What is the ground state electron configuration of oxygen?

1s² 2s² 2p⁴

The following diagram represents the relative energies of the atomic orbitals in the first three shells. Using arrows to represent electrons, show the most stable electron arrangement of the oxygen atom. Label the core electrons and the valence electrons.

Briefly explain how your diagram illustrates the Pauli exclusion principle, Aufbau principle and Hund’s rule.

Pauli exclusion principle: there’s a maximum of 2 electrons in each orbital with opposite spins, ensuring that no two electrons have the same set of quantum numbers.

Aufbau principle: lowest energy orbitals fill first.

Hund’s rule: electrons in degenerate orbitals (i.e. orbitals with the same energy) have the maximum number of parallel spins to minimise electron / electron repulsion.

Draw an oxygen molecule showing the shapes of the σ-orbital and the π-orbital present.

Oxygen and sulfur are both Group 16 elements with a valence of two. Oxygen is a diatomic molecule at room temperature, whilst the bonding in solid sulfur consists only of σ-bonds. Suggest reasons why, at room temperature, the O=O molecule is stable and the S=S molecule is not.

Sulfur would use 3p orbitals to form a π-bond. These orbitals are diffuse and overlap is poor and so it is more stable to use σ-bonds to 2 other atoms. Good overlap of the 2p orbitals in oxygen means that the π-bond is stable.
Glycine, $\text{NH}_2\text{CH}_2\text{COOH}$, the simplest of all naturally occurring amino acids, has a melting point of 292 °C. The $pK_a$ of the acid group is 2.35 and the $pK_a$ associated with the amino group is 9.78. Draw a Lewis structure that indicates the charges on the molecule at the physiological pH of 7.4.

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{N} \text{C} \text{O} \text{O} \\
\end{array}
\]

Use your structure to illustrate the concept of resonance.

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{N} \text{C} \text{O} \text{O} \\
\end{array} \quad \longrightarrow \quad \begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{N} \text{C} \text{O} \text{O} \\
\end{array}
\]

Describe the hybridisation of the two carbon atoms and the nitrogen atom in glycine and the molecular geometry of the atoms surrounding these three atoms.

N: $sp^3$ hybridised; tetrahedral geometry  
CH$_2$: $sp^3$ hybridised; tetrahedral geometry  
CO$_2^-$: $sp^2$ hybridised; trigonal planar geometry

Glycine has an unusually high melting point for a small molecule. Suggest a reason for this.

In its zwitterionic state, glycine has very strong electrostatic attractions (i.e. ionic bonds) between the NH$_3^+$ and CO$_2^-$ groups giving it very high melting point.

Do you expect glycine to be water soluble? Give a reason for your answer.

Yes. It is ionic so dissolves in the very polar solvent water.
• The autoionisation of water conforms to the following balanced equation:

\[ 2\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq) \quad \Delta H = 56.3 \text{ kJ mol}^{-1} \]

Is this an exothermic or endothermic reaction?

**Endothermic (as \( \Delta H \) is positive).**

What will happen to the equilibrium if the temperature is raised?

The reaction will shift to the right. From le Chatelier’s principle, the equilibrium will shift to reduce the effect of the change. As the forward reaction is endothermic, it is able to mitigate the increase in temperature by shifting forwards.

The equilibrium constant, \( K \), for this reaction is \( 1.8 \times 10^{-16} \) at 25 °C. Calculate \( \Delta G \).

Using \( \Delta G = -RT\ln K \),

\[ \Delta G = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times ((25 + 273) \text{ K}) \times 1.8 \times 10^{-16} = +89 \text{ kJ mol}^{-1} \]

Answer: +89 kJ mol\(^{-1}\)

Why is \( \Delta G \) not equal to \( \Delta H \) for this reaction?

By definition, \( \Delta G = \Delta H - T\Delta S \). As the entropy change for the reaction and the temperature are not zero, so \( \Delta G \neq \Delta H \).

The pH of pure water is 6.81 at 37 °C. Is water acidic, basic or neutral at this temperature? Explain.

**Neutral.** Pure water is neutral at all temperatures as the chemical equation always gives \([\text{H}_3\text{O}^+(aq)] = [\text{OH}^-(aq)]\). A pH value of 7.0 only corresponds to a neutral solution at 25 °C.
The radioactive isotopes $^{131}$I and $^{137}$Cs have been detected in drinking water near the Japanese Fukushima nuclear reactor. They have half lives of 8 days and 30 years, respectively. What is the definition of half-life?

**Half-life** is the amount of time required for the amount (or activity) of a sample to decrease to half its initial value.

What percentage of both isotopes will still be detectable after 25 years?

The number of nuclei, $N$, decays with time, $t$, according to $\ln(N_0/N_t) = \lambda t$ where $\lambda$ is the activity coefficient. This is related to the half life, $t_{1/2}$ by $\lambda = \ln(2)/t_{1/2}$.

For $^{131}$I, $t_{1/2} = 8$ days $= 8/365$ years:

$$\lambda = \ln(2) / (8/365) \text{ years}^{-1} = 32 \text{ years}^{-1}$$

When $t = 25$ years,

$$\ln(N_0/N_t) = \lambda t = (32 \text{ years}^{-1})(25 \text{ years})$$

$$N_0/N_t = e^{790} \quad \text{or} \quad N_t / N_0 \approx 0$$

$N_t$ is very close to zero and effectively all of the $^{131}$I has decayed.

For $^{137}$Cs, $t_{1/2} = 30$ years:

$$\lambda = \ln(2) / (30) \text{ years}^{-1} = 0.023 \text{ years}^{-1}$$

When $t = 25$ years,

$$\ln(N_0/N_t) = \lambda t = (0.023 \text{ years}^{-1})(25 \text{ years})$$

$$N_0/N_t = 1.8 \quad \text{or} \quad N_t / N_0 = 0.56 = 56\%$$

$^{131}$I: 0\%

$^{137}$Cs: 56\%

If you were exposed to equal concentrations of both isotopes for 1 hour, which isotope would do more damage? Explain.

$^{131}$I would do more damage.

It has the shorter half-life so undergoes more disintegrations and produces more radiation in a given time period.
• The concentration of a dissolved gas is related to its partial pressure by \( c = kp \). What is the concentration of CO\(_2\) dissolved in blood if the partial pressure of CO\(_2\) in the lungs is 0.053 atm? The \( k \) for CO\(_2\) is 0.034 mol L\(^{-1}\) atm\(^{-1}\).

Using \( c = kp \),

\[
   c = (0.034 \text{ mol L}^{-1} \text{ atm}^{-1})(0.053 \text{ atm}) = 0.0018 \text{ mol L}^{-1}
\]

Answer: \(0.0018 \text{ mol L}^{-1}\)

Calculate the pH of blood if all of this CO\(_2\) reacted to give H\(_2\)CO\(_3\). The \( K_a \) of H\(_2\)CO\(_3\) is \(4.5 \times 10^{-7}\).

If \([\text{H}_2\text{CO}_3(aq)] = 0.0018 \text{ mol L}^{-1}\), the pH can be calculated using the reaction table:

<table>
<thead>
<tr>
<th></th>
<th>H(_2)CO(_3)</th>
<th>H(_2)O</th>
<th>(\leftrightarrow)</th>
<th>H(_3)O(^+)</th>
<th>HCO(_3^-))</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.0018</td>
<td>large</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>-x</td>
<td>negligible</td>
<td>+x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>final</td>
<td>0.0018 (-x)</td>
<td>large</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

The equilibrium constant \( K_a \) is given by:

\[
   K_a = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{x^2}{0.0018-x}
\]

As \( K_a = 4.5 \times 10^{-7} \) and is very small, \(0.0018-x \sim 0.0018\) and hence:

\[
   x^2 = 0.0018 \times (4.5 \times 10^{-7}) \quad \text{or} \quad x = 2.8 \times 10^{-5} \text{ M} = [\text{H}_3\text{O}^+]\]

Hence:

\[
   \text{pH} = -\log_{10} [\text{H}_3\text{O}^+ (aq)] = -\log_{10}(2.8 \times 10^{-5}) = 4.54
\]

Answer: \(4.54\)

Hyperventilation results in a decrease in the partial pressure of CO\(_2\) in the lungs. What effect will this have on the pH of the blood? Use a chemical equation to illustrate your answer.

If the CO\(_2\) partial pressure decreases, the equilibrium below will shift to the left. This will decrease \([\text{H}^+(aq)]\) and the pH will increase.

\[
   \text{CO}_2(aq) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3(aq) \leftrightarrow \text{HCO}_3^-(aq) + \text{H}^+(aq)
\]

Answer continues on the next page
The pH of blood is maintained around 7.4 by the H₂CO₃ / HCO₃⁻ buffer system. Explain how a buffer works, illustrating your answer with chemical equations.

A buffer resists changes in pH. It contains substantial quantities of a weak acid and its conjugate base. In the H₂CO₃/HCO₃⁻ buffer, added acid is removed by the reaction:

\[ \text{HCO}_3^-(aq) + \text{H}^+(aq) \rightarrow \text{H}_2\text{CO}_3(aq) \]

Added base is removed by the reaction:

\[ \text{H}_2\text{CO}_3(aq) + \text{OH}^-(aq) \rightarrow \text{HCO}_3^-(aq) + \text{H}_2\text{O} \]
A structural formula for Warfarin, an anticoagulant, showing all atoms and bonds is shown below. Draw a stick representation of the formula in the box provided.

Give the constitutional formula(s) of the major organic products formed in each of the following reactions:

1. \(\text{Br} \quad \xrightarrow{N(\text{CH}_3)_3} \quad \text{N}^+ \text{Br}^-\)

2. \(\text{C}_3\text{H}_7\text{CH} = \text{CH}_2 \quad \xrightarrow{\text{Br}_2} \quad \text{C}_3\text{H}_7 \text{CH} \quad \text{Br}\quad \text{Br}\)

3. \(\text{C}_3\text{H}_7\text{CH} = \text{CH}_2 \quad \xrightarrow{\text{H}_2\text{SO}_4} \quad \text{C}_3\text{H}_7 \quad \text{OH}\)

4. \(\text{C}_4\text{H}_9\text{OH} \quad \xrightarrow{1) \text{LiAlH}_4} \quad \text{C}_4\text{H}_9\text{OH} \quad \xrightarrow{2) \text{H}_3\text{O}^+} \quad \text{C}_4\text{H}_9\text{OH}\)

5. \(\text{S} \quad \text{S} \quad \xrightarrow{\text{Zn metal, HCl}} \quad 2 \times \text{C}_2\text{H}_5\text{SH}\)
Complete the following table.

<table>
<thead>
<tr>
<th>Starting material</th>
<th>Reagent / Conditions</th>
<th>Major organic products(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Molecule" /></td>
<td><img src="image" alt="Reagent" /></td>
<td><img src="image" alt="Product" /></td>
</tr>
<tr>
<td><img src="image" alt="Molecule" /></td>
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<tr>
<td><img src="image" alt="Molecule" /></td>
<td><img src="image" alt="Reagent" /></td>
<td><img src="image" alt="Product" /></td>
</tr>
</tbody>
</table>

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.
• (+)-Citronellal is a widely occurring natural product present in citronella oil, lemon and lemon grass. It is used as a soap perfume and in insect repellents.

\[
\text{citronellal}
\]

Give the molecular formula of citronellal. \[\text{C}_{10}\text{H}_{18}\text{O}\]

Identify the functional groups present in citronellal.

**Aldehyde and alkene**

Draw the constitutional formula of the product(s) formed when citronellal is treated with each of the following reagents.

- \(\text{Cr}_2\text{O}_7^{2-} / \text{H}^\oplus\)

- Excess CH\(_3\)OH / catalytic amount H\(_2\)SO\(_4\)

• NADH is the most important reducing agent in Nature. It is itself oxidised to NAD\(^+\).

Complete the scheme below by:

(a) drawing in curly arrows to show the movement of electrons during the first step in the reduction of acetone with NADH, and

(b) drawing the structure of NAD\(^+\).
- Show clearly the reagents you would use to carry out the following chemical conversions. Note that more than one step is required and you should indicate all necessary steps and the constitutional formulas of any intermediate compounds.

<table>
<thead>
<tr>
<th>Reagents Used</th>
<th>Chemical Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexene, dilute H₂SO₄, heat</td>
<td>Cyclohexene → Cyclohexanol → Cyclohexanone</td>
</tr>
<tr>
<td>2-Cyclohexen-1-ol, Cr₂O₇²⁻/H⁺</td>
<td>2-Cyclohexen-1-ol → Cyclohexanone</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>1-Butanol → Butyl formate</td>
</tr>
<tr>
<td>2-Butanol, Cr₂O₇²⁻/H⁺</td>
<td>2-Butanol → 2-Butanone</td>
</tr>
<tr>
<td>2-Butanone, SOCl₂</td>
<td>2-Butanone → 2-Butanoyl chloride</td>
</tr>
<tr>
<td>2-Butanoyl chloride, CH₃CH₂OH</td>
<td>2-Butanoyl chloride → 1-Butanol → Butyl formate</td>
</tr>
</tbody>
</table>
• Consider the tripeptide phenylalanylglutamyltyrosine (Phe-Glu-Tyr) (F), whose constitutional formula is shown below.

![Constitutional formula of Phe-Glu-Tyr](image)

Draw the constitutional formula(s) of the product(s) obtained when the tripeptide (F) is subjected to the following conditions. Make sure you show the products in the appropriate ionic states.

**cold 2 M NaOH**

![Product structure for cold 2 M NaOH](image)

**5 M HCl / heat**

![Product structures for 5 M HCl / heat](image)
The pKₐ values of tyrosine are pKₐ₁ = 2.20 (α-COOH), pKₐ₂ = 9.11 (α-NH₃⁺) and pKₐ₃ = 10.07 (-CH₂C₆H₄OH). Draw the structure of the zwitterionic form of tyrosine.

\[
\text{H}_3\text{N}^+\text{CO}_2^- \\
\text{O} \quad \text{CO}_2^- \quad \text{CH}_2\text{Ph}
\]

At what pH will this be the predominant species in aqueous solution? 5.66 (halfway between pKₐ₁ and pKₐ₂)

The naturally occurring isomer of phenylalanine is (l)-phenylalanine. Draw the zwitterionic structure of (l)-phenylalanine and indicate the stereogenic centre with an asterisk (*). Determine whether this amino acid has the (R) or (S) configuration. Show your working.

Horizontal bonds in Fischer projections are out of the paper, vertical bonds are into the paper. Order of priority of substituents is NH₃⁺ > CO₂⁻ > CH₂Ph > H. Reorient the molecule so that the lowest priority group (H) is at the back. Viewing down the C–H bond, the orientation of NH₃⁺ → CO₂⁻ → CH₂Ph is anticlockwise. Therefore (l)-phenylalanine has (S) configuration.
• Draw a tautomer of the structure of thymine, shown below.

[Diagram of thymine and tautomers]

• Rank the following compounds in order of base strength and explain your reasoning. You may use diagrams to assist your explanation.

[Diagrams of pyridine, pyrrole, and N-phenylacetamide]

Order of base strength is:

pyrrole (non-basic) < pyridine (basic) < N-phenylacetamide (essentially non-basic)

Pyridine is the most basic as the lone pair of electrons on nitrogen is available to bond with H⁺.

Pyrrole is the least basic as the “lone pair” of electrons on nitrogen is part of the aromatic π-electron system and is delocalised around the ring. It is not available for bonding with H⁺ ions.

N-Phenylacetamide is essentially non-basic as the lone pair of electrons is involved in resonance forms (including delocalisation of the positive charge into the aromatic ring, which is not shown).
• Consider the following two monosaccharides, (A) and (B).

\[ \beta\text{-D-altropyranose} \quad \alpha\text{-D-xylofuranose} \]

Draw Fischer projections of the open chain forms of (A) and (B).

(A)  
\[
\begin{align*}
\text{CHO} \\
\text{HO} & \quad \text{H} \\
\text{H} & \quad \text{OH} \\
\text{H} & \quad \text{OH} \\
\text{H} & \quad \text{OH} \\
\text{CH}_2\text{OH}
\end{align*}
\]

(B)  
\[
\begin{align*}
\text{CHO} \\
\text{H} & \quad \text{OH} \\
\text{HO} & \quad \text{H} \\
\text{H} & \quad \text{OH} \\
\text{CH}_2\text{OH}
\end{align*}
\]

Draw the major organic product of the reaction of D-altropyranose with the following reagents.

1. $\text{NaBH}_4$  
2. $\text{H}^+ / \text{H}_2\text{O}$  

\[
\begin{align*}
\text{CHO} \\
\text{HO} & \quad \text{H} \\
\text{H} & \quad \text{OH} \\
\text{H} & \quad \text{OH} \\
\text{H} & \quad \text{OH} \\
\text{CH}_2\text{OH}
\end{align*}
\]

\[
\begin{align*}
\text{CHO} \\
\text{HO} & \quad \text{H} \\
\text{H} & \quad \text{OH} \\
\text{H} & \quad \text{OH} \\
\text{CH}_2\text{OH}
\end{align*}
\]

\[
\begin{align*}
\text{CHO} \\
\text{HO} & \quad \text{H} \\
\text{H} & \quad \text{OH} \\
\text{H} & \quad \text{OH} \\
\text{CH}_2\text{OH}
\end{align*}
\]