2

Atomic structure and properties

Answers to worked examples

WE 2.1 Interconverting wavelength and frequency

What is the frequency of red light with a wavelength of 680 nm?

Strategy

Use Equation 2.1, $c = \lambda\nu$, and rearrange to find the frequency, ν.

The wavelength, λ, must be in metres.

Solution

Rearranging Equation 2.1 by dividing both sides by λ gives

$$\nu = \frac{c}{\lambda}$$

$$c = 2.998 \times 10^8 \text{ m s}^{-1}$$

$$\lambda = 680 \text{ nm} = 680 \times 10^{-9} \text{ m}$$

$$\nu = \frac{2.998 \times 10^8 \ \cancel{\text{m}}\ \text{s}^{-1}}{680 \times 10^{-9} \ \cancel{\text{m}}}$$

$$\nu = 4.41 \times 10^{14} \text{ s}^{-1} = 4.41 \times 10^{14} \text{ Hz}$$

WE 2.3 The photoelectric effect

Calculate the kinetic energy of the ejected electrons (in kJ mol^{-1}) if ultraviolet radiation of wavelength 450 nm is used in this experiment.

Strategy

By rearranging Equation 2.1, $c = \lambda v$, the frequency, v. can be calculated.
This value of v, can then be combined with Equation 2.2, $E = hv$, to calculate the energy (in J) of a single photon.
The value of the work function, Φ, for sodium has already been calculated in Worked example 2.3 as 3.68×10^{-19} J.
Using Equation 2.3, where $hv = \Phi + E_{KE}$, allows E_{KE} for a single electron to be calculated.
Finally, the value for a mole of electrons can be calculated by multiplying E_{KE} by the Avogadro constant.

Solution

Rearranging Equation 2.1 by dividing both sides by λ gives

$$v = \frac{c}{\lambda}$$

$$c = 2.998 \times 10^{8} \text{ m s}^{-1}$$

$$\lambda = 450 \text{ nm} = 450 \times 10^{-9} \text{ m}$$

$$v = \frac{2.998 \times 10^{8} \text{ m s}^{-1}}{450 \times 10^{-9} \text{ m}}$$

$$v = 6.66 \times 10^{14} \text{ s}^{-1}$$

Using Equation 2.2, $E = hv$, calculate the energy of one photon where h = Planck's constant = 6.626×10^{-34} J s

$$E = (6.626 \times 10^{-34} \text{ J s}) \times (6.66 \times 10^{14} \text{ s}^{-1})$$

$$E = 4.41 \times 10^{-19} \text{ J}$$

Since from Equation 2.3, $hv = \Phi + E_{KE}$, and the value of Φ, for sodium has already been calculated in the worked example (pp.82-83) as 3.68×10^{-19} J, rearranging for E_{KE} gives

$E_{KE} = hv - \Phi$

$E = (4.41 \times 10^{-19} J) - (3.68 \times 10^{-19} J)$

$E = 7.3 \times 10^{-20} J$

To convert this value for a single photon to a mole of electrons, requires multiplication by the Avogadro constant, N_A.

$E_{KE} = (7.3 \times 10^{-20} J) \times (6.022 \times 10^{23} mol^{-1})$

$E_{KE} = 4.4 \times 10^{4} J$ or $44 kJ mol^{-1}$

WE 2.5 The ionization energy of hydrogen

What is the ionization energy for hydrogen when the electron has already been promoted to the $n = 2$ level?

Strategy

Use the Rydberg equation, Equation 2.6, to work out the frequency of the line corresponding to the transition $n_1 = 2$ to $n_2 = \infty$ (infinity). Then use Equation 2.2, $E = hv$, to convert the frequency to the energy of the transition. Finally, this energy for a single atom needs to be converted to a molar quantity by multiplying by the Avogadro constant.

Solution

Using Equation 2.6,

$$v = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{ and } R_H = 3.29 \times 10^{15} \text{ Hz}$$

$n_1 = 2$ to $n_2 = \infty$ (infinity)

$$v = R_H\left[\frac{1}{2^2} - \frac{1}{\infty^2}\right] = \left[\frac{1}{4} - 0\right] = 8.23 \times 10^{14} \text{ Hz } (s^{-1})$$

Using Equation 2.2, $E = h\nu$, to find the energy of the transition.

$$E = (8.23 \times 10^{14}\ \text{s}^{-1}) \times (6.626 \times 10^{-34}\ \text{J s})$$

$$E = 5.45 \times 10^{-19}\ \text{J} \quad \text{or} \quad 5.45 \times 10^{-22}\ \text{kJ}$$

Finally multiply by the Avogadro constant to determine the value for a mole in kJ mol^{-1}.

$$E = (5.45 \times 10^{-22}\ \text{kJ}) \times (6.022 \times 10^{23}\ \text{mol}^{-1})$$

$$E = 328\ \text{kJ mol}^{-1}$$

WE 2.7 The Heisenberg uncertainty principle

Calculate the uncertainty in the position of an electron whose velocity is known to within 1×10^{6} m s^{-1}.

Strategy

Since the momentum (p) = mass × velocity, the uncertainty in the momentum is calculated using $\Delta p = m\Delta v$.

Rearrange Equation 2.10 and use it to calculate the uncertainty Δq, in the position of the electron.

Solution

The uncertainty in the momentum $\Delta p = m\Delta v$, where the mass of an electron = 9.1094×10^{-31} kg (Table 2.1, p.76)

$$\Delta p = (9.1094 \times 10^{-31}\ \text{kg}) \times (1 \times 10^{-6}\ \text{ms}^{-1})$$

$$\Delta p = 9.1094 \times 10^{-37}\ \text{kg m s}^{-1}$$

Using Equation 2.10

$$\frac{h}{4\pi} \leq \Delta p \Delta q$$

Rearrange by dividing both sides by Δp to give

$$\Delta q = \frac{h}{4\pi\Delta p} = \frac{6.626 \times 10^{-34}\ \cancel{\text{kg}}\ \text{m}\ \cancel{\text{s}^{-1}}}{4 \times 3.1416 \times 9.1094 \times 10^{-37}\ \cancel{\text{kg}\ \text{m}\ \text{s}^{-1}}}$$

$\Delta q = 57.9$ m

WE 2.9 Radial wavefunctions

How many radial nodes does a 7*s* orbital have?

<u>Strategy</u>

The number of radial nodes is directly related to the type of orbital. For an *s* orbital, there are $(n - 1)$ nodes where n is the principal quantum number.

<u>Solution</u>

As $n = 7$, the number of nodes for this s orbital is simply $(n - 1)$, therefore the 7*s* orbital has 6 nodes.

WE 2.11 Effective nuclear charge

What is the effective nuclear charges for (a) chlorine ($Z = 17$) and (b) bromine ($Z = 35$)?

Strategy

First establish the electronic configuration of the elements using the Aufbau principle and Figure 2.25. Consider one electron in the outer set of orbitals and the effect the other electrons has on it and apply Slater's rules to calculate the shielding constant, S. The other electrons in the same set of orbitals shield at 0.35, in the ($n - 1$) set of orbitals shield at 0.85 and the ($n - 2$) set of orbitals (or below) shield at 1.0. Finally, use Equation 2.19 to calculate Z_{eff}.

Solution

(a) The electronic configuration of chlorine ($Z = 17$) is $1s^2 2s^2 2p^6 3s^2 3p^5$.

Considering one of the electrons in the $3p$ orbitals and the effect the other electrons have on it gives the following.

There are four other electrons in the $3p$ orbitals and two electrons in the $3s$ orbital. As these electrons are in orbitals of the same principal quantum number they shield at 0.35. i.e. 6×0.35.

Each of the eight electrons in the $2s$ and $2p$ orbitals contribute 0.85 to the shielding as they are in the ($n - 1$) set of orbitals. This gives 8×0.85 for this shielding contribution.

Finally the two $1s$ electrons are in the ($n - 2$) set of orbitals and hence each contribute 1.0 to the shielding. This gives 2×1.0.

Overall the shielding is therefore $(6 \times 0.35) + (8 \times 0.85) + (2 \times 1.0) = 10.9$.

Using Equation 2.19, where $Z_{eff} = Z - S$ gives $17 - 10.9 = 6.1$.

(b) The electronic configuration of bromine ($Z = 35$) is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$.

Considering one of the electrons in the 4*p* orbitals and the effect the other electrons have on it gives the following.

There are four other electrons in the 4*p* orbitals and two electrons in the 4*s* orbital. As these electrons are in orbitals of the same principal quantum number they shield at 0.35. i.e. 6×0.35.

Each of the eighteen electrons in the 3*s*, 3*p* and 3*d* orbitals contribute 0.85 to the shielding as they are in the $(n - 1)$ set of orbitals. This gives 18×0.85 for this shielding contribution.

Finally the there are ten electrons in a combination of the 1*s*, 2*s* and 2*p* orbitals which are in the $(n - 2)$ (or below) set of orbitals and hence each contribute 1.0 to the shielding. This gives 10×1.0.

Overall the shielding is therefore $(6 \times 0.35) + (18 \times 0.85) + (10 \times 1.0) = 27.4$.

Using Equation 2.19, where $Z_{eff} = Z - S$ gives 35–27.4 = 7.6.

Answers to boxes

Box 2.1 Radiation from the Sun

Why does the Sun appear yellow?

Strategy

Examine the solar spectrum and examine the maximum intensity in comparison to the visible region.

Solution

All colours are present in sunlight, but the maximum intensity of the solar spectrum occurs at around 500 nm which is in the yellow region of the visible region.

Box 2.3 The composition of stars

How would the emission spectrum from the elements surrounding the Sun differ from the absorption spectrum obtained by Fraunhofer?

Strategy

Read the details of the Fraunhofer experiment given in Box 2.3 (p.91-92). The absorption spectrum gave missing lines in the visible spectrum according to the gases absorbing certain wavelengths of light. The emission spectrum should show the opposite behaviour where the missing lines corresponding to certain wavelengths are now emitted.

Solution

The emission spectrum at the Sun would be series of coloured lines on a dark background. The positions of the coloured lines (previously missing wavelengths) would exactly correspond to the position of the dark lines in the absorption spectrum

Box 2.7 Atomic numbers and the Periodic Table

Moseley showed that copper emits X-rays with $\lambda = 1.549 \times 10^{-10}$ m. Calculate the energy of a photon with this wavelength.

Strategy

Use Equation 2.1, $c = \lambda\nu$, to calculate the frequency of this X-ray and then Equation 2.2, $E = h\nu$, to calculate the energy of the photon.

Solution

Rearranging Equation 2.1 by dividing each side by λ gives and inputting the wavelength ($c = 2.998 \times 10^{8}$ ms^{-1})

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{8}\ \text{\sout{m}s}^{-1}}{1.549 \times 10^{-10}\ \text{\sout{m}}} = 1.935 \times 10^{18}\ \text{s}^{-1}\ \ (\text{Hz})$$

Using Equation 2.2 to determine the energy of the photon where $E = h\nu$ and $h = 6.626 \times 10^{-34}$ J s

$E = (6.626 \times 10^{-34}\ \text{J}\ \cancel{\text{s}}) \times (1.935 \times 10^{18}\ \cancel{\text{s}^{-1}})$

$E = 1.282 \times 10^{-15}\ \text{J}$

Box 2.9 Smoke detectors

What is the nuclear equation of the α decay of an atom of ^{241}Am?

<u>Strategy</u>

An alpha decay (see Table 2.7, p.121) is associated with a change of 4 in the atomic number and 2 in the atomic mass (i.e. the same as a He atom). Therefore the product must reflect these changes.

<u>Solution</u>

$^{241}_{95}\text{Am} \rightarrow\ ^{237}_{93}\text{Np} +\ ^{4}_{2}\text{He}$

Answers to end of chapter questions

1. What is the energy (in kJ mol^{-1}) of X-ray photons with a wavelength of 100 pm?

<u>Strategy</u>

Use Equation 2.1, $c = \lambda\nu$, and rearrange to find the frequency, ν. The wavelength, λ, must be in metres. The frequency can then be converted to energy for a single photon using Equation 2.2, $E = h\nu$ and then multiplied by the Avogadro constant to find the energy of a mole of photons. (Where the Avogadro constant, N_A, is the number of entities in a mole, see Section 1.3, p.16.)

<u>Solution</u>

Rearranging Equation 2.1 by dividing both sides by λ gives

$$\nu = \frac{c}{\lambda}$$

$c = 2.998 \times 10^{8}$ m s^{-1}

$\lambda = 100$ pm $= 100 \times 10^{-12}$ m

$$\nu = \frac{2.998 \times 10^{8} \text{ m s}^{-1}}{100 \times 10^{-12} \text{ m}}$$

$\nu = 2.998 \times 10^{18}$ s^{-1} $= 2.998 \times 10^{18}$ Hz

Using Equation 2.2, $E = h\nu$ to then calculate the energy of one photon where
h = Planck's constant $= 6.626 \times 10^{-34}$ J s

$E = (6.626 \times 10^{-34}$ J s$) \times (2.998 \times 10^{18}$ s$^{-1})$

$E = 1.986 \times 10^{-15}$J

The value for a single photon can then be converted into the energy for one mole of photons by multiplying by the Avogadro constant, 6.022×10^{23} mol^{-1}.

$E = 1.986 \times 10^{-15}$ J $\times 6.022 \times 10^{23}$ mol^{-1}

$E = 1.196 \times 10^{9}$ J mol^{-1} or 1.196×10^{6} kJ mol^{-1}

3. What is the wavelength of light for a line in the atomic spectrum of hydrogen for which $n_1 = 2$ and $n_2 = 4$? What part of the electromagnetic spectrum does this correspond to?

<u>Strategy</u>
Comparing these data to Table 2.4 (p.87) shows that this line is from the Balmer series of the atomic spectrum of hydrogen. Numerically this can be proven using Equation 2.6 to calculate the frequency of the line and then using Equation 2.1, $c = \lambda\nu$, to convert the frequency to wavelength.

Solution

Using Equation 2.6,

$$\nu = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{ and } R_H = 3.29 \times 10^{15} \text{ Hz}$$

$$\nu = R_H\left[\frac{1}{2^2} - \frac{1}{4^2}\right] = R_H\left[\frac{1}{4} - \frac{1}{16}\right] = 6.169 \times 10^{14} \text{ Hz } (\text{s}^{-1})$$

From Equation 2.1 dividing each side by ν gives

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{6.169 \times 10^{14} \text{ s}^{-1}} = 4.86 \times 10^{-7} \text{ m} = 486 \text{ nm}$$

This is at the violet end of the visible region.

5. Which of the following sets of quantum numbers are allowed? What atomic orbitals do the allowed combinations correspond to?

(a) $n = 2, l = 2, m_l = 2$

(b) $n = 5, l = 3, m_l = -2$

(c) $n = 3, l = -1, m_l = 1$

(d) $n = 2, l = 1, m_l = 1$

(e) $n = 4, l = 0, m_l = 1$

Strategy

Use the definitions given for n, l and m_l on page 96 to identify permitted values n takes integral values starting from 1 upwards and l can then take value from 0 up to (n – 1). m_l can take integral values between $+l$ and $-l$.

Solution

(a) These values are not allowed, the maximum value of l is $(n - 1)$.

(b) These values are allowed and with $n = 5$ and $l = 3$, combine to give a 5*f* orbital.

(c) These values are not allowed as l cannot be negative.

(d) These values are allowed and with $n = 2$ and $l = 1$, combine to give a 2*p* orbital.

(e) The values are not allowed as m_l can only take values from $+l$ to $-l$. In this case as l is zero, $m_l = 1$ is not allowed.

7. The value of m_l for a particular orbital is –2. What are the smallest possible values for n and l ?

Strategy

Use the definitions given for n, l and m_l on page 96 to identify permitted values n takes integral values starting from 1 upwards and l can then take value from 0 up to $(n - 1)$. m_l can take integral values between $+l$ and $-l$.

Solution

For m_l to have a value of –2, where m_l takes values from $+l$ to $-l$, the smallest l can be is 2. As l takes values up to $(n - 1)$, the smallest value of n where $l = 2$, must be $l + 1 = 3$.

9. Of the following arrangement of *p* electrons, which represents the ground state, which are excited states and which are impossible?

Strategy

Apply the Pauli exclusion principle (no two electrons may have the same four quantum numbers) and Hund's Rule (the lowest energy configuration is the one with maximum number of parallel electrons) to the different configurations to determine which are allowed. Note in the answers that the difference between an allowed excited state (in violation of Hund's Rule) as opposed to a disallowed state (in violation of the Pauli exclusion principle).

Solution

(a) As one of the electrons could be placed in another orbital in a spin parallel configuration (according to Hund's rule) this is not the lowest energy configuration. This is therefore an excited state.

(b) This is the ground state configuration with a maximum number of parallel electrons in agreement with Hund's rule.

(c) Although electrons are in separate orbitals, the spins are not parallel and hence this configuration does not obey Hund's rule. It is therefore an excited state.

(d) This configuration has two electrons with the same four quantum numbers and disobeys the Pauli exclusion principle. This configuration is disallowed.

11. Which elements would you expect to have the following electronic configurations: (a) [Ar] $4s^2$, (b) [Ne]$3s^2 3p^5$, (c) [Kr]$5s^2 4d^7$. The actual configuration for the element in (c) is [Kr] $5s^1 4d^8$. Suggest a reason for this.

Strategy

Use Figure 2.25 (p.105) to determine the order in which the orbitals are filled. Use the Periodic Table (on the inside front cover) to pinpoint the period of the element in question. E.g. from the noble gas configuration shorthand the element must be in the period after the last full noble gas configuration.

Solution

(a) This element has two more electrons than argon, it is therefore calcium.

(b) This element has seven more electrons than neon, it is therefore chlorine.

(c) This element has nine more electrons than krypton, it is therefore rhodium.

The unexpected configuration for rhodium is due to Hund's rule. This configuration has a greater number of parallel electrons.

13. ^{210}Pb decays into ^{206}Pb in a pathway involving two β emissions followed by an α emission. What are the two intermediate isotopes?

Strategy

A β emission causes a rise by 1 unit in the atomic mass. Use the Periodic Table (on the inside front cover) to determine which two elements are created after each emission.

Solution

$$^{210}_{82}Pb \rightarrow\ ^{210}_{83}Bi +\ ^{0}_{-1}e$$

$$^{210}_{83}Bi \rightarrow\ ^{210}_{84}Po +\ ^{0}_{-1}e$$

$$^{210}_{84}Po \rightarrow\ ^{206}_{82}Pb +\ ^{4}_{2}He$$

The two intermediate isotopes are bismuth-210 and polonium-210.