Group 1A: The alkali metals

The elements of group 1A, lithium, sodium, potassium, rubidium, caesium and francium are called the **alkali metals**. Not much is known about the last one mentioned, since it is radioactive and all its isotopes are exceedingly short-lived: It is formed during the radioactive decay of actinium. Some physical properties of group 1A elements are given in the table 1 below:

Table 1 Some physical properties of alkaline metals

Elements	Atomic number	Electronic configuration	M.P. /^0C	B.P. /^0C	Atomic radius (nm)	ionic radius (nm)	1st Ionization energy /kJ mol^{-1}	Std. Electrode potential /V
Li	3	2.1	180	1326	0.133	0.060	520	-3.04
Na	11	2.8.1	98	883	0.157	0.096	496	-2.71
K	19	2.8.8.1	64	756	0.203	0.133	418	-2.92
Rb	37	2.8.18.8.1	39	688	0.216	0.148	403	-2.92
Cs	55	2.8.18.18.8.1	29	690	0.235	0.169	374	-3.02

Properties of group one elements

1. All alkali metals have one electron in the outermost shell proceeded by a closed shell containing eight electrons except lithium which has a closed shell of two.

2. The alkali metals are extremely reactive and electropositive metals. In chemical combinations, this single electron is very readily transferred, giving a metal ion of single positive charge with a stable electronic configuration of a noble gas. Compounds of the alkali metals are therefore ionic and exist as high melting point solids. Li^+ due to its smallest size polarizes anions most strongly and thus its compounds are highly covalent which is why they are soluble in organic solvents.

3. Alkali metals have lower ionization energies than any other group of similar elements. This is the reason why the single electron is readily transferred during chemical reactions.

4. The atoms and ions of alkali metals increase in size with increasing atomic number, since each succeeding member has an extra closed shell of electrons.

5. All the alkali metal compounds give characteristic flame colorations that can be used to identify them e.g. lithium (red), sodium (yellow), potassium (lilac), rubidium (red) and caesium (blue).

7. The alkali metals are soft and silvery coloured: They are good-conductors of heat and electricity. Because they rapidly tarnish in air, they are generally stored under oil.

8. Lithium has extraordinary higher while sodium has lower electrode potentials than expected:

Reason: An element with a high negative electrode potential value is the one that readily loses electrons and forms positive ions. Such elements are however, said to be electropositive. Electropositivity increases down a group of the periodic table.

The ease of formation of M^+ (aq) ion from M(s) in its standard state is measured by the standard electrode potential for M^+ (aq)/M (s) couple; or less accurately, by the standard enthalpy of formation of M^+ (aq). The order is Li 〉 K = Rb 〉 Cs 〉 Na, as shown below:

Table 2 The enthalpy of formation of hydrated ion (M^+ (aq)) and standard electrode potential of group 1 elements

	Li	K	Rb	Cs	Na
Enthalpy of formation of M^+ (aq) / $KJmol^{-1}$	-279	-252	-251	-248	-240
Electrode potential, M^+ (aq)/M (s) /V	-3.045	-2.925	-2.925	-2.923	-2.714

The figures are quoted on arbitrary basis of zero enthalpy of formation for H^+ (aq) and a zero electrode potential for the H^+ (aq)/$\frac{1}{2}H_2$ (g) couple.

The irregularity of the order comes about because three enthalpy terms are involved.

Enthalpy of atomization	Ionization enthalpy	Enthalpy of hydration of ions
M (s) → M (g)	M (g) → M^+ (g)	M^+ (g) →M^+ (aq)

Each of these varies, as shown below:

Table 3 Energy changes contributing to enthalpy of formation of hydrated ions of group 1 elements

	Li	**Na**	**K**	**Rb**	**Cs**
M (s) → M (g)	161	108	90	82	78
M (g) → M^+ (g)	526	502	426	409	382
M^+ (g) →M^+ (aq)	-520	-406	-320	-296	-264
M (s) → M^+ (aq)	167	204	196	195	196

The figures quoted in table 3 for the enthalpy of formation of the M^+ (aq) ion differ from those quoted in table 2 by approximately 444 *kJ mol*$^{-1}$ as these figures are not on the arbitrary scale of H^+ (aq), having a zero enthalpy of formation.

The enthalpy of atomization, and hydration, and the ionization enthalpy, all increase numerically in passing from caesium to lithium, as the ionic size decreases, but the variations are not regular.

Therefore, it is particularly the **large value for the enthalpy of hydration of Li^+ (g)**, that is, mainly responsible for the high negative electrode potential of Li^+ (aq)/Li (g) couple. **The high ionisation enthalpy of Na (g)** causes the low value of negative electrode potential for the Na^+ (aq)/Na (g) couple.

Trial 1

Explain the following observation. (4 marks)

(a) The standard electrode potential of lithium is greater than that of potassium although potassium reacts vigorously with water than lithium.

Extraction of sodium

It is manufactured by electrolysis of fused sodium chloride in the Downs' cell (fig. 1) (MPt. 800^0C).

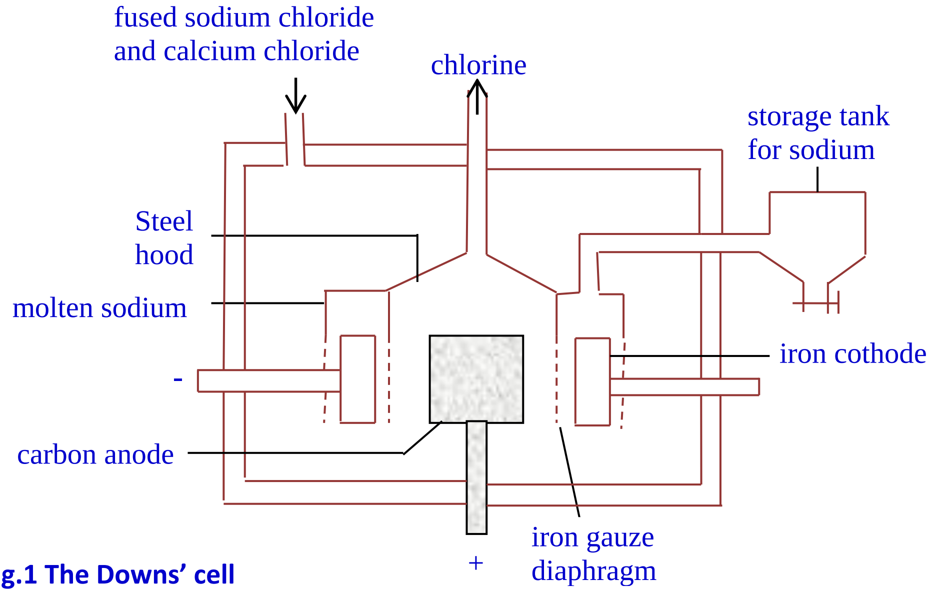

Fig.1 The Downs' cell

At first there were four difficulties;

- (i) It was expensive to keep the electrolyte over 800^0C.
- (ii) The molten sodium chloride was corrosive.
- (iii) Sodium is fairly soluble in its molten chloride at 800^0C
- (iv) The vapour pressure of sodium at 800^0C is very high, about ½ atmosphere of 400 *mmHg*.

The difficulties were all overcome by adding calcium chloride to sodium chloride to form a mixture that melts below 600^0C. It is cheaper to maintain this temperature, the mixture is non-corrosive, sodium is almost insoluble and the vapour pressure is about 15 mmHg.

The iron gauze cylinder between the anode and cathode prevents the sodium and chlorine from mixing. Liquid sodium leaves the cell in the raised pipe high enough for the lower density metal but not high enough for the higher density chloride mixture to overflow continuously into the receiver.

The reactions are
At cathode: Na^+ (l) + e ⟶Na(l)
Anode: $2Cl^-$(l) - 2e ⟶ Cl_2 (g)

Uses of sodium

- Molten sodium is used as a coolant in some types of nuclear reactors because of its good thermal conductivity, low melting point and its higher boiling point than that of water.
- Sodium wire is used in the electrical circuit for special application.
- Sodium vapour lamps are used for street lighting.
- Sodium cyanide is used in the extraction of silver and gold.

Chemical properties

Reaction of alkali metals with water.

Alkali metals react with water to form alkali hydroxides. Reactivity with water increases with increasing atomic numbers. Thus, lithium reacts quietly with water, sodium and potassium react with increased vigour and rubidium and caesium react with exceptional violence.

$$2K\ (s) + 2H_2O(l) \longrightarrow 2KOH\ (aq) + H_2\ (g)$$

They react with a variety of non-metals when heated to give sulphides, halides, hydrides, etc.

$$4Li\ (s) + O_2\ (g) \longrightarrow 2Li_2O\ (s)$$
$$2Na\ (s) + S\ (s) \longrightarrow Na_2S\ (s)$$
$$2Na\ (s) + Cl_2\ (g) \longrightarrow 2NaCl\ (s)$$
$$2Rb\ (s) + H_2\ (g) \longrightarrow 2RbH\ (s)$$

Lithium alone reacts with nitrogen to give a nitride.

$$6Li\ (s) + N_2\ (g) \longrightarrow 2Li_3N(s)$$

The metals burn in a stream of hydrogen chloride and react with ammonia when heated.

$$2Na\ (s) + 2HCl\ (g) \longrightarrow 2NaCl\ (s) + H_2\ (g)$$
$$2Na\ (s) + 2NH_3\ (g) \longrightarrow 2NaNH_2\ (s) + H_2\ (g)$$

Reaction alkali metals with hydrochloric acid

They react to form hydrogen and salt, e.g.

$$2Na\ (s) + 2HCl(g) \longrightarrow 2NaCl(s) + H_2(g)$$

Reaction alkali metals with sodium hydroxide

Lithium and sodium have no reaction with sodium hydroxide.
Ptassium, rubidium displace sodium from sodium hydroxide

$$K(s) + Na+(l) \longrightarrow K+ + Na(l)$$

Oxides of alkali metals

It is only lithium that forms the monoxide, Li_2O, when heated in oxygen. Sodium forms a monoxide, and peroxide, Na_2O_2, if an excess of oxygen is used. The other alkali metals give the super oxides when heated with oxygen, e.g., KO_2.

$4Li (s) + O_2 (g) \rightarrow 2Li_2O (s)$
$4Na (s) + O_2 (g) \rightarrow 2Na_2O (s) + O_2 (g) \rightarrow 2Na_2O_2 (s)$
$K (s) + O_2 (g) \rightarrow KO_2 (s)$

A lithium ion, by virtue of its small size, is not able to accommodate peroxide ions to give a stable crystal lattice and consequently only the monoxide exists. The ions of potassium, rubidium and caesium get progressively larger in this order and can form stable structures with the superoxide ions - the largest of the three oxide anions.

Reactions of oxides of alkali metals with water

i) Monoxides react with water to give alkali hydroxides.

$Li_2O (s) + H_2O (l) \rightarrow 2LiOH (aq)$
$Na_2O (s) + H_2O (l) \rightarrow 2NaOH (aq)$

ii) The peroxides react with water to give alkali hydroxides and hydrogen peroxide.

$Na_2O_2 (s) + 2H_2O (l) \rightarrow 2NaOH (aq) + H_2O_2 (l)$

iii) The superoxides react with water to give alkali hydroxides, hydrogen peroxide and oxygen.

$2KO_2 (s) + 2H_2O (l) \rightarrow 2KOH (aq) + H_2O_2 (aq) + O_2 (g)$

The hydroxides of alkali metals

They have a general formula of M^+OH^-. Sodium hydroxide is manufactured by electrolysis of brine (a solution of sodium chloride) using **titanium/carbon as the anode** and **mercury as the cathode**. During electrolysis, chlorine (due to its high concentration) is discharged at the anode and sodium at the cathode, where it forms sodium amalgam.

Anodic reaction: $2Cl^- (aq) \rightarrow 2e^- + Cl_2 (g)$
Cathodic reaction: $Na^+ (aq) + e^- \rightarrow Na (s)$

The sodium amalgam is passed through water where the sodium reacts with water to form 50% sodium hydroxide solution of high purity. The reaction is catalysed by presence of iron grids.

$2Na/Hg (s) + 2H_2O (l) \rightarrow 2NaOH (aq) + H_2 (g) + 2Hg (l)$

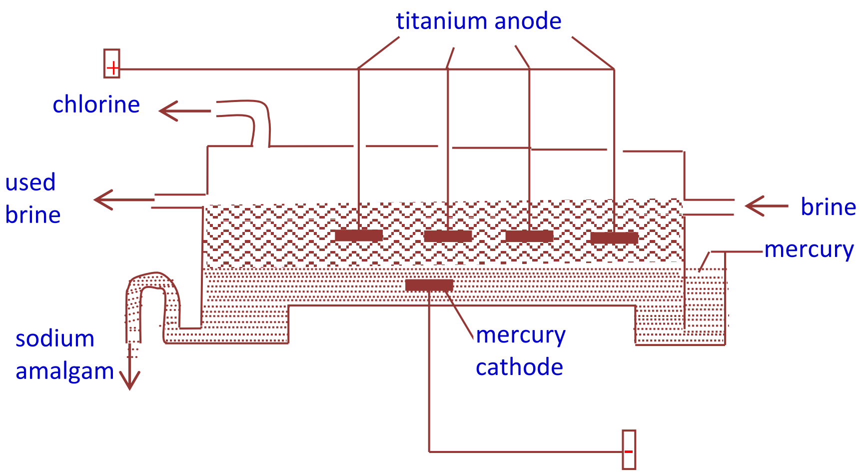

Fig. 2 Apparatus for production of sodium hydroxide

Reaction of hydroxides of alkali metals with water

i) Alkali metal hydroxides readily dissolve in water with vigorous evolution of heat.

$$NaOH\ (s) + (aq) \longrightarrow Na^+\ (aq) + OH^-\ (aq)$$

ii) They are neutralized by acids.

$$NaOH\ (aq) + HCl\ (aq) \longrightarrow NaCl\ (aq) + H_2O\ (l)$$
$$2KOH\ (aq) + H_2SO_4\ (aq) \longrightarrow K_2SO_4\ (aq) + 2H_2O\ (l)$$
$$\text{or } OH^-\ (aq) + H^+\ (aq) \longrightarrow H_2O\ (l)$$

iii) They displace ammonia from ammonium salts.

$$NaOH\ (aq) + NH_4Cl\ (aq) \longrightarrow NaCl\ (aq) + H_2O\ (l) + NH_3\ (g)$$
$$\text{or } NH_4^+\ (aq) + OH^-\ (aq) \longrightarrow NH_3\ (g) + H_2O\ (l)$$

iv) They react with many salts in aqueous solutions and precipitate the corresponding basic hydroxides.

$$CuSO_4\ (aq) + 2NaOH\ (aq) \longrightarrow Cu(OH)_2\ (s) + Na_2SO_4\ (aq)$$
$$\text{Or } Cu^{2+}\ (aq) + 2OH^-\ (aq) \longrightarrow Cu(OH)_2\ (s)$$

The hydroxides of less electropositive metals are amphoteric and dissolve in excess alkali e.g., the hydroxides of aluminium, lead (II), tin (II) and zinc.

$$Al^{3+}\ (aq) + 3OH^-\ (aq) \longrightarrow Al(OH)_3\ (s)$$
$$Al(OH)_3\ (s) + OH^-\ (aq) \longrightarrow \underbrace{[Al(OH)_4]^-}_{\text{Aluminate ion}}\ (aq)$$

$$Zn^{2+}\ (aq) + 2OH^-\ (aq) \longrightarrow Zn(OH)_2\ (s)$$
$$Zn(OH)_2\ (s) + 2OH^-\ (aq) \longrightarrow \underbrace{[Zn(OH)_4]^{2-}}_{\text{Zincate ion}}\ (aq)$$

$$Sn^{2+}\ (aq) + 2OH^-\ (aq) \longrightarrow Sn(OH)_2\ (s)$$
$$Sn(OH)_2\ (s) + 2OH^-\ (aq) \longrightarrow \underbrace{[Sn(OH)_4]^{2-}}_{\text{Stannate ions}}\ (aq)$$

Uses of alkali metal hydroxides.

1. Sodium hydroxide is used to absorb CO_2 and other acidic gases in the laboratory.
2. Potassium and sodium hydroxides are used in most organic reactions involving alkaline hydrolysis and in volumetric analysis.
3. Sodium and potassium alkalis are used in making soap (fig.8.3)

Fig. 3 Bar soap manufactured using sodium hydroxide

Reactions of carbonates of alkali metals

i) They react with some salts in solution and precipitate corresponding carbonates.

$$CaCl_2(aq) + Na_2CO_3\ (aq) \longrightarrow CaCO_3\ (s) + 2NaCl\ (aq)$$

ii) Sodium and potassium carbonates frequently precipitate basic carbonates.

$$3Zn^{2+}(aq) + CO_3^{2-}(aq) + 4OH^-\ (aq) + 2H_2O(l) \longrightarrow ZnCO_3.2Zn(OH)_2.2H_2O\ (s)$$

Uses of alkali metal carbonates

Sodium carbonate is often used in the laboratory as a volumetric reagent. Industrially it is used in a variety of ways, including the manufacture of glass.

Potassium carbonate is used as a drying agent in organic Chemistry since it is not deliquescent.

Hydrogen carbonates of alkali metals.

They can be obtained by passing carbon dioxide through a cold concentrated solution of corresponding carbonates.

$$Na_2CO_3\ (aq) + CO_2\ (g) + H_2O\ (l) \longrightarrow 2NaHCO_3(s)$$

These are the only hydrogen carbonates that can be obtained in solid form and even these tend to decompose readily.

$$2KHCO_3\ (s) \longrightarrow K_2CO_3\ (s) + CO_2\ (g) + H_2O\ (l)$$

Sodium hydrogen carbonate is less soluble in water than potassium hydrogen carbonate and both solutions are affected by hydrolysis but not to the same extent as corresponding carbonate.

HCO_3^- (aq) + H_2O (l) $\rightleftharpoons$ H_2CO_3 (aq) + OH^- (aq)

Because sodium hydrogen carbonate solution is less alkaline than sodium carbonate solution, the former is often used to precipitate normal carbonates that would otherwise be formed as basic carbonates.

Cu^{2+} (aq) + $2HCO_3^-$ (aq) → $CuCO_3$ (s) + H_2O (l) + CO_2 (g)

Halides of alkali metals

Preparation:

Can be prepared by reacting hydroxides with hydrogen halides HX (X = F, Cl, Br, I).

NaOH (aq) + HCl (aq) → NaCl (aq) + H_2O (l)

On large scale:

1. Sodium chloride is obtained by crystallization from seawater in which it exists extensively.
2. Potassium chloride is obtained by fractional crystallizations of carnallite, $KCl.MgCl_2.6H_2O$, deposits found in Germany.

Uses:

1. Sodium chloride is used for curing food. It is also a raw material for sodium hydroxide, sodium carbonate, sodium chlorate (I) and (V), etc.
2. Potassium chloride is used to counteract potassium deficiency in soil and humans, and in the production of KOH.
3. Potassium bromide is used as a sedative. In addition, it is used in production of silver bromide, which is used in photography.
4. Potassium iodide is used in laboratory for dissolving iodine in aqueous solution.

The nitrates and nitrites of alkali metals

Sodium and potassium nitrates are obtained by fractional crystallizations of chile saltpetre. Both sodium and potassium nitrates are used as nitrogen fertilizers. Potassium nitrate is a constituent of gun powder and is also used as a meat preservative. Nitrates decompose to give nitrites when heated strongly.

$2KNO_3$ (s) → $2KNO_2$ (s) + O_2 (g)

Nitrites.

The nitrites can be made by the thermal decomposition of corresponding nitrates.

$2NaNO_3$ (s) → $2NaNO_2$ (s) + O_2 (g)

On a large scale, a 50:50 mixture of nitrogen dioxide and nitrogen oxide is absorbed in sodium hydroxide solution.

2NaOH (aq) + NO_2 (g) + NO (g) → $2NaNO_2$ (aq) + H_2O (l)

Reactions of sodium nitrites

On treating cold aqueous solutions of nitrites with dilute HCl, a blue colour develops and, on warming, a mixture of nitrogen oxide and nitrogen dioxide is evolved:

$$2NaNO_2\ (aq) + 2HCl\ (aq) \longrightarrow 2NaCl\ (aq) + H_2O\ (l) + NO\ (g) + NO_2\ (g)$$

The blue colour is presumably due to the presence of N_2O_3 which readily decomposes into NO (g) and NO_2 (g).

Uses

Sodium nitrite is used in production of organic dyes and diazonium salts.

The sulphates and hydrogen sulphates of alkali metals

a. The sulphates of alkali metals have a general formula $(M^+)_2SO_4^{2-}$.

Preparation:

They are prepared by neutralization of aqueous solutions of alkali metal hydroxides with dilute H_2SO_4.

$$2KOH\ (aq) + H_2SO_4\ (aq) \rightarrow K_2SO_4\ (aq) + 2H_2O\ (l)$$
$$2NaOH\ (aq) + H_2SO_4\ (aq) \rightarrow Na_2SO_4\ (aq) + 2H_2O\ (l)$$

Sodium sulphate crystallizes as a decahydrate, $Na_2SO_4.10H_2O$, which effloresces to give an anhydrous salt when heated above 32.5^0C.

Uses

Potassium sulphate is used for making up potassium deficiency in soil, as a drying agent and for making potash alum, $KAl(SO_4)_2.12H_2O$, which is used as a mordant in dyeing.

b. The hydrogen sulphates, $M^+HSO_4^-$.

They are prepared by crystallizing corresponding sulphates from concentrated sulfuric acid.

$$Na_2SO_4\ (s) + H_2SO_4\ (l) \rightarrow 2NaHSO_4\ (l)$$

Reactions

i) The hydrogen sulphates are decomposed by heat to give first pyrosulphates and water and, then sulphate and sulphur trioxide, e.g.

$$2NaHSO_4\ (s) \rightarrow Na_2S_2O_7\ (s) + H_2O\ (l)$$
$$\text{then,}\quad Na_2S_2O_7\ (s) \rightarrow Na_2SO_4\ (s) + SO_3\ (g)$$

Hydrolysis of alkali metal salts

Salts of alkali metals with weak acids hydrolyze in water to give alkaline solutions.

$$CO_3^{2-}\ (aq) + H_2O\ (l) \rightarrow HCO_3^-\ (aq) + OH^-\ (aq)$$
$$HCO_3^-\ (aq) + H_2O\ (l) \rightarrow H_2CO_3\ (aq) + OH^-\ (aq)$$
$$CN^-\ (aq) + H_2O\ (l) \rightarrow HCN\ (aq) + OH^-\ (aq)$$
$$S^{2-}\ (aq) + H_2O\ (l) \rightarrow HS^-\ (aq) + OH^-\ (aq)$$
$$HS^-\ (aq) + H_2O\ (l) \rightarrow H_2S\ (aq) + OH^-\ (aq)$$

When alkali metal cyanides and sulphides are warmed with water, volatile hydrogen cyanide and hydrogen sulphide are given off as gases; the hydrolysis therefore goes to completion and solutions of alkali hydroxides remain.

Additional exercise

1. *The properties of the first member of a group of elements in the periodic table, are not typical of the group as a whole. Discuss this statement concerning the Chemistry of elements of groups 1A, (Li - Cs) and 2A (Be - Ba).*

   Include in your answer specific properties that differentiate lithium and beryllium from other members of their respective groups as well as the reasons for the differentiation.

2. *(a) Write the electronic structure of the group 1A elements, lithium to caesium, in terms of s, p, and d orbitals.*
   (b) For the elements lithium to caesium, state and explain quantitatively the general trends in:
      (i) first ionisation energy.
      (ii) atomic radii.
   (c) Give reasons for the following:
      (i) The large negative standard electrode potential of lithium.
      (ii) The differences in the structures of the crystal lattices of NaCl and CsCl.
      (iii) The fact that lithium salts are often hydrated but hydrated caesium salts are rare.

   (d) Give two chemical properties of lithium or its compounds that are not typical of the other group 1A elements and their compounds.
   By means of descriptions or equations, show the ways in which these properties are not typical.

3. *Outline an electrolytic method for industrial preparation of sodium hydroxide from brine. How, and under what conditions, does sodium hydroxide react with (i) carbon dioxide (ii) ammonium alum, (iii) silicon (iv) phosphorus?*

4. *Give a concise account of the extraction of sodium from sodium chloride. How may the following be prepared from the metal?*
   (a) sodium sulphide (c) sodium peroxide
   (b) sodium hydride (d) sodamide

   Write equations to show the action of water on these compounds.

5. *Define the term* ***ionisation energy*** *and* ***standard electrode*** *potential and discuss the relationship between them. The values for the ionisation energies of the alkali metals, Li, Na, and K are respectively 5.39, 5.14 and 4.34 eV. The corresponding standard values for the* M^+ *(aq)/M (s) couples are -3.0 V, -2.7 V, and -2.9 V. Comment on these values.*

8. *Predict the structures of the following compounds:* H_2O, CO_2, $AlCl_3$, *and* SO_4^{2-}.

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