Descriptive chemistry of 3d metals

Chemistry has come a long way from early alchemy

Paracelsus; father of modern medicine used chemicals to treat people in 1526.

| TABLE 24.1 Selected Properties of Elements of the First Transition Series |
|-----------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                           | Sc  | Ti  | V   | Cr  | Mn  | Fe  | Co  | Ni  | Cu  | Zn  |
| Atomic number             | 21  | 22  | 23  | 24  | 25  | 26  | 27  | 28  | 29  | 30  |
| Electron config.          | 3d^24s^2| 3d^24s^2| 3d^24s^2| 3d^24s^2| 3d^24s^2| 3d^24s^2| 3d^24s^2| 3d^24s^2| 3d^24s^2| 3d^24s^2|
| Metallic radius, pm        | 161 | 145 | 132 | 125 | 124 | 124 | 124 | 125 | 126 | 133 |
| Ionization energy, kJ/mol  |     |     |     |     |     |     |     |     |     |     |
| First                      | 631 | 658 | 650 | 653 | 717 | 759 | 758 | 737 | 745 | 906 |
| Second                     | 1235| 1310| 1414| 1592| 1509| 1561| 1646| 1753| 1958| 1733|
| Third                      | 2389| 2663| 2828| 2987| 2957| 3252| 3893| 3554| 3833|
| E°, V                      | -2.03| -4.63| -11.03| -0.90| -1.18| -0.440| -0.277| -0.257| -0.340| -0.763|
| Common positive oxidation states | 3  | 2, 3, 4 | 2, 3, 4, 5 | 2, 3, 4 | 2, 3, 4, 5 | 2, 3, 4, 5 | 2, 3, 4, 5 | 2, 3, 4, 5 | 2, 3, 4, 5 | 2, 3, 4, 5 |
| mp, °C                     | 1397| 1672| 1710| 1900| 1424| 1530| 1495| 1455| 1083| 420 |
| Density, g/cm³             | 3.00| 4.50| 6.11| 7.14| 7.43| 7.87| 8.90| 8.91| 8.95| 7.14|
| Hardness†                  |     |     |     |     |     |     |     | 9.0 | 5.0 | 4.5 |
| Electrical conductivity‡   | 3   | 4   | 6   | 12  | 1   | 16  | 25  | 23  | 33  | 27  |

* Each atom has an argon inner-core configuration.
† For the reduction process, M^+(aq) + e^- → M(s) [except for scandium, where the ion is Sc^3+(aq)].
‡ The most important oxidation states are printed in red.
§ Hardness values are on the Mohs scale (see Table 22.2).
‖ Electrical conductivity compared with an arbitrarily assigned value of 100 for silver.
i) Density
- Generally greater than 5 gm mL\(^{-1}\), e.g.,
  - Vanadium: 6.10 gm mL\(^{-1}\)
  - Niobium: 8.56 "
  - Molybdenum: 10.28 "
- Max Osmium: 22.7 gm mL\(^{-1}\)
- Except for:
  - Scandium: -3.01 gm mL\(^{-1}\)
  - Yttrium: -4.47 "
  - Titanium: -4.51 "
- As the atomic weight increases across the periodic table, the density increases and the atomic size decreases (e\(^{-}\)'s are filling in the same shell)

ii) Atomic & Ionic Radii
- From left to right on the PT, the atomic size decreases due to the increase in nuclear charge.
- Down the group, the size of the 3\(^{rd}\) element is expected to be greater than the 2\(^{nd}\) element.
- But it is not the case:
  - Cr: 1.28 Å, Mn: 1.27 Å
  - Mo: 1.39 Å, Tc: 1.36 Å
  - W: 1.39 Å, Re: 1.37 Å
- The reason is due to the lanthanide contraction (e\(^{-}\)'s are entering the 4\textit{f} electron shell i.e. inner shell)
- Poor shielding of nuclear charge by 4\textit{f} electrons
iii) Melting & boiling point

- High melting point compared to group 1 and 2 metals

<table>
<thead>
<tr>
<th>Element</th>
<th>Mp (°C)</th>
<th>Bp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scandium (Sc)</td>
<td>1539</td>
<td>2748</td>
</tr>
<tr>
<td>Vanadium (V)</td>
<td>1915</td>
<td>3350</td>
</tr>
<tr>
<td>Manganese (Mn)</td>
<td>1240</td>
<td>2060</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>1535</td>
<td>2750</td>
</tr>
<tr>
<td>Ruthenium (Ru)</td>
<td>2280</td>
<td>4050</td>
</tr>
<tr>
<td>Osmium (Os)</td>
<td>3045</td>
<td>5025</td>
</tr>
</tbody>
</table>

- The reason is due to their closed packed structure and strong metallic bonding

iv) Ionization potential (IP)

- Across from Left to right on the PT, there is slight increase of the IP (decrease in radii and increase in nuclear charge)
- Down the group the IP decreases (however, in the lanthanide group the IP goes up due to lanthanide contraction)

v) Magnetic properties

- In paramagnetic atoms and ions, there are unpaired spins.
- The magnetic fields are randomly arranged, though, unless placed in an external magnetic field.
vi) Thermal and Electroconductivity

Electron-Sea Model

- Metals can be thought of as cations suspended in “sea” of valence electrons.
- Attractions hold electrons near cations, but not so tightly as to impede their flow.
- This explains properties of metals:
  - Conductivity of heat
  - Electricity
  - Deformation

Solid ionic compound

Molten ionic compound

Ionic compound dissolved in water
i) Noble

- Generally are not reactive. This is due to their relatively:
  - Small in size
  - High ionization energy
  - High heat of atomization
  - High hydration energy

- This tendency increases down the group. E.g.
  - **Mn** reacts readily with dilute H$_2$SO$_4$ or HCl while **Tc** and **Re** will only react with strong acid.
  - **Cr** reacts readily with dilute HCl while **W** will only react with a mixture of strong HF/HNO$_3$ acid.
  - **Fe** most reactive. Reacts readily with O$_2$ and moist air (rust) while **Ru** and **Os** will not react readily with O$_2$ only at high temp and not also with dilute acids.


ii) Catalytic activity

- Transition metals and their compounds are good catalysts due to the fact that they have:
  - Large surface area
  - Variable oxidation state

\[
\begin{align*}
PdCl_2 + C_2H_4 & \rightarrow CH_3CHO \\
Pd + HCl & \rightarrow PdCl_2 \\
CH_3CHO + Pd + HCl & \rightarrow H_2O
\end{align*}
\]
• Down the group the catalytic activity increases (due to increase in surface area)

• T-metals have variable oxidation state. The energy difference between the suborbital is very small. Hence any electron can be used for bonding (chemical reaction)

• Down the group the lower oxidation state decreases in stability. Implying that Ti-acceptor stabilize T-metal in lower oxidation state. (in other words higher oxidation state are more stable and they offer better distribution of high charge density)

• The lower oxidation state are reducing (basic) while the higher oxidation state are oxidizing (acidic)

• The various oxidation state and energy level provide many pathways (intermediates)

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**Summary of some properties**

1. Have large charge/radius ratio
2. Are hard and have high densities
3. Have high melting and boiling points
4. Form compounds which are often paramagnetic
5. Show variable oxidation states
6. Form coloured ions and compounds
7. Form compounds with profound catalytic activity
8. Form stable complexes.
Platinum Group Metals

- **Rhodium**, **Iridium**, **Palladium** and **Platinum** are all face-centered cubic.
  - They are all oxidized by O₂, F₂ and Cl₂.

**Palladium**

- Pd has a highest oxidation state of +4 but +2 is the most common.
- \([\text{Pd(H}_2\text{O)}_4\text{]}^{2+}\) occurs in aqueous solution.
- The coordination number rarely exceeds six and Pd(II) is a “class b” (soft) metal. *(read HSAB concept)*
- Pd⁰ is employed like Pt⁰ as a heterogeneous reduction catalyst dispersed on activated charcoal.
- Coordinates to alkynes to alkenes to alkanes, nitro groups to amines.

**The Trans effect**

- This refers to a particular effect on selectivity of reaction products.
- In square planar arrangements the ligand *trans* to the new incoming ligand affects the regiospecificity of the reaction and thus the geometry of the final product.

- In the following reaction there are two possible products, *cis* and *trans*.
• Surprisingly, only a single major product is formed, in this case a **Cis product**.

• Experimentally a number of square planar reactions were carried out and *priority* or *order* of ligands and their **trans directing effect** was measured relative to each other.

• From this a series was elucidated.

  *i.e.* the order of increasing **trans** directing ability:

  \[
  F^- < OH^- < H_2O < NH_3 < py < Cl^- < Br^- < I^- < SCN^- < NO_2^- < CH_3^- < H^- < PR_3^- < C(NH_2)_3^- < CO < C_2H_4
  \]

• Another example is shown below: NO_2 > Cl^- so the **trans** product predominates.

• Therefore in the previous example Cl^- > NH_3 so the **cis** product predominates.

Another example is shown below: NO_2 > Cl^- so the **trans** product predominates.
Exercise

Use the trans effect series to suggest synthetic routes to cis- and trans-\([\text{PtCl}_2(\text{NH}_3)_2]\) from \([\text{Pt(NH}_3)_4]^{2+}\) and \([\text{PtCl}_4]^{2-}\).

Solution

- Reaction of \([\text{Pt(NH}_3)_4]^{2+}\) with HCl leads to \([\text{PtCl(NH}_3)_3]^+\)
- Because the trans effect of Cl\(^-\) is greater than that of NH\(_3\), substitution reactions will occur trans to Cl\(^-\) and further addition of HCl will give trans-\([\text{PtCl}_2(\text{NH}_3)_2]\)
- To synthesize the cis- compound use the starting material \([\text{PtCl}_4]^{2-}\).
- Reaction with NH\(_3\) leads to \([\text{PtCl}_3(\text{NH}_3)]^-\).
- The second step will involve substitution of one of the two trans Cl\(^-\) ligands with NH\(_3\) to give the cis- \([\text{PtCl}_2(\text{NH}_3)_2]\)

Homework exercise

- Given the reactants PH\(_3\), NH\(_3\) and \([\text{PtCl}_4]^{2-}\), propose an efficient route to both cis- and trans-\([\text{PtCl}_2(\text{NH}_3)(\text{PH}_3)]\).

Isolation of Palladium and Platinum

Ores: Braggite (Pt, Pd, Ni - sulfides); Cooperite (Pt, Pd – sulfides); Sperrylite (PtAs\(_2\)) and Laurite (RuS\(_2\))

Overall process:
1. Crushing of ore followed by floatation (concentration techniques)
2. Gravity filtration followed by roasting of the sulfide aggregates
3. Chlorination of the solids at 500 °C to make them water soluble
Separation methodology

Metal concentrates
Aqua regia → Residue Ru, Rh, Ir and AgCl
H₂AuCl₄
H₂PdCl₄
H₂PtCl₆
FeCl₂ or HCl; Cl₂; 550°C → ppt H₂AuCl₄
H₂PdCl₄
H₂PtCl₆
NH₄Cl → Solution of H₂PdCl₄
ppt (NH₄)₂PtCl₆ → 1. Excess Ammonium hydroxide
2. "Trans" product
Repurify → cis-[PtCl₂(NH₃)₂]²⁻
H₂O → Ignite → ppt trans-[PtCl₂(NH₃)₂]²⁻
Pt metal → Ignite → Pd metal

Homework exercise

- Write full balance equations and explain each reaction given in the previous chat.

Actinides
- Thorium to lawrencium (14 elements) Z = 90-103
- Analogous to lanthanides but the valence electrons are found in the 5f orbitals.
- Thorium, protactinium and uranium are the only naturally occurring species; the rest are generated synthetically (known as the trans-uranium elements or transuranic elements i.e. with atomic numbers greater than 92)
- All the natural elements are generated by the decay of ²³⁸U.

\[ \text{α = alpha particle, He}^{2⁺}; \quad \beta^- = \text{electron emission}; \quad \beta^+ = \text{positron emission} \]

\[
\begin{align*}
²³⁸\text{U} & \xrightarrow[92]{\text{α}} ²³⁴\text{Th} \\
²³⁴\text{Th} & \xrightarrow[90]{\beta^-} ²³⁴\text{Pa} \\
²³⁴\text{Pa} & \xrightarrow[91]{\beta^-} ²³⁴\text{U} \\
²³⁴\text{U} & \xrightarrow[92]{\beta^-} ²³⁰\text{U}
\end{align*}
\]
Oxidation states

- Thorium (Th) +4
- Protactinium (Pa) +5 (most stable)
- Uranium (U) +6 (higher achievable, +2, +3 more common)

The metals tarnish in air forming an oxide "coat"

They react with steam evolving H₂ gas

Common compounds include halides, carbides and nitrides

Lattice structures are:
- Th = Face-centered cubic (FCC)
- Pa = Cubic
- U = Cubic

Isolation of Uranium

- Ore is mined in South Africa
- The ore is crushed (ground down) and concentrated (floatation)
- Leaching is next performed with sulfuric acid

\[
\text{UO}_2^+ + \text{H}_2\text{SO}_4 \rightarrow [\text{UO}_2(\text{SO}_4)_3]^{4+}
\]

- An extraction process which employs an organic soluble ligand is added to the solution. This will allow the isolation of the uranium by selective solubility into an organic layer.
- The complex dissolves in a paraffin type hydrocarbon solvent e.g. kerosene, hexane, etc.
The types of ligands used can form a “ion pair” arrangement with the overall negative complex ion species
e.g. tertiary trioctylamine (alamine 336)

\[
[HN(C_8H_{17})_3]_4^+ + [HN(C_8H_{17})_3]_4^-
\]

This in turn leads to the complex:

- The kerosene can be re-used as dilute ammonia will precipitate UO$_2^+$ (i.e. removes the alamine 336).
- This “yellow goop” is allowed to dry and form a “cake”, this is sometimes sold as is.
- The material is then “roasted” giving off H$_2$O and N$_2$.
- The final product is usually thus U$_3$O$_8$ (Triuranium octoxide)
- U$_3$O$_8$ Olive green to black, odorless solid