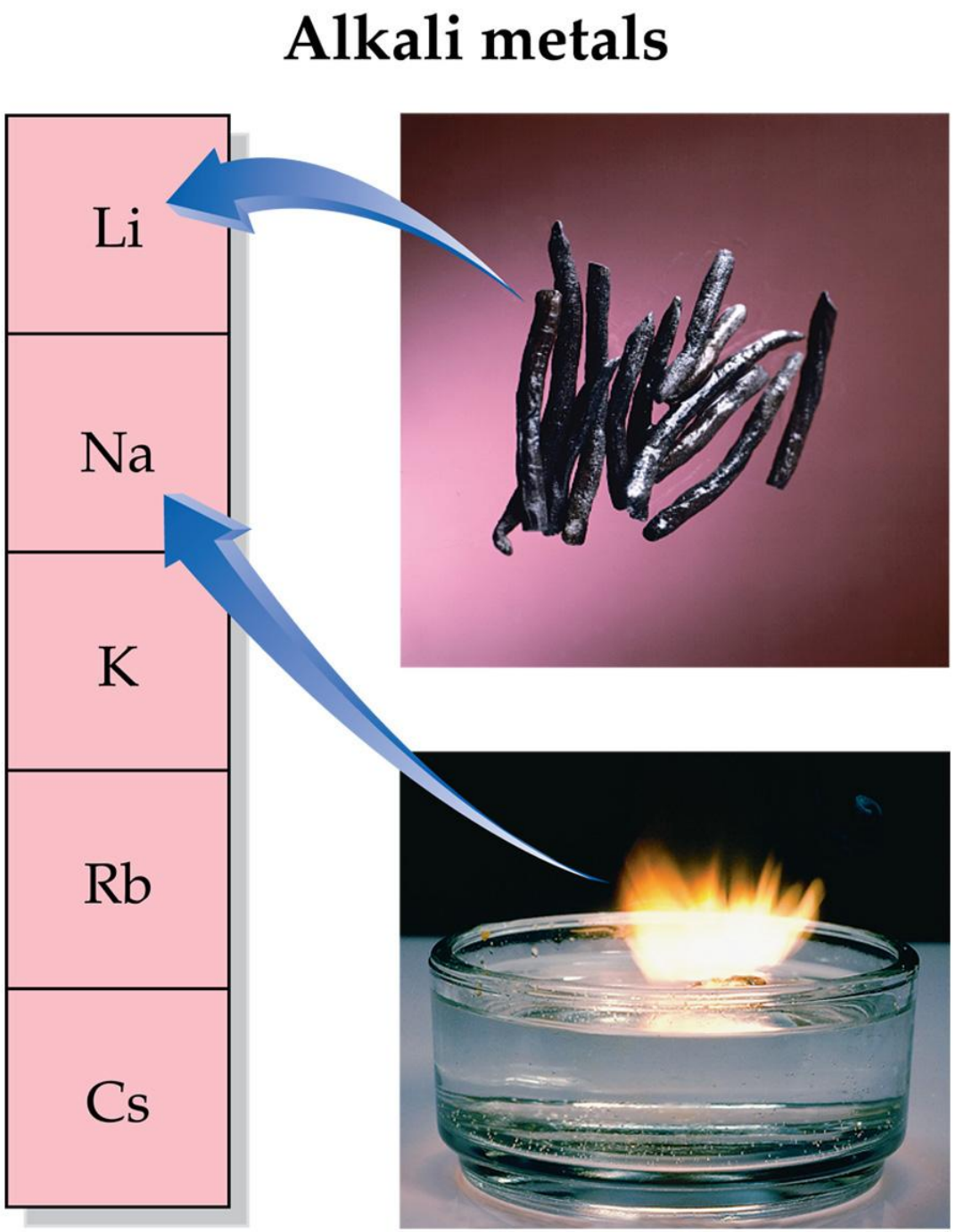
# *Alkali Group*

*pranjoto utomo*



# General Properties

- The Group 1A metals exhibit regular trends for a number of properties.
  - The atomic/ionic radii increase from Li to Cs
  - The first ionization energy and electronegativity decrease from Li to Cs

# General Properties

- The Group 1A metals exhibit regular trends for a number of properties.
  - From Li to Cs, the atoms become more metallic
  - The alkali metals are soft, conduct electricity well and have low melting points

# General Properties

- Each element produces characteristic flame
  - Li : carmine (red)
  - Na : yellow
  - K : lilac
  - Rb : bluish red
  - Cs : blue
- They are quite reactive metals

# General Properties

- Cations of +1 charge are formed, the compounds are stable, colorless (except to those colored anions, e.g. $KMnO_4$, $K_2CrO_4$)
- Hydration energy <<<
- Almost all of alkali compounds are soluble


- e.g.

$$4Li\ (s) + O_2\ (g) \rightarrow 2Li_2O\ (s)$$
$$Li_2O\ (s) + CO_2\ (g) \rightarrow Li_2CO_3\ (s)$$

- REACTION WITH WATER → exothermic
  - Li (calmly)
  - Na (violent)
  - K, Rb, Cs, Fr (explosive)

# Solubility

- Solubility depends on: enthalpy parameters → (lattice energy, hydration energy of anion and cation, entropy change)
- Soluble salt

  free energy ($\Delta G^0$) = negative

  ($\Delta H - T\Delta S$) = negative

# Solubility

| Compounds | $E_{lattice}$ | $E_{hydration}$ | $\Delta H$ | $S_{lattice}$ | $S_{hydration}$ | $T\Delta S$ | $\Delta G^0$ | Solubility (Mol $L^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| | ($kJ\ mol^{-1}$) | | | | | | | |
| NaF | +930 | -929 | +1 | +72 | -74 | -2 | +3 | 0.009 |
| NaCl | +788 | -784 | +4 | +68 | -55 | +13 | -11 | 0.62 |
| NaBr | +752 | -753 | -1 | +68 | -50 | +18 | -19 | 0.92 |
| NaI | +704 | -713 | -9 | +68 | -45 | +23 | -32 | 1.23 |

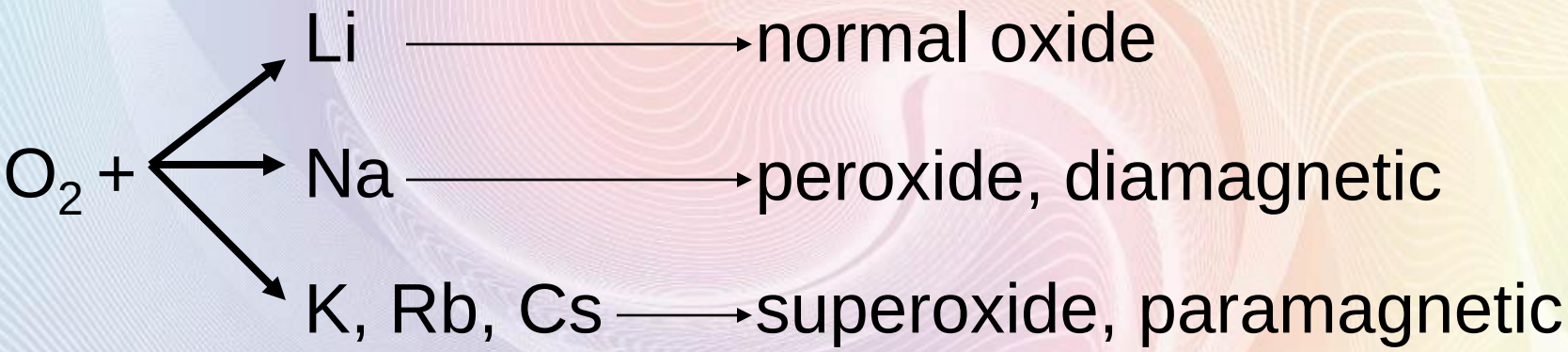
# Solubility

- Solubility of alkali salts depend on cation – anion radii ratio
  - cation – anion radii differences >>>
    - soluble
  - cation – anion radii differences <<<
    - slightly soluble

# Solubility

| Com-pounds | $R_{cation}$ (pm) | $R_{anion}$ (pm) | $\Delta r$ | Relative solubility |
|---|---|---|---|---|
| LiF | 90 | 119 | 29 | Slightly soluble |
| LiI | 90 | 206 | 116 | Soluble |
| CsF | 181 | 119 | 62 | Soluble |
| CsI | 181 | 206 | 25 | Slightly soluble |

# Alkali Oxide



# Alkali Oxide

- Normal oxide
  - $2Li(s) + \frac{1}{2} O_2(g) \rightarrow Li_2O(s)$
  - $Li_2O(s) + H_2O(\ell) \rightarrow 2LiOH(aq)$

- Peroxide
  - $2Na(s) + O_2(g) \rightarrow Na_2O_2(s)$
  - $Na_2O_2(s) + 2H_2O(\ell)$
    $\rightarrow 2NaOH(aq) + H_2O_2(aq)$

# Alkali Oxide

- Superoxide
  - $K(s) + O_2(g) \rightarrow KO_2(s)$
  - $2KO_2(s) + 2H_2O(\ell) \rightarrow 2KOH(aq) + H_2O_2(aq) + O_2(g)$

# Alkali Oxide

- Potassium dioxide → emergency oxygen source (life support system) → *oxygen masks*

  $2KO_2(s) + 2CO_2(g) \rightarrow 2K_2CO_3(s) + 3O_2(g)$

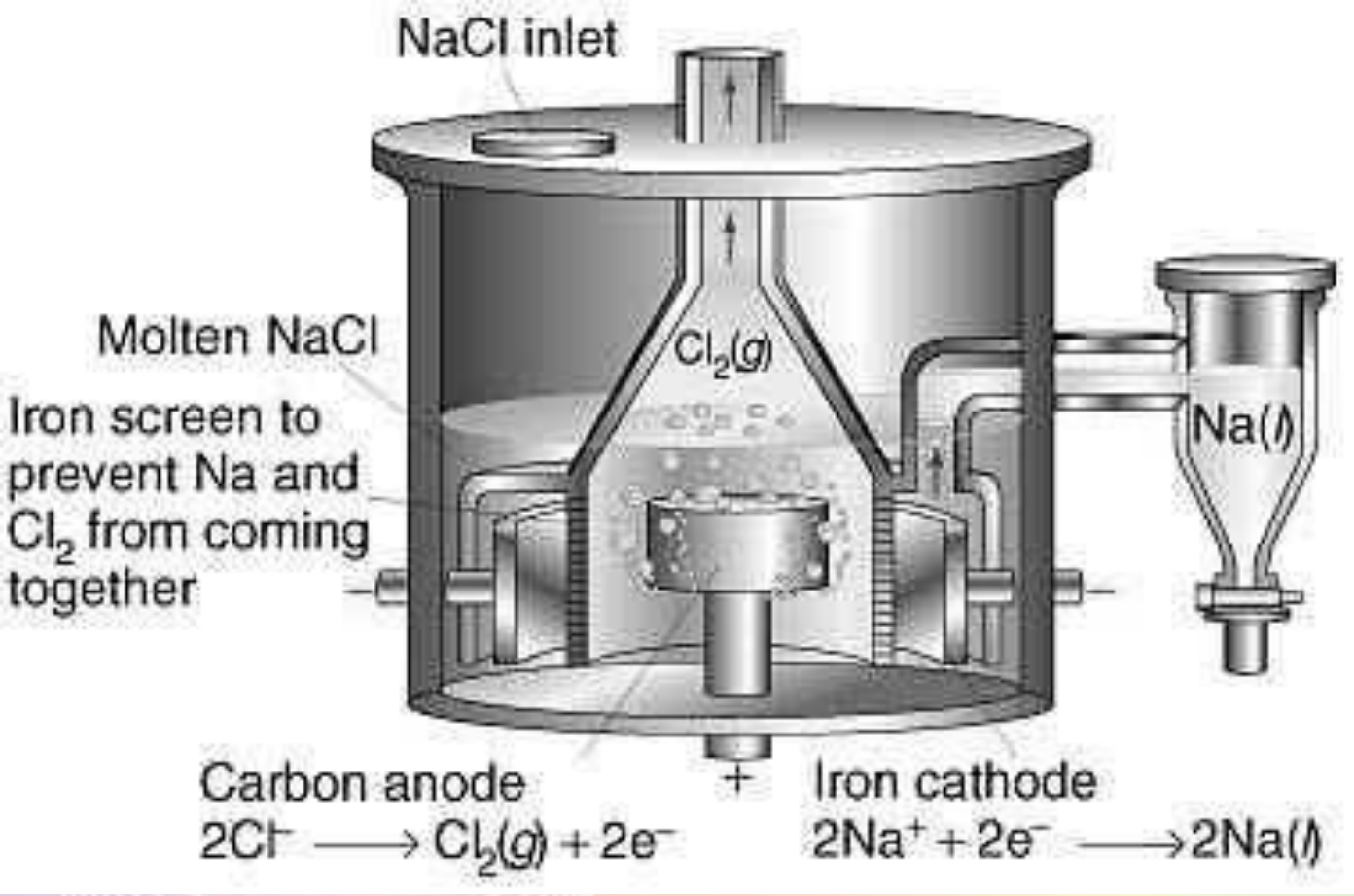
  $2K_2CO_3(s) + 2CO_2(g) + 2H_2O(g) \rightarrow 4KHCO_3(s)$

- Net reaction:

  $4KO_2(s) + 4CO_2(g) + 2H_2O(g) \rightarrow 4KHCO_3(s) + 3O_2(g)$

# Sodium

## Preparation: Downs Process



# Sodium

Uses :

- extraction of other metals → reduction potential >>>

  $TiCl_4$ ($\ell$) + 4Na ($s$) → Ti ($s$) + 4NaCl ($s$)

  NaCl rinsed with water → soluble → pure Ti metal

# Sodium

Uses

- production of TEL (tetra ethyl lead)

$$4Na\text{-}Pb(s) + 4C_2H_5Cl(g) \rightarrow (C_2H_5)_4Pb(\ell) + 3Pb(s) + 4NaCl$$

# Alkali salts

1. Chlor – alkali industry

Material : NaCl (brine) most important

Preparation: electrolysis of NaCl

$$NaCl(aq) + 2H_2O(\ell) \xrightarrow{\text{electrolysis}} 2NaOH(aq) + H_2(g) + Cl_{2(}g)$$

Caustic-soda: concentrated commercial NaOH for soap making, paper and pulp industry.

# Alkali salts

2. Sodium sulfate ($Na_2SO_4$)

Other name : salt cake

Preparation :

$$2NaCl(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(s) + 2HCl(aq)$$

# Alkali salts

3. Sodium carbonate ($Na_2CO_3$)

Other name : soda ash → anhydrate

Source :

- washing soda ($Na_2CO_3.10H_2O$)
  - hydrated
- trona/sodium sesquicarbonate
  - (90% $Na_2CO_3.NaHCO_3.2H_2O$)

# Alkali salts

3.Sodium carbonate ($Na_2CO_3$)

Preparation : Solvay process

Reaction:

$2NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2$

brine limestone soda ash

# Alkali salts

## 3.Sodium carbonate ($Na_2CO_3$)

Uses :

- glass industry

  $Na_2CO_3(\ell) + x\ SiO_2(s)$

  $\rightarrow Na_2O.xSiO_2(\ell) + CO_2(g)$ (T ± 1500$^oC$)

- water softener

  $Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$

# Alkali salts

4.Sodium hydrogen carbonate ($NaHCO_3$)

Other name : sodium bicarbonate,
baking soda

Preparation :

- Solvay process
- Adding $CO_2$ to saturated solution of sodium carbonate (inexpensive)

$Na_2CO_3(aq) + CO_2(g) + H_2O(\ell) \rightarrow 2NaHCO_3(s)$

# Alkali salts

4. Sodium hydrogen carbonate ($NaHCO_3$)

Uses :

- extinguisher

  $NaHCO_3(s) \xrightarrow{\triangle} Na_2CO_3(aq) + CO_2(g) + H_2O(\ell)$

- cake swelling

  $2\ NaHCO_3(s) + Ca(H_2PO_4)_2(s) \rightarrow Na_2HPO_4(s) + CaHPO_4(s) + 2CO_2(g) + 2H_2O(\ell)$

# Alkali salts

4.Sodium hydrogen carbonate ($NaHCO_3$)

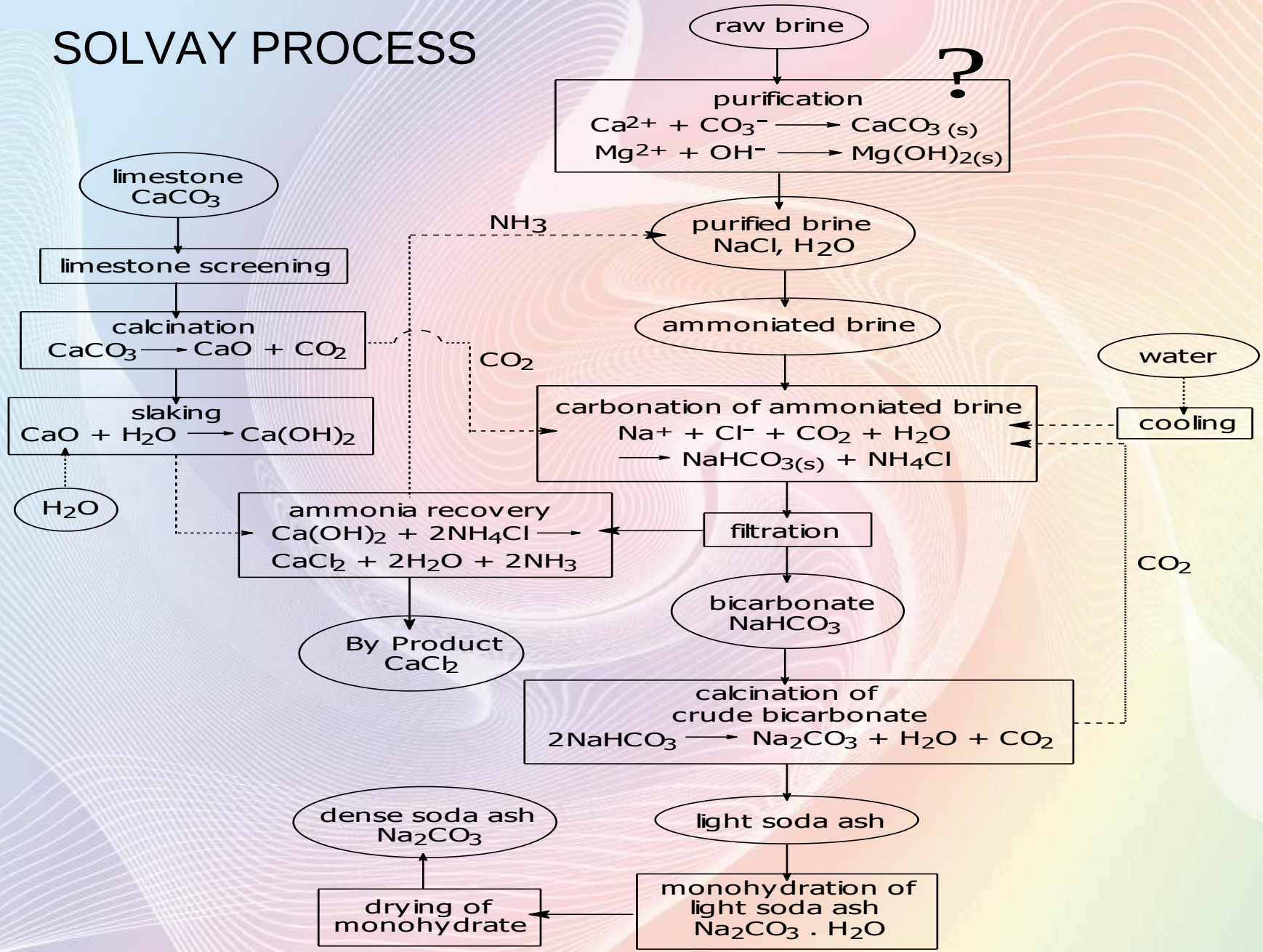
Uses

- prevent salt clotting

  $MgCl_2(s) + 2NaHCO_3(s)$

  $\rightarrow MgCO_3(s) + 2\ NaCl(s) + H_2O(l) + CO_2(g)$

# SOLVAY PROCESS



# Alkali salts

5.Sodium nitrate ($NaNO_3$)

Other name : Chile saltpeter

Origin :

$NH_3(g) + 2O_2(g) \rightarrow NO_3^-(aq) + H_3O^+(aq)$

$NO_3^-(aq) + NaCl(aq) \rightarrow NaNO_3(s) + Cl^-(aq)$

Uses: production of $KNO_3$

# Alkali salts

6.Kalium nitrat ($KNO_3$)

Preparation : exchange reaction

$NaNO_3(aq) + KCl(aq) \rightarrow KNO_3(aq) + NaCl(aq)$

Uses : gun powder making (+ carbon and sulfur)

$2\ KNO_3(s) + 4C(s) \rightarrow K_2CO_3(s) + 3CO_3(g) + N_2(g)$

$2\ KNO_3(s) + 2S(s) \rightarrow K_2SO_4(s) + SO_2(g) + N_2(g)$

# The Alkali Metals And Living Matter

- Oxygen, carbon, hydrogen, and nitrogen are the most abundant elements in the human body, in the order listed.

- Sodium ions are found primarily in fluids outside cells and potassium ions are abundant in fluids within cells.

# The Alkali Metals And Living Matter

- Because most alkali metal compounds are water soluble, many acidic drugs are administered in the form of their sodium or potassium salts.

- Lithium carbonate is used in medicine to level out the dangerous manic “highs” that occur in manic-depressive psychoses.

# Diagonal Relationships: The Special Case Of Lithium

- In some of its properties, lithium resemble magnesium
  - Lithium carbonate, fluoride, hydroxide, and phosphate are much less water-soluble than those of other alkali metals, insoluble to those of alkaline earth metals.
  - Lithium is the only alkali metal that forms a nitride ($Li_3N$)

# Diagonal Relationships: The Special Case Of Lithium

- In some of its properties, lithium resemble magnesium.
  - When it burns in air, lithium forms a normal oxide ($Li_2O$) rather than a peroxide or a superoxide.
  - Lithium carbonate and lithium hydroxide decompose to form the oxide on heating, while the carbonates and hydroxides of other Group 1A metals are thermally stable.