Chemistry 1Adv/1SSP   (Chem1901/1903)   June 2007

2007-J-2

- a) A description of an atom or molecule with no unpaired electron spins and hence no nett magnetic moment.

  b) A low energy arrangement of two or more atoms arising from the delocalisation of electrons in molecular orbitals.

  c) The generation of heavier nuclei by the fusion of lighter nuclei.

  d) The attraction between a hydrogen atom bonded to a very electronegative atom (F, O or N) and electron lone pairs on another atom.

  e) The requirement that degenerate orbitals are all half-filled with electrons with parallel spins before any of the degenerate orbitals is filled.

  f) A material in which charged groups can flow in response to an applied electric field or potential. In the case where the material is a solid and the charged "groups" are electrons, this requires a small to zero band gap.

2007-J-3

- $^{36}_{16}S$

  $^{234}_{90}Th$

  $^{246}_{98}Cf$

- 92 Bq

- $^{33}_{17}Cl$ - A half life of 2.5 s is too short to allow for synthesis of host molecules, administration of the nuclide to the patient and measurement of the radiation emitted.

  $^{77}_{36}Kr$ - Krypton is noble gas and cannot be incorporated into a suitable host molecule for administration to the patient.

  $^{27}_{12}Mg$ - This nuclide is a β-emitter so little useful radiation would escape the body and local radiation damage would occur.

2007-J-4

- 1

  diamagnetic - all electrons are paired

  12

  $\sigma^2 \sigma^{*2} \sigma^2 \sigma^{*2} \sigma^2 \pi^4 \pi^{*4}$
  $\qquad \uparrow \uparrow \qquad \uparrow \uparrow$

2007-J-5

A	0	3	trigonal planar
B	2	2	bent
C	1	3	trigonal pyramidal

- 3.68×10^{-18} J   54.0 nm

2007-J-6

- 1. Solid is less dense than liquid.
  2. Density of liquid can decrease on cooling.
  3. Boiling point significantly higher than predicted by dispersion forces.
  4. Capable of dissolving ionic solids.

  Properties 1 and 2 are due to the tetrahedral arrangement of H atoms and lone pairs about the O. This results in a low density tetrahedral network being the most stable arrangement of H_2O molecules.

  Property 3 is due to the strong hydrogen bonds present in water.

  Property 4 is due to the strong ion-dipole interactions involving water.

  Biological specificity, *eg* smell, drug action
  Formation of liquid crystal phases.

- The presence of resonance Lewis structures indicates the presence of molecular orbitals that extend over more than a pair of atoms. This greater delocalisation of electrons produces lower energies and hence increased stabilisation of the molecule.

2007-J-7

- $CH_3NHNH_2(g) + {}^5\!/_2 O_2(g) \rightarrow CO_2(g) + N_2(g) + 3H_2O(g)$

  -1231 kJ mol^{-1}

  9.8 kJ g^{-1}

  N_2O_4 has b.p. of 21 °C, so no problems associated with handling cryogenic liquids. N_2O_4 and methylhydrazine are hypergolic - the reaction occurs spontaneously on contact.

2007-J-8

- 441 K
- 1.2×10^{-8} M $\qquad$ 3.0×10^{-14} M

2007-J-9

- 82 J K^{-1} (78 J K^{-1} if you fail to realise the density of water is 0.997 g cm^{-3} at 25 °C)
  16.1 kJ mol^{-1}

2007-J-10

- $NiO(s) + C(s) \;\rightleftharpoons\; Ni(l) + CO(g)$

  Spontaneous above 620 K

  Tungsten forms tungsten carbide if smelted with coke. Usually another reductant such as H_2 is used.

  Al is usually recovered electrolytically as smelting only occurs at temperatures well above 1800 K, which are not readily achieved.
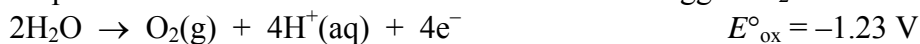
2007-J-11

- $$S(l) + O_2(g) \rightleftharpoons SO_2(g) \qquad K_p = \dfrac{p_{SO_2}}{p_{O_2}}$$
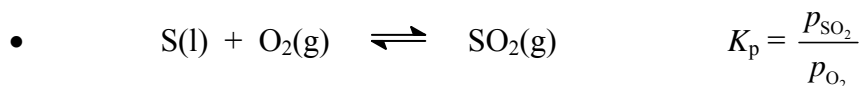
  High temperature drives the reaction to the left (exothermic), but high temp is used to increase the reaction rate. High pressure of O_2 drives reaction to the right.

  $$H_2SO_4(l) + H_2S(g) + O_2(g) \rightarrow 2SO_2(g) + 2H_2O(l)$$

  $$2MS(s) + 3O_2(g) \rightarrow 2MO(s) + 2SO_2(g)$$
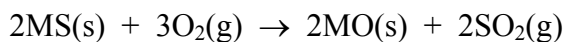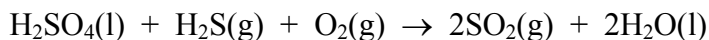
  The direct reaction between SO_3 and H_2O is too exothermic and boils the water creating a mist of sulfuric acid.

2007-J-12

- Relative kinetics of the two reactions; the overpotential for the formation of $O_2(g)$ is much greater than that for the formation of $Cl_2(g)$. Hence Cl_2 produced preferentially, despite the $E°$ values of the two oxidations which suggest O_2 should form.

  $$2H_2O \rightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad\qquad E°_{ox} = -1.23\ V$$
  $$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^- \qquad\qquad E°_{ox} = -1.36\ V$$

- 17.7 tonne
  5.91 tonne

2007-J-13

- In any spontaneous reaction, the entropy of the universe always increases.

  The enthalpy of reaction defines the heat released into or absorbed from the surroundings at constant temperature and pressure.

  The entropy change of the surroundings arises from the heat released:

  $$\Delta S_{surr} = q_{out} / T$$

  $$q_{out} = -\Delta H_{rxn} \text{ at constant } P$$

  Hence $\qquad \Delta S_{surr} = -\Delta H_{rxn} / T$

  The dimer is favoured at lower temperature.