Chemistry 1Adv/1SSP (Chem1901/1903) June 2006

2006-J-2

a) The principle that states that no 2 electrons in an atom can have the same set of quantum numbers.

b) A measure of the ability of an atom to attract the electron density in a covalent bond.

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

d) A description of an atom or molecule that has an unpaired electron spin that results in a net magnetic moment.

e) A semiconductor made by doping with Group 15 atoms. The extra electrons occupy orbitals in the conductance band. These few electrons are free to move and carry the current.

e) A bond formed by the end-to-end overlap of atomic orbitals. The maximum electron density is between the nuclei along the bond axis. It has lower energy than the atomic orbitals from which it was formed.

2006-J-3

• $^{55}_{25}$ Mn

 ${}^{0}_{-1}\beta$ or ${}^{0}_{-1}e$

• β^{-} decay

 β^+ decay or electron capture

 α decay

Electrons occupy certain stable "orbits" that correspond to the standing waves obtained by solving the Shrödinger Equation. Each solution (orbital) corresponds to a different allowed energy level. As a consequence of this;

(a) atoms do not spiral in towards the nucleus despite the electrostatic attraction between them.

(b) the light emitted by excited atoms is a series of discrete spectral lines corresponding to the energy differences between the allowed energy states.

2006-J-4

- LiF LiCl KF NaCl
- Each has a 1:1 ratio of cations to anions. The different crystal structures arise because of the relative differences in sizes between the cations and anions. eg the small Na⁺ ions can fit between the large Cl⁻ ions, whereas the larger Cs⁺ ions cannot.

2006-J-5

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 σ to π^* or π^* to σ^* (You can't really tell which is the smaller energy gap on the diagram.)

2006-J-6

- A 1 2 bent
 B 0 3 trigonal planar
 C 1 3 trigonal pyramidal
- $4.84 \times 10^{-18} \text{ J}$ 41.0 nm

2006-J-7

• $N_2(g) + 2H_2(g) \rightarrow N_2H_4(g)$ $N_2H_4(g) + O_2(g) \rightarrow N_2(g) + 2H_2O(g)$ 96 kJ mol⁻¹

• 216 K

2006-J-8

• NaNO₃(s) \rightarrow Na⁺(aq) + NO₃⁻(aq) 20.3 kJ mol⁻¹ 1.68 s

2006-J-9

• 0.631 atm 1.89 atm 8.07×10^{-3} atm

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 $\begin{array}{ll} {\rm Fe}^{2+}({\rm aq}) \to {\rm Fe}^{3+}({\rm aq}) \, + \, {\rm e}^{-} & E^{\circ}_{\rm ox} = -0.77 \ {\rm V} \\ {\rm O}_2({\rm g}) \, + \, 4{\rm H}^+({\rm aq}) \, + \, 4{\rm e}^{-} \to \, 2{\rm H}_2{\rm O} & E^{\circ}_{\rm red} = +1.23 \ {\rm V} \\ {\rm 4Fe}^{2+}({\rm aq}) \, + \, {\rm O}_2({\rm g}) \, + \, 4{\rm H}^+({\rm aq}) \to {\rm 4Fe}^{3+}({\rm aq}) \, + \, 2{\rm H}_2{\rm O} & E^{\circ}_{\rm cell} = +0.46 \ {\rm V} \\ {\rm Reaction is spontaneous so \ Fe}^{2+} \ {\rm unstable \ in \ presence \ of \ O_2/{\rm H}^+}. \end{array}$

 $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-}$ $E^{\circ}_{ox} = +0.44 V$

 $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$ $E^{\circ}_{ox} = +0.76 V$

So Zn(s) is oxidised preferentially to Fe(s).

$Cu^+(aq) + e^- \rightarrow Cu(s) \times 2$	$E^{\circ}_{red} = +0.53 \text{ V}$
$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$	$E^{\circ}_{ox} = -0.34 \text{ V}$
$2\mathrm{Cu}^{+}(\mathrm{aq}) \rightarrow \mathrm{Cu}^{2+}(\mathrm{aq}) + \mathrm{Cu}(\mathrm{s})$	$E^{\circ}_{cell} = +0.19 \text{ V}$

Therefore spontaneous disproportionation into Cu²⁺ ions and Cu metal.

2006-J-11

At the cathode, water is reduced to H_2 rather than sodium being reduced to Na metal due to the relative reduction potentials.

 $Na^{+}(aq) + e^{-} \rightarrow Na(s) \times 2 \qquad \qquad E^{\circ}_{red} = -2.71 V$ 2H₂O + 2e⁻ \rightarrow H₂(g) + 2OH⁻(aq) $E^{\circ}_{red} = -0.83 V$

At the anode, the overpotential for the formation of $O_2(g)$ is much greater than the overpotential 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.

 $\begin{array}{ll} 2H_2O \rightarrow O_2(g) + 4H^+(aq) + 4e^- & E^{\circ}_{ox} = -1.23 \text{ V} \\ 2Cl^-(aq) \rightarrow Cl_2(g) + 2e^- & E^{\circ}_{ox} = -1.36 \text{ V} \end{array}$

 $1.33 \times 10^{6} \text{ A}$ $1.44 \times 10^{8} \text{ kJ}$

2006-J-12

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 is $q / T = \Delta H_{\text{rxn}} / T$

melting of ice:	$H_2O(s) \rightarrow H_2O(l)$
burning of ethane	$2C_2H_6(g) \ + \ 7O_2(g) \ \rightarrow 4CO_2(g) \ + \ 6H_2O(g)$
freezing of water:	$H_2O(l) \rightarrow H_2O(s)$