2012-N-2

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- In the unit cell there are: 4 Pd atoms
 - 1 O atom in the centre

 $2 \times \frac{1}{2} = 1$ O atom at the top and bottom faces

 $4 \times \frac{1}{4} = 1$ O atom at the equatorial edges

 $8 \times \frac{1}{8} = 1$ O atom at the corners

This gives unit cell formula of Pd₄O₄ and thus empirical formula of PdO.

Pd: 4 Ni: 6

 $Pd^{2+}(d^8)$ prefers square planar coordination and thus has a lower coordination number than Ni²⁺. Also, the smaller Ni²⁺ can fit inside the interstitial sites of the close packed O²⁻ structure of NiO. Pd²⁺ is too large to pack like this.



2012-N-3

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.

potassium octachloridodimolybdate(II)



Oxidation is the loss of 1 electron which is removed from the HOMO δ bonding orbital to give a paramagnetic species. This reduces the bond order from 4.0 to 3.5, thus weakening and lengthening the Mo–Mo bond.

2012-N-5

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First order with respect to BrO_3^- First order with respect to Br^- Second order with respect to H^+ $3.6 \times 10^{-3} \text{ M s}^{-1}$ Rate = $k[BrO_3^-][Br^-][H^+]^2$ $k = 12 \text{ M}^{-3} \text{ s}^{-1}$

2012-N-6

• It has 2 triple points.

There is no gas/solid equilibrium line (*i.e.* Helium does not sublime). There is a liquid/liquid equilibrium line. The triple points involve 2 liquid phases. Helium cannot exist as a solid at atmospheric pressure.

No. If T > 5.2 K, helium exists as a supercritical fluid above $\sim 2 \times 10^5$ Pa and as a gas below this pressure.

The electrons are held very tightly in the 1*s* orbital as there is no shielding of the nucleus. The atom is therefore very small and the electron cloud is not very polarisable. As a result, the interatomic dispersion forces required for liquefaction are very weak and they can only operate at temperatures approaching absolute zero.



Markovnikov's rule. The H^+ of HBr adds to C1 leading to a secondary carbocation rather than to C2 which leads to a primary carbocation. The more substituted carbocation is more stable due to hyperconjugation.

2012-N-8

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sp

 sp^3

P is more basic. The sp^3 hybridised N has more *p* orbital character (75%) compared to sp (50%). **P** therefore has a more diffuse lone pair that is more available for protonation. Conversely, the lone pair in **Q** is more tightly bound and **Q** is therefore a weaker base.



 \mathbf{P} is more basic. The lone pair in \mathbf{R} contributes to the resonance structure and is partially delocalised into the carbonyl group and is therefore unavailable for protonation.

2012-N-9





C₂: (*R*)- Around C₂, the order of priorities is: a: C₁(O,O,C) > b: C₃(C,H,H) > c: C_{methyl}(H,H,H) > d: H Looking down C₂-H bond, a \rightarrow b \rightarrow c is clockwise

C₅: (*R*)- Around C₅, the order of priorities is: a: C(C,C,C) > b: C₆(C,H,H) > c: C₄(C,H,H) > d: H As C₄ and C₆ are equivalent, C₁ > C₃ is used to prioritise them. Looking down C₅-H bond (*i.e.* out of paper), a \rightarrow b \rightarrow c is clockwise •



A and B are constitutional isomers. A and C are constitutional isomers. B and C are diastereoisomers.



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 \mathbf{K} (the tertiary carbocation) is more stable than \mathbf{J} (the secondary carbocation) as it is more substituted and hence more stabilised by hyperconjugation.



Substitution at positions 2 and 4 is favoured over position 3 due to the relative stabilities of the Wheland intermediates. There are 4 resonance contributors for substitution at positions 4 (or 2), but only 3 for substitution at position 3. Position 4 is favoured over position 2 due to steric effects - the methoxy group attached to C1 physically blocks approach of the attacking carbocation.





2012-N-12



Steric effects. The CH_2 group is more accessible than the $CH(CH_3)$ group for S_N2 attack by the Cl^- nucleophile.

2012-N-13

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H = 4.2 I = 15.2 J = 9.9
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Four aromatic resonance stabilised structures.



Only 2 aromatic resonance stabilised structures. The non-aromatic structures are minor resonance contributors

K will be more acidic than **J** as the negative charge of the phenoxide ion can be delocalised into the nitro group, increasing the resonance stabilisation.

