

# Aristo chemistry flashcard



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Detecting the presence of chemical species Action of heating solid sample strongly Chapter 64 Separation and purification methods Centrifugation Sublimation Partition equilibrium of a solute between two immiscible solvents Two-dimensional thin-layer chromatography 2 3 6 Chapter 65 Quantitative methods of analysis Detection of end point in acid-alkali titration 8 Chapter 66 Instrumental analytical methods More about infrared spectroscopy More about mass spectrometry 12 15 Chapter 67 Contribution of analytical chemistry to our society Gas chromatography- mass spectrometry 32 Heating the solid sample strongly is one of the preliminary tests of substances. This can be done by heating the sample over a non-luminous Bunsen flame in the laboratory. In case there is any gas evolved, further tests can be done to identify the gas. See Table ASS. 1. Observation Inference Yellow sublimate Sulfur Violet vapor and dark grey shiny sublimate Iodine Dark red sublimate Iron(III) chloride, Ferric White sublimate Ammonium halides e. g. Ammonium Chloride Water vapor evolved Hydrated salts; hydrogenation's; some hydroxides Color change Some hydrated salts Rust red residue

Effie formed (from decomposition of iron compounds) Black residue from blue or green sample CoO formed (from decomposition of copper(II) compounds) Yellow residue when hot, white when cold ZnO formed (from decomposition of zinc compounds) Orange residue when hot, yellow when cold PbO formed (from decomposition of lead(II) compounds) Ammonia evolved Some ammonium salts Carbon dioxide evolved Some carbonates; hydrogenation's Nitrogen dioxide evolved Nitrates and nitrites (except those of potassium, sodium and ammonium) Oxygen evolved Nitrates (except

INHUMAN); some oxides of metals (e. G. EBPP, Hog, Gaga); chlorate's e. G. KICKS) Sulfur dioxide evolved Culprits (except those of sodium and potassium); some caliphates Table ASS. 1 Observation and inference from the action of heating solid sample strongly. Chapter 64 Separation and purification methods Centrifugation can be used instead of filtration to separate a solid from a liquid. It is particularly useful when there is only a small amount of material, or when very fast separation is required.

Firstly, the mixture containing an undisclosed solid and a liquid is put into a centrifuge tube. Then the centrifuge tube, together with other tubes, are put into the be holders in a centrifuge (Figure ASS. 1). The holders and tubes are spun around very rapidly, and are thrown outwards. The undisclosed solid and the liquid in the mixture are spun at the same time (Figure ASS. 2). Finally, the denser solid is collected as a lump at the bottom of the tube. Then the liquid can be removed by declaration. Figure ASS. 2 Centrifugation. A few substances change directly from solid to vapor on heating, without going through the liquid state. This physical change is called sublimation. On cooling, the vapor changes back to solid directly.

Consider the following example. If a mixture of iodine and sand is heated in a beaker, the iodine changes from solid to vapor directly (Figure ASS. 3). The vapor changes back to solid directly on a cool surface. The sand is not affected by the heat and remains in the beaker. Figure ASS. 3 Sublimation of iodine. Other substances which sublime include solid carbon dioxide (dry ice') (Figure ASS. 4), anhydrous iron(III) chloride, anhydrous aluminum chloride and some ammonium salts. Since only a few solids sublime, this method of separation is limited in use. Partition equilibrium of a solute

between two immiscible solvents Water and heptanes re immiscible solvents.

When iodine is extracted from an aqueous solution using heptanes, the heptanes layer will become pink in color and the aqueous layer will become brown in color. After shaking the mixture for several times, the colors of the layers will remain unchanged. We say that an equilibrium system has been established (Figure ASS. 5). Figure ASS. 5 Partition of iodine between water and heptanes. At the interface of the aqueous layer and the heptanes layer, some solute (iodine) particles move ' up' and some move ' down'. The solute particles are moving at the same rate. A dynamic equilibrium is established. If the concentrations of solute in both layers are found, we may find that there is a constant ratio between them no matter how much solute or solvent is used in each layer.

The ratio is a constant at a particular temperature as stated by the partition law. Partition law states that when a non-volatile solute is distributed between two immiscible solvents, the ratio of concentrations of the solute in the two solvents, at equilibrium, is a constant at a constant temperature. The constant is known as partition coefficient. The partition coefficient (KDE) can be represented by the following equation:  $KDE = \frac{C_1}{C_2}$  It should be noted that KDE carries no unit. It is a constant dependent on temperature only and can only apply for dilute solutions. The partition law only applies to systems where the solute has the same molecular form in both solvents.

For example, the partition law cannot be applied to the partition of ethanol acid between water and benzene. It is because ethanol acid exists as

discrete molecules or ions in water but it forms dimers in benzene. See Figure ASS. 6. Another example that partition law cannot apply is the partition of hydrogen chloride between water and chloroform (COACH). It is because hydrogen chloride unionizes in water to give hydrogen ions and chloride ions which are different from the molecular form of HCl in chloroform.

Example ASS. 1 Determining the mass of solute extracted by a solvent

At 298 K, the partition coefficient of an organic compound X between ethyl ether and water is 5.60.

A) Calculate the mass of X that can be extracted by ethyl ether when 50 cm<sup>3</sup> of an aqueous solution containing 5.00 g of X is shaken with 50 cm<sup>3</sup> of ethyl ether. (b) Calculate the mass of X that can be extracted in each of two further extractions using 50 cm<sup>3</sup> of ethyl ether each time. C) Calculate the mass of X extracted by three successive extractions with 50 cm<sup>3</sup> of ethyl ether. (d) Calculate the mass of X extracted when 150 cm<sup>3</sup> of ethyl ether is used. (e) Comment on the difference of results from (c) and (d).

Solution Let  $m$  be the mass of compound X extracted by 50 cm<sup>3</sup> of ethyl ether.

$$5.60 = \frac{m}{5.00 - m} \Rightarrow m = 4.24$$

Mass of compound X extracted by 50 cm<sup>3</sup> of ethyl ether is 4.24 g.

B) Let  $m_1$  be the mass of compound X extracted by 50 cm<sup>3</sup> of ethyl ether in the second extraction, the mass of X left in the aqueous layer is  $5.00 \text{ g} - 4.24 \text{ g} = 0.76 \text{ g}$ .

$$5.60 = \frac{m_1}{0.76 - m_1} \Rightarrow m_1 = 0.64$$

Mass of compound X extracted by 50 cm<sup>3</sup> of ethyl ether in the second extraction 0.64 g.

Let  $m_2$  be the mass of compound X extracted by 50 cm<sup>3</sup> of ethyl ether in the third extraction. The mass of X left in the aqueous layer is  $0.76 \text{ g} - 0.64 \text{ g} = 0.12 \text{ g}$ .

$$5.60 = \frac{m_2}{0.12 - m_2} \Rightarrow m_2 = 0.10$$

Mass of compound X extracted by 50 cm<sup>3</sup> of ethyl ether in the third extraction is 0.10 g.

Alternative method: The fraction of X extracted in the first extraction =  $\frac{4.24}{5.00} = 0.848$

Since there is  $(5.00 - 4.24) \text{ g} = 0.76 \text{ g}$  of X left in water. Mass of X

extracted with 50 cm of ethyl ether in the second extraction = 0.76 g  
 0.64 g After the second extraction, there is  $(0.76 - 0.64) \text{ g} = 0.12 \text{ g}$  of X left in water. Mass of X extracted with 50 cm of ethyl ether in the third extraction =  $0.12 \text{ g} \times 0.848 = 0.10 \text{ g}$  (c) The mass of X extracted by three successive extractions with 50 cm of ethyl ether =  $4.24 \text{ g} + 0.64 \text{ g} + 0.10 \text{ g} = 4.98 \text{ g}$  (d) Let  $n$  be the mass of compound X extracted by 150 cm of ethyl ether. On = 4.72 Mass of compound X extracted by 150 cm of ethyl ether is 4.72 g. (e) Mass of X extracted by three successive extractions with 50 cm of ethyl ether is  $4.98 \text{ g} - 4.72 \text{ g} = 0.6 \text{ g}$  more than by one extraction with 150 cm of ethyl ether.

Thus, using three successive extractions is more efficient than using just one extraction.

**Two-dimensional thin-layer chromatography**

Two-dimensional thin-layer chromatography uses the thin-layer chromatographic method twice to separate spots that are unresolved by only one solvent. After running a sample in one solvent, the thin-layer chromatography plate is removed, dried, rotated 90°, and run in another solvent. Any of the spots from the first run that contain mixtures can now be separated. The finished chromatogram is a two-dimensional array of spots. See Figure ASS. 7.

**Figure ASS. 7 Developing a two-dimensional thin-layer chromatogram. Example**

**ASS. Separating amino acids by two-dimensional thin-layer chromatography**

In an experiment to analyse amino acids, thin-layer chromatography was carried out. A mixture of three amino acids, X, Y and Z was separated by a two-dimensional thin-layer chromatography. In the first chromatographic analysis, a mix solvent of ethanol acid and butane-1-OL was used. While in the second chromatographic analysis, phenol was used as the solvent. The

RFC values of these three amino acids are as follows: Amino acid First chromatographic analysis (RFC value in ethanol acid/butane-1-OL) Second chromatographic analysis (RFC value in phenol) x z 0. 25 0. 40 0. 65 0. 30 0. 55 0. 0 Draw a labeled diagram to show the positions of X, Y and Z in the chromatogram. Detection of end point in acid-alkali titration To detect the end point of an acid-alkali titration, several methods may be used. These involve use of indicators, use of pH meter, thermometric titration, etc. (1) Detecting the end point by use of indicators Many acids, alkalis and their products are colorless in nature. There is no obvious change when the reaction is completed. Thus, an indicator is added to the reaction mixture to tell whether the reaction is completed. An indicator is a substance, usually a weak acid or weak base, which changes color within a specific pH range.

The point at which the acid and the alkali have just reacted completely during titration is called the equivalence point. During a titration, the point at which the indicator changes color is called the end point. When carrying out a titration, the indicator is chosen so that the end point appears as close as possible to the equivalence point. The pH value of a solution is a number indicating the degree of acidity or alkalinity of the solution. pH is equal to  $\text{Log}[\text{H}^+]$ , where  $[\text{H}^+]$  is the concentration of hydrogen ions in mole per dm<sup>3</sup> (mol dm<sup>-3</sup>). pH values usually range from 0 to 14. During an acid-alkali titration, there will be a marked change in the pH at the end point.

A suitable indicator will give a noticeable color change at the end point. (2) Detecting the end point by using pH meter A pH meter can be used to follow the course of a titration and thus indicate the end point. Suppose 0. 1 M hydrochloric acid is added slowly to 25. 0 cm<sup>3</sup> of 0. M sodium hydroxide

solution, and the pH of the resultant solution after each addition is found by a pH meter (Figure ASS. 1). Figure ASS. 1 Detecting the end point off titration using a pH meter. When the pH values are plotted against the volume of hydrochloric acid added, a graph as shown in Figure ASS. 2 is obtained. Figure ASS. 2 A graph of pH against volume of hydrochloric acid added.

During an acid-alkali titration, there is often a marked change in pH at the end point, which can thus be easily located on the graph. The volume of acid used to neutralize the alkali can then be read from the graph. 3) Detecting the end point by thermometric titration When an acid reacts with an alkali, heat is given out. The greatest temperature rise occurs at the end point. Consider 50.0 cm<sup>3</sup> of 0.1 M sodium hydroxide solution in an expanded polystyrene cup which is supported in a beaker as shown in Figure ASS. 3. The temperature of the sodium hydroxide solution is measured. 0.1 M hydrochloric acid is then added from a burette, 5.00 cm<sup>3</sup> at a time, and the solution is stirred with a thermometer.

Figure ASS. 3 Detecting the end point by thermometric titration. The temperature readings after addition of each 5.0 cm<sup>3</sup> portion are recorded, and a graph of temperature against volume of hydrochloric acid added is plotted (Figure ASS. 4). Figure ASS. 4 A graph of temperature against volume of hydrochloric acid added. Interpretation of the graph: This indicates the original temperature of sodium hydroxide solution. A to E Temperature rises as more heat is liberated by adding more acid. (Neutralization is an exothermic reaction which releases heat. ) At E This is the end point. The temperature rise is maximum when the reaction is just completed.



E to B Temperature drops as any more acid added will not react but will absorb heat from the solution and cool it. Electromagnetic spectrum

Electromagnetic radiation is not a 'stranger' in daily life. Visible light comes from a light source in our homes; radio waves come from a radio station.

They are two examples of electromagnetic radiation. Other examples of electromagnetic radiation are microwaves, infrared, ultraviolet light, X-rays and gamma-rays. Different types of radiations can be grouped together to form an electromagnetic spectrum (Figure ASS. 1). Figure ASS. 1 An electromagnetic spectrum. The frequency ( $\nu$ ) of an electromagnetic radiation can be expressed in terms of its wavelength ( $\lambda$ ) and velocity ( $c$ ). The energy of a particular electromagnetic radiation can be expressed according to the following equation:  $E = h\nu$  where  $c$  is the speed of light ( $c = 3.0 \times 10^8 \text{ m s}^{-1}$ ) and  $h$  is Planck's constant ( $h = 6.626 \times 10^{-34} \text{ J s}$ ). Using a hydrogen atom as an example, when electromagnetic radiation falls onto a hydrogen atom, radiation of certain frequency will be absorbed. The electron in the hydrogen atom will be excited from the ground state to a higher energy level. The atom is said to be in an excited state. The electron in the higher energy level is unstable. It quickly returns to its lower energy level, the ground state. The energy is released in the form of light (electromagnetic radiation) which is equal to the energy difference between the higher and lower energy levels (Figure ASS. 2).

The energy is quantized and can be represented as:  $E_{\text{excited}} - E_{\text{ground}}$  = Energy difference  
- Ground state Figure ASS. 2 Light is emitted when an electron moves from a higher energy level to a lower energy level. Similarly, when electromagnetic radiation falls onto a molecule, radiation of certain frequency will be

absorbed. Electrons in the molecules are excited to higher energy levels and quantized energies are absorbed in a similar way as in hydrogen atom. In addition to the excitation of electrons, the absorption of energy can increase the extent of vibration of the bonds and the speed of rotation of the molecule. The energy involved in the changes in vibration and rotation is smaller than that resulting from the excitation of electrons.

The excitation of electrons fall into the energy range of ultraviolet light or visible light region, while the vibration change and rotational change of molecules only require energy in the infrared region and microwaves respectively. Vibration of molecules The atoms in a molecule are not static. Instead, they vibrate about their equilibrium positions. The covalent bonds in molecules act like springs in continuous, high- frequency vibration (Figure ASS. 3). When a molecule absorbs infrared radiation, the vibration of atoms will increase in amplitude. The molecule is said to be in an excited vibration state (Figure ASS. 4). The molecule will return to its ground state by the dissipation of heat. Figure ASS. 4 The change in vibration state of molecule after the absorption of infrared radiation. Figure ASS. 5 The structure of a mass spectrometer.

Formation of molecular ions To obtain a mass spectrum, a sample is introduced into a mass spectrometer. The sample is then vaporized to the gaseous state in the vaporization chamber. The molecules of the gaseous sample are then bombarded with a beam of fast-moving electrons. Some of the collisions are energetically enough to knock one or more electrons out of the molecule to give a positively-charged molecular ion. The chambers in the mass spectrometer should be kept under vacuum so that the molecular ions

produced can pass through the chambers without hitting any air molecules. The molecular ion is basically a radical action with an unpaired electron. It is not only a action, but also a radical.

A radical action is a free radical species that carries a positive charge.

Although it is possible that the bombardment of electrons with the molecules can give molecular ions with +2 charges, most of the molecular ions carry a +1 charge. This is because it is much more difficult to remove further electrons from a positive ion. The mass-to-charge ratio ( $m/e$ ) is different if the ions carry a +2 charge. For example, if a molecular ion has a mass of 30 and a charge of +1, the  $m/e$  would be 30. If the molecular ion has a charge of +2, the  $m/e$  would be 15. The molecular ions formed in the unionization chamber may undergo a series of fragmentation reactions.

The fragments generated may be carbonation's, radical actions, radicals or neutral molecules. Only the radical actions and carbonation's can be deflected by the magnetic field and detected by the detector in the mass spectrometer. Carbonation's/radical actions are then accelerated by the electric field towards a magnetic field. Ions with different  $m/e$  are deflected to different extents by the magnetic field. The extent of deflection depends on:

1. Mass of ions: the lighter the ions, the greater is the deflection.
2. Charge of ions: the higher the charge of the ions, the greater is the deflection.

Thus, ions with a greater  $m/e$  will be deflected to a lesser extent than an ion with a smaller  $m/e$ .

Since only positively charged ions are deflected, the mass spectrometer can detect the presence of radical actions and carbonation's only. Fragmentation

of molecular ions Molecular ions undergo a series of fragmentation reactions in the mass spectrometer to generate different positively charged fragment ions. These fragment ions are then separated in the mass spectrometer according to their  $m/e$ . Figure ASS. 6 shows the mass spectrum of methane. The peak at  $m/e = 16$  corresponds to the molecular ion  $\text{CH}_4^+$ . The peaks at  $m/e = 15, 14, 13$  and  $12$  correspond to the fragment ions produced. Figure ASS. 6 The mass spectrum of methane. We can easily identify the fragmentation patterns from the mass spectrum.

The methane radical cation loses a hydrogen radical to generate the methyl cation as shown below: methane radical cation methyl cation  $m/e = 16$   $m/e = 15$  hydrogen radical A signal at  $m/e = 15$  which represents the  $\text{CH}_3^+$  carbonation can be observed clearly in the mass spectrum. Further fragmentation reactions give fragment ions with lower  $m/e$ . The interpretation of the mass spectrum of methane is summarized in Table ASS.

1. Fragment carbonation/radical cation  $m/e$  16 14 13 Table ASS. 1

Interpretation of the mass spectrum of methane. Fragmentation patterns 1.

Straight-chain alkanes The mass spectrum of pentane is shown in Figure ASS.

7. It shows the typical characteristics of straight-chain alkanes.