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The s -Block Elements

Those elements in which the last electron enters in s-orbital of the outermost shell are called s-block elements. These elements have been placed in extreme left of the Periodic Table under the Group 1 (alkali metals) and group 2 (alkaline earth metals).

The general electronic configuration of s-block elements is ns^{1-2}.

Along with p-block elements, these elements are called representative elements.

Group- 1 Elements – The Alkali Metals

Group 1 of the Periodic Table consists of the six elements, namely lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs) and francium (Fr), of which Fr is radioactive. The hydroxides of these elements are highly soluble in water and their aqueous solutions are strongly alkaline in nature. Hence, these elements are also called Alkali metals.

The atomic, physical and chemical properties of alkali metals are discussed below-

Atomic Properties

1. Electronic Configuration-

The general outer shell electronic configuration of alkali metals is ns^1 . Thus, they have only one valence electron in their valence shell. They readily lose this electron to form mono-valent M^+ ions.

The loosely held s-electron in the outermost valence shell of these elements makes them the most reactive and most electropositive metals. Hence they are never found in free state in nature.

ELEMENT	SYMBOL	ELECTRONIC CONFIGURATION
Lithium	Li	$1s^2 2s^1$
Sodium	Na	$1s^2 2s^2 2p^6 3s^1$
Potassium	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
Rubidium	Rb	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$
Caesium	Cs	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^1$ or $[Xe]6s^1$
Francium	Fr	$[Rn]7s^1$

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2. **Atomic and Ionic Radii**

The alkali metals have the biggest atomic and ionic sizes in respective period of the periodic table. The atomic and ionic radius increases on moving down the group.

The ionic size of monovalent ions (M^+) is smaller than the parent atom.

3. **Ionization Enthalpy**

The alkali metals have least ionization enthalpy in respective period and it decrease down the group from Li to Cs. It is because, the effect of increasing size outweighs the increasing nuclear charge and the outermost electron is very well screened from the nuclear charge.

4. **Hydration Enthalpy**

The hydration enthalpies of alkali metal ions decrease with increase in ionic sizes and follows following order-

$$\mathbf{Li^+ > Na^+ > K^+ > Rb^+ > Cs^+}$$

Because of its smallest ionic size , Li^+ has highest degree of hydration and for this reason its salts are mostly hydrated, e.g., $LiCl \cdot 2H_2O$

Physical Properties

1. Appearance

All the alkali metals are silvery white, in appearance.

2. Density

These are soft and light metals. Because of the large atomic size, these elements have low density which increases down the group from Li to Cs. However, potassium is exceptionally lighter than sodium.

3. Melting and Boiling point

The melting and boiling points of the alkali metals are low indicating weak metallic bonding in them. It is due to the presence of only a single valence electron in them.

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4. Flame Colouration

The alkali metals and their salts impart characteristic colour to an oxidizing flame (Bunsen flame). For example,

Metal	Li	Na	K	Rb	Cs
Color	Crimson red	Yellow	Violet	Red violet	Blue
Emitted wavelengh (λ/nm)	670.8	589.2	766.5	780.0	455.5

This is because, the heat of Bunsen flame excites the outermost orbital electron to a higher energy level. When the excited electron comes back to the ground state, there is emission of radiation in the visible region.

This property makes caesium and potassium useful as electrodes in making photo-electric cells.

Chemical Properties

Reactivity-

Due to bigger atomic size and least ionization enthalpy, the alkali metals are highly reactive in nature. When they are exposed to air they react with atmospheric oxygen to form their oxides, with water to form hydroxides and with carbon dioxide to form carbonates.

$$2M + \tfrac{1}{2} O_2 \rightarrow M_2O$$

$$2M + 2H_2O \rightarrow 2MOH + H_2$$

$$M_2O + CO_2 \rightarrow M_2CO_3$$

These reactions are very violent and exothermic where hydrogen released, usually catches fire. Hence, to avoid the contact with air, these elements (except Li) are placed in kerosene oil. Li being lighter, floats over kerosene oil. Hence, it is placed in paraffin wax.

The reactivity of these metals goes on increasing on moving down the group.

(1) Reactivity towards air

The alkali metals get tarnished in dry air due to the formation of their oxides which in turn react with moisture to form hydroxides. The alkali metals burn vigorously in oxygen forming oxides. Here, lithium forms its monoxide, sodium

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forms peroxide, while the other metals form their super oxides. The super oxide ion (O_2^-) is stable only in the presence of large cations such as K^+, Rb^+, Cs^+.

$4Li + O_2 \rightarrow 2Li_2O$ (Simple oxide)

$2Na + O_2 \rightarrow Na_2O_2$ (Peroxide)

$M + O_2 \rightarrow MO_2$ (Superoxide), Where, M = K, Rb or Cs

In all these oxides the oxidation state of the alkali metal is +1.

Here, Li shows exceptional behaviour and reacts directly with nitrogen of air to form its nitride, Li_3N. Because of their high reactivity towards air and water, the alkali metals are normally kept in kerosene oil.

Q. -What is the oxidation state of K in KO_2?

Ans.- The superoxide ion is represented as O_2^-. Since the compound is neutral, therefore, the oxidation state of potassium is +1.

(2) Reactivity towards water

The alkali metals react vigourously with water to form their hydroxides and release dihydrogen.

$$2M + 2H_2O \rightarrow 2MOH + H_2 \qquad (M = \text{an alkali metal})$$

Here, although lithium has most negative E^0 value (-3.04V), its reaction with water is less vigorous than that of sodium which has the least negative E^0 value among the alkali metals. This behaviour of lithium is due to its small ionic size and very high hydration enthalpy. Other metals of the group react explosively with water.

They also react with proton donors such as alcohol, gaseous ammonia and alkynes.

(3) Reactivity towards dihydrogen

The alkali metals react with dihydrogen at about 673K (lithium at 1073K) to form ionic hydrides with high melting points.

$$2M + H_2 \rightarrow 2M^+H^-$$

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(4)Reactivity towards halogens

The alkali metals react vigorously with halogens to form ionic halides, M^+X^-. Here, lithium halides are somewhat covalent due to high polarizing power of Li^+ ion.

The Li^+ ion is very small in size and has high tendency to distort electron cloud around the negative halide ions. Since anion with large size can be easily distorted, amongst halides, lithium iodide is the most covalent in nature.

Atomic and Physical Properties of the Alkali Metals						
PROPERTY	**Li**	**Na**	**K**	**Rb**	**Cs**	**Fr**
Atomic number	3	11	19	37	55	87
Atomic mass ($g\ mol^{-1}$)	6.94	22.99	39.10	85.47	132.91	(223)
electronic configuration	[He] $2s^1$	[Ne] $3s^1$	[Ar] $4s^1$	[Kr] $5s^1$	[Xe] $6s^1$	[Rn] $7s^1$
Ionization enthalpy ($kJ\ mol^{-1}$)	520	496	419	403	376	~375
Hydration enthalpy ($kJ\ mol^{-1}$)	-506	-406	-330	-310	-276	-
Metallic radius (pm)	152	186	227	248	265	-
Ionic radius M^+ (pm)	76	102	138	152	167	(180)
m.p. (K)	454	371	336	312	302	-
b.p. (K)	1615	1156	1032	961	944	-
Density ($g\ cm^{-3}$)	0.53	0.97	0.86	1.53	1.90	-
Standard potentials for (M^+/ M), E^Θ (V)	-3.04	-2.714	-2.925	-2.930	-2.297	-

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(5) Reducing nature

The alkali metals have very high negative value of their standard electrode potential and are strong reducing agents. Here, Li is strongest while Na is the least powerful reducing agent in the group.

In fact, the standard electrode potential (E^0) which measures the reducing power of metal is dependent on following three factors-

$M(s) \rightarrow M(g)$, $\Delta_{sub}H$ (sublimation enthalpy)

$M(g) \rightarrow M^+(g) + e^-$, Δ_iH (ionization enthalpy)

$M^+(g) + xH_2O \rightarrow M^+(aq)$, $\Delta_{hydration}H$ (hydration enthalpy)

Because of smaller ionic size, lithium has the highest hydration enthalpy. It accounts for its highest negative value of E^0 and therefore, its highest reducing power.

Q. The standard electrode potentials, E^0 for Cl_2/Cl^- is +1.36, for I_2/I^- is + 0.53, for Ag^+/Ag is +0.79, Na^+/Na is -2.71 and for Li^+/Li is -3.04. Arrange the following species in decreasing order of reducing strength.

I^-, Ag, Cl^-, Li, Na

Ans.- The greater the negative value of E^0 for a species, more is its reducing strength. Thus, the decreasing order of reducing strength of given species will be as under-

$Li > Na > I^- > Ag > Cl^-$

(6) Solutions in liquid ammonia

The alkali metals dissolve in liquid ammonia to give deep blue solutions which are conducting in nature. The blue colour of the solution is due to the presence of solvated (ammoniated) electrons in the solution, which absorbs energy in the visible region and impart blue colour to the solution.

$$M \rightarrow M^+ + e^-$$

$$M^+ + xNH_3 \rightarrow [M(NH_3)_x]^+$$

$$e^- + yNH_3 \rightarrow [e(NH_3)_y]^-$$

$$M + (x+y)NH_3 \rightarrow [M(NH_3)_x]^+ + [e(NH_3)_y]^-$$

Ammoniated cation Ammoniated electron

These solutions are paramagnetic and are strongly reducing in nature due to the presence of ammoniated electrons.

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On standing, they slowly liberate hydrogen resulting in the formation of amide.

$$M^{+}_{(am)} + e^{-}_{(am)} + xNH_3(1) \rightarrow MNH_{2(am)} + \tfrac{1}{2}H_2\,(g)$$

(where, 'am' stands for solution in liquid ammonia)

In concentrated solution, the blue colour changes to bronze colour and becomes diamagnetic.

These solutions are good conductor of electricity due to the presence of both ammoniated cations and ammoniated electrons.

Uses-

(1) Lithium is used to make useful alloys. For example with lead to make 'white metal' bearings for motor engines, with aluminium to make aircraft parts, and with magnesium to make armour plates. It is used in thermonuclear reactions. Lithium is also used to make electrochemical cells.

(2) Sodium is used to make a Na/Pb alloy needed to make $PbEt_4$ and $PbMe_4$. These organolead compounds were earlier used as anti-knock additives to petrol, but nowadays vehicles use lead-free petrol. Liquid sodium metal is used as a coolant in fast breeder nuclear reactors.

(3) Potassium has a vital role in biological systems. Potassium chloride is used as a fertilizer. Potassium hydroxide is used in the manufacture of soft soap. It is also used as an excellent absorbent of carbon dioxide.

(4) Caesium is used in devising photoelectric cells.

General Characteristics of the Compounds of Alkali Metals

The compounds of the alkali metals are generally ionic in nature. General characteristics of some of their compounds are discussed here-

1. Oxides and Hydroxides

On combustion in excess of air, lithium forms mainly the simple oxide, Li_2O (with some peroxide, Li_2O_2), sodium forms the peroxide, Na_2O_2 (and some superoxide NaO_2) while potassium, rubidium and caesium form the superoxides of type MO_2.

Under appropriate conditions pure compounds M_2O, M_2O_2 and MO_2 may be prepared.

These oxides are readily soluble in water and are easily hydrolysed by water to form the hydroxides as per the following reactions-

$$M_2O + H_2O \rightarrow 2M^{+} + 2OH^{-}$$

$$M_2O_2 + 2H_2O \rightarrow 2M^{+} + 2OH^{-} + H_2O_2$$

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$$2MO_2 + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2O_2 + O_2$$

These hydroxides are white coloured crystalline solids. These are the strongest of all bases and dissolve freely in water with evolution of much heat on account of intense hydration.

The stability of the peroxides or superoxide increases with increase of the size of the metal ion. It is due to the stabilization of large anions by larger cations through lattice energy effects.

The oxides and hydroxides of these elements are highly soluble in water and their aqueous solutions are strongly alkaline in nature. Hence, these elements are also called Alkali metals.

Water solubility and basic nature of oxides and hydroxides of these elements goes on increasing on moving down the group. It is because of the increase of ionic character in compounds on moving down the group.

The oxides and the peroxides are colourless when pure, but the superoxides are yellow or orange in colour. The superoxides are also paramagnetic.

Sodium peroxide is widely used as an oxidising agent in inorganic chemistry.

Q. Why is KO_2 paramagnetic ?

Ans.-The superoxide ions, O_2^- contain an unpaired electron in π^*2p molecular orbital. Hence, they are attracted in magnetic field and are paramagnetic in nature.

2. Halides

All the alkali metals form ionic halides of type MX (where, X = F,Cl,Br,I). These halides can be prepared by the reaction of the appropriate oxide, hydroxide or carbonate with aqueous hydrohalic acid (HX). All of these halides have high negative enthalpies of formation ($\Delta_f H^0$). On going down the group the negative value of $\Delta_f H^0$ goes on increasing for chlorides, bromides and iodides while reverse is observed for for fluorides,. For a given metal $\Delta_f H^0$ always becomes less negative from fluoride to iodide.

These halides are colourless crystalline solids having high melting points. For a definite metal, the melting and boiling points always follow following order-

Fluoride > Chloride > Bromide > Iodide

All these halides are highly soluble in water except LiF and CsI. The low solubility of LiF in water is due to its high lattice enthalpy whereas the low solubility of CsI is due to smaller hydration enthalpy of its two ions. Other halides

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of lithium are soluble in ethanol, acetone and ethylacetate. LiCl is also soluble in pyridine.

3. Salts of Oxo-Acids

Such compounds in which at least an oxo group as well as a hydroxyl group with an acidic proton remains attached to a polyvalent atom are called oxo acids. For example, carbonic acid, H_2CO_3 [$(O=C(OH)_2$] sulphuric acid, H_2SO_4 [$(O_2S(OH)_2)$], etc.

The alkali metals form salts with all the oxo-acids. These salts, in general are stable to heat and are soluble in water. For example, their carbonates (M_2CO_3) and in most cases the hydrogencarbonates ($MHCO_3$) also are highly stable to heat and therefore do not decompose on heating. Due to increase of ionic character, the stability of the carbonates and hydorgencarbonates increases down the group.

Due to more covalent character, lithium carbonate is relatively less stable to heat and therefore gets decomposed on heating to form more stable Li_2O and CO_2.

Its $LiHCO_3$ does not exist as a solid.

Anomalous Behaviour of Lithium

Li shows dissimilarities in properties with other elements of its group. The anomalous behaviour of lithium is due to following reasons-

(i) Exceptionally smaller atomic and ionic sizes

(ii) High polarizing power (i.e., charge/ radius ratio) of Li^+ ion

Thus, the compounds of Li are predominantly covalent while those of other alkali metals are predominantly ionic. It is responsible for their solubility in organic solvents.

Difference between Lithium and other Alkali Metals

(i) Alkali metals are soft while Li is relatively harder.

(2) Its m.p. and b.p. are higher than the other alkali metals.

(3) Lithium is least reactive but the strongest reducing agent among all the alkali metals. On combustion in air it forms mainly monoxide, Li_2O and the nitride, Li_3N unlike other alkali metals.

(4) LiCl is deliquescent and crystallises as a hydrate, $LiCl.2H_2O$ whereas other alkali metal chlorides do not form hydrates.

(5) Lithium hydrogencarbonate is not obtained in the solid form while all other elements form solid hydrogencarbonates.

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(v) Lithium unlike other alkali metals forms no ethynide on reaction with ethyne.
(vi) Lithium nitrate when heated gives lithium oxide, Li_2O, whereas other alkali metal nitrates decompose to give the corresponding nitrite.

$$4LiNO_3 \xrightarrow{\text{Heat}} 2Li_2O + 4NO_2 + O_2$$

$$2NaNO_3 \xrightarrow{\text{Heat}} 2NaNO_2 + O_2$$

(vii) LiF and Li_2O are comparatively much less soluble in water than the corresponding compounds of other alkali metals.

Similarities between Li and Mg
OR
Diagonal relationship of Li with Mg

Li shows similarities in properties with Mg in many respects. This is called diagonal relationship of Li with Mg.

The similarity between lithium and magnesium arises because of their similar atomic and ionic sizes :-

Atomic radii - Li = 152 pm, Mg = 160 pm
Ionic radii - Li^+ = 76 pm, Mg^{2+}= 72 pm.

The important similarities between lithium and magnesium are as under-

(i) Both lithium and magnesium are harder and lighter than other elements in the respective groups
(ii) Lithium and magnesium react slowly with water.
(iii) The oxides and hydroxides of both Lithium and magnesium are feebly soluble in water and are weakly basic in nature.
(iv) The hydroxides of both Lithium and magnesium decompose on heating to form their oxides.
(v) Both Lithium and magnesium combine directly with nitrogen to form their nitrides, Li_3N and Mg_3N_2
(vi) The oxides of both Li and Mg (Li_2O and MgO) do not combine with excess oxygen to give their superoxide.
(vii) The carbonates of both lithium and magnesium decompose easily on heating to form the oxides and CO_2.
(viii) Both lithium and magnesium do not form solid hydrogencarbonates.
(ix) Both LiCl and $MgCl_2$ are soluble in ethanol.

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(x) Both LiCl and $MgCl_2$ are deliquescent and crystallise from their aqueous solution as hydrates, $LiCl \cdot 2H_2O$ and $MgCl_2 \cdot 8H_2O$.

Some Important Compounds of Sodium

(1) Sodium Carbonate (Washing Soda), $Na_2CO_3 \cdot 10H_2O$

Preparation (Solvay Process)

Sodium carbonate is generally prepared by Solvay Process. In this process, ammonical brine (concentrated solution of sodium chloride saturated with ammonia) is carbonated with CO_2, where sodium hydrogencarbonate gets precipitated because of its low solubility as compared to ammonium hydrogencarbonate. The reactions involved in the complete process are as under-

$$2NH_3 + H_2O + CO_2 \rightarrow (NH_4)_2CO_3$$

$$(NH_4)_2CO_3 + H_2O + CO_2 \rightarrow 2NH_4HCO_3$$

$$NH_4HCO_3 + NaCl \rightarrow NH_4Cl + NaHCO_3$$

Sodium hydrogencarbonate crystal thus separated on calcinations (heating) gives sodium carbonate.

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

In this process NH_3 is recovered by treating the solution containing NH_4Cl with $Ca(OH)_2$. Here, calcium chloride is obtained as a by-product.

$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + H_2O$$

Solvay process cannot be extended to the manufacture of potassium carbonate because potassium hydrogencarbonate is too soluble to be precipitated by the addition of ammonium hydrogencarbonate to a saturated solution of potassium chloride.

Properties

(1) Sodium carbonate is a white crystalline solid which exists as a decahydrate, $Na_2CO_3 \cdot 10H_2O$. This is also called washing soda.

(2) It is readily soluble in water.

(3) On heating, the decahydrate loses its water of crystallisation to form monohydrate. Above 373K, the monohydrate becomes completely anhydrous and changes to a white powder called soda ash.

(4) Carbonate part of sodium carbonate gets hydrolysed by water to form an alkaline solution.

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^-$$

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Uses-

(i) It is used in water softening, laundering and cleaning.
(ii) It is used in the manufacture of glass, soap, borax and caustic soda.
(iii) It is used in paper, paints and textile industries.
(iv) It is an important laboratory reagent both in qualitative and quantitative analysis.

(2) Sodium Hydrogencarbonate (Baking Soda), $NaHCO_3$

Chemically,sodium hydrogencarbonate is known as baking soda because it decomposes on heating to give carbon dioxide which produces holes in cakes or pastries and therefore makes them light and fluffy.

Preparation

Sodium hydrogencarbonate is prepared by saturating a solution of sodium carbonate with carbon dioxide. Here, sodium hydrogencarbonate, being less soluble, gets separated.

$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3$$

Properties and uses

(1) Sodium hydrogencarbonate is a white coloured crystelline solid.
(2) It is a mild antiseptic for skin infections.
(3) It is used in fire extinguishers.

(3) Sodium Hydroxide (Caustic Soda), NaOH

Preparation

On commercial scale sodium hydroxide is usually prepared by the electrolysis of sodium chloride (brine) in Castner-Kellner cell using a mercury cathode and a carbon anode. Here, sodium metal discharged at the cathode combines with mercury to form sodium amalgam. Chlorine gas is evolved at the anode.

The amalgam is taken out from the cell and is treated with water to give sodium hydroxide and hydrogen gas.

$$2Na\text{-amalgam} + 2H_2O \rightarrow 2NaOH + 2Hg + H_2$$

Properties

(1) Sodium hydroxide is a white, translucent solid.
(2) It melts at 591 K.
(3) It is readily soluble in water to give a strong alkaline solution.

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(4) Crystals of sodium hydroxide are deliquescent.
(5) The sodium hydroxide solution at the surface reacts with the atmospheric CO_2 to form Na_2CO_3.

Uses-

It is used in-

(i) the manufacture of soap, paper, artificial silk and a number of chemicals,
(ii) in petroleum refining,
(iii) in the purification of bauxite
(iv) in the textile industries for mercerising cotton fabrics,
(v) for the preparation of pure fats and oils
(vi) as a laboratory reagent.

(4) Sodium Chloride, NaCl

The most abundant source of sodium chloride is sea water which contains 2.7 to 2.9% by mass of the salt. In tropical countries like India, common salt is generally obtained by evaporation of sea water. Approximately 50 lakh tons of salt are produced annually in India by solar evaporation. Crude sodium chloride, generally obtained by crystallisation of brine solution, contains sodium sulphate, calcium sulphate, calcium chloride and magnesium chloride as impurities. Calcium chloride, $CaCl_2$, and magnesium chloride, $MgCl_2$ are impurities because they are deliquescent (absorb moisture easily from the atmosphere). To obtain pure sodium chloride, the crude salt is dissolved in minimum amount of water and filtered to remove insoluble impurities. The solution is then saturated with hydrogen chloride gas. Crystals of pure sodium chloride separate out. Calcium and magnesium chloride, being more soluble than sodium chloride, remain in solution.

Properties

(1) Sodium chloride melts at 1081K.
(2) It has a solubility of 36.0 g in 100 g of water at 273 K. The solubility does not increase appreciably with increase in temperature.

Uses-

(i) It is used as a common salt or table salt for domestic purpose.
(ii) It is used for the preparation of Na_2O_2, NaOH and Na_2CO_3.

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Biological Importance of Sodium and Potassium

A typical 70 kg man contains about 90 g of Na and 170 g of K compared with only 5 g of iron and 0.06 g of copper.

Sodium ions are found primarily on the outside of cells in blood plasma and in the interstitial fluid which surrounds the cells. These ions participate in-

(i) Transmission of nerve signals

(ii) Regulating the flow of water across cell membranes

(iii) Transport of sugars and amino acids into cells.

Although Sodium and potassium are chemically similar, they differ quantitatively in their ability to penetrate cell membranes, in their transport mechanisms and in their efficiency to activate enzymes.

Potassium ions are the most abundant cations within cell fluids, where they activate many enzymes, participate in the oxidation of glucose to produce ATP and, with sodium, are responsible for the transmission of nerve signals.

There is considerable variation in the concentration of sodium and potassium ions found on the opposite sides of cell membranes. For example, in blood plasma, the concentration of Na^+ is 143 $mmolL^{-1}$, while that of K^+ is only 5 $mmolL^{-1}$In the red blood cells the concentrations of these ions are 10 $mmolL^{-1}$ and 105 $mmolL^{-1}$ respectively. These ionic gradients demonstrate that a discriminatory mechanism, called the sodium-potassium pump, operates across the cell membranes which consumes more than one-third of the ATP used by a resting animal and about 15 kg per 24 h in a resting human.

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