# **Ionization Enthalpies**

- Fairly low I. E
- First ionization enthalpy is around 600 kJ mol<sup>-1</sup>, the second about 1200 kJ mol<sup>-1</sup> comparable with those of calcium.
- Due to low I. E, lanthanides have high electropositive character

# **Coloured ions**

- Many of the lanthanoid ions are coloured in both solid and in solution due to f – f transition since they have partially filled f – orbitals.
- Absorption bands are narrow, probably because of the excitation within f level.
- La<sup>3+</sup> and Lu<sup>3+</sup> ions do not show any colour due to vacant and fully filled f- orbitals.

### Magnetic properties

- The lanthanoid ions other then the f<sup>0</sup> type (La<sup>3+</sup> and Ce<sup>3+</sup>) and the f<sup>14</sup> type (Yb<sup>2+</sup> and Lu<sup>3+</sup>) are all paramagnetic. The paramagnetism rises to the maximum in neodymium.
- Lanthanides have very high magnetic susceptibilities due to their large numbers of unpaired *f*-electrons.

### **Oxidation States**

- Predominantly +3 oxidation state.
- +3 oxidation state in La, Gd, Lu are especially stable (Empty half filled and Completely filled f – subshell respectively)
- Ce and Tb shows +4 oxdn state (Ce <sup>4+</sup> 4f<sup>o</sup> & Tb <sup>4+</sup>
  4f<sup>7</sup>)
- Occasionally +2 and +4 ions in solution or in solid compounds are also obtained.
- This irregularity arises mainly from the extra stability of empty, half filled or filled f subshell.

- The most stable oxidation state of lanthanides is +3. Hence the ions in +2 oxidation state tend to change +3 state by loss of electron acting as reducing agents whereas those in +4 oxidation state tend to change to +3 oxidation state by gain of electron acting as a good oxidising agent in aqueous solution.
- Why Sm<sup>2+</sup>, Eu<sup>2+</sup>, and Yb<sup>2+</sup> ions in solutions are good reducing agents but an aqueous solution of Ce<sup>4+</sup> is a good oxidizing agent?

### properties

- Silvery white soft metals, tarnish in air rapidly
- Hardness increases with increasing atomic number, samarium being steel hard.
- Good conductor of heat and electricity.
- Promethium Radioactive

# **Chemical Properties**

- Metal combines with hydrogen when gently heated in the gas.
- The carbides, Ln<sub>3</sub>C, Ln<sub>2</sub>C<sub>3</sub> and LnC<sub>2</sub> are formed when the metals are heated with carbon.
- They liberate hydrogen from dilute acids and burn in halogens to form halides.
- They form oxides and hydroxides, M<sub>2</sub>O<sub>3</sub> and M(OH)<sub>3</sub>, basic like alkaline earth metal oxides and hydroxides.



## **The Actinides**

- All isotopes are radioactive, with only <sup>232</sup>Th, <sup>235</sup>U, <sup>238</sup>U and <sup>244</sup>Pu having long half-lives.
- Only Th and U occur naturally-both are more abundant in the earth's crust than tin.
- The others must be made by nuclear processes.

- The dominant oxidation state of actinides is +3. Actinides also exhibit an oxidation state of +4. Some actinides such as uranium, neptunium and plutonium also exhibit an oxidation state of +6.
- The actinides show actinide contraction (like lanthanide contraction) due to poor shielding of the nuclear charge by 5f electrons.
- All the actinides are radioactive. Actinides are radioactive in nature.

### **Actinoide Contraction**

- The size of atoms / M<sup>3+</sup> ions decreases regularly along actinoid seris. The steady decrease in ionic/ atomic radii with increase in atomic number is called Actinoide Contraction.
- The contraction is greater from element to element in this series – due to poor shielding effect by 5 f electron.

### **Electronic configuration**

Element name S	Symbol	Z	Ln	Ln <sup>3+</sup>	Radius Ln <sup>3+</sup> / pm		
Actinium	Ac	89	[Rn] 6d <sup>1</sup> 7s <sup>2</sup>	[Rn]4f <sup>0</sup>	111		
Thorium	Th	90	[Rn ]5d <sup>2</sup> 7s <sup>2</sup>	[Rn]4f <sup>1</sup>			
Protactinium	Ра	91	[Rn]5f <sup>2</sup> 6d <sup>1</sup> 7s <sup>2</sup>	[Rn]4f <sup>2</sup>			
Uranium	U	92	[Rn]5f <sup>3</sup> 6d <sup>1</sup> 7s <sup>2</sup>	[Rn]4f <sup>3</sup>	103		
Neptunium	Np	93	[Rn]5f <sup>4</sup> 6d <sup>1</sup> 7s <sup>2</sup>	[Rn]4f <sup>4</sup>	101		
Plutonium	Pu	94	[Rn]5f <sup>6</sup> 7s <sup>2</sup>	[Rn]4f⁵	100		
Americium	Am	95	[Rn]5f <sup>7</sup> 7s <sup>2</sup>	[Rn]4f <sup>6</sup>	99		
Curium	Cm	96	[Rn]5f <sup>7</sup> 6d <sup>1</sup> 7s <sup>2</sup>	[Rn]4f <sup>7</sup>	99		
Berkelium	Bk	97	[Rn]5f <sup>9</sup> 7s <sup>2</sup>	[Rn]4f <sup>8</sup>	98		
Californium	Cf	98	[Rn]5f <sup>10</sup> 7s <sup>2</sup>	[Rn]4f <sup>9</sup>	98		
Einsteinium	Es	99	[Rn]5f <sup>11</sup> 7s <sup>2</sup>	[Rn]4f <sup>10</sup>			
Fermium	Fm	100	[Rn]5f <sup>12</sup> 7s <sup>2</sup>	[Rn]4f <sup>11</sup>			
Mendelevium	Md	101	[Rn]5f <sup>13</sup> 7s <sup>2</sup>	[Rn]4f <sup>12</sup>			
Nobelium	No	102	[Rn]5f <sup>14</sup> 7s <sup>2</sup>	[Rn]4f <sup>13</sup>			
Lawrencium	Lr	103	[Rn]5f <sup>14</sup> 6d <sup>1</sup> 7s <sup>2</sup>	[Rn]4f <sup>14</sup>			

### **Magnetic properties**

- Paramagnetic behaviour
- Magnetic properties are more complex than those of lanthanoids.

### M.P and B.P

High M.P and B.P

Do not follow regular gradation of M.P or B.P with increase in atomic number

### **IONISATION ENTHALPY**

• Low I.E. so electropositiity is High

**COLOUR** 

- Generally coloured
- Colour depends up on the number of 5 f electrons
- The ions containing 5 f ° and 5 f <sup>7</sup> are colouress

Eg –

U<sup>3+</sup> (**5** f<sup>3</sup>) – Red

NP <sup>3+</sup> (**5 f** <sup>4</sup>) – Bluish

Chemistryof Coordination Compounds

# Bonding in Coordination Compounds

- ✓ Review: ionic vs. covalent bond
- ✓ Review: electronic structure and periodic table
- ✓ Crystal Field Theory
- ✓ Spectrochemical Series
- ✓ Ligand Field Theory

Where are metals and non-metals in the periodic table ?

Where are the transition metals ?

Which elements form cations and which anions ?



1 H	<b>←</b> IA	E	N	Electronegativity (EN) VIIIA→											2		
2.2	IIA	0.7-	1.4				-		_	•		IIIA	IVA	VA	VIA	VIIA	110
3 Li	4 Be	1.5-	1.9									5 R	6 C	7 N	0 0	9 FI	10
1.0	1.5	20.	29									2.0	2.5	3.0	3.5	4.0	ive
11 Na	12 Mg	3.0-	4.0									13 Al	14 Si	15 P	16 6	17 CI	18 Ar
0.9	1.2	IIIB	IVB	VB	VIB	VIIB	<u>r</u>	VIIIB-		IB	IIB	1.5	1.8	2.1	2.5	3.0	~1
19 K 0.8	20 Ca 1.0	21 Sc 1.3	22 Ti 1.5	23 V	24 Cr 1.5	25 Mn 15	26 Fe	27 Co 1.8	28 Ni 1.8	29 Cu 1.9	30 Zn 1.6	31 Ga 1.6	32 Ge 1.8	33 As 2 0	34 So 24	35 Br 2 &	36 Kr
37 Ru 0.8	38 Sr 1.0	39 Y 1.2	40 Zr 1.4	41 Nb 1.6	42 Mo 1.8	43 Tc 1.9	44 Ru 2.2	45 Rh 2.2	46 Pd 2.2	47 Ag 1.9	48 Cd 1.7	49 In 1.7	50 Sn 1.8	51 Sb 1.9	52 Te 2.1	53 1 2.5	54 Xe
55 Cs 0.7	56 Ba 0.9	57 La 1.1	72 Hf 1.3	73 Ta 1.5	74 W 1.7	75 Re 1.9	76 Os 2.2	77 Jr 2,2	78 Pt 2.2	79 Au 2,4	80 Hg 1.9	81 TI 1.8	82 Pb 1.9	83 Bi 1.9	84 Po 2.0	85 At 2.2	86 Rn

Tutorial Video about chemical bonding

## How atoms form bonds ?

Atoms use their VALENCE ELECTRONS to exchange or share electrons to form bonds ! Examples: <u>how many VE</u> are in these elements ? Na Ca Cl Ar C N S P

Which rule can we find for the main group elements ?

# 8 electron rule (main group

Each elemente in group tends to get 8 valence electrons.

2 ways to do this:

- 1. Exchange electrons between 2 atoms
- 2. Share electrons

Example: NaCl vs. HCl vs. PCl3

### **Review:**

### Oxidation Numbers of Transition Metal Ions



In the ions, the energy of the 4s is higher than the 3d  $\Rightarrow$  in the ions the 4s electrons are removed first !

 $\Rightarrow$  +1 ONLY for Cu/Ag/Au ! (-1 for Au possible !)  $\Rightarrow$  +2 possible for nearly ALL metals ( => remove the two s electrons)

### Oxidation Numbers of Transition Metal Ions



Write the d electron number for each metal in the highest common ox. state (highest big dot for each element)

### 18 electron rule Transition metals (TM)

TM have d-orbitals which should be filled together with s and p orbitals -> 8 + 10 electrons !

### **Excurs: Hückel's rule**

"A planar ring system with  $4n+2\pi$ -electrons is aromatic" (n=0,1,2,...)

Are these molecules aromatic ? Cyclobutadiene Cyclopropene Cyclopentadienyl (-) ion Cyclooctatetraene

# **Ionic Bonding**

Two atoms <u>exchange electrons</u> ⇒ionic bond

Combination Metal – Non-Metal:

Fe 1.8  $\Leftrightarrow$  Cl 3.0 =>  $\Delta$ EN = 1.2 Na 0.9  $\Leftrightarrow$  Cl 3.2 =>  $\Delta$ EN = 2.3

High EN difference → high ionic character *(exceptions possible !)* 

# **Covalent Bond**

If the EN difference between two atoms is small (smaller than 1.7 as a rule), then the atoms SHARE unpaired electrons instead of exchanging them.

Number of valence electrons = number of bonds



form  $PCl_3$  ( $PCl_5$  also possible)

# Which kind of bond ?

Depends on the EN difference ("END") between 2 atoms:



CI-CI  $(\delta+)H-CI(\delta-)$  Na(+) CI(-)

# What kind of bond ? And which oxidation numbers ?

- Calciumcarbide Ca<sub>2</sub>C
- Methyl Lithium LiCH<sub>3</sub>
- Boronhydride BH<sub>3</sub>
- Tungstencarbide WC
- Nickelchloride NiCl<sub>2</sub>
- Ironpentacarbonyl Fe(CO)<sub>5</sub>
- Xenonflouride XeF<sub>4</sub>

# Hemoglobin

Iron(2+) ions are used to transport Oxygen in our bodies –

without Iron, no life !



### Chlorophyll



### Sun Protection Cream

... is made of Titanium Dioxide as very fine particles in a cream:



### **Cancer Treatment**

The growth of living cells can be blocked by a platinum complex:





### The d-block elements: transition **Metals** is sites of enzymes – hemoglobin (oxygen transport), nitrogenases (nitrogen fixation), hydrogenases, etc.



#### Hemoglobin Green shows Fe-containing site



Heme b

# **Nitrogen fixation**



Heterogeneous catalysis: *Haber-Bosch* process Homogeneous catalysis:



Nitrogenase structure





Vitamin B<sub>12</sub> is an example of an organometallic compound (containing metal-carbon bonds).



#### Fe(II) and Ti(IV) impurities in Al<sub>2</sub>O



Ruby Cr(III) impurities in Al<sub>2</sub>O<sub>3</sub>



#### Al(II) and Al



Hematite A mineral form of Fe<sub>2</sub>O<sub>2</sub>



How many groups of transition metals exist ? (compare to the 8 MAIN GROUP elements) And why ?

### d-Orbitals



#### Review of orbitals

### **VSEPR model**

### **Electron-Pair Geometries**





120°

109.5°

### **Electron-Pair Geometries**

<u>#E.P.s</u> Geometry

5 Trigonal Bipyramidal

6 Octahedral



### **The Trigonal Bipyramid**

There are two positions, axial and equatorial, and two bond angles - 90° and 120°.











Bonding e: 6 Non-bonding e: 0

Bonding e: 5 Non-bonding e: 1

Bonding e: 4 Non-bonding e: 2

### Energy Levels of d-Orbitals "Crystal

### In an atom, the d-orbitals have the same energy ("degenerated")

BUT: if molecules with high electron density approach the atom, then the energy levels for these 2 d-orbitals go up:



### Look from

the top down:



# Energy Change in "crystal field"









# **Colour of**



Depends on the energy difference between the lower and higher metal d-orbital levels !

Visible light is absorbed and pushes electrons up

=> The higher  $\Delta$ , the more "blue" is the light absorbed



Green colour => red is absorbed

#### **Conclusion:**

The energy absorbed by the green complex is lower than by the yellow complex.

Calculate the absorbed light energy – example red light absorbed (700 nm wavelength)

E = h \* c /  $\lambda$  = 6.6\*10^(-34) \* 3\*10^8 m/s / 700 \* 10^-9 m = 2.82 \* 10^(-19) J or 1.76 eV

Blue light absorbed (400 nm wavelength) E =

# **Spectrochemical Series**

The splitting energy depends on:

1. metal ion: high charge => high splitting : Ni(3+) > Ni(2+) high period => high splitting : Pd > Ni

```
Pt^{4+} > Ir^{3+} > Rh^{3+} > Co^{3+} > Cr^{3+} > Fe^{3+} > Fe^{2+} > Co^{2+} > Ni^{2+} > Mn^{2+}
```

2. ligands:
 empirical order by measurements = "spectrochemical series"
 CO S CN<sup>-</sup> > NO<sub>2</sub><sup>-</sup> > NH<sub>3</sub> > -NCS<sup>-</sup> > H<sub>2</sub>O > OH<sup>-</sup> F<sup>-</sup> -SCN<sup>-</sup> S Cl<sup>-</sup> > Br<sup>-</sup>
 strong-field ligands

# **Energy Calculations**

UV/VIS spectra: scala in cm<sup>-1</sup>=1/ $\lambda$  =v "wavenumber" BECAUSE: the wavenumber ~ energy (h\* v)

10.000 cm<sup>-1</sup> ≈ 120 kJ/mol ≈ 1.24 eV ≈

Example: Fe(H2O)62 + = d?

Compare the energy of low and high spin ! ( $\Delta = 10.400 \text{ cm} \cdot 1 / \text{P} = 17.600 \text{ cm} \cdot 1$ )

Is the complex dia- or paramagnetic ?

# **Coordination Numbers**

How many ligands will a metal ion have ?

### Tetrahedral Complexes ML<sub>4</sub>

In a tetrahedron, the ligands have the maximum distance to each other !

A tetrahedral complex, ML<sub>4</sub>



#### Which set of d-orbitals comes in closer contact to the ligands (and is therefore

#### de-stabilized ?



(draw typical orbitals into this picture and estimate the distances)

# **Energy Level Splitting**

How do we expect the d-energy levels to split up in a tetrahedral field ?



How many d-electrons are OK for tetrahedral?

# **Tetrahedral complexes**

Write ox.number of the metal and no. of d electrons:

[MnO<sub>4</sub>]<sup>■</sup> (permanganate) [CrO<sub>4</sub>]2- (chromate) [FeCl<sub>4</sub>]2-[CoCl4]2-[NiCl4]2-[ZnCl4]2-[ZnCl4]2-Ni(CO)4

Which 2 factors determine the geometry ??



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# Square planar from Octahedral

How would the d-orbitals split from an octahedral complex ?



How many d-electrons are OK for square-planar?





Identify the d-orbitals for each coordination !