

- An atomic absorption spectrometer with a path length of 1.0 cm is used to measure the concentrations of copper in tap water. The results are shown below. The standard solution contains 5.0 ppm Cu.

**Marks**  
**3**

Sample	Absorbance reading
Standard solution (5.0 ppm Cu)	22.3
Unknown tap water	14.5

Assuming the Beer-Lambert Law is applicable, what is the concentration of Cu in the unknown tap water?

**According to the Beer-Lambert Law, absorbance,  $A$ , is proportional to concentration,  $c$ :  $A \propto c$ . The proportionality constant can be obtained from the standard solution:**

$$\text{constant} = A / c = 22.3 / 5.0 = 4.46 \text{ ppm}^{-1}$$

**Using  $A = 4.46c$ , the concentration of copper in the tap water is:**

$$c = A / 4.46 = 14.5 / 4.46 = 3.3 \text{ ppm}$$

Answer: **3.3 ppm**

What is the absorption process that AAS measures?

**AAS measures the excitation of valence electrons into higher energy states.**

- The diagram on the left of page 15 depicts the three lowest energy levels of the hydrogen atom. Consider an excited hydrogen atom with an electron in the 3s orbital.
- (A) Indicate all possible jumps this electron can make as the atom returns to the ground state. One possible jump (a) is shown for you as an example.
- (B) Calculate the energy associated with each of these jumps and mark it on the diagram on the right on page 15. Label the transitions. Again, jump (a) is shown as an example.

**Marks**  
**3**

Working

The energy of a level is given by  $E_n = -Z^2 E_R (1/n)^2$  where  $Z = 1$  for hydrogen. The energies of the  $n = 1, 2$  and  $3$  levels are therefore:

$$E_{n=1} = -(1)^2 \times (2.18 \times 10^{-18} \text{ J}) \times (1/1)^2 = -2.18 \times 10^{-18} \text{ J}$$

$$E_{n=2} = -(1)^2 \times (2.18 \times 10^{-18} \text{ J}) \times (1/2)^2 = -5.45 \times 10^{-19} \text{ J}$$

$$E_{n=3} = -(1)^2 \times (2.18 \times 10^{-18} \text{ J}) \times (1/3)^2 = -2.42 \times 10^{-19} \text{ J}$$

Alongside (a), two jumps are possible:

$$\begin{aligned} \text{(b) } n = 3 \rightarrow 2: \Delta E &= E_{n=2} - E_{n=3} = (-5.45 \times 10^{-19} \text{ J}) - (-2.42 \times 10^{-19} \text{ J}) \\ &= 3.06 \times 10^{-19} \text{ J} = 30.6 \times 10^{-20} \text{ J} \end{aligned}$$

$$\begin{aligned} \text{(c) } n = 2 \rightarrow 1: \Delta E &= E_{n=1} - E_{n=2} = (-2.18 \times 10^{-18} \text{ J}) - (-5.45 \times 10^{-19} \text{ J}) \\ &= 1.64 \times 10^{-18} \text{ J} = 164 \times 10^{-20} \text{ J} \end{aligned}$$

List all of the transitions that are in the visible region and identify the colour associated with each. For reference, the relationship between colours and wavelengths is shown below.

UV	violet	blue	green	yellow	orange	red	IR
400	450	490	560	590	630	700 nm	

The energy is related to the wavelength of the light through Planck's relationship,  $\Delta E = hc / \lambda$ . For the three transitions:

$$\begin{aligned} \text{(a)} \quad \Delta E &\sim 194 \times 10^{-20} \text{ J (estimated from graph):} \\ \lambda &= hc / \Delta E = (6.626 \times 10^{-34} \times 2.998 \times 10^8) / (194 \times 10^{-20}) \text{ m} \\ &= 1.02 \times 10^{-7} \text{ m} = 102 \text{ nm} \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad \Delta E &\sim 30.6 \times 10^{-20} \text{ J:} \\ \lambda &= hc / \Delta E = (6.626 \times 10^{-34} \times 2.998 \times 10^8) / (30.6 \times 10^{-20}) \text{ m} \\ &= 1.21 \times 10^{-7} \text{ m} = 121 \text{ nm} \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad \Delta E &\sim 164 \times 10^{-20} \text{ J:} \\ \lambda &= hc / \Delta E = (6.626 \times 10^{-34} \times 2.998 \times 10^8) / (164 \times 10^{-20}) \text{ m} \\ &= 6.56 \times 10^{-7} \text{ m} = 656 \text{ nm} \end{aligned}$$

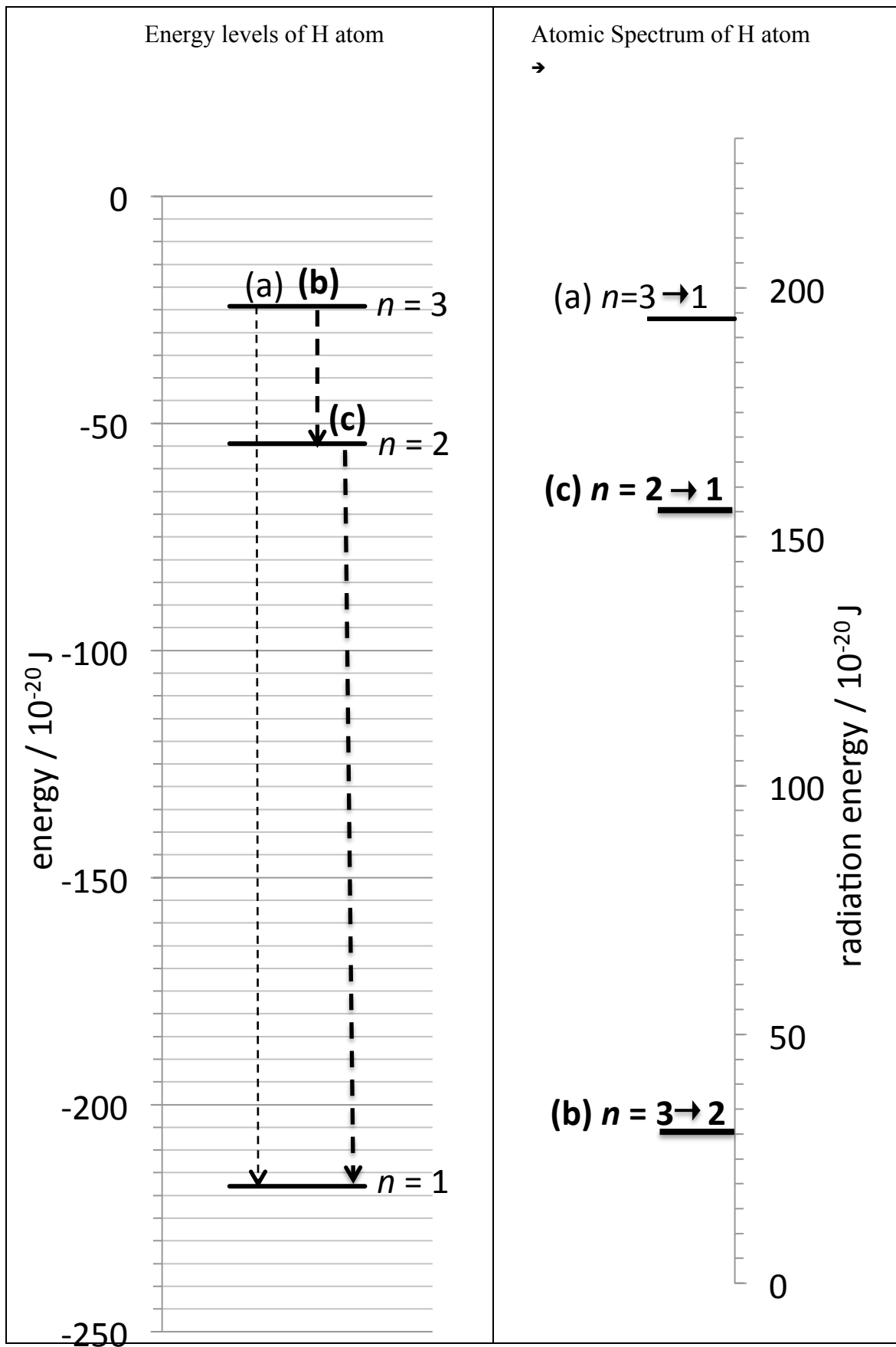
Transitions (a) and (b) are at shorter wavelength than the visible region. They occur in the UV. Transition (c) occurs in the visible and is in the orange / red region.

ANSWER CONTINUES ON THE NEXT PAGE

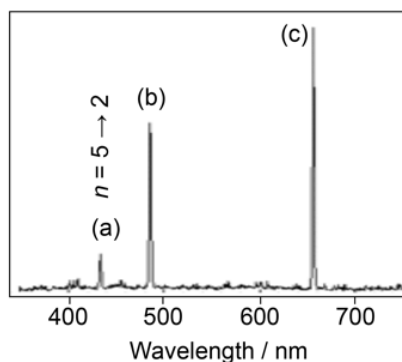
If the corresponding transitions were obtained from  $\text{He}^+$  instead of H, would they occur at longer or shorter wavelengths? Give a reason for your answer.

**$Z = 2$  for He. The energies of the levels and their separation will be greater for  $\text{He}^+$  than for H. Higher energy corresponds to shorter wavelength.**

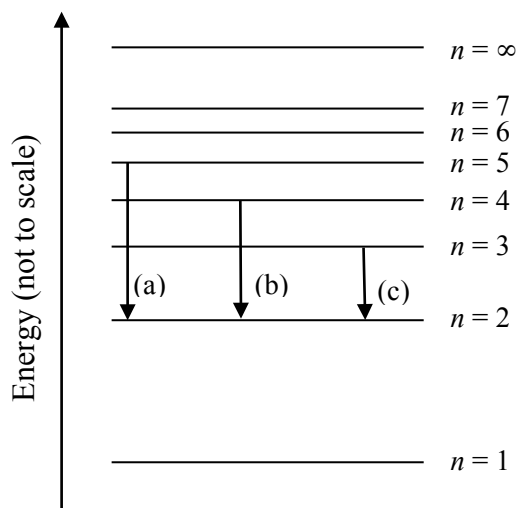
**ANSWER CONTINUES ON THE NEXT PAGE**

**Marks**  
**3**

- The emission spectrum of an H atom in the visible region of the electromagnetic spectrum is shown below, showing three clear transitions, labelled (a), (b) & (c). The quantum numbers associated with one of the transitions is assigned for you.

**Marks****4**

Complete the energy level diagram below to illustrate the energy levels of an H atom associated with all three transitions



Calculate the wavelength (in nm) of transition (a).

The energy levels of the electron in a H atom vary with the  $n$  quantum number according to the Rydberg relationship,  $E_n = -Z^2 E_R(1/n^2)$  where  $Z = 1$  for hydrogen and  $E_R = 2.18 \times 10^{-18}$  J.

Transition (a) corresponds to  $n = 5 \rightarrow n = 2$  and its energy is the difference between  $E_{n=2}$  and  $E_{n=5}$ :

$$E_{n=2} = -(1)^2 \times (2.18 \times 10^{-18} \text{ J}) \times (1/2^2) = 5.45 \times 10^{-19} \text{ J}$$

$$E_{n=5} = -(1)^2 \times (2.18 \times 10^{-18} \text{ J}) \times (1/5^2) = 8.72 \times 10^{-20} \text{ J}$$

$$\Delta E = E_{n=2} - E_{n=5} = (5.45 \times 10^{-19} - 8.72 \times 10^{-20}) \text{ J} = 4.58 \times 10^{-19} \text{ J}$$

**ANSWER CONTINUES ON THE NEXT PAGE**

The wavelength of light is related to the energy through Planck's relationship,  $E = hc/\lambda$ :

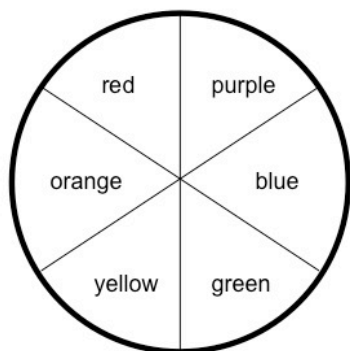
$$4.58 \times 10^{-19} \text{ J} = (6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^8 \text{ m s}^{-1}) / \lambda$$

$$\lambda = 4.34 \times 10^{-7} \text{ m} = 434 \text{ nm.}$$

Answer: **434 nm**

**Marks**  
**1**

- Nitrogen dioxide,  $\text{NO}_2$ , is formed in the atmosphere from industrial processes and automobile exhaust. It is an indicator of poor quality air and is mostly responsible for the brown haze seen in large cities. This question about  $\text{NO}_2$  extends over many pages, but each sub-question is essentially independent of the others.
- a)  $\text{NO}_2$  is a pungent red-orange coloured gas. According to the colour wheel for human vision, reproduced below, what colour light does  $\text{NO}_2$  absorb?



**From the question,  $\text{NO}_2$  has a red-orange colour. This is the complementary colour of the light that is absorbed.**

**On the colour wheel, blue / green is opposite to red-orange so these colours are absorbed.**

Answer: **Blue / green**

**3**

- b) An atmospheric chemist, monitoring pollution in Sydney, measured the absorption of light at 425 nm due to  $\text{NO}_2$ . Measured over a distance of 100 m, 425 nm light was attenuated by 5 % (*i.e.* 95 % transmission). What is the concentration of  $\text{NO}_2$  in the atmosphere? Give your answer in  $\text{mol L}^{-1}$ .  
Data:  $\epsilon(\text{NO}_2, 425 \text{ nm}) = 300 \text{ M}^{-1} \text{ cm}^{-1}$ .

**As the transmittance is 95%;  $I / I_0 = 0.95$  and so the absorbance,  $A$ , is:**

$$A = -\log_{10}(I / I_0) = -\log_{10}(0.95) = 0.0223$$

**From the Beer-Lambert law, absorbance,  $A$ , is related to the extinction coefficient for the substance,  $\epsilon$ , concentration,  $c$ , and the path length,  $l$ :**

$$A = \epsilon cl$$

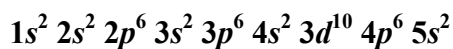
**With  $A = 0.0223$ ,  $\epsilon = 300 \text{ M}^{-1} \text{ cm}^{-1}$  and  $l = 100 \text{ m}$  or  $100 \times 10^2 \text{ cm}$ :**

$$c = A / \epsilon l = 0.0223 / ((300 \text{ M}^{-1} \text{ cm}^{-1}) \times (100 \times 10^2 \text{ cm})) \\ = 7.4 \times 10^{-9} \text{ M} = 7.4 \times 10^{-9} \text{ mol L}^{-1}$$

Answer:  **$7.4 \times 10^{-9} \text{ mol L}^{-1}$**

**Marks**  
**10**

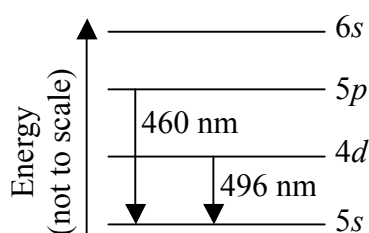
- Both strontium and strontianite are named after Strontian, a village in Scotland near which the mineral was first discovered. Strontium displays crimson (red) colouration in a flame. Give the ground state configuration for Sr.



Indicating only valence electrons, the electronic transition  $5s5p \rightarrow 5s^2$  in strontium brings about 460 nm photons. Can this transition be responsible for the crimson colour of Sr flames? Explain.

**No. 460 nm radiation is blue.**

Another transition,  $5s4d \rightarrow 5s^2$ , occurs at 496 nm. Show the transitions responsible for 460 nm and 496 nm photons on the energy level diagram to the right.



Calculate, in eV, the energy gap between the 4d and 5p orbitals of strontium.

**The gap between 5p and 5s is 460 nm. This corresponds to an energy difference of:**

$$E_1 = hc / \lambda = (6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1}) / (460 \times 10^{-9} \text{ m}) \\ = 4.32 \times 10^{-19} \text{ J}$$

**The gap between 4d and 5s is 496 nm. This corresponds to an energy difference of:**

$$E_2 = hc / \lambda = (6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1}) / (496 \times 10^{-9} \text{ m}) \\ = 4.00 \times 10^{-19} \text{ J}$$

**The 4d – 5p gap is, from the figure above, the difference between these:**

$$E = (4.32 \times 10^{-19} - 4.00 \times 10^{-19}) \text{ J} = 3.31 \times 10^{-20} \text{ J}$$

**As 1 eV = 1.602 × 10<sup>-19</sup>, this corresponds to:**

$$E = (3.31 \times 10^{-20} / 1.602 \times 10^{-19}) \text{ eV} = 0.20 \text{ eV}$$

Answer: **0.20 eV**

**ANSWER CONTINUES ON THE NEXT PAGE**



Explain why the  $4d$  orbitals of strontium are of a higher energy than the  $5s$  orbitals.

**The  $5s$  orbital experiences a higher nuclear charge more than the  $4d$  as it is more penetrating – it has more spherical nodes and spends a higher amount of time near the nucleus.**

**This stabilises the  $5s$  orbital, pulling it down in energy.**

Electron spins cannot flip easily during a transition. Explain why the excited state of Sr,  $5s5p$  with parallel spins, is long-lived.

**A spin up  $5p$  electron cannot drop into a  $5s$  orbital if a spin up electron is already there as this would violate the Pauli Exclusion principle.**

**As there is no lower energy orbital available that it can drop into, the species is long-lived.**

**Marks**  
**3**

- Calculate the energy (in J) and the wavelength (in nm) of the photon of radiation absorbed when the electron in  $B^{4+}$  jumps from the  $n = 3$  state to the  $n = 4$  state.

As  $B^{4+}$  has one electron, the equation  $E_n = \frac{-E_R Z^2}{n^2}$  where  $E_R = 2.18 \times 10^{-18}$  J can be used. Boron has  $Z = 5$ . The energies of the  $n = 3$  and  $n = 4$  levels are:

$$E_3 = \frac{-E_R (5)^2}{(3)^2} = -\frac{25}{9} E_R = -2.778 E_R \quad \text{and} \quad E_4 = \frac{-E_R (5)^2}{(4)^2} = -\frac{25}{16} E_R = 1.5625 E_R$$

The separation is:

$$\Delta E = (2.7778 - 1.5625) E_R = 1.2153 E_R = 1.2153 \times (2.18 \times 10^{-18}) = 2.65 \times 10^{-18} \text{ J.}$$

$$\text{As } E = \frac{hc}{\lambda}, \lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34}) \times (2.998 \times 10^8)}{(2.65 \times 10^{-18})} = 7.50 \times 10^{-8} \text{ m} = 75.0 \text{ nm}$$

Energy:  $2.65 \times 10^{-18}$  J

Wavelength: 75.0 nm

2

- Explain why the atomic radius of elements are observed to decrease from left to right across a period.

**The number of electrons and protons increase across a period. As all electrons are being added to the same shell, the nuclear charge increases with minimal increase in shielding and the attraction between the nucleus and the electron cloud increases. This results in smaller atoms as we move from left to right across a period.**

2

- Explain why samples must be atomised for atomic absorption spectrometry, but not for X-ray spectrometry.

**X-ray spectrometry investigates high energy transitions involving core electrons. These electrons are not involved in bonding and hence insensitive to whether atom is bonded or not. The X-ray spectrum of an element is approximately the same whatever compound the element is in.**

**Atomic absorption spectrometry measures transitions involving the valence electrons. These change depending upon the bonding of the atom, so samples must be atomised. The atomic absorption spectrum of an element depends crucially on the compound the element is in.**