

Describe the periodic trends exhibited by atomic radii. Justify these trends in terms of principal quantum number, n , and effective nuclear charge, Z_{eff} .

Marks
2

Atomic radius decreases across a period as the number of protons and electrons is increasing. As the electrons are all be added to the same shell, they do not shield each other from the increasing nuclear charge and consequently Z_{eff} increases and the electrons are pulled closer to the nucleus.

Atomic radii increase going down a group. As n increases, the size of the orbitals increases and the electrons in these orbitals are shielded from the nuclear charge by electrons with smaller n . They are thus less tightly held and further from the nucleus.

Giving reasons, order either the set of oxyacids or the binary acids in terms of increasing acidity.

HClO , HClO_2 , HClO_3 , HClO_4 or H_2O , H_2S , H_2Se , H_2Te

Marks
2

All HClO_n acids have the structure HOClO_{n-1} . As the number of oxygens increases, more electron density is drawn away from the O–H bond and weakens it. The weaker the O–H bond, the stronger the acid, so the order is $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$.

In binary acids such as H_2S and H_2Se , the H–Se bond is longer than the H–S bond as Se is larger than S. The H–Se bond is therefore weaker than the H–S bond and H_2Se is thus a stronger acid than H_2S . The order is therefore $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$.

- Explain why HClO_4 is a stronger Brønsted acid than HBrO_4 , but HCl is a weaker acid than HBr .

In Group 17 oxyacids, electron density is drawn away from the O atom as the electronegativity of the halogen increases. This in turn draws electron density away from the O–H bond and weakens it. The weaker the O–H bond, the stronger the acid. Cl is more electronegative than Br so HOClO_3 is stronger acid than HOBrO_3 .

In binary acids such as HBr and HCl , the H–Br bond is longer than the H–Cl bond as Br is larger than Cl. The H–Br bond is therefore weaker than the H–Cl bond and HBr is thus a stronger acid than HCl .

- Describe the periodic trends of **either** atomic radius **or** of ionisation energy. Explain the trend in the property selected.

Atomic radius:

Atomic radius decreases across a period and increases down a group. The numbers of protons and electrons increase as you move across a row. Electrons in s or p orbitals are not shielded from the increasing nuclear charge and hence the effective nuclear charge (Z_{eff}) is increasing. This results in smaller orbitals and decreasing atomic radius. At the end of the row, the next electron goes into an s orbital of greater n . This orbital is shielded by electrons in the lower energy orbitals and there is a consequent big drop in Z_{eff} . The atomic radius thus increases going down a group.

Ionisation energy:

Ionisation energies increase across a row as the atoms become smaller. The smaller the atom, the more strongly the outer electrons are attracted to the nucleus and hence the higher the ionisation energy. Similarly, ionisation energies decrease down a group as the atoms become larger.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
2

- Order **either one** of the two following sets of oxides in terms of increasing acidity. Explain the reasons for your order.

1. HBrO_4 , H_3AsO_4 , H_2SeO_4 2. HClO_2 , HClO , HClO_4 , HClO_3 .**1. $\text{H}_3\text{AsO}_4 < \text{H}_2\text{SeO}_4 < \text{HBrO}_4$**

The acidic protons are all bonded to an O atom that in turn is bonded to the As, Se or Br. The more electronegative the central atom, the more electron density is drawn out of the O–H bond and the weaker this bond becomes. The weaker this bond, the stronger the acid. Acid strength therefore follows the electronegativity of the central atoms: $\text{Br} > \text{Se} > \text{As}$.

2. $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$

All are structurally $\text{H}-\text{O}-\text{Cl}(\text{O})_x$, where x is 0, 1, 2 or 3. Oxygen is a very electronegative atom and pulls electron density towards itself. The more O's bonded to the chlorine, the more pronounced this effect and the weaker the O–H bond becomes. The weaker this bond, the stronger the acid.

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Marks
2

- Explain in terms of their electronic configurations **and** ionisation energies why the halogens (Group 17) are powerful *oxidising* agents.

Oxidising agents are themselves reduced (*i.e.* they gain electrons).

The electronic configuration of the halogens (Group 17) is np^5 . They are small atoms (atomic size decreases across a period as the nuclear charge increases). In each period, the halogen is the element with the highest number of protons in the nucleus that also has an incomplete shell.

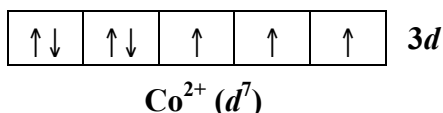
As a result, they will readily gain a single electron to form the X^- ion.

Similarly, the high nuclear charge and small size means that they have high ionisation energies. Hence halogens are poor reducing agents.

2

- Compounds of *d*-block elements are frequently paramagnetic. Using the box notation to represent atomic orbitals, account for this property in compounds of Co^{2+} .

A cobalt atom has 9 valence electrons: it is in Group 9 of the Periodic Table. A Co^{2+} cation has lost 2 electrons so has $(9 - 2) = 7$ valence electrons. The configuration of Co^{2+} is $3d^7$. These occupy the five *d*-orbitals to maximize the number of unpaired electrons (to minimize the electron-electron repulsion):



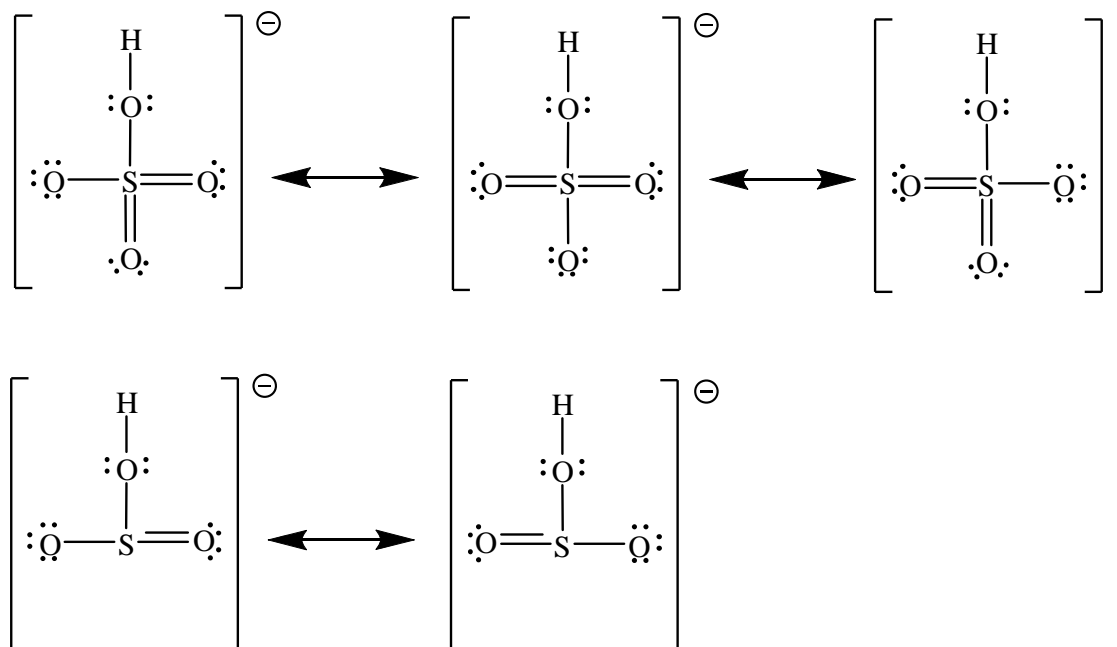
Paramagnetism arises as a result of the presence of 1 or more unpaired electrons. Co^{2+} has 3 unpaired electrons and so is paramagnetic.

Marks
2

- Explain why H_2SO_4 is a stronger acid than H_2SO_3 .

The acidity of oxo-acids increases as the number of oxygen atoms increases.

This is best understood in terms of the relative stability of the negative charge on the conjugate base, HSO_4^- and HSO_3^- :



The negative charge in HSO_4^- is delocalized over 3 oxygen atoms whereas that in HSO_3^- is delocalized over only 2 oxygen atoms. The greater stability of the HSO_4^- anion leads to the higher acidity of the conjugate acid, H_2SO_4 .

- Explain in terms of their electronic configurations **and** ionisation energies why the alkali metals (Group 1) are powerful *reducing* agents.

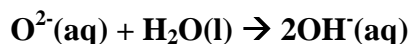
The alkali metals have a single electron in an *s*-orbital outside a noble gas full shell. As this electron occupies a new shell and orbits further from the nucleus, it can be removed (*ionized*) much more easily than for the noble gas.

As the alkali metals are in Group 1, they have the smallest nuclear charge in each period, and hence the lowest ionization energy in each period.

As the alkali metals have low ionization energies for removal of their single valence electron, they are powerful reducing agents – they cause electron gain in substances they react with.

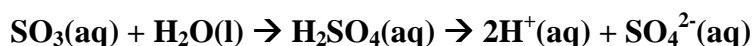
- Briefly explain how the concept of electronegativity can rationalise the existence of acidic, basic and amphoteric oxides.

Oxides of the *least* electronegative elements (the *most* electropositive elements – the metals) are very ionic. They consist of a cation and the oxide, O^{2-} , ion. The oxide ion is *extremely* basic. For example, it will react rapidly with water:

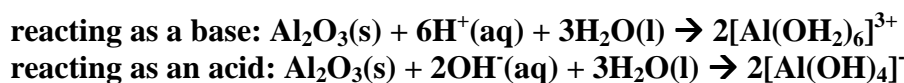


Dissolution of the oxide of an element of low electronegativity will result in a strongly basic solution.

The oxides of the *most* electronegative elements (the non-metals) are covalent and contain $E=O$ bonds (where E is the electronegative element). They react with water to form acids. For example, sulfur trioxide reacts with water to produce sulfuric acid which rapidly ionizes to give an acidic solution:



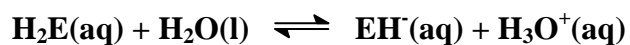
Elements with intermediate electronegativity form oxides which react with both acids and bases. As a result, they are classified as being amphoteric. Aluminium oxide is an example. It will dissolve in acidic and in alkaline solutions according to the reactions:



You would *not* have needed to remember these reactions of SO_3 or Al_2O_3 to get full marks on this question. They are given here as examples.

- Briefly explain why H₂Se is a stronger Brønsted-Lowry acid than H₂O and a weaker acid than H₂Te.

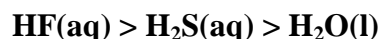
In general, when comparing binary acids within the same group, the strength of the bond E-H between the element (E) and hydrogen determines the acidity:



As the atomic size of E becomes larger, the E-H becomes longer and weaker. Thus H₃O⁺ is more readily formed in aqueous solution and acidity increases.

Marks
2

- Rank $\text{H}_2\text{O}(\text{l})$, $\text{H}_2\text{S}(\text{aq})$ and $\text{HF}(\text{aq})$ in order of their Brønsted acid strengths. Explain your reasoning.



The H–F bond is more polar than H–O so is easier to break HF into H^+ and F^- than to break H_2O into H^+ and OH^- . Hence HF is stronger acid than H_2O .

S is much larger atom than O, so the H–S bond is much longer and weaker than H–O; hence H_2O is weaker acid than H_2S .

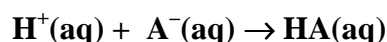
HF is stronger than H_2S because the small F^- ion bonds more strongly to the water molecules than does the larger HS^- ion.

4

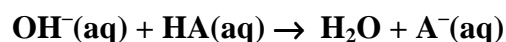
- Buffer systems are frequently used in chemistry. Briefly describe a buffer system and how it functions? Use equations where appropriate.

Buffer systems resist changes in pH. They consist of a weak acid (HA) and its conjugate base (A^-) in high concentrations.

If H^+ is added, it is consumed by the A^- ions:



If OH^- is added, it is consumed by the acid present:



If the amount of H^+ or OH^- added is too great, there may be insufficient HA or A^- present and so the buffer may not work.

What ratio of concentrations of acetic acid to sodium acetate would you require to prepare a buffer with $\text{pH} = 4.00$? The K_a of acetic acid is 1.8×10^{-5} M.

The pH of a buffer can be calculated using the Henderson-Hasselbalch equation can be used:

$$\text{pH} = \text{p}K_a + \log_{10} \left(\frac{[\text{base}]}{[\text{acid}]} \right)$$

For acetic acid, $\text{p}K_a = -\log_{10} K_a = -\log_{10}(1.8 \times 10^{-5}) = 4.74$. Thus to achieve pH 4.00, the ratio of base to acid must be:

$$4.00 = 4.74 + \log_{10} \left(\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \right)$$

$$\log_{10} \left(\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \right) = -0.74 \quad \text{or} \quad \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = 5.6$$

Answer: $\text{CH}_3\text{COOH} : \text{CH}_3\text{COO}^- = 5.6$

Marks
2

- Briefly explain why HF is a weaker Brønsted acid than HI and a stronger acid than H₂O.

F is more electronegative than O, so the H–F is more polarised bond than the O–H. This facilitates dissociation into F[−] and H⁺ ions.

I is much larger atom than F, so the H–I bond is much longer and weaker than H–F, so HF is weaker acid than HI.