**Marks
3**

- Consider the melting points of the following solids, which all have the halite crystal structure type.

solid	AgCl	KBr	KCl	NaCl
m.p. (°C)	455	734	770	801

Rationalise the order of the melting points of KBr, KCl and NaCl in terms of the size of the constituents and the strength of the interactions holding them together.

Melting an ionic solid involves breaking up the lattice: the more energy it takes to do this, the higher the melting point will be. The lattice energy depends on the:

- **The crystal structure adopted: as these salts all adopt the same halite crystal structure type, this is not a factor here.**
- **The charges on the cations and anions: as these salts all have a +1 cation and a -1 anion, this is not a factor here.**
- **The size of the cation and anion: the smaller these are, the closer they can approach and the larger the lattice energy will be:**

    (i)   **Br^- is bigger than Cl^- so KCl has a higher lattice energy and a higher melting point than KBr.**

   (ii)   **K^+ is larger than Na^+ so NaCl has a higher lattice energy and a higher melting point than KCl.**

The Ag^+ ion is intermediate in size between Na^+ and K^+. Why does AgCl have a melting point considerably lower than both KCl and NaCl?

When the relative electronegativity of the anion and cation are very different as in NaCl and KCl, the bonding is predominately ionic. Melting the solid requires breaking up the ionic lattice with its strong and long distance interactions.

As Ag^+ is much less electronegative than Na^+ and K^+, AgCl is much less ionic than NaCl and KCl and has the lowest melting point. There is considerable ionic character to the bonding in AgCl.

**Marks
3**

- Explain, with the aid of a diagram labelling all the key components, how sodium stearate ($C_{17}H_{35}COONa$) can stabilise long-chain non-polar hydrocarbons ("grease") in water.

Sodium stearate dissolves in water to give stearate ions which act as surfactants. They have non-polar (hydrophobic) "tails" that associate with grease and charged, polar (hydrophilic) "heads" that associate with water. This leads to the formation of stable spherical micelles in which the grease molecules are contained within a monolayer of stearate anions with their heads pointing outwards.
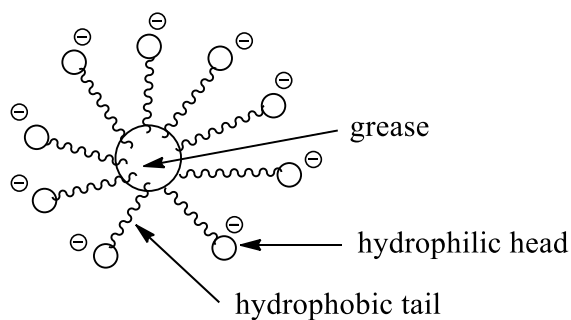
- Consider the complex $K_4[Mn(CN)_6]$. Describe and contrast the origin, strength and directionality of the chemical bonds in this compound (a) between C and N; (b) between the manganese and cyanide ions; and (c) between the complex and the potassium counterions.

6

C–N bonds are covalent. They are relatively short, strong and highly directional.

Mn–CN coordination bonds are due to the donation of the lone pair of electrons on C to the Mn^{2+}. These bonds are weaker, longer and less directional than covalent bonds.

$[Mn(CN)_6]^{4-}$ and K^+ are ionically bonded in the solid state due to coulombic attraction between the oppositely charged ions. These bonds are strong but not directional.

- The ionic solids NaCl, LiF, KF and LiCl, all have the same crystal structure. Assuming only electrostatic interactions are involved, use the information below to organise these four ionic solids in order of increasing energy of the crystal lattice.

ion	radius (10^{-12} m)	ion	radius (10^{-12} m)
Li^+	76	F^-	133
Na^+	102	Cl^-	181
K^+	138		

Working

The electrostatic attraction between the cations and anions in an ionic solid depends on:

- **The ionic charges: higher cation and anion charges lead to higher lattice energies. In these systems, the cations are all +1 and the anions all -1.**

- **The lattice structure: higher coordination numbers lead to higher Madelung constants and higher lattice energies. These systems all adopt the same structure (the rocksalt or NaCl structure).**

- **The separation of the cations and anions: higher ionic radii lead to longer separations and lower lattice energies.**

The cation – anion separation is given by the sum of the ionic radii:

- **NaCl: (102 + 181) = 283 pm, LiF: (76 + 133) = 209 pm,**
  KF: (138 + 133) = 271 pm, LiCl: (76 + 181) = 257 pm.

The order of the lattice energies is the same as that of these separations.

Increasing energy of the crystal lattice →

NaCl	**KF**	**LiCl**	**LiF**

- Explain why CsCl, NaCl and ZnS have different crystal structures.

1

The lattice energy is higher when the number of cations around the anions and the number of anions around the cations are both maximised. The relative sizes of the ions controls how many can be fitted around each one.

Cs^+ is the largest cation and can fit 8 Cl^- ions around it.
Na^+ is smaller and can only fit 6 Cl^- ions around it.
Zn^{2+} is even smaller and S^{2-} is larger than Cl^- so that only 6 anions can fit around the cation.

These 'radius – ratio' rules work best in very ionic systems. In those where covalency is also important, orbital overlap can also play a role. For example, ZnS is likely to be significantly more covalent than the alkali metal chlorides. The tetrahedral coordination of Zn^{2+} in ZnS may be partly due to covalency.

	Marks 5
• In the spaces provided, explain the meaning of the following terms. You may use an example, equation or diagram where appropriate.	

(a) antibonding orbital

A molecular orbital formed from 2 atomic orbitals with a nodal plane perpendicular to the interatomic axis and between the nuclei. It is higher in energy than the original atomic orbitals and occupation of it weakens the bond.

(b) paramagnetic

Materials that are attracted towards a magnetic field but have no magnetism in the absence of an applied field. Paramagnets are atoms, molecules or solids that have one or more unpaired electron spins resulting in a net magnet moment.

(c) ionic bond

The low energy state found in ionic solids associated with the Coulombic attraction of unlike charged ions.

(d) nuclear fission

The splitting of an unstable, neutron rich nucleus into smaller nuclides and neutrons and releasing energy in the process.

(e) electron affinity

The energy change that occurs when a mole of gaseous atoms or ions gains a mole of electrons. For example, the first electron affinity of an atom is the energy change accompanying the reaction $M(g) + e^- \rightarrow M^-(g)$. Electron affinities are positive if this process is favourable and negative if this process is unfavourable.