Chemistry 1Adv/1SSP (Chem1901/1903) June 2005

- 2005-J-2
 - a) 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.

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

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

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

e) The enthalpy change that occurs when an atom gains an electron.

ie ΔH for the reaction M(g) + e⁻ \rightarrow M⁻(g)

2005-J-3

- 55_{25}^{55} Mn
 - $^{228}_{88}$ Ra
 - $^{218}_{85}At$
- 29 years

• non-toxic

not α or β^- emitter, ie either γ or β^+ emitter

half-life within range of 1 minute to 10 hours

chemically capable of being incorporated into appropriate molecule

easily produced or produced onsite

2005-J-4

• It showed that two pure substances could react in specific ratios to form another pure substance, indicating that chemicals were composed of smaller fundamental units (atoms) which could recombine to form other chemicals.

• atomic volume, stoichiometry of oxides, hydroxides, chloride and other compounds, melting points of elements and compounds, chemical reactivity, atomic mass

For atomic volume: Atomic volume increases going down the groups of the table as new valence shells are filled.

For stoichiometry of compounds: Compounds of elements in the same group show the same stoichiometry because they have the same configuration of valence electrons and therefore combine with the same number of atoms of another element to form a stable electronic configuration. Moving across a period, the stoichiometry changes as the number of valence electrons changes.

 $\bullet \qquad \qquad \mathrm{Na^+} \ < \ \mathrm{N} \ < \ \mathrm{P} \ < \ \mathrm{Na} \ < \ \mathrm{K}$



- Long-range Coulomb or electrostatic repulsion between protons acts to push them apart, but the short-range strong nuclear force between all nucleons (protons and neutrons) acts to hold the nucleus together. Neutrons thus contribute to the binding of the nucleus without also contributing to the electrostatic destabilisation.
- SiO_2 has no energy states separated by the energy of the photons in visible light, so it doesn't absorb light in the visible wavelength range and transmits it instead. Crystalline Fe has many energy states separated by the energies of all the photons in visible light, so it absorbs light across the entire visible wavelength range.

2005-J-6

•	А	0	3	trigonal planar
	В	1	3	trigonal pyramidal
	С	0	4	tetrahedral

 $n = 2 \rightarrow n = 1$ transition

3
4 (2 lone pairs)
$$\sigma^2 \sigma^{*^2} \overset{\downarrow}{\sigma^2} \overset{\downarrow}{\sigma^{*^2}} \pi^4 \sigma^2$$

2005-J-8

•
$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightarrow NO(g)$$

00.4 bJ m 1^{-1}

 90.4 kJ mol^{-1}

$$K_{c} = \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}} = \frac{\left[\frac{P_{C}}{RT}\right]^{c}\left[\frac{P_{D}}{RT}\right]^{d}}{\left[\frac{P_{A}}{RT}\right]^{a}\left[\frac{P_{B}}{RT}\right]^{b}} = \frac{P_{C}^{c}P_{D}^{d}}{P_{A}^{a}P_{B}^{b}} \times \frac{(RT)^{a+b}}{(RT)^{c+d}}$$
$$= \frac{P_{C}^{c}P_{D}^{d}}{P_{A}^{a}P_{B}^{b}} \times (RT)^{(a+b)-(c+d)} = \frac{P_{C}^{c}P_{D}^{d}}{P_{A}^{a}P_{B}^{b}} \times (RT)^{-\Delta n}$$

ie
$$K_c = K_p (RT)^{-\Delta n}$$
 or $= K_p = K_c (RT)^{\Delta n}$

2005-J-9

• $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ -55.8 kJ mol-1 Bond enthalpy refers to the reaction $H(g) + O(g) \rightarrow OH(g)$

2005-J-10

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2005-J-11

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$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^{-}$	$E^{\circ}_{ox} = -0.77 \text{ V}$
$H_2O + e^- \rightarrow \frac{1}{2}H_2(g) + OH^-(aq)$	$E^{\circ}_{\rm red} = -0.83 {\rm V}$
$Fe^{2+}(aq) + H_2O \rightarrow Fe^{3+}(aq) + \frac{1}{2}H_2(g) + OH^{-}(aq)$	$E^{\circ}_{\text{cell}} = -1.60 \text{ V}$
$Fe^{2+}(aq) + 2e^{-} \rightarrow Fe(s)$	$E^{\circ}_{red} = -0.44 \text{ V}$
$2H_2O \rightarrow O_2(g) + 4H^+(aq) + 4e^-$	$E^{\circ}_{ox} = -1.23 \text{ V}$
$Fe(s) + 2H_2O \rightarrow Fe^{2+}(aq) + O_2(g) + 4H^+(aq)$	$E^{\circ}_{\text{cell}} = -1.67 \text{ V}$

Both possible cell reactions are non spontaneous so Fe^{2+} stable in absence of O₂.

 5.02×10^{-3} atm

$\mathrm{Fe}^{2+}(\mathrm{aq}) \rightarrow \mathrm{Fe}^{3+}(\mathrm{aq}) + \mathrm{e}^{-}$	$E^{\circ}_{ox} = -0.77 \text{ V}$			
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O$	$E^{\circ}_{red} = +1.23 \text{ V}$			
$4 \text{Fe}^{2+}(aq) \text{ O}_2(g) + 4 \text{H}^+(aq) \rightarrow 4 \text{Fe}^{3+}(aq) + 2 \text{H}_2 \text{O}$	$E^{\circ}_{\text{cell}} = +0.46 \text{ V}$			
Reaction is spontaneous so Fe^{2+} unstable in presence of O ₂ .				

$\operatorname{Fe}^{2+}(\operatorname{aq}) \rightarrow \operatorname{Fe}^{3+}(\operatorname{aq}) + e^{-}$	$E^{\circ}_{ox} = -0.77 \text{ V}$
$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-}$	$E^{\circ}_{ox} = +0.44 \text{ V}$

So Fe(s) is oxidised preferentially to $Fe^{2+}(aq)$.

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

Therefore spontaneous disproportionation into Cu^{2+} ions and Cu metal.

2005-J-12

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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.

0.418 L

2005-J-13

The entropy of the universe always increases: ie $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$ At constant pressure, $\Delta S_{surr} = -\Delta H_{sys} / T$ Therefore $\Delta S_{univ} = \Delta S_{sys} - \Delta H_{sys} / T$ Therefore $-T\Delta S_{univ} = \Delta H_{sys} - T\Delta S_{sys}$ The Gibbs Free Energy is defined as $\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$ As *T* and *S*_{univ} are always positive for spontaneous reactions, ΔG_{sys} must be negative. melting of ice at 300 K: $H_2O(s) \rightarrow H_2O(1)$ burning of ethane $C_2H_6(g) + \frac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$ freezing of water at 200 K: $H_2O(1) \rightarrow H_2O(s)$