Metal Oxides

Metal oxides are the compounds of oxygen and metals:
The study of metal oxides is central to solid state chemistry due to:
  ➔ stability
  ➔ ease of synthesis
  ➔ variable structure and composition

Properties:
1. Electrical properties are wide and varied
   ➔ insulators, e.g. CaO, TiO$_2$
   ➔ semiconductors, e.g. FeO
   ➔ metallic, e.g. TiO
   ➔ superconductors e.g. YBa$_2$Bu$_3$O$_7$.
2. Structural diversity
Metal Oxides

3. Variable magnetic properties
4. Compositional non-stoichiometry: many metal oxides show varied compositions that are often non-stoichiometric, e.g. Na$_{0.7}$WO$_3$.
5. Mixed valency: this is a common feature of TM oxides often associated with non-stoichiometry, e.g. Fe$_3$O$_4$.

Types of metal oxides:
1. Metal monoxides (MO) such as TiO and NiO

2. Binary- Most transition metals form binary oxides of formula $M_xO_y$

3. Ternary-These are composed of transition and pre- or post-transition elements forming an oxide. E.g. LaNiO$_3$ and PbTiO$_3$
Binary TM oxides- MO, MO₂ and MO₃

All of the 3d elements from Ti to Cu form a **monoxide**, either by direct combination of the elements or by reduction of a higher oxide by the metal.

- Most have the NaCl structure
- The oxides are basic, hence react with acids.
No oxides are known of the later transition elements 4dⁿ and 5dⁿ where n=7 or 9 (PGMs)

**Structural types:**
All binary oxides have structural forms in which the metal atom is octahedrally coordinated. These include:
1. Rock salt: The NaCl structure is the simplest for simple binary oxides  
   [REFER TO CHEM 210 NOTES FOR A REVISION]
2. Rutile: TiO₂.
Rutile (TiO$_2$) type

Rutile is the most important crystal form of titania, TiO$_2$.

Rutile or distorted rutile structures is also the common structure for metal dioxides (MO$_2$) $M = V$, Cr, Nb, Mo and Mn.

Remember: CrO$_2$ is ferromagnetic and used in the production of magnetic ‘chrome’ tapes.
Corundum ($\text{Al}_2\text{O}_3$) type

All the 3d elements from Ti to Fe give stable oxides with corundum type structures ($\text{M}_2\text{O}_3$). The relative closeness of pairs of metal atoms allows for intermetallic bonding with direct M-M bonds formed for e.g. with $\text{Ti}_2\text{O}_3$. All the oxides are ionic and predominantly basic. In air corundum is the most stable oxide for Cr, Mn and Fe.

Ternary variants are also important: formed by metallic substitution.

- ilmenite: $\text{FeTiO}_3$  
  Fe-Ti substitutes Al-Al pairs
- lithium niobate: $\text{LiNbO}_3$  
  Li-Nb substitutes Al-Al pairs.
**ReO$_3$ type**

Few TMs adopt the +6 oxidation state in an oxide, hence oxides of the stoichiometry MO$_3$ are very rare. ReO$_3$ and WO$_3$ are few examples. ReO$_3$ is a metallic binary oxide. This is important because it is parent of the perovskite structure to be discussed later.

The lattice can be viewed in several ways:

**Re-based** A cubic Re array with oxygens in the middle of each ’bond’ & Re at the corners.

**O-based** cubic array of oxygen octahedra with Re in the centre of each octahedron
Ternary oxides

Ternary oxides contain more than one metal ion, also referred to as complex oxides.

Structural types:
The structural types for ternary oxides are more complex than binary oxides, coordination around the metals vary.

Basically we will consider the two important types:

1. Spinels and inverse spinels
2. Perovskites
Spinels (MgAl₂O₄) and inverse spinels (NiFe₂O₄)

Spinels are compounds containing metals and group 16 elements of general formulae AB₂X₄.

A = metal ion in II, IV or VI formal oxidation state
B = metal ion in III, II or I formal oxidation state
X = O, S, Se or Te. Most spinels are O based.

\(X^{2-}\) anions form an almost perfect cubic close packed array

Total cation charge \((A + B) = 8\). **Remember A = 2B**

Unlike perovskites below the cations A and B are of similar size.

Most spinels are formed with a combination of \(A^{2+}\) and \(B^{3+}\) cations

ie \(A^{2+}B^{3+}_2O_4\) also possible is \(A^{4+}B^{2+}_2O_4\)

Normal spinel = \(A^{\varepsilon}B^{\sigma}_2O_4\) ➔
Inverse spinel = \(B^{\varepsilon}(AB)^{\sigma}O_4\) ➔
Spinels and inverse spinels

Typical examples are:

Fe$_3$O$_4$

Co$_3$O$_4$

Mn$_3$O$_4$

and mixed –metal oxides:

ZnFe$_2$O$_4$

All possess useful magnetic properties

**Fig. 23.24** A segment of the spinel (AB$_2$O$_4$) unit cell showing the tetrahedral environment of A ions and the octahedral environments of B ions. (Compare with Fig. 3.40.)
### Spinels and inverse spinels

**Occupation factor, $\lambda$, in some spinels**

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>Mg$^{2+}$</th>
<th>Mn$^+$</th>
<th>Fe$^{2+}$</th>
<th>Co$^{2+}$</th>
<th>Ni$^{2+}$</th>
<th>Cu$^{2+}$</th>
<th>Zn$^{2+}$</th>
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<td>$d^5$</td>
<td>$d^6$</td>
<td>$d^7$</td>
<td>$d^8$</td>
<td>$d^9$</td>
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<td>0</td>
<td>0</td>
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<tr>
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</tr>
<tr>
<td>Fe$^{3+}$</td>
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<tr>
<td>Co$^{3+}$</td>
<td>$d^6$</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

$\lambda = 0 \Rightarrow$ normal spinel; $\lambda = 0.5 \Rightarrow$ inverse spinel.

**The role of LFSE in determining spinel and inverse spinel structures**
Spinels and inverse spinels

Recall LFSE except for d⁰, d⁵ and d¹⁰ configurations where Δoct = Δtet, for all other configurations Δoct > Δtet.

Therefore the LFSE of d-metal ions can be used to explain site occupancies leading to either normal or inverse spinel structures.

Normal spinels:
1. Co₃O₄ ➔ Co(III) d⁶ ➔ (Co²⁺)ₜ(2Co³⁺)₀O₄
2. CdAl₂O₄ ➔ Cd(II) d¹⁰ ➔ (Cd²⁺)ₜ(2Al³⁺)₀O₄
3. Zn²⁺Al³⁺₂O₄
4. Mn²⁺Al³⁺₂O₄
5. Zn²⁺Fe³⁺O₄.

Inverse spinels:
1. Fe₃O₄ (Fe²⁺Fe⁺³₂O₄) ➔ Fe(II) d⁶ ➔ (Fe³⁺₀.₅)ₜ(Fe²⁺Fe³⁺₁.₅)₀O₄
2. NiFe₂O₄ ➔ Ni(II) d⁸ ➔ (Fe³⁺₀.₅)ₜ(Ni²⁺Fe³⁺₁.₅)₀O₄

Random structure:
NiAl₂O₄ ➔ Ni(II) d⁸ ➔ (Al³⁺₀.₇₅Ni²⁺₀.₂₅)ₜ(Ni²⁺₀.₇₅Al³⁺₁.₂₅)₀O₄
Spinels and inverse spinels

Q. Using LFSE predict which of the following is are normal and which are inverse spinels: You are given the oxidation state of one metal ion each as a guide.
Assume [Al(III)] and [Fe(II)]

1. CdAl$_2$O$_4$
2. MnAl$_2$O$_4$
3. ZnFeO$_4$
4. NiFe$_2$O$_4$
5. ZnAl$_2$O$_4$
6. NiAl$_2$O$_4$
7. Fe$_3$O$_4$

Applications:

- e.g. in Fe$_3$O$_4$ which is an inverse spinel $(Fe^{3+})(Fe^{2+}Fe^{3+})O_4$
- the Fe$^{2+}$ and Fe$^{3+}$ occupy the same lattice site making it a **good electrical conductor**.

Fe$^{3+}$ having an LFSE = 0 forms many inverse spinels of general formula AFe$_2$O$_4$ which are classified as **ferrites**
Perovskite (CaTiO$_3$) type

Perovskite is a ternary oxide structural type with the formula (ABO$_3$). Named after L. A. Perovski who identified the mineral CaTiO$_3$. The oxygens can be considered as cubic close packed, around which:

- $B$ is octahedrally coordinated to 6 oxygen atoms
- $B$ is a TM ion of high charge $+3$, $+4$ or $+5$
- $A$ is usually the larger cation
- $A$ occupies a site with 12-fold oxygen coordination.
- $A$ is most likely to be a pre- or post-transition element of lower charge $+1$, $+2$ or $+3$

Examples include of $A$ $\Rightarrow$ K (KTaO$_3$), Sr (SrRuO$_3$), La (LaVO$_3$)
Perovskite (CaTiO$_3$) type

(a) 12-fold coordination of the larger A cation (blue).
(b) 6-fold coordination of the B cation (red).
(c) The BO$_6$ octahedra link all vertices forming the same cubic framework as in the comparable ReO$_3$ structure.
**Perovskite (ABO$_3$) type**

Tolerance Factor ($t$) and conditions for a perovskite structure:

A is larger than B  
The overall charge sums ($A + B$) = 6  

The tolerance factor for perovskite structure,  

$$t = \frac{\sqrt{2} \times (r_A + r_O)}{2 \times (r_B + r_O)}$$

$r_A$, $r_B$ and $r_O$ = ionic radii of cations A, B and oxygen respectively.

For a perfect fit for A and B into the perovskite structure $t = 1$  
Deviations from $t = 1$ mean ions are too big or too small to fit this structural pattern due to strain which is often manifested as a distortion of the perovskite structure.

Acceptable $t$ limit for a perovskite structure is: $0.85 < t < 1.06$. 
Metal Oxides: Perovskite (CaTiO$_3$) type

Q.
(a) Use the following ions to write the structures of perovskite structures obtainable:
Y$^{3+}$, V$^{4+}$, Ba$^{2+}$, Fe$^{3+}$.

Answer: $\rightarrow$ YVO$_3$; YFeO$_3$; BaVO$_3$; BaFeO$_3$

(b) From the values Sr$^{2+}$ ($r = 158$ pm); Ti$^{4+}$ ($r = 74.5$ pm) and O$^{2-}$ ($r = 126$ pm) determine the value of the perovskite tolerance factor $t$, is this a perovskite?, write the possible formula of the compound formed.

Answer: $\rightarrow$ A = Sr and B = Ti, $t = 1.002$, a near perfect perovskite is formed. Sum of charges = 6. Therefore, formula = SrTiO$_3$.

(b) Determine whether the following are perovskites: LiNbO$_3$ and FeTiO$_3$. HAVE FUN.
Perovskites: LiNbO$_3$

This a typical example of an ABO$_3$ non-perovskite compound.

The Li$^+$ and the Nb$^{5+}$ ions are too small to fit into the perovskite structure producing a very small tolerance ratio.

Lithium cannot occupy the A site of 12-coordination. 4-6 is preferred.

Lithium niobate is also ferroelectric due to displacement of Li ions within the octahedral sites of six coordinated oxygens.

It is also electro-optic → application of an external electric field aligns the lithium ion displacements and also changes the refractive index of the material.

This has led to applications in optical devices.
Perovskites: $\text{BaTiO}_3$

Tolerance factor $= 1.06 \rightarrow$ distortion from a perfect spinel structure.

Ti ion occupies a site that is larger than it would prefer.

Ti is displaced by about $0.12 \text{Å}$ from the central site towards one of the oxide ions.

This displaces the charge distribution in the unit cell.

The displacement of charges results in tetragonal $\text{BaTiO}_3$ being ferroelectric due to the ordering of the resulting dipole moments.

The polarisation results in a very high dipole moment, hence $\text{BaTiO}_3$ is widely used in capacitors.

Charge displacement is common in perovskites:

$\rightarrow$ In $\text{PbZrO}_3$ the lead is displaced in opposite directions in adjacent unit cell

$\rightarrow$ antiferroelectric
Magnetic properties

**Paramagnetism:** is the magnetism associated with the random orientation of electron spins in partially filled d-orbitals with unpaired electrons. Paramagnetism is generally observed in:

1. solutions of TM compounds where discrete metal centres exist.
2. in solid materials at high temps. ⇒ any interaction of e⁻s btw metal centres is removed by thermally induced disorder.

In solid materials of ordered lattice, the unpaired electrons on individual metal centres can interact, resulting in any of the following alignments:

- **Ferromagnetism:** Parallel concerted orientation of magnetic moments.
- **Antiferromagnetism:** Anti-parallel orientation. Average mag. moment = 0.
- **Ferrimagnetism:** The individual electron spins is not parallel, but a measurable total mag. moment > 0 persists.
Magnetic properties

Superexchange via intervening ligands

Paired spins

Polarization (favourable alignment)

Paramagnetic
Ferromagnetic
Antiferromagnetic

Magnetic susceptibility, $\chi$

Temperature, $T$

$T_N$
$T_C$

antiferromagnetic
ferromagnetic
The temperature dependence of magnetic susceptibility

**Curie Temperature** $T_C$: The temperature at which a material undergoes a transition to a state where all the individual magnetic moments align (ferromagnetic) to an external field. This is accompanied by a surge in magnetic susceptibility as all the electrons line up in the same direction. Above $T_C$ the material is paramagnetic.

**Néel Temperature** $T_N$: The temperature at which a material undergoes a transition to a state where the individual electrons align half parallel and half antiparallel (antiferromagnetic) to an external field. This is accompanied by a marked drop in magnetic susceptibility. $T_N$ is often the temperature at which antiferromagnetism sets in when a paramagnetic material is cooled. This occurs by the mechanism of superexchange via an M-O-M link.

E. g., MnO (122 K); Cr$_2$O$_3$ (310 K); FeO (198 K); CoO (271 K) and NiO (523 K).
Electrical properties

Electronic structure of a solid is characterized by bands of orbitals separated by gaps in the energy where there are no orbitals.
The band gap

Whether there is a gap or not depends on the separation of the orbitals and the strength of the interaction between the atoms. With a stronger interaction the bands widen and may overlap.

The Fermi level ($E_F$) is the highest occupied state in a solid at $T = 0$. It is simply the level to which a band structure is filled.

It lies near the centre of the band and if the band is partially full, the electrons close to $E_F$ can easily be promoted to any empty levels, resulting in electrical mobility $\rightarrow$ conduction.
The band gap arises from molecular orbitals being slightly different in energy, which arises from the different degrees of bonding in each.

At the bottom of the band you have the lowest energy MO which has all bonding character. At the top, with highest energy is a MO with all anti-bonding character.

Therefore the rest of the band is formed from all the MO’s with intermediate bonding character between the two extremes.

Band gap determines the minimum photon energy required to excite an electron up to the conduction band from the valence band.

The band gap is important as the size of it determines whether you are looking at an insulator, semiconductor or a metallic conductor.
IONIC SOLIDS – bonding due to transfer of charge from one atom to another. Energy bands formed from the atomic orbitals of anions and cations.

COVALENT SOLIDS – bonding due to overlap and sharing of electrons. Bands formed from bonding molecular orbitals (filled bands) and antibonding orbitals (empty bands).

METALLIC SOLIDS – bonding due to orbital overlap forming a delocalised cloud of electrons. Overlap of atomic orbitals can be so strong that bands are formed which are much broader than the original energy separation of the orbitals, thereby ensuring conduction.
Insulators have a full valence band separated from the next energy band, which is empty, by a large, forbidden gap.

Diamond is an excellent insulator. It has a band gap of approximately 6eV which is very large.

This means very few electrons have sufficient energy to be promoted and the conductivity is negligibly small.

When conductivity of insulators is able to be measured it is found to increase with temperature.

Therefore this classification is often disregarded for the TM oxides.
Semiconductors

Semiconductors have a similar band structure to insulators but the band gap is not very large and some electrons have sufficient thermal energy to be promoted up to the empty conduction band.

Semiconductors can be split into two groups. **intrinsic** and **extrinsic** semiconductors.

Intrinsic semiconductors are pure materials. The number of electrons in the conduction band is determined only by the size of the band gap and the temperature.

Higher Temp. ➔ more electrons ➔ more conduction.

Extrinsic semiconductors are materials where the conductivity is controlled by adding dopants with different numbers of valence electrons to that of the original material.
Doping semiconductors

There are two fundamental differences between extrinsic and intrinsic semiconductors:

1) At standard temperatures extrinsic semiconductors tend to have significantly greater conductivities than comparable intrinsic ones.

2) The conductivity of an extrinsic semiconductor can easily and accurately be controlled simply by controlling the amount of dopant which is introduced. Therefore materials can be manufactured to exact specifications of conductivity.

The doping process may produce n- or p-type semiconductors.
Controlled valency semiconductors

p-type semiconductors: low oxidation state TM oxides → e. gs. MnO, Cr$_2$O$_3$, CuO, and FeO.

n-type semiconductors: higher oxidation state TM oxides → e. gs. Fe$_2$O$_3$, MnO$_2$, and CuO.

Some transition metal compounds can be conductors due to the presence of an element in more than one oxidation state. NiO is a very good example.

On oxidation the compound goes black and becomes a relatively good conductor. Some of the Ni$^{2+}$ ions have been oxidised to Ni$^{3+}$ and some Ni$^{2+}$ ions diffuse out to maintain charge balance leaving cation holes.

The reason for the conduction is the ability of electrons to transfer from Ni$^{2+}$ to Ni$^{3+}$ ions.
Q. Predict p- or n-type semi conductivity: \( V_2O_5, CoO, MgO, WO_3 \) and CdO.

Q. Predict p- or n-type semi conductivity: Ga-doped Ge, As-doped Ge

Ga-doped Ge.
Gallium has three valence electrons while germanium has four. Therefore each gallium atom introduced will create one less electron in the germanium lattice \( \Rightarrow \) **p-type semi conductor** is predicted

As-doped Ge.
Arsenic has five valence electrons compared to four in germanium, hence every atom of As introduced will create one more electron in the Ge lattice \( \Rightarrow \) **n-type semi conductor** is predicted

**Summary:** Doping any material with another material of lower oxidation state \( \Rightarrow \) **n-doping**
Doping with a higher oxidation state material \( \Rightarrow \) **p-doping**

THINK ABOUT THIS \( \Rightarrow \)
Is As-doped Bi n- or p-type or NONE?
Metallic conductors vs. semiconductors

A metallic conductor has electric conductivity that decreases with an increase in temperature. This is because higher $T \rightarrow$ increased vibration of atoms $\rightarrow$ disrupted orderliness $\rightarrow$ lower conduction. An ordered lattice is necessary for metallic conductivity $\rightarrow$ E.g. TiO.

This is opposite the conductivity of semiconductors. Higher $T \rightarrow$ increased vibration $\rightarrow$ increased ability of electrons or holes to migrate from one localised metal atom to another $\rightarrow$ e.g. NiO.
Conditions for good overlap of d band

(1) The formal charge of the cations is small.
Therefore TiO is metallic whereas TiO$_2$ is an insulator.

(2) The cation occurs early in the transition series.
Therefore TiO and VO are metallic whereas NiO and CuO are poor semiconductors.

(3) The cation is in the 2nd or 3rd transition series.
Therefore Cr$_2$O$_3$ is a poor conductor whereas the lower oxides of Mo and W are good conductors.

(4) The anion is reasonably electropositive.
Therefore NiO is a poor conductor whereas NiS and NiSe are good conductors.
**High temperature superconductors (HTSC)**

Characteristics of superconductors (SC):

1. For each SC material there exist a critical temperature $T_c$ below which it is SC ($T_C$ is different from $T_c$).

2. SC means the material has zero electrical resistance.

3. SC materials also exhibit an exclusion of magnetic field—Meissner effect.

4. SC in metals (K): Zn (0.88); Cd (0.56); Hg (4.15); Pb (7.19); Nb (9.50).

Examples of HTSCs include: $YBa_2Cu_3O_{7-x}$ ($T_c = 93$ K)—YBCO 123 and $Tl_2Ba_2Ca_2Cu_3O_{10}$ ($T_c = 134$ K).

Both are built on some form of the perovskite structure with layers of CuO$_n$ ($n= 4, 5, 6$) forming part of the structure.
Rechargeable battery materials

\[
\text{LiC}_6 + \text{LiCoO}_2 \xleftrightarrow{\text{charge}} \text{C}_6 + \text{Li}_{x+1}\text{CoO}_2
\]

This is the lithium ion rechargeable battery used in laptop computers and cell phones.

Anode: \[
\text{LiCoO}_2 \rightarrow \text{CoO}_2 + \text{Li}^+ + e^-
\]

Cathode: \text{graphitic carbon} \[
\text{C}_6 + \text{Li}^+ + e^{-} \rightarrow \text{LiC}_6
\]

Lithium (very light; standard potential = -3.04) ions move between the anode (cobalt \text{Co}^{\text{III}} \text{ to Co}^{\text{IV}}) and the cathode (graphite).

Battery is rechargeable because both anode and cathode host Li$^+$ ions.

The layered structure of the anode ensures the ease of mobility of the Li$^+$ ions between charging and discharging cycles.

High capacity and great reversibility (about 500 charge/discharge cycles)

Main drawback is the high price and toxicity of cobalt.
Synthesis of metal oxides

Direct synthesis

Many complex inorganic solids including complex oxide materials can be synthesised by direct reaction of the components at high temperature for extended periods of time. Even complex oxides may be easily obtained by simply grinding together and heating component oxides of each metal precursor over several days:

**$\text{BaTiO}_3$:** $\text{BaCO}_3(s) + \text{TiO}_2(s) \xrightarrow{\text{1000 °C}} \text{BaTiO}_3(s) + \text{CO}_2(g)$

**$\text{YBa}_2\text{Cu}_3\text{O}_7$:** \(\frac{1}{2} \text{Y}_2\text{O}_3(s) + 2 \text{BaCO}_3(s) + 3 \text{CuO} \xrightarrow{\text{930 °C/air and 450 °C C/O}_2} \text{YBa}_2\text{Cu}_3\text{O}_7(s) + 2 \text{CO}_2(g)\)

**$\text{Tl}_2\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{12}$:** $\text{Tl}_2\text{O}_3(l) + 2 \text{BaO}(s) + 3\text{CaO}(s) + 4 \text{CuO}(s) \xrightarrow{\text{400 °C}} \text{Tl}_2\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{12}(s)$

High temperatures and long reaction times are often required since the energy required to overcome lattice enthalpies and ensure diffusion of the ions through the solid structures are enormous.
Q. Briefly describe using a chemical equation how you would synthesize the following quaternary oxides:

1. \( \text{Ca}_4\text{Mn}_3\text{O}_{10} \)

2. \( \text{NdBa}_2\text{Cu}_3\text{O}_7 \)

3. \( \text{SrMoO}_4 \)

4. \( \text{Sr}_3\text{Fe}_2\text{O}_7 \)

\[ \text{Chemical vapour deposition (CVD) techniques} \]