Chem Factsheet

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Inorganic Reaction Trends

The importance of reaction trends in chemistry cannot be overstated. In 1869 Dmitri Ivanovich Mendeleev (1834-1907) published his periodic table of the elements. He did this when only some sixty-odd elements were known. He arranged these elements into horizontal rows (periods) and vertical columns (groups) based on their properties. Mendeleev understood the importance of trends by leaving gaps for elements yet to be discovered (e.g. gallium and germanium). He used the properties of known elements in the missing element's groups and periods to predict the properties of the missing elements. Understanding trends greatly reduces the number of chemical facts that need to be remembered and, just as for Mendeleev, allows prediction of properties of elements and compounds not actually studied.

The chemical properties of the elements principally depend upon their electronic configurations plus the proton numbers of the atoms.

1. Trends in Chemical Properties of Elements in the Same Group

The following statements apply to atoms of elements on moving down a group.

(i) The atoms have the same number and type(s) of electrons in their outer shell. e.g. All electronic configurations for Group VII atoms end ns^2np^5 where n is the energy level.

(ii) There is one extra shell of electrons that is further from the nucleus than the outer shell of electrons of the previous element. The atomic radius increases down a group. Also, since there are more inner shells, shielding of the outer electrons from the nuclear charge increases. Hence, for atoms of metallic elements, electrons are easier to lose and, for atoms of non-metallic elements, electrons are harder to gain as the attraction for outer electrons weakens.

(iii) The numbers of protons (Z) increases. Although an increase in Z would be expected to make electrons harder to lose and easier to gain it is out-weighed by the weakening effects of the previous two factors; increased atomic radius and increased shielding.

(a) The Redox (Displacement) Reactions of Group 7 - the Halogens with AQUEOUS Halide Ions (X^-)

Trend 1

The elements become weaker oxidising agents on moving down Group 7.

The lower the element is in the group, the less it will displace halogens from halide solutions.

Reason

Electrons are less readily gained by the halogen atom (i.e. poorer oxidant) —because the atomic radius increase and shielding increase out-weigh the increase in Z— resulting in an overall decreased attraction between nucleus and outer electrons.

When halogens are added to separate solutions of halides ions (e.g. NaX(aq)) the ionic equations ($Na^+(aq)$ is a spectator ion) for the reactions are:

$Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$.

Orange solution formed (red solution in organic solvent)

$Cl_2(aq) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$.

Brown solution formed (purple solution in organic solvent)

$Br_2(aq) + 2I^-(aq) \rightarrow 2Br^-(aq) + I_2(aq)$.

Brown solution formed (purple solution in organic solvent)

Chlorine displaces both bromine and iodine, bromine displaces iodine but not chlorine and iodine displaces neither chlorine nor bromine. Hence, $Cl_2 > Br_2 > I_2$ in its ability to displace halogens from halides. i.e. $Cl_2 > Br_2 > I_2$ in oxidising power since the halogen takes electrons from the halide.

Being redox reactions, these displacement reactions can be described in terms of half-equations.

Hence, for example, chlorine reacting with sodium bromide solution gives:

Reduction: $Cl_2(aq) + 2e^- \rightarrow 2Cl^-(aq)$ and

Oxidation: $2Br^-(aq) - 2e^- \rightarrow Br_2(aq)$ (Na^+ is a spectator ion)

Trend 2

The halide ions become stronger reducing agents on moving down the group. (The lower the halide ion in the group the more halogens it will reduce.)

Reason

Electrons are more easily lost by the halide ion on moving down the group (i.e. stronger reductant) — because the atomic radius increase and shielding increase out-weigh the increase in Z — resulting in an overall decreased attraction between nucleus and outer electrons.

Note: The greater the oxidising power of a halogen, the weaker the reducing power of its halide ion. e.g. F_2 is the most oxidising halogen in group 7 but F^- is the least reducing halide.

b) The Acid-Base and Redox Reactions of SOLID Ionic Halides with Concentrated Sulfuric Acid

When concentrated sulfuric acid is added to a solid ionic halide the initial observation is the production of faint white fumes due to the production of colourless hydrogen halide gases which then "fume" on reacting with water vapour in moist air.

Thus KF, KCl, KBr and KI produce HF, HCl, HBr and HI respectively. Bronsted-Lowry acid-base reactions have occurred since the sulfuric acid has donated a proton to the halide ion which has accepted it to form the hydrogen halide.

The equation with KF is

$KF(s) + H_2SO_4(l) \rightarrow KHSO_4(aq) + HF(g)$.

Similar acid-base reactions occur with the other solid halides.

Having formed the hydrogen halide, it *may* then reduce the concentrated sulfuric acid as it bubbles through it..

Trend

As trend 2 above. i.e. the lower the halide in the group, the greater the amount of reduction of conc. H_2SO_4.

For KF and NaF:

The halides of HF and HCl are too weakly reducing to reduce the conc. H_2SO_4 so no further reaction occurs.

For KBr:

HBr reduces the H_2SO_4 to SO_2 (pungent smell). The HBr is oxidised to Br_2 (orange vapour).The oxidation state of S has decreased by 2 units (+6 in H_2SO_4 to +4 in SO_2) and that of Br has increased by 1 unit (-1 in HBr to 0 in Br_2)

Half-equations:

$2Br^- - 2e^- \rightarrow Br_2$ and $SO_4^{2-} + 4H^+ + 2e^- \rightarrow SO_2 + 2H_2O$

(+2 e^- since Ox No +6 to +4)

Ionic equation:

$SO_4^{2-} + 4H^+ + 2Br^- \rightarrow SO_2 + Br_2 + 2H_2O$;

(or $H_2SO_4 + 2HBr \rightarrow SO_2 + Br_2 + 2H_2O$)

For KI:

HI reduces the H_2SO_4 firstly to SO_2 (pungent smell), then to S (yellow solid) and finally to H_2S (bad-eggs smell). The HI is oxidized to I_2 (purple vapour which may sublime to a black solid). The oxidation state of S has decreased by 8 units overall (+6 in H_2SO_4 to -2 in H_2S) and that of I has increased by 1 unit (-1 in HI to 0 in I_2). Half-equations and equations can be written to any of the reduction products. Those to H_2S are:

Half-equations:

$2I^- - 2e^- \rightarrow I_2$ and $SO_4^{2-} + 10H^+ + 8e^- \rightarrow H_2S + 4H_2O$

(+8 e^- since Ox No +6 to -2)

Ionic equation:

$SO_4^{2-} + 10H^+ + 8I^- \rightarrow H_2S + 4I_2 + 4H_2O$

(or $H_2SO_4 + 8HI \rightarrow H_2S + 4I_2 + 4H_2O$)

2. Trends in the Chemical Properties of the Elements in Period 3.

a) The Redox Reactions of Sodium and Magnesium with Water.

Sodium reacts very rapidly with water. Because of the exothermic nature of the reaction, it melts to a silvery ball which shoots about the surface, becoming smaller until it has all reacted producing a colourless solution. The pH of this solution is 14 showing a high concentration of hydroxide ions has been produced.

The half-equations are:

$Na - e^- \rightarrow Na^+$ and $H_2O + e^- \rightarrow OH^- + \frac{1}{2}H_2$.

Ionic equation:

$Na + H_2O \rightarrow Na^+ + OH^- + \frac{1}{2}H_2$

The reaction of magnesium with cold or hot water is very, very slow. Heated Mg and *steam* produce a bright white light and a white solid.

The half-equations are:

$Mg - 2e^- \rightarrow Mg^{2+}$ and $H_2O + 2e^- \rightarrow O^{2-} + H_2$.

Equation: $Mg(s) + H_2O(g) \rightarrow MgO(s) + H_2(g)$

Sodium is a stronger reducing agent than magnesium since the sodium atom only has to lose one outer electron whereas the magnesium atom must lose two outer electrons. The energy required to ionise Na (I_1) is considerably less than that to ionise Mg ($I_1 + I_2$).

b) The Redox Reactions of Na, Mg, Al, Si, P and S Elements of Period 3 with Oxygen.

All these elements combine directly with oxygen to form oxides. Some of these elements form more than one oxide but only one oxide of each element will be considered. All the elements form an oxide which is a white solid except for sulfur which forms an oxide that is a colourless, pungent smelling gas.

Sodium when heated burns with a yellow flame:

$2Na(s) + \frac{1}{2}O_2(g) \rightarrow Na_2O(s)$

Magnesium when heated burns with a bright white flame:

$Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$

Aluminium when heated burns with a bright white flame:

$2Al(s) + 1\frac{1}{2}O_2(g) \rightarrow Al_2O_3(s)$

Silicon when strongly heated reacts: $Si(s) + O_2(g) \rightarrow SiO_2(s)$

White phosphorus when warmed burns with a very bright white flame: $P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$

Sulfur when heated burns with a blue flame:

$S(s) + O_2(g) \rightarrow SO_2(g)$

Trend

The oxidation state of the *atom in the oxide* increases from left to right across the period. It increases in steps of 1 from +1 in Na_2O to + 5 in P_4O_{10}. Sulfur breaks this trend since the oxidation state of S in SO_2 is +4.

c) The Reaction of Certain Period 3 Oxides with Water

Trend
If the oxide reacts with water the pH of the resulting solution decreases from left to right.
The pH of the solutions begin at 14 for group 1 and decrease to 0 (SO_3) for group VI.

The degree of acidity is related to the type of bonding in the oxide. The less ionic / more covalent the bond the lower the pH of the solution.

Electronegativity difference (Δ_{en}), bond type, structure, solubility of oxide and pH of any aqueous solution.

	Na & O	Mg & O	Al & O	Si & O	P & O	S & O
Δ_{en}	2.6	2.3	2.0	1.7	1.4	1.0
Bonding	Most ionic	Less ionic	Least ionic	Least covalent	More covalent	Most covalent
Structure	Giant ionic	Giant ionic	Giant ionic	Macromolecular	Simple molecular	Simple molecular
Solubility	V. soluble	Sparingly	Insoluble	Insoluble	Very soluble	Very soluble
pH solution	14	8-9	insoluble	insoluble	0	0(SO_3); 3(SO_2)

Sodium oxide is very soluble in water. The oxide ion is a base and accepts a proton from a water molecule. A high concentration of hydroxide ions is produced making the solution very alkaline, pH = 14.

Hydrolysis of the oxide ion:
$O^{2-}(aq) + H_2O(l) \rightarrow 2OH^-(aq)$ - - - (1) (Na^+ is a spectator ion)

The equation: $Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$ fails to show that only the oxide ion reacts and OH^- ions are formed thus making the solution alkaline.

Magnesium oxide is very sparingly soluble in water so there fewer free oxide ions to hydrolyse by equation (1).
The concentration of hydroxide ions is much lower and so the pH is about 8/9.

- Aluminium oxide is insoluble in water. The pH is that of water, pH 7.
- The oxides with ionic bonding ,when they are soluble, produce alkaline solutions.
- Silicon dioxide, a macromolecule, is insoluble in water. The pH is that of water, pH 7.

The molecular oxides are all hydrolysed by water forming acidic, colourless solutions.

$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$. Strong acid, pH = 0,
$H_3PO_4(aq) \rightarrow H^+(aq) + H_2PO_4^-(aq)$

$SO_3(l) + H_2O(l) \rightarrow H_2SO_4(aq)$. Strong acid, pH = 0,
$H_2SO_4(aq) \rightarrow H^+(aq) + HSO_4^-(aq)$

$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$. Weak acid, pH = 2-3,
$H_2SO_3(aq) \rightleftharpoons H^+(aq) + HSO_3^-(aq)$

- `The *covalent, molecular oxides* of non-metallic elements produce acidic solutions.

3) Thermal Decomposition of Carbonates and Nitrates of Groups I and II

Trend 1
On moving down either group, carbonates and nitrates become more thermally stable.

Reason
The polarising power of the cation (its ability to distort the electron distribution in the anion) decreases as its charge density decreases because its size increases whilst its ionic charge is constant).

Trend 2
Moving across a period from Group 1 to Group II the thermal stability of the carbonates and nitrates decrease.

Reason
The polarising power of the cation increases as its charge density increases because its charge increases (1+ to 2+) and its size decreases.

At sufficiently high temperatures, all carbonates decompose to produce a white solid oxide and a colourless gas. Those with cations of high charge density are more likely to decompose. Experiment shows that only Li_2CO_3, $MgCO_3$ and $CaCO_3$ are decomposed at the temperature of a Bunsen flame – only Li^+, Mg^{2+} and Ca^{2+} are charge dense enough to polarise and destabilise the carbonate anion.

The general equation are:
Gp I: $M_2CO_3(s) \rightarrow M_2O(s) + CO_2(g)$;
Gp II: $MCO_3(s) \rightarrow MO(s) + CO_2(g)$

Using a Bunsen flame, all Group II nitrates and *only lithium nitrate* from group I decompose to produce a white solid oxide and a reddish brown mixture of nitrogen dioxide and oxygen gas. This is because the charge density of the M^{2+} cation is high enough to polarise the N-O bond and break it and form an O^{2-} ion.

Group II general equation:
$M(NO_3)_2(s) \rightarrow MO(s) + 2NO_2(g) + ½O_2(g)$.

$2LiNO_3(s) \rightarrow Li_2O(s) + 2NO_2(g) + ½O_2(g)$.

The other nitrates of Group I decompose as follows:
$MNO_3(s) \rightarrow MNO_2(s) + ½O_2(g)$ since the polarising powers of their cations is not sufficiently high to produce oxide ions.

Practice Questions

1. Aqueous solutions of chlorine, bromine and iodine are separately added to aqueous solutions of sodium fluoride, sodium chloride, sodium bromide and sodium iodide. Describe what is seen in the test tubes where a reaction occurs and name the products responsible for the observations. Write any one ionic equation with state symbols. State and explain two trends that this experiment illustrates.

2. Describe what is seen when concentrated sulphuric acid is added to separate samples of solid sodium fluoride, sodium chloride, sodium bromide and sodium iodide. Write ionic equations for any two redox reactions that occur. Give two reasons why these reactions should be done in a fume cupboard. Explain why the observations show that the reducing ability of the halide ion increases from Cl^- to I^-.

3. Two compounds, both with the formula X_2O_2, produced solutions when added to separate samples of water. One solution had a pH of 0 and the other a pH of 14. What type of bonding is present in each oxide and suggest which groups of the periodic table the elements X may be found.

4. Explain, including equations, why different types of products occur when sodium nitrate and magnesium nitrate are heated.

Answers

1.

	to aq NaF	to aq NaCl to	aq NaBr	to aq NaI
Chlorine added	Pale green of Cl_2 remains	Pale green of Cl_2 remains	Orange solution of Br_2 produced	Brown solution of I_2 produced
Bromine added	Orange of Br_2 remains	Orange of Br_2 remains	Orange of Br_2 remains	Brown solution of I_2 produced
Iodine added	Brown solution of I_2 remains	Brown solution of I_2 remains	Brown solution of I_2 remains	Brown solution of I_2 remains

$Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$
or $Cl_2(aq) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$
or $Br_2(aq) + 2I^-(aq) \rightarrow 2Br^-(aq) + I_2(aq)$.

The *halogens become less oxidising down group VII* because their atoms gain electrons less easily as the radius increases and the shielding of the nuclear attraction increases.

The *halides become more reducing down group VII* because these ions lose electrons more easily as the radius increases and the shielding of the nuclear attraction increases.

2. See 2 b). Other equations: $SO_4^{2-} + 4H^+ + 2I^- \rightarrow SO_2 + I_2 + 2H_2O$; $SO_4^{2-} + 8H^+ + 6I^- \rightarrow S + 3I_2 + 4H_2O$.
Hydrogen halides are acidic choking gases. SO_2 has a pungent smell. H_2S smells of bad eggs/is poisonous.

3. pH = 0. X_2O_2 has covalent bonding. Groups 5, 6 or 7. pH = 14. X_2O_2 has ionic bonding. Groups 1 or 2.

4. $NaNO_3 \rightarrow NaNO_2 + \frac{1}{2}O_2$ and $Mg(NO_3)_2 \rightarrow MO + 2NO_2 + \frac{1}{2}O_2$

Mg^{2+} has a higher charge and a smaller ionic radius (a higher charge density) than Na^+ and so has a higher polarising power. Mg^{2+} polarises the N-O bond sufficiently for it to break and form an oxide ion.

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