are functions of *T*.

$$\frac{d(uv)}{dT} = u\frac{dv}{dT} + v\frac{du}{dT}$$

$$\frac{d(-RT\ln K/K^\circ)}{dT} = -RT\frac{d\ln K/K^\circ}{dT} + \ln K/K^\circ . -R$$

So finally, the original equation becomes

$$-R\ln K/K^\circ - RT\frac{d\ln K/K^\circ}{dT} = -R\ln K/K^\circ - \frac{\Delta H_m^o}{T}$$

Hence

$$RT\frac{d\ln K/K^\circ}{dT} = \frac{\Delta H_m^o}{T}$$

And

$$\frac{d\ln K/K^\circ}{dT} = \frac{\Delta H_m^o}{RT^2}$$

Which on integration yields

$$\ln K/K^\circ = -\frac{\Delta H_m^o}{RT} + C$$ ⑬

So a plot of $\ln K/K^\circ$ vs $1/T$ will yield a straight line of slope $-\Delta H_m^o/R$.

Also equilibrium constants at two temperatures may be related:

$$\ln K_1/K_2 = \frac{\Delta H_m^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$ ⑭

Chemical Potential

The Gibbs free energy is an important quantity for determining whether a reaction will go or not.

Chemical potentials may be thought of as the contribution of each component of a system to its total Gibbs free energy. Symbol: μ (mu)

For example:

$$2H_2O\ (l) \rightleftarrows H_3O^+\ (aq) + OH^-\ (aq)$$

$$\Delta G_m = \mu_{H_3O^+(aq)} + \mu_{OH^-(aq)} - 2\mu_{H_2O(l)}$$

For an ideal gas, chemical potential may be defined as follows:

$$\mu = \mu^\circ + RT\ln\left(\frac{p}{p^\circ}\right)$$ ⑮

For an ideal liquid mixture of A and B:

$$\mu_A = \mu_A^* + RT\ln x_A$$ ⑯

The asterisk denotes the pure substance.

A similar equation may be written for substance B

$$\mu_B = \mu_B^* + RT\ln x_B$$ ⑰

The Thermodynamics of Mixing

Consider an ideal liquid mixture of A and B.

N.b. An ideal liquid mixture forms if net intermolecular forces remain unchanged upon mixing. Few solutions exhibit such behaviour, though the concept provides a useful reference point for REAL behaviour.

The Gibbs free energy prior to mixing is

$$n_A\mu_A^* + n_B\mu_B^*$$

After mixing this becomes

$$n_A\mu_A + n_B\mu_B$$

The change in Gibbs free energy is termed the Gibbs free energy of mixing:

$$\Delta G_{mix} = \left(n_A\mu_A + n_B\mu_B\right) - \left(n_A\mu_A^* + n_B\mu_B^*\right)$$

Using equations ⑯ and ⑰

$$\Delta G_{mix} = n_A\mu_A^* + n_ART\ln x_A + n_B\mu_B^* + n_BRT\ln x_B$$
$$- n_A\mu_A^* - n_B\mu_B^*$$

$$\Delta G_{mix} = n_A RT \ln x_A + n_B RT \ln x_B$$

$$\Delta G_{mix} = nRT\left(x_A \ln x_A + x_B \ln x_B\right)$$ ⑱

Since mole fractions lie between 0 and 1, the logarithmic terms are negative or zero. Thus the Gibbs energy of mixing is ALWAYS negative or zero and ideal mixtures form spontaneously from their components.

The entropy of mixing may be obtained from equation ⑫.

$$\Delta S_{mix} = -\frac{d\Delta G_{mix}}{dT}$$

$$\Delta S_{mix} = -nR\left(x_A \ln x_A + x_B \ln x_B\right)$$

For the same reasons as before the entropy of mixing is ALWAYS positive or zero.

It is this entropy change which is the driving force for the formation of ideal mixtures since there is no enthalpy of mixing.

The volume of mixing can also be evaluated.

$$\Delta V_{mix} = \frac{d\Delta G_{mix}}{dp} \tag{19}$$

Which in this case equals zero, consistent with the idea of identical interactions between molecules of the components.

Ideal Dilute Solutions

When we have a small quantity of B dissolved in a large quantity of A, the behaviour of B is different from A.

B molecules are almost always surrounded by A molecules. This situation will persist as the concentration of B increases until it is large enough to permit a high probability of B molecules adjacent to one another.

Hence the interactions of the B molecules will be almost entirely of the A-B type, and until the point described above is reached, will be independent of composition.

A molecules are almost always surrounded by other A molecules and consequently will experience interactions of the A-A type almost exclusively until B molecules become more numerous. Again, up to this point, the interactions will be independent of composition.

This means that A obeys ideal solution behaviour when $x_A \rightarrow 1$. Thus from ⑯

$$\mu_A = \mu_A^* + RT \ln x_A$$

A similar relationship exists for B molecules. The chemical potential of pure B is however not involved because the majority of interactions will be A-B rather than B-B.

Hence we write:

$$\mu_B = \mu_B^\circ + RT \ln x_B$$ ⑳

Where μ_B° is called the standard chemical potential of B.

The physical explanation of this quantity is that it is what μ_B would become if ideal solution behaviour persisted to $x_B = 1$, i.e. it corresponds to a hypothetical (not a real) state.

Thus the two relations for ideal dilute solutions are

$$\mu_A = \mu_A^* + RT \ln x_A$$

$$\mu_B = \mu_B^\circ + RT \ln x_B$$

Non-ideal Solutions

In general solutions are neither dilute or ideal…

We try to treat non-ideal solutions as we treat ideal ones regarding variations as deviations from ideal behaviour.

Equation ⑯ becomes

$$\mu_A = \mu_A^* + RT \ln a_A$$

The mole fraction has now been replaced by a_A termed the activity of A.

Think of a_A as a modified mole fraction that makes real solutions behave as ideal ones.

In this course we shall mainly be concerned with solutions of solids (usually ionic) in liquids. Consequently, the ideal dilute model is best.

Thus equations ⑯ and ⑳ become:

$$\mu_A = \mu_A^* + RT \ln a_A$$ ㉑

$$\mu_B = \mu_B^\circ + RT \ln a_B$$ ㉒

Q. How do we define activity for the solvent?

A. $a_A = x_A \gamma_A$ ㉓

γ_A is termed the activity coefficient and varies from 0 to 1.

All solvents become increasingly ideal as they approach purity, $x_A \to 1$. $\gamma_A \to 1$ as $x_A \to 1$.

From ㉑ and ㉓ we get

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

$$\mu_A = \underbrace{\mu_A^* + RT\ln x_A}_{\text{IDEAL BEHAVIOUR}} + \underbrace{RT\ln\gamma_A}_{\text{DEVIATION}}$$ ㉔

Q. Generally we talk in terms of concentration for solutes so how do we define activity for the solute?

A. $a_B = x_B f_B$ ㉕

f_B is the activity coefficient referred to the concentration scale.

$$\mu_B = \underbrace{\mu_B^\circ + RT\ln\frac{c_B}{c^\circ}}_{\text{IDEAL BEHAVIOUR}} + \underbrace{RT\ln f_B}_{\text{DEVIATION}}$$ ㉖

c° is the standard concentration arbitrarily defined as 1 mol dm^{-3}

In both cases γ and f represent the deviation of a real solution from an ideal one. $RT\ln\gamma_A$ and $RT\ln f_B$ are labelled the excess chemical potentials of A and B.

Suppose we reconsider our earlier example of a weak acid dissociating in water.

$$HA\ (aq) + H_2O\ (l) \rightleftarrows H_3O^+\ (aq) + A^-\ (aq)$$

$$K_{true} = \frac{a_{H_3O^+}a_{A^-}}{a_{HA}a_{H_2O}}$$ ㉗

or if ionisation is only slight…

$$K_{true} = \frac{a_{H_3O^+}a_{A^-}}{a_{HA}}$$

since the activity of water here is only slightly different from that of pure water which is by definition 1.

This equilibrium constant applies to ALL solutions and not just ideal or ideal dilute.

In the same way we related the activity of a solute to concentration:

$$a_i = \frac{c_i}{c^\circ} f_i$$ ㉘

We can do a similar thing with the equilibrium constant:

$$K_{true} = \frac{K_c}{K_c^\circ} K_f$$ ㉙

Ionic Solutions

Activity Coefficients & Ionic Activities

Ionic solutions are widespread. They are also non-ideal due to the coulombic interaction between the charged species.

Equation ㉒ and ㉘ tell us that

$$\mu_i = \mu_i^\circ + RT\ln a_i$$

$$\mu_i = \mu_i^\circ + RT\ln\frac{c_i}{c^\circ}f_i$$

where $f_i \rightarrow 1$ as $c_i \rightarrow 0$ (more dilute)

However, difficulties arise for ions, that do not arise for covalent molecules…

- Individual ions cannot be measured

An ion in solution can only exist in conjunction with a counter ion. We cannot formulate or define effects of change in concentration of only one ion without considering the other.

Hence, a mean value of the activity is used…

Consider a uni-univalent electrolyte (M^+X^-) The concentration of each ion must be the same:

$$c_+ = c_- = c$$

The total chemical potential is given by

$$\mu_{total} = \mu_+ + \mu_- = \mu_+^\circ + RT\ln a_+ + \mu_-^\circ + RT\ln a_-$$

The mean chemical potential $\mu_\pm$ is given by

$$\mu_\pm = \frac{\mu_{total}}{2} = \frac{\mu_+^\circ + \mu_-^\circ}{2} + \frac{1}{2}\left(RT\ln a_+ + RT\ln a_-\right)$$

$$\mu_\pm = \frac{\mu_+^\circ + \mu_-^\circ}{2} + \frac{1}{2}RT\ln a_+ a_-$$

$$\mu_\pm = \mu_\pm^\circ + RT\ln\sqrt{a_+ a_-} = \mu_\pm^\circ + RT\ln a_\pm \tag{30}$$

Where $\mu_\pm = \frac{1}{2}\left(\mu_+^\circ + \mu_-^\circ\right)$ **and** $a_\pm^2 = a_+ a_-$

$a_{\pm}$ is the mean ionic activity.

In a similar manner to equation ㉘

$$a_{\pm} = \frac{c}{c^{\circ}} f_{\pm}$$ ㉛

and thus

$$\mu_{\pm} = \mu_{\pm}^{\circ} + RT \ln \frac{c}{c^{\circ}} + RT \ln f_{\pm}$$ ㉜

We can also write

$$f_{\pm}^{2} = f_{+} f_{-}$$ ㉝

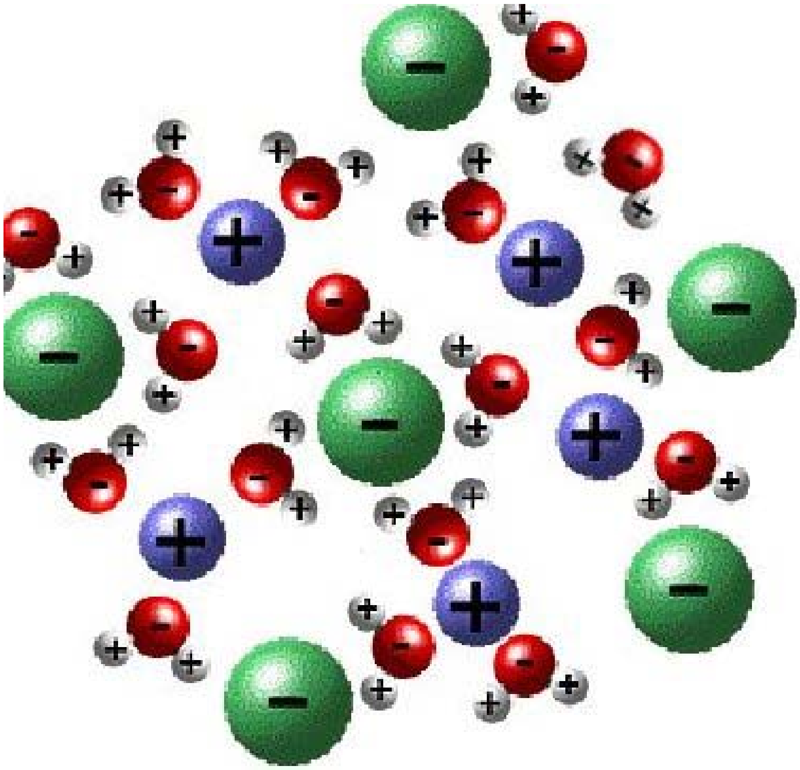
The above expressions are valid only for 1:1 electrolytes. For the general case they are considerably more complicated.

The Debye-Hückel Theory

Provides a way to calculate the mean ionic activity coefficients of an ionic solute at low concentration.

The important features of the theory are:

- Each ion is surrounded by an ionic atmosphere containing largely ions of opposite charge.



- The solution is treated as a continuum (a homogeneous continuous medium) with a uniform electric potential and charge density.

- Ions have negligible size.

- The charge density is related to the ionic number density (i.e. the number of ions in a given volume).

We have already established that the mean solute chemical potential is given by

$$\mu_B = \mu_B^\circ + RT\ln\frac{c_B}{c^\circ} + RT\ln f_\pm$$

If the solution were ideal dilute, then

$$\mu_B = \mu_B^\circ + RT\ln\frac{c_B}{c^\circ}$$

$$\ln f_\pm = \left(\mu_B - \mu_{B(\text{ideal dilute})}\right)/RT = W/RT$$

Where *W* represents the molar interaction between solute ions.

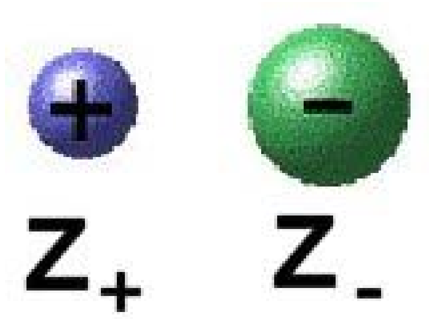
W can be evaluated in this way and eventually the following simple equation can be obtained:

$$\log_{10} f_{\pm} = -\left|z_{+}z_{-}\right| A\sqrt{I}$$ ㉞

(only true for very dilute solutions)

where

z_+ and z_- are the ionic charge numbers



A is the Debye-Huckel constant which depends only on properties of the solvent (dielectric constant, density, temperature) and not the solute ions

I is the ionic strength defined as follows

$$I = \frac{1}{2}\sum_{i=1}^{i=n} c_i z_i^2$$ ㉟

Example Calculation of Ionic Strength

Calculate *I* for a 0.05 mol dm^{-3} solution of $AlCl_3$.

$$I = \frac{1}{2}\sum_{i=1}^{i=n} c_i z_i^2$$

$$AlCl_3 \rightarrow Al^{3+}_{(aq)} + 3Cl^-_{(aq)}$$

$$= \frac{1}{2}\left(0.05 \text{ mol dm}^{-3} \times (+3)^2 + 0.15 \text{ mol dm}^{-3} \times (-1)^2\right)$$

$$= \frac{1}{2}\left(0.45 \text{ mol dm}^{-3} + 0.15 \text{ mol dm}^{-3}\right)$$

$$= 0.3 \text{ mol dm}^{-3}$$

For a 1:1 electrolyte equation ㉞ reduces to the Debye-Hückel Limiting Law:

$$\log_{10} f_{\pm} = -A\sqrt{I}$$ ㊱

For aqueous solutions at 25 °C

$$A \approx 0.51\,\mathrm{dm}^{3/2}\,\mathrm{mol}^{-1/2}$$

In general for aqueous solutions of 1:1 electrolytes it applies for $I \leq 0.01\,\mathrm{mol\,dm}^{-3}$

Assumptions of the limiting law:

- Continuum electrostatics
- Central ion as point charge
- Neglect of non-ideality apart from electrostatic effects
- No ion pairs (or molecules)

Uses of the Debye-Hückel Theory and the Limiting Law

ALL equilibria involving ions are affected by ionic activities…

Returning once again to the example of the dissociation of a weak acid HA:

$$HA\,(aq) + H_2O\,(l) \rightleftarrows H_3O^+\,(aq) + A^-\,(aq)$$

As stated before, as equation ㉗ , the true ionisation constant is:

$$K_{true} = \frac{a_{H_3O^+}a_{A^-}}{a_{HA}a_{H_2O}}$$

If we replace the ionic activities $a_{H_3O^+}$ and a_{A^-} by expressions derived from equation ㉘ and if we assume ideal behaviour for the undissociated acid (i.e. $a_{HA} = c_{HA}/c^\circ$), and that H_2O is in its standard state (the activity of pure water being 1), then

$$K_a = \frac{c_{H_3O^+} c_{A^-} f_\pm f_\pm}{c_{HA}} \cdot \frac{c^\circ}{\left(c^\circ\right)^2}$$

$$K_a = \frac{K_c}{K_c^\circ} f_\pm^2$$

where $K_c = \frac{c_{H_3O^+} c_{A^-}}{c_{HA}}$ and $K_c^\circ = \frac{c^\circ c^\circ}{c^\circ}$

Q. Are these assumptions reasonable?

A. Yes, they probably are for sufficiently dilute solutions of sufficiently weak acids.

The point of all this is that K_a is the true or thermodynamic equilibrium constant. It is however NOT easily measured.

$$\log_{10} K_a = \log_{10} \frac{K_c}{K_c^\circ} f_\pm^2 \tag{37}$$

$$\log_{10} K_a = \log_{10} \frac{K_c}{K_c^\circ} + 2\log_{10} f_\pm \tag{38}$$

$$\log_{10} K_a = \log_{10} \frac{K_c}{K_c^\circ} - 2A\sqrt{I} \tag{39}$$

We can however measure K_c by various experimental techniques, e.g. conductivity, and spectrophotometry.

In conjunction with the Debye-Hückel limiting law K_a may thus be calculated.

The conductivity method relies on the dissociation of an acid HA into conducting ions. The simple Arrhenius expression relating degree of dissociation α with the measured molar conductivity Λ_c is

$$\alpha = \frac{\Lambda_c}{\Lambda_0}$$

where Λ_c is the limiting molar conductivity (i.e. the value at infinite dilution) is not sufficient because molar conductivity varies with concentration, irrespective of ionisation. This variation is given by the Onsager equation

$$\Lambda_c = \Lambda_0 - \left(B_1\Lambda_0 + B_2\right)\sqrt{c}$$

By a process of computer iteration these equations allow accurate measurement of K_c.

Spectrophotometry is the measurement of intensity of transmitted light through a solution of an absorbing material. Beer's law states that absorbance is proportional to concentration of the absorbing species

$$\log_{10}\frac{I'}{I} = \varepsilon c l$$

Where I and I' are the incident and transmitted light intensities, l is the path length of the cell used and ε is the molar absorption coefficient.

Thus the concentrations of any coloured (or UV-absorbing) undissociated acid or ions formed can be readily obtained.

Solubility Products

Similar arguments can be applied to the idea of solubility product.

If a salt MX is sparingly soluble, then the process of solution may be written

$$MX_{(s)} \rightleftarrows M^+_{(aq)} + X^-_{(aq)}$$

The activity product K_s may be written from equation ㉛ as follows

$$K_s = a_{M^+} a_{X^-} = \frac{c_{M^+} c_{X^-}}{\left(c^\circ\right)^2} \cdot f_\pm^2$$

accepting that solids are always in their standard states and so $a_{MX} = 1$.

The expression $c_{M^+} c_{X^-}$ is normally termed the solubility product, whilst the true constant is called the activity product.

Once again, although the activity product is difficult to measure, we can measure the solubility product quite easily then use the limiting law to calculate K_s.

$$\log_{10} K_s = \log_{10}\left(\frac{c_{M^+}c_{X^-}}{\left(c^\circ\right)^2}\right) f_\pm^2 \qquad (40)$$

$$\log_{10} K_s = \log_{10}\left(\frac{c_{M^+}c_{X^-}}{\left(c^\circ\right)^2}\right) + 2\log_{10} f_\pm \qquad (41)$$

$$\log_{10} K_s = \log_{10}\left(\frac{c_{M^+}c_{X^-}}{\left(c^\circ\right)^2}\right) - 2A\sqrt{I} \qquad (42)$$

the process is analogous to that of calculating a thermodynamic equilibrium constant.

The Salt Effect

Take a solution of a salt MX. Adding a salt BX with a common ion will alter the solubility of MX. This effect is well known as the common ion effect.

The reason for this is simply that

$$c_{M^+} \neq c_{X^-}$$

However, addition of a salt with NO common ion will increase the solubility of MX and this phenomenon is called the salt effect.

The reason for this is that while K_s remains constant, the ionic strength, I, increases (due to there being more ions in solution) and hence according to the Debye-Hückel theory the mean ionic activity, $f_{\pm}$, must decrease and thus solubility must increase.

Q. At 25 °C the solubility product of silver bromide in water is about 2 x 10^{-13} mol^2 dm^{-6}. What is the solubility of silver bromide in 0.1 mol dm^{-3} aqueous nitric acid?

First consider the AgBr alone…

From the definition of solubility product

$$c_{Ag^+}c_{Br^-} = 2\times10^{-13}\,\mathrm{mol^2\,dm^{-6}}$$

but

$$c_{Ag^+} = c_{Br^-}$$

$$\therefore c_{Ag^+} = c_{Br^-} = \sqrt{2\times10^{-13}\,\mathrm{mol^2\,dm^{-6}}}$$

$$= 4.5\times10^{-7}\,\mathrm{mol\ dm^{-3}}$$

Use of the Debye-Huckel Limiting Law for a $4.5\times10^{-7}\,\mathrm{mol\ dm^{-3}}$ aqueous solution of AgBr gives a value $f_\pm = 0.9992$. So the activity product effectively equals the solubility product.

$$\log_{10} K_s = \log_{10}\left(\frac{c_{Ag^+}c_{Br^-}}{(c^\circ)^2}\right)f_\pm^2$$

$$K_s = 2\times10^{-13}$$

Now consider the AgBr in the nitric acid…

$$\log_{10} K_s = \log_{10}\left(\frac{c_{Ag^+} c_{Br^-}}{\left(c^\circ\right)^2}\right) + 2\log_{10} f_\pm$$

The activity product will no longer equal the solubility product because the mean ionic activity coefficient will no longer be unity.

To calculate the extent of the change we use the Debye-Hückel Limiting Law to rewrite $f_\pm$.

$$\log_{10} K_s = \log_{10}\left(\frac{c_{Ag^+} c_{Br^-}}{\left(c^\circ\right)^2}\right) - 2A\sqrt{I}$$

Remember, for aqueous solutions at 25 °C

$$A \approx 0.51\,\mathrm{dm}^{3/2}\ \mathrm{mol}^{-1/2}$$

From equation ㉟

$$I = \frac{1}{2}\sum_{i=1}^{i=n} c_i z_i^2$$

$$I = \frac{1}{2}\left(0.1\,\text{mol dm}^{-3} \times (+1)^2 + 0.1\,\text{mol dm}^{-3} \times (-1)^2\right)$$

$$= 0.1\,\text{mol dm}^{-3}$$

Assuming the nitric acid to be fully ionised…

$$\log_{10} K_s = \log_{10}\left(\frac{c_{Ag^+} c_{Br^-}}{(c^\circ)^2}\right) - 2A\sqrt{I}$$

becomes

$$\log_{10}\left(2 \times 10^{-13}\right) = \log_{10}\left(\frac{c_{Ag^+} c_{Br^-}}{(c^\circ)^2}\right) - 2 \times 0.51\,\text{dm}^{3/2}\,\text{mol}^{-1/2} \times \sqrt{0.1\,\text{mol dm}^{-3}}$$

$$\log_{10}\left(2 \times 10^{-13}\right) = \log_{10}\left(\frac{c_{Ag^+} c_{Br^-}}{(c^\circ)^2}\right) - 1.02\,\text{dm}^{3/2}\,\text{mol}^{-1/2} \times 0.32\,\text{mol}^{1/2}\,\text{dm}^{-3/2}$$

$$\log_{10}\left(2 \times 10^{-13}\right) = \log_{10}\left(\frac{c_{Ag^+} c_{Br^-}}{(c^\circ)^2}\right) - 0.33$$

$$-12.70 = 2\log_{10}\left(\frac{c_{Ag^+}}{c^\circ}\right) - 0.33$$

$$\frac{0.33 - 12.70}{2} = \log_{10}\left(\frac{c_{Ag^+}}{c^\circ}\right)$$

$$\log_{10}\left(\frac{c_{Ag^+}}{c^\circ}\right) = -6.19$$

$$\frac{c_{Ag^+}}{c^\circ} = 6.5 \times 10^{-7}$$

$$\frac{c_{Ag^+}}{1\ \text{mol dm}^{-3}} = 6.5 \times 10^{-7}$$

$$c_{Ag^+} = 6.5 \times 10^{-7}\ \text{mol dm}^{-3}$$

Compared with the value in the absence of the nitric acid, this represents a 44% increase in solubility.

Obtaining Accurate values for K_s & K_a

This is normally done graphically. From equation ㊷, plotting the log of the solubility product against the square root of the ionic strength,

$$\log_{10}\left(\frac{c_{M^+}c_{X^-}}{\left(c^\circ\right)^2}\right) \quad \text{vs} \quad \sqrt{I}$$

should yield a straight line of gradient 2*A* and intercept $\log_{10} K_s$.

Similarly, from equation ㊴, plotting the log of the equilibrium constant against the square root of the ionic strength,

$$\log_{10}\frac{K_c}{K_c^{\circ}} \quad \text{vs} \quad \sqrt{I}$$

should yield a straight line of gradient $2A$ and intercept $\log_{10} K_a$.

Q. What experiments should be carried out in order to achieve this?

A. Measure K_c in solutions of the acid HA with varying amounts of added salt (chosen without any common ion with HA) – and hence varying ionic strengths. If only the concentration of HA is varied, the effect on the ionic strength will be negligible, assuming HA to be a weak acid. If HA is not a weak acid then the Debye-Hückel theory collapses anyway! The largest amount of added salt should not be very great…

This procedure will not only obtain a value for K_a but will also test the validity of the Limiting Law. Results of such experiments reveal that the points fit well to the Limiting Law straight line at lower concentrations but deviate from it at higher ones.

Q1. At 25 °C the solubility product of silver iodide in water is about 1.5×10^{-16} mol^2 dm^{-6}. Calculate the percentage increase in solubility of silver iodide in 0.5 mol dm^{-3} aqueous hydrochloric acid?

Q2. At 25 °C the solubility product of mercury chloride in water is about 2×10^{-18} mol^2 dm^{-6}. What is the solubility of mercury chloride in 0.3 mol dm^{-3} aqueous nitric acid?

First consider the AgI alone…

From the definition of solubility product

$$c_{Ag^+} c_{I^-} = 1.5 \times 10^{-16} \text{mol}^2 \text{dm}^{-6}$$

but

$$c_{Ag^+} = c_{I^-}$$

$$\therefore c_{Ag^+} = c_{I^-} = \sqrt{1.5 \times 10^{-16} \text{mol}^2 \text{dm}^{-6}}$$

$$= 1.2 \times 10^{-8} \text{mol dm}^{-3}$$

Use of the Debye-Huckel Limiting Law for a 1.2×10^{-8} mol dm^{-3} aqueous solution of AgI gives a value $f_{\pm} = 0.9999$. So the activity product effectively equals the solubility product.

$$\log_{10} K_s = \log_{10} \left(\frac{c_{Ag^+} c_{I^-}}{(c^{\circ})^2} \right) f_{\pm}^2$$

$$K_s = 1.5 \times 10^{-16}$$

Now consider the AgI in the hydrochloric acid…

$$\log_{10} K_s = \log_{10}\left(\frac{c_{Ag^+} c_{I^-}}{\left(c^\circ\right)^2}\right) + 2\log_{10} f_\pm$$

The activity product will no longer equal the solubility product because the mean ionic activity coefficient will no longer be unity.

To calculate the extent of the change we use the Debye-Hückel Limiting Law to rewrite $f_\pm$.

$$\log_{10} K_s = \log_{10}\left(\frac{c_{Ag^+} c_{I^-}}{\left(c^\circ\right)^2}\right) - 2A\sqrt{I}$$

Remember, for aqueous solutions at 25 °C

$A \approx 0.51\,\mathrm{dm}^{3/2}\ \mathrm{mol}^{-1/2}$

From equation ㉟

$$I = \frac{1}{2}\sum_{i=1}^{i=n} c_i z_i^2$$

$$I = \frac{1}{2}\left(0.5\,\text{mol dm}^{-3} \times (+1)^2 + 0.5\,\text{mol dm}^{-3} \times (-1)^2\right)$$

$$= 0.5\,\text{mol dm}^{-3}$$

Assuming the hydrochloric acid to be fully ionised…

$$\log_{10} K_s = \log_{10}\left(\frac{c_{Ag^+} c_{I^-}}{\left(c^\circ\right)^2}\right) - 2A\sqrt{I}$$

becomes

$$\log_{10}\left(1.5 \times 10^{-16}\right) = \log_{10}\left(\frac{c_{Ag^+} c_{I^-}}{\left(c^\circ\right)^2}\right) - 2 \times 0.51\,\text{dm}^{3/2}\,\text{mol}^{-1/2} \times \sqrt{0.5\,\text{mol dm}^{-3}}$$

$$\log_{10}\left(1.5 \times 10^{-16}\right) = \log_{10}\left(\frac{c_{Ag^+} c_{I^-}}{\left(c^\circ\right)^2}\right) - 1.02\,\text{dm}^{3/2}\,\text{mol}^{-1/2} \times 0.71\,\text{mol}^{1/2}\,\text{dm}^{-3/2}$$

$$\log_{10}\left(1.5 \times 10^{-16}\right) = \log_{10}\left(\frac{c_{Ag^+} c_{I^-}}{\left(c^\circ\right)^2}\right) - 0.72$$

$$-15.82 = 2\log_{10}\left(\frac{c_{Ag^+}}{c^\circ}\right) - 0.72$$

$$\frac{0.72 - 15.82}{2} = \log_{10}\left(\frac{c_{Ag^+}}{c^\circ}\right)$$

$$\log_{10}\left(\frac{c_{Ag^+}}{c^\circ}\right) = -7.55$$

$$\frac{c_{Ag^+}}{c^\circ} = 2.8 \times 10^{-8}$$

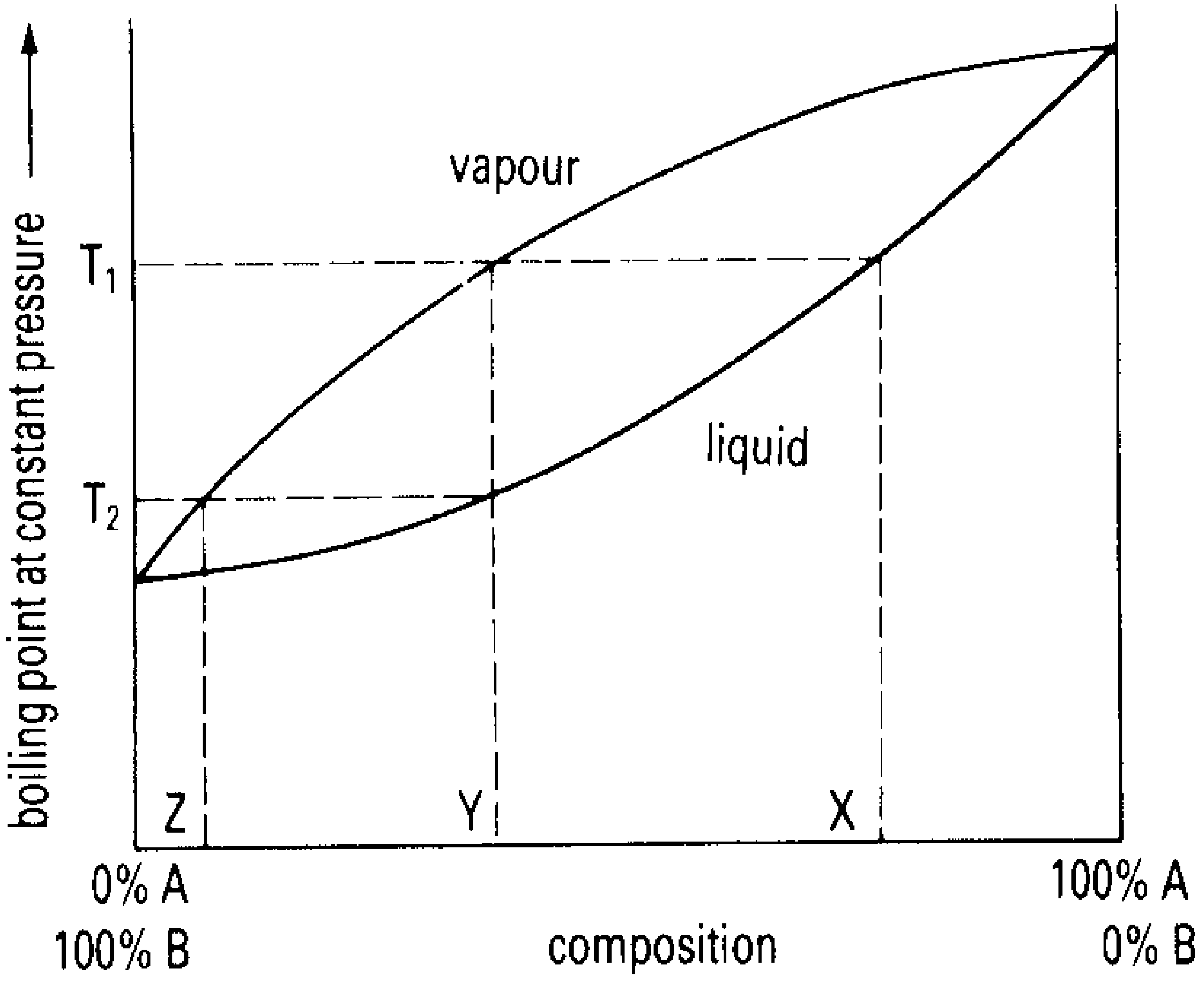
$$\frac{c_{Ag^+}}{1\ \text{mol dm}^{-3}} = 2.8 \times 10^{-8}$$

$$c_{Ag^+} = 2.8 \times 10^{-8}\ \text{mol dm}^{-3}$$

Compared with the value in the absence of the hydrochloric acid, this represents a 133% increase in solubility.

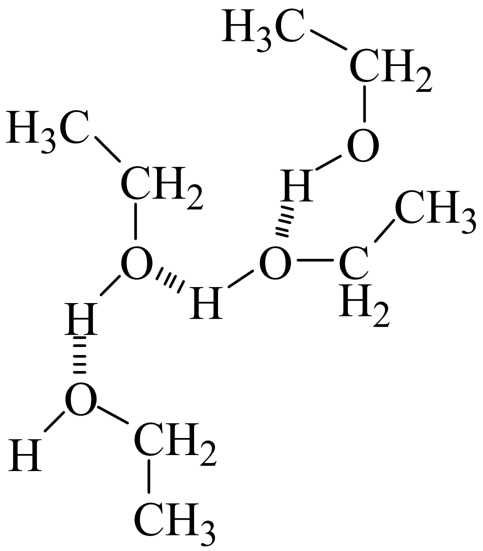
Raoult's Law

"The vapour pressure of a constituent of an ideal solution is equal to the vapour pressure exerted by the pure constituent at that temperature multiplied by the mole fraction of that constituent."



Positive deviation

Pure ethanol is strongly H-bonded



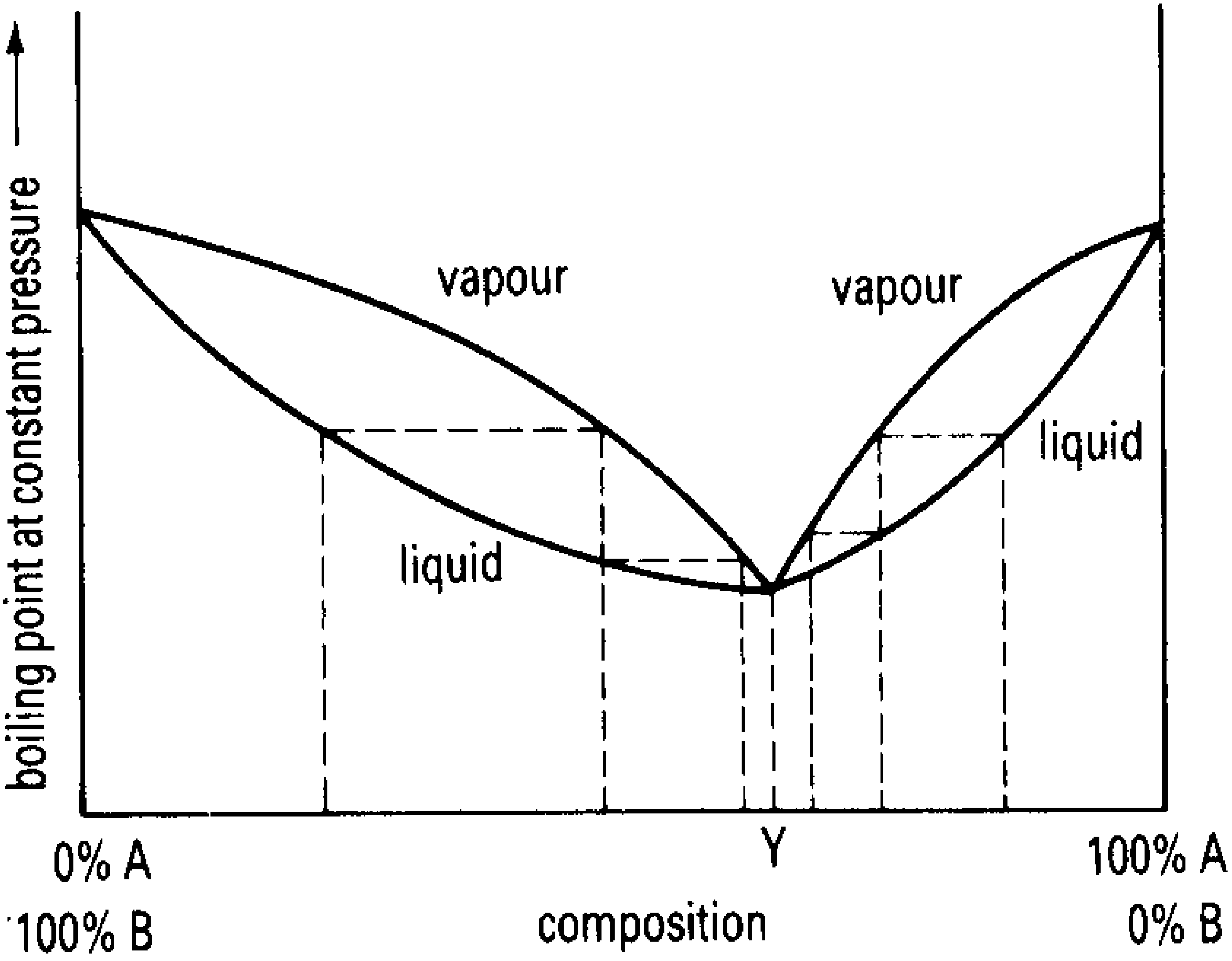
Mix ethanol with chloroform and the temperature *falls*

$CHCl_3$ and CH_3CH_2OH

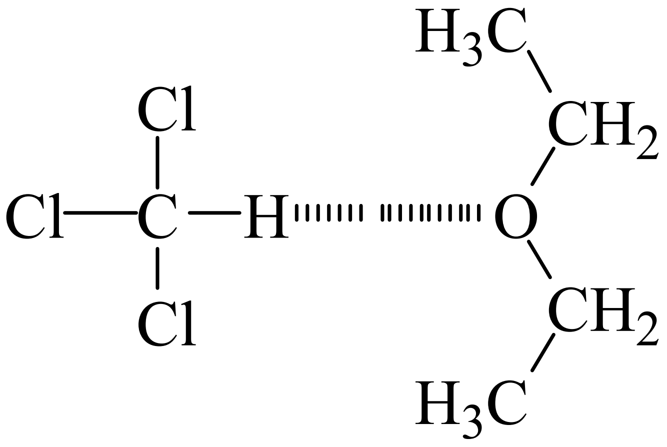
Q. Why?

A. Because the chloroform disturbs the H bonding network of the ethanol… It is like breaking bonds – and that costs energy.

vapour pressure INCREASES
hence POSITIVE deviation
and boiling point DECREASES


boiling point at constant pressure
vapour
vapour
liquid
liquid
0% A
100% B
Y
composition
100% A
0% B

Negative deviation



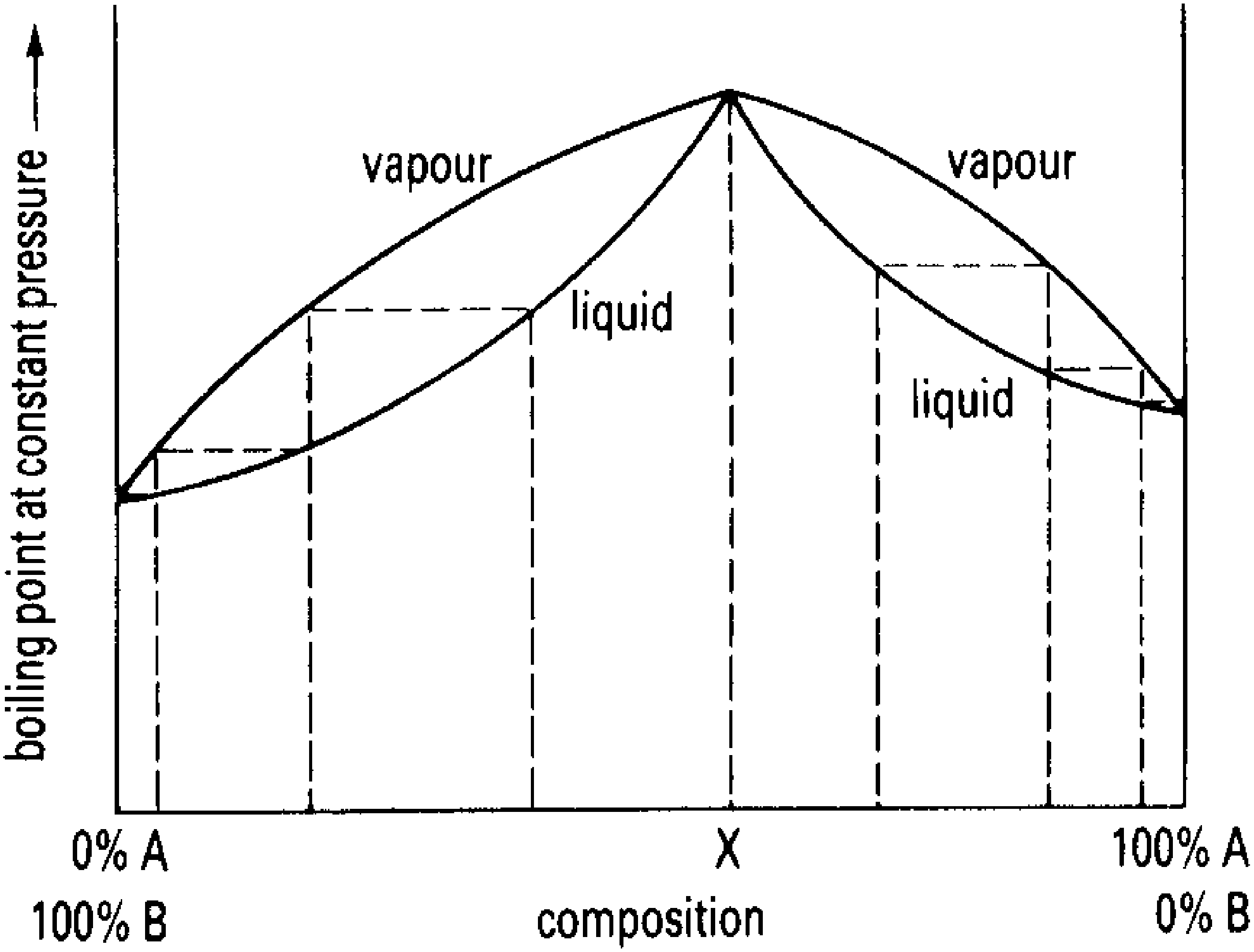
Mix diethylether with chloroform and the temperature *rises*

$CHCl_3$ and $CH_3CH_2OCH_2CH_3$

Q. Why?

A. Because of new intermolecular hydrogen bonding. Bonds are being created and energy is given out.

vapour pressure DECREASES
hence NEGATIVE deviation
and boiling point INCREASES


boiling point at constant pressure
vapour
vapour
liquid
liquid
0% A
100% B
X
composition
100% A
0% B