Chem Factsheet

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# Colour in Chemistry

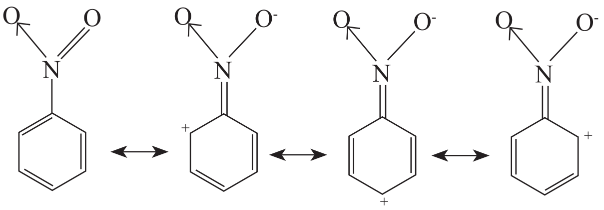
## Which substances are coloured?

Amongst inorganic compounds any coloured substance will be a compound involving a transition element. These may be in the form of compound ions (e.g. manganate(VII) – $MnO_4^-$ – purple) or complex ions (e.g. tetrachlorocuprate(II) ion – $CuCl_4^-$ – yellow).
Further Examples

| Compound ions | | | Complex ions | | |
|---|---|---|---|---|---|
| Dichromate(VI) | $Cr_2O_7^{2-}$ | Orange | Hexaaquanickel (II) ion | $Ni(H_2O)_6^{2+}$ | Green |
| Chromate(VI) | $CrO_4^{2-}$ | Yellow | Hexamminecobalt(II) ion | $Co(NH_3)_6^{3+}$ | Red |
| Vanadate(V) | $VO_3^-$ | Yellow | Hexhydroxochromate(III) ion | $Cr(OH)_6^{3-}$ | Green |
| Manganate(VI) | $MnO_4^{2-}$ | Green | Tetrachlorocobaltate(II) ion | $CoCl_4^-$ | Blue |

Simple organic molecules are rarely coloured. Nitrobenzene, 2,4,6-trinitromethylbenzene, 1,3-dinitrobenzene etc are all pale yellow indicating that the nitro group is responsible for the colour. However, compounds such as nitromethane and nitroethane are colourless which shows that it is the nitro group in conjunction with a benzene ring that causes colour. As shown in fig.1, the delocalised electron system of the benzene ring is extended to include the atoms in the nitro group – they are said to be *conjugated*.

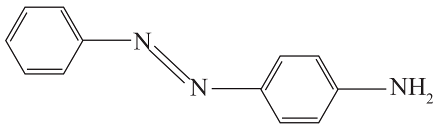
**Fig 1 Extended delocalisation in nitrobenzene**



Together the nitro group and the benzene ring produce a *chromophore* which, in general, is any group of atoms and bonds that causes a molecule to be coloured. Most chromophores are much more complex but, in general they consist of long sequences of alternating double and single bonds – this is referred to as a *conjugated system*. These structures allow extended delocalisation of p-orbital electrons across all of the atoms in the conjugated system to form a π molecular orbital (and a π antibonding [*] molecular orbital).
As seen in fig.2, dyes and many naturally occurring coloured molecules show this aspect of structure.

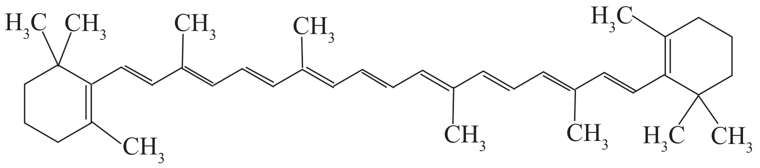
**Fig 2**

Analine yellow dye



Yellow

ß-carotene



Orange

Q1 How many p-orbitals are involved in the delocalisation process to form a π molecular orbital in (a) analine yellow dye (b) ß-carotene

## Why are they coloured?

A solution appears coloured as a result of its interactions with the various wavelengths ($\lambda \approx 700 - 400$nm) / frequencies ($f \approx 430 - 790$ THz ; THz = terahertz = $10^{12}$ Hz) in visible light (ROYGBIV – red, orange, yellow, green, blue, indigo, violet).
Note: Higher energy (E) radiation → shorter wavelength (λ) → higher frequency (f)

$E = hf$ where h = Planck's constant = $6.626 \times 10^{-34}$ Js (4sf)

Example: For a frequency of 450THz in the red region of the visible spectrum

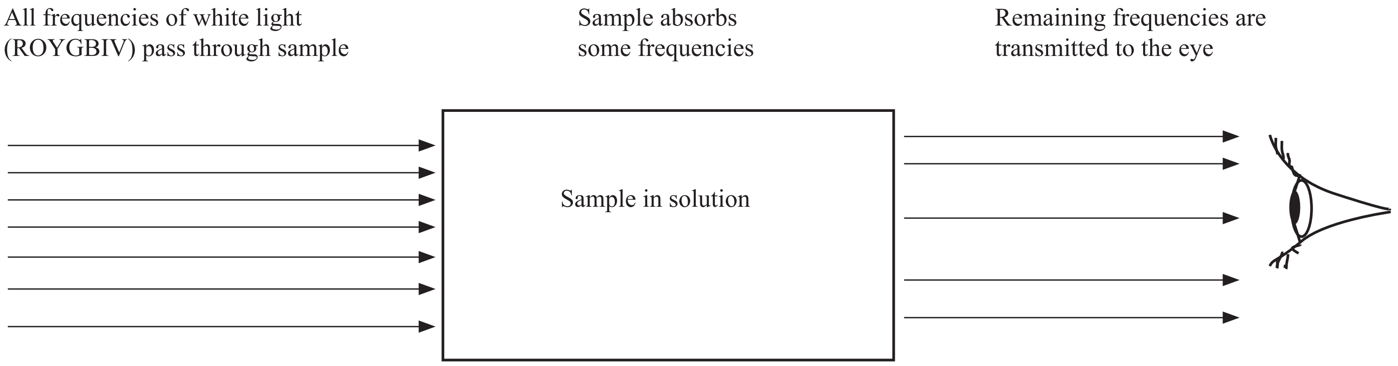
Energy per photon $= 6.626 \times 10^{-34} \times 450 \times 10^{12}$

$= 2.98 \times 10^{-19}$ J (3sf)

Q2 Calculate the energy per photon of violet light with frequency 750THz.

As shown in fig. 3, when the entire range of frequencies in white light pass through a solution, some are absorbed as a result of interaction with the sample. The *remaining* frequencies reach the observer resulting in the observed colour.

**Fig 3**

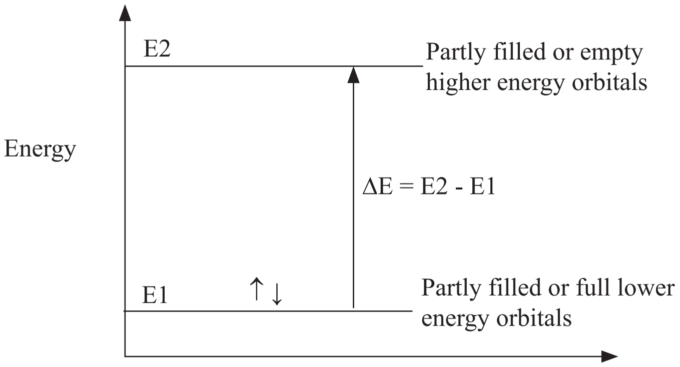


For example, if the sample absorbs frequencies from the red end of the visible spectrum the solution will be a shade of blue or purple. Similarly, absorption at the violet end results in a red or orange solution.

## Why are some frequencies absorbed?

As indicated in fig. 4, all coloured chemical substances have one thing in common in terms of electron orbitals. This is the existence of 2 sets of atomic or molecular orbitals (energy levels) that are separated by a difference in energy (ΔE) which corresponds to the energies of photons found in the visible region of the spectrum. This will be approximately (see previous calculations) in the range $2.85 – 5.25 \times 10^{-19}$ J.

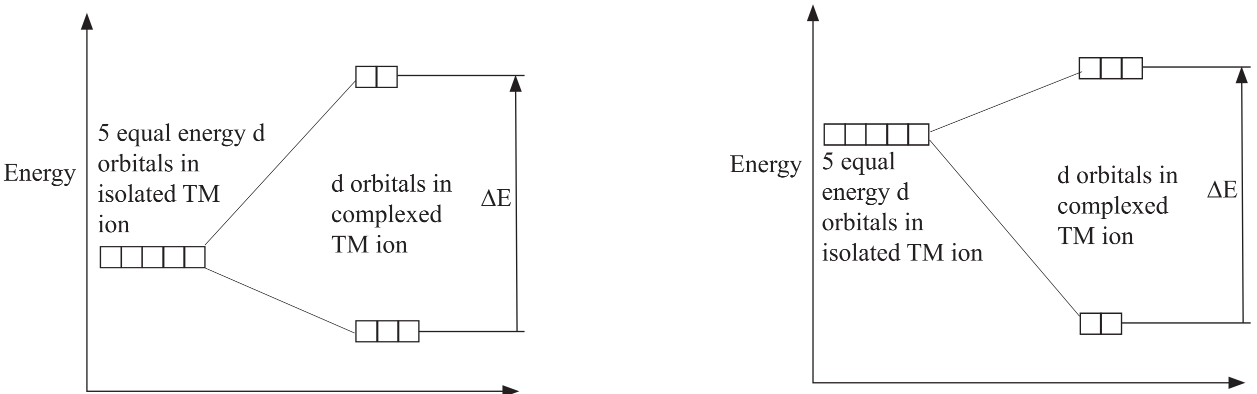
**Fig 4**



The lower levels must be occupied (partially or fully) by electrons and the upper levels must be empty or partially filled, but not full.
In the case of transition metal complexes this configuration is provided by atomic d-orbitals that are split into the two sets of levels when the ligands become bonded to the transition metal ion. This is illustrated for two different complex shapes in fig. 5.

The size of ΔE depends on (a) the identity of the transition metal (TM) ion (b) the oxidation state of the TM ion (c) the size of the ligand (d) the charge on the ligand (e) the strength of the ligand to TM ion coordinate bonds.

**Fig 5**

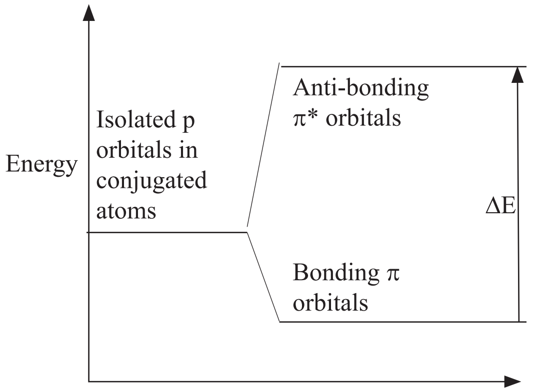


d-Orbital splitting for an octaheral complex

d-Orbital splitting for a tetrahedral complex

In the case of coloured organic molecules, the configuration is provided by bonding and anti-bonding (*) π molecular orbitals created by the overlap of p-orbitals on adjacent atoms as illustrated in the simplified fig. 6.

**Fig 6**



d-Orbital splitting for a tetrahedral complex

The size of ΔE depends on (a) the number of p orbitals involved in the conjugated system : more p orbitals → smaller ΔE (b) the identities of the conjugated atoms.

Given either of these situations, when exposed to all the frequencies of white light, the particle will absorb those frequencies (f) which have energies corresponding to ΔE according to the relationship $\Delta E = hf$. Each photon absorbed causes an electron to be "excited" from one of the lower energy levels to one of the higher energy levels. The remaining frequencies are transmitted and together, constitute the observed colour of the substance.

Q3 Write the electron configurations of (a) $Sc^{3+}$ (b) $Zn^{2+}$ (c) $Cu^{+}$ ions.
Explain why compounds containing these ions are NOT coloured.

Once excited to higher levels, the electrons return to the lower, more stable energy levels by dissipating the excess energy as heat. Hence, the electrons can be excited again.

## Answers to questions

Q1 (a) 14 (b) 22
Q2 $5.00 \times 10^{-19}$ J
Q3 (a) $Sc = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1 \rightarrow Sc^{3+} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^0$
(b) $Zn = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10} \rightarrow Zn^{2+} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^{10}$
(c) $Cu = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10} \rightarrow Cu^{+} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^{10}$
$Sc^{3+}$ has no d electrons to be excited. Excitation of the 3p electrons would result in absorptions in the ultra violet region.
The upper energy levels in $Zn^{2+}$ and $Cu^{+}$ are full and cannot therefore accept excited electrons from the lower levels.
Excitations to even higher levels (e.g. 4p) would also result in absorptions in the ultra violet region.

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