2013-N-2

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4. The unit cell is the simplest repeating unit of a lattice. Examination of the diagram shows there are 4 such units present.

Cu₂O

+I

 Cu^+ has 10 electrons in its 3*d* subshell. They are all paired as shown, so Cu^+ is diamagnetic, not paramagnetic.

$\uparrow \downarrow$	↑↓	↑↓	↑↓	$\uparrow\downarrow$
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The anionic radius of O^{2-} is the main factor determining the solid state structure of the oxides. The cations (Ag⁺ or Cu⁺) fit in the holes within the O^{2-} lattice.

2013-N-3

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potassium octachloridorhenate(III)-2-water





Reduction is the gain of 1 electron which is added to the LUMO δ^* anti-bonding orbital to give a paramagnetic species. This reduces the bond order from 4.0 to 3.5, thus weakening and lengthening the Re–Re bond.

2013-N-4

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The boron atom in B(OH)₃ is electron deficient. It acts as a Lewis acid by readily accepting the lone pair from the oxygen in a water molecule to go from sp^2 to sp^3 hybridisation.

2013-N-5

 $3.4 \times 10^{-7} \text{ M}$

 $\operatorname{Cu}^{2+}(\operatorname{aq}) + 4\operatorname{NH}_3(\operatorname{aq}) \quad \Longrightarrow \quad [\operatorname{Cu}(\operatorname{NH}_3)_4]^{2+}(\operatorname{aq})$

 $1.6 \times 10^{-6} \text{ M}$

No. Equilibrium constant K is very small so the reaction lies heavily in favour of reactants.

2013-N-6

There are 3 triple points:

rhombic, monoclinic and vapour (at 95.31 °C and 5.1×10^{-6} atm); monoclinic, liquid and vapour (at 115.18 °C and 3.2×10^{-5} atm); rhombic, monoclinic and liquid (at 153 °C and 1420 atm);

Rhombic is denser. If you start in the monoclinic region and increase the pressure at constant temperature *(i.e.* draw a vertical line upwards) you move into the rhombic region. Rhombic is thus the more stable form at higher pressures, so must be denser.

Rhombic sulfur is formed.

Correct reason. Plastic sulfur is not shown as it is a metastable state and changes into a more stable state over time. Phase diagrams only show stable states that are in equilibrium with other stable states. There are no conditions of temperature and pressure in which plastic sulfur **is in equilibrium** with another state of sulfur, so it does not appear on the phase diagram.

Based on the information provided, it is reasonable to assume that plastic sulfur is a compound formed by reaction of water with sulfur or some form of sulfur involving water in its crystal structure. Arguing that, and that the phase diagram for sulfur only shows pure forms of sulfur, was also awarded full marks.

2013-N-7

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The double bond is equally substituted, so attack of the electrophile H^+ is equally likely at C2 or C3. The carbocations at C3 and C2 should therefore be formed in equal amounts. Subsequent attack of the trigonal planar carbocation by Br⁻is equally likely from above or below the molecule. Attack at C3 produces only one compound. Attack at C2 produces either the (*R*)- or (*S*)- enantiomer in equal amounts.

Constitutional isomers

Enantiomers

The higher priority groups are methyl (at C2) and ethyl (at C3). These are on opposite sides of the double bond and hence the molecule has (E) stereochemistry.

Same ratio as for the (*E*) isomer, *i.e.* 50% A, 25% B, 25% C.



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 sp^2

 sp^3

sp

D is most basic. The sp^3 hybridised N has more *p* orbital character (75%) compared to sp^2 (67%) or sp (50%). **D** therefore has a more diffuse lone pair that is more available for protonation.





2013-N-9 (cont.)

• 1:1. Both products are formed from a common carbocation intermediate. There is no real preference for which H⁺ will be lost as both products (**H** and **I**) have the same degree of substitution (Saytsev's rule).

Elimination (E1) Addition (or catalytic hydrogenation) Oxidation

Nucleophilic addition (A_N)

2013-N-10

3-methylcyclohexanol

4



C₁: (*S*)- Around C₁, the order of priorities is: a: O > b: C₂(C,H,H) > c: C₆(C,H,H) > d: H To distinguish between C₂ and C₆, compare next C in chain b: C₃(C,C,H) > c: C₅(C,H,H) Looking down C₁-H bond, a \rightarrow b \rightarrow c is anticlockwise

C₃: (*R*)- Around C₃, the order of priorities is: a: C₂(C,H,H) > b: C₄(C,H,H) > c: C_{methyl}(H,H,H) > d: H As C₂ and C₄ are equivalent, C₁ > C₅ is used to prioritise them. Looking down C₃-H bond, a \rightarrow b \rightarrow c is clockwise





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2013-N-12

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substitution

H ₂ O or CH ₃ OH	H⊕	or	€ Line
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