Production of bromine compounds

General
Most of the bromine produced in Israel is used for the manufacture of bromine compounds. The Dead Sea Bromine Group produces about 70 different bromine compounds. Some are produced at Ramat Hovav and others in plants abroad: Broomchemie in Holland and Clearon in the USA.
The products are marketed in about 100 different countries through an extensive marketing and sales network, with headquarters in the Dead Sea Bromine Group management offices in Beer-Sheba and local offices in international commercial centers in Europe, America, South Africa and the Far East.
The Group’s principal products are manufactured in the Ramat Hovav plant. Most are consumer products and a few are intermediates for production of other materials.
The plant in Holland also manufactures fine chemicals and custom-made products. The USA plant is devoted mainly to water treatment products. Recently the Dead Sea Bromine Group acquired part of Chemada, a company located in the south of the Israel. This company specializes in the production of small quantities of custom-made organic bromine compounds used for specific purposes.
The following scheme classifies the different materials produced by the Bromine Group:
Production of bromine compounds

Although at present the USA is still the main producer of bromine compounds, Israel’s share is increasing every year. This is due to the great advantage Israel has in being able to produce bromine from a surface brine source, as compared to the relatively low bromine ion concentrations of the brine in the USA and the growing need for deeper drillings with steadily increasing production costs.

As we see from this data, the USA and Israel are the most important bromine producers in the world. Today, the Dead Sea Bromine Group is the second largest bromine and bromine compounds producing company in the world (in the USA there are two companies).

In this chapter we shall focus on the production of a number of bromine compounds. We shall do this by applying the principles presented in previous chapters of this book and by studying the problems posed by the industrial production of these compounds. We shall describe the common principles of these processes and highlight the unique features of each of them. We have selected a few relatively simple, inorganic and organic compounds. Some are produced in continuous processes, others in batch processes or by a combination of both, but all processes are computerized, using advanced technologies.
We shall describe the chemical principles underlying these processes and the
supporting technologies, as well as safety, ecological and economic aspects. The
following scheme briefly illustrates the various aspects of production processes
as performed in the Dead Sea Bromine Group, at the same time providing a
generalized framework applicable to many other industrial production processes:

As the products become more advanced and the production processes more
complex, the accompanying problems get increasingly complicated. Nevertheless,
it should be kept in mind that advanced products have a higher **economic added
value**, meaning a higher price of the product relative to the price of the raw
material, which increases projected profits.

**Economic added value of product**: Price of product relative to price of raw
materials. The price of sophisticated products, whose production requires
considerable know-how, is high relative to the price of raw materials. In such
cases the products have a high added value.
Production of bromine compounds

The following price table (from 1998) illustrates the significance of the economic added value of sophisticated products compared to the price of the raw material, bromine:

<table>
<thead>
<tr>
<th>Product</th>
<th>Price in US$ per ton</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromine</td>
<td>900-1000</td>
</tr>
<tr>
<td>Methyl bromide</td>
<td>2000-3000</td>
</tr>
<tr>
<td>Flame retardants</td>
<td>2000-4500</td>
</tr>
<tr>
<td>Fine chemicals¹</td>
<td>10,000 and more</td>
</tr>
</tbody>
</table>

5.1 - Production of hydrogen bromide, HBr

¹ Fine chemicals – Products sold in relatively small quantities at high prices whose syntheses involve many stages.
Production of bromine compounds

Properties

Name of material: Hydrogen bromide – HBr
Molar mass: 80.9 g/mol
Melting point: -88.5°C
Boiling point: gas –67°C
   solution (48%): 126°C
Solubility in water: high
   221 g in 100 cm³ water (at 0°C)
   130 g in 100 cm³ water (at 100°C)
Solubility in other solvents: Soluble in alcohol and acetic acid
Density: Heavier than air
Flammability: Non-flammable, non-explosive
Stability: Stable under regular conditions
Toxicity: Gas causes burns and is very toxic on inhalation
   concentrated solution causes burns
Neutralizing agent: 10% solution of NaHCO₃
Typical reactions:
- Reacts with bases
- Reacts with metals
- Reacts with strong oxidants
- Reacts with many carbon compounds such as alkanes, alkenes and alcohols
Applications: Usually marketed as a 48% or 62% aqueous solution.
   The solution is used as a bromine source in organic and inorganic chemical industry

Hydrogen bromide itself is not used as final product, but serves as a very important bromine source for many organic and inorganic compounds. Although hydrogen bromide is usually supplied as an aqueous solution, the actual product is a gas, which is subsequently absorbed in water. It is produced in all the group’s plants.

Hydrogen bromide gas is formed by the reaction between hydrogen and bromine according to the following equation:

\[ \text{H}_2 + \text{Br}_2 \rightleftharpoons 2\text{HBr}_\text{g}, \quad \Delta \text{H} = -103 \text{ kJ for the forward reaction} \]

Following are the values for the equilibrium constants \( K \), for formation of hydrogen bromide gas at three different temperatures:
Is this a thermodynamically spontaneous reaction at all three temperatures?
In industry the selected reaction temperature is 500ºC. Why?
What is the ratio of the concentrations of products and reactants at this temperature? Is the process at 500ºC, as carried out by the Dead Sea Bromine Group in equilibrium or does it go to completion? Explain.

To obtain hydrogen bromide gas from bromine and hydrogen, both reactants must be pure. The starting materials selected are:

a. Hydrogen, for the most part a byproduct of a hydrocarbon cracking process in a nearby plant, partly a byproduct of the production of sodium bromate, NaBrO₃(s), in the Dead Sea Bromine Group plant, and partly a byproduct of chlorine production.

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2 For details see Page 182
b. Chlorine-free bromine, vaporized before entering the reaction tower. Hydrogen bromide production is a continuous process described in the following scheme:

- Why is hydrogen bromide produced in a continuous process?
- What kind of construction materials must be used for an aqueous hydrogen bromide production facility?
- Why is hydrogen bromide marketed as solution and not as compressed gas?

As we can see, the process consists of three main stages: the hydrogen bromide production reaction; bromine absorption; and, hydrogen bromide absorption in water.

**Stage A: The hydrogen bromide reaction**
The first stage consists of hydrogen bromide gas formation, which occurs by the reaction between bromine gas and hydrogen in a tube-shaped reactor. As mentioned before, although the reaction between hydrogen and bromine is exothermic, its activation energy is high. Since the reaction proceeds without a catalyst, prior heating to a temperature sufficiently high to start the reaction is necessary.

As in any industrial process, the aim is to obtain the highest possible amount of hydrogen bromide per time unit. Although theoretically it is an equilibrium reaction, examination of the reaction conditions will show that we are actually
Production of bromine compounds

dealing with a reaction going to completion. We can influence the amount of hydrogen bromide formed simply by increasing the concentration of reactants, which in accordance with the collision theory increases the reaction rate. It is possible to increase the concentrations of both reactants and to keep the molar ratio of reactants the same as in the reaction equation. Alternatively, we can use an excess of one of the reactants and so increase the reaction rate. What we see here is an example of a kinetically controlled reaction rate.

- What are the advantages and disadvantages of increasing the concentration of both the reactants, hydrogen and bromine?

- What are the advantages and disadvantages of increasing the concentration of only one reactant?

Addition of excess bromine is not advisable for the following reasons:
a. Bromine is expensive and all production processes are planned to make the fullest possible use of the material in order to increase profits.
b. For environmental reasons it is impossible to release excess bromine into the atmosphere, but hydrogen can be released if it does not contain polluting substances.
c. The final product must be pure, without residual bromine.
Production of bromine compounds

For these reasons excess hydrogen is used.

- **Hydrogen bromide is generated at a pressure of 1 atmosphere. Explain why increasing the pressure is not advantageous.**
- **Which properties should the construction materials of the hydrogen and bromide reactor have?**

Reactants and reaction temperature determine the type of **construction materials** for the reactor. The reactor is made from quartz, which is resistant to bromine and capable of enduring the high temperatures prevailing inside. Since the reaction is exothermic, there is no need to insulate the reactor to keep the temperature at 500°C (the temperature is kept constant by exposing the reactor to air). Under these conditions the conversion rate of the bromine is relatively high, but as mentioned earlier, excess hydrogen and traces of non-reacted bromine are left. Although for certain purposes this product can be used without further purification, separating the excess bromine and hydrogen is usually necessary. The hydrogen and bromine must be separated from the gas mixture leaving the reactor. According to the flow diagram, the bromine is separated first, followed by the hydrogen.

- **How is the bromine separated?**
- **How is the hydrogen separated?**
- **Why is the hydrogen not separated before the bromine?**

**Stage B: Removal of bromine**
The bromine adsorption stage is of great importance for the purity of the final product. Adding the reaction mixture to water without pre-adsorption of the bromine leads to complete absorption of the bromine by the bromide solution. Remember that we get a solution rich in bromine ions, Br\(^{-}\)\(_{aq}\), and therefore Br\(_3\)\(_{aq}\) ions are formed, which are highly soluble in water (see Page 64).
The reaction mixture containing hydrogen bromide, hydrogen and traces of bromine is cooled off while flowing into the bromine adsorption reactor. The adsorption proceeds very similarly to the adsorption to activated carbon, performed in the experiment in Section 4.3 of Chapter 4. The pH of the resulting waste solution, which also contains some hydrogen bromide acid, must be adjusted to neutral before entering the waste or being recycled.
- How would you neutralize this solution? Suggest a suitable neutralizing agent.

**Stage C: Hydrogen bromide absorption in water**

After leaving the adsorption reactor the hydrogen bromide, together with non-reacted hydrogen, enters the water-containing absorption column.

- Write the reaction equation for the absorption in water.
- Explain why the excess hydrogen leaves the absorption column.

This glass-made column is filled with polymer (PVDF) disks.

- The gas mixture enters the column from below and the water enters from above. Explain why.
- What is the purpose of the disks?

A 48%, or more concentrated 62%, solution of hydrogen bromide is obtained. The excess hydrogen is released into the atmosphere, but in a planned improvement of the process it will be returned to the reactor after compression. The aqueous hydrogen bromide is stored in polyethylene-coated steel containers or containers made from durable plastics, such as PVC (polyvinyl chloride). The hydrogen bromide is stored and supplied in plastic containers of different sizes. These containers are either made from durable plastics or have an interior plastic coating.

- Why are aqueous hydrogen bromide solutions stored in plastic-coated containers?
- Can aqueous hydrogen bromide be kept in steel containers? Explain.
- Adjacent to the hydrogen bromide production plant, drums containing base can be seen. Explain.
- Which bases can be used for this purpose? Explain.
- What are the arguments for choosing a particular base? Explain.
Spilled aqueous hydrogen bromide can be quickly and efficiently neutralized with slaked lime, quicklime, or a sodium hydroxide solution in water. A leak of hydrogen bromide gas is neutralized with ammonia.

- Give the equations for the reactions of aqueous hydrogen bromide with: slaked lime, quicklime, and sodium hydroxide solution.
- Give the equation for the reaction between hydrogen bromide gas and ammonia.
- What are the advantages and disadvantages of using each of these substances?
- Why is the use of calcium carbonate for neutralization of aqueous hydrogen bromide not recommended?
- If no ammonia is available, spraying with water may be used to neutralize hydrogen bromide gas. Explain why.
Production of bromine compounds

As we have seen before, hydrogen bromide is used as precursor for many different compounds, some of which are produced by the Dead Sea Bromine Group. For example, hydrogen bromide can be used for the synthesis of:

\[
\text{CH}_3\text{CHBrCH}_3(\text{g}) \quad \text{HBr} \quad \text{LiBr}_{(\text{aq})} \quad \text{NaBr}_{(\text{s})} \quad \text{CaBr}_2(\text{aq}) \quad \text{KBr}_{(\text{s})}
\]

The question marks in the above scheme represent production processes of a number of compounds using hydrogen bromide as starting material.
- Which methods would you suggest to synthesize these compounds from hydrogen bromide?
- Which other starting materials are needed? Give reaction equations and explain.
- On which chemical principles are the methods you suggest based?
Production of bromine compounds

Hydrogen bromide is a strong acid, which reacts with bases to form inorganic bromides. Examples of such reactions are the formation of calcium bromide, CaBr₂, or lithium bromide, LiBr, which we shall discuss later. Hydrogen bromide can also react with various organic compounds. With alkenes, addition reactions take place and with alcohols or alkanes, substitution reactions.

Give reaction equations for the reaction of hydrogen bromide with:
- alkenes
- alcohols
- halo-alkanes

An example of a substitution reaction is the formation of methyl bromide, which we shall describe in greater detail later in this chapter.

Hydrogen bromide is also formed as a byproduct of various organic reactions. For example, hydrogen bromide is formed as a result of the reaction between an alkane and bromine.

- Give the equation (by way of example) between propane and bromine.
- What are the proper reaction conditions?
- Do you think that pure hydrogen bromide is obtained? Explain.
- This reaction is likely to generate more than one product.
- What are the possible products? Give the formulas.
- How can the hydrogen bromide obtained in this reaction be purified? Explain.

The hydrogen bromide generated as a byproduct of various organic reactions is collected, purified and absorbed in water. The aqueous solution obtained is relatively pure and can be used as raw material for the synthesis of different compounds.

Read about the use of bromide solutions for oil drillings on Page 255.
- Why can aqueous hydrogen bromides obtained as byproducts of organic reactions be used for the production of oil drilling products?

For production of a lithium bromide solution, which is used for air conditioning and cooling systems (see Page 265) aqueous hydrogen bromide produced in the plant from hydrogen and bromide is used, and not solutions obtained as byproduct.
- Explain why.
- Give two advantages of using aqueous hydrogen bromide obtained as byproduct of one process, as raw material for another process. Explain.
5.2 - Production of Calcium Bromide, CaBr$_2$ (solution and solid)

**Properties**

Name of material: Calcium bromide – CaBr$_2$

- Clear and viscous, odorless and non-volatile solution
- White, odorless solid
- Molar mass (of solid): 200 g/mol
- Melting point: solid – less than 760ºC
  - solution (52%) -7ºC
- Boiling point: solid 810ºC
  - solution (52%) 130ºC
- Density: solid 3.35 g/cm$^3$
  - solution 52% 1.7 g/cm$^3$
- Solubility in water: Good
  - 142 g in 100 cm$^3$ water (at 30ºC)
- Solubility in other solvents: Dissolves well in alcohol and acetone
- Flammability: Non-flammable, non-explosive
- Stability: Stable under regular conditions
- Toxicity: The solution may cause slight irritation of eyes and skin
  - Inhalation of powder may cause severe irritation of respiratory system
  - Swallowing may cause damage to the central nervous system

Typical reactions (of the solution):
- Hygroscopicity
- Strong heating can release bromine and hydrogen bromide vapors
- Can react with strong acids or oxidants

Applications: Usually supplied as a 52% aqueous solution.
The solution is used as pressure regulator in oil drillings.

In the Section 5.1 we saw that the Dead Sea Bromine Group produces two kinds of hydrogen bromide solutions. One is obtained by dissolving hydrogen bromide, formed by the reaction between hydrogen and bromine, in water. The second is a byproduct obtained from the industrial production of various organic compounds.

Which type of aqueous hydrogen bromide should be used? This question can only be answered if we know the use and the required purity of the product. The choice of raw materials for any product depends on its final application. It
Production of bromine compounds

is not economical to use an ultrapure, expensive material, if there is no need for it. Using alternative, cheaper raw materials reduces production costs e.g., in the case of calcium bromide solution.

Calcium bromide solutions are used in the oil industry as auxiliaries for oil drillings (see Chapter 6). These solutions, which are pumped in the ground do not of course have to be as pure as those used for production of medicines, foodstuffs, air conditioners, etc.

Nevertheless, to satisfy market requirements regarding environmental protection and prevention of soil and water pollution, it is necessary to purify these solutions. It is important to note that we benefit twice from using byproducts. First because we save on production costs by using cheaper raw materials obtained from byproducts. Second, because we save on the treatment of acid solutions which, if not used, would be hazardous waste requiring neutralization.

For formation of a calcium bromide solution a base is needed, in addition to aqueous hydrogen bromide.

- Which bases can be used? Give the reaction equations.
- Which criteria would determine the appropriate base for the production of calcium bromide?

For many years calcium bromide solutions have been prepared by an acid-base reaction between an aqueous solution of hydrogen bromide and solid calcium hydroxide, which is also called slaked lime.

Calcium hydroxide is called slaked lime because of the way it is produced. The material is obtained from quarried calcium carbonate, CaCO₃. The calcium carbonate is first decomposed by heating with a formation of carbon dioxide and calcium oxide, which is called quicklime:

\[ \text{CaCO}_3 \rightarrow \text{CaO}_{(s)} + \text{CO}_2_{(g)} \]

The calcium oxide is reacted with water, yielding calcium hydroxide which is called slaked lime.

\[ \text{CaO}_{(s)} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2_{(s)} \]

By reacting slaked lime with aqueous hydrogen bromide one obtains a calcium bromide solution:

\[ \text{Ca(OH)}_2_{(s)} + 2\text{H}_3\text{O}_3_{(aq)} + 2\text{Br}^-_{(aq)} \rightarrow \text{Ca}^{2+}_{(aq)} + 2\text{Br}^-_{(aq)} + 4\text{H}_2\text{O}_{(l)} \]

Aqueous solution of HBr
The choice fell on this raw material because, as we shall see later, compared to other raw materials, it allowed the development of a simpler technological process. Actually slaked lime is an inhomogeneous material, since it contains traces of calcium carbonate, CaCO$_3$\(\text{aq}\), which also reacts with hydrogen bromide in an acid-base reaction:

$$\text{CaCO}_3(\text{s}) + 2\text{H}_3\text{O}^+ + 2\text{Br}^- \rightarrow \text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l}) + \text{Ca}^{2+} + 2\text{Br}^-$$

- **What is the source of the calcium carbonate in the slaked lime?**
- **Which problems can the presence of calcium carbonate in slaked lime cause?**
  **Explain**

The main problem is the release of carbon dioxide. Small quantities of this gas, like those obtained during production of calcium bromide, do not cause environmental damage. The release of gas, however, can cause serious technological problems.

- **What kind of problems can the release of carbon dioxide cause?**
- **Suggest methods to solve these problems.**
Production of bromine compounds

Sampling points in the installation

The carbon dioxide generated by the system can build up pressure in the reactor. This fact must be taken into account during the design of the reactor. The gas may also contain different materials found in the reactor: water droplets, hydrogen bromide vapor and even slaked lime particles. The combined effect of these materials and the gas formed during the reaction can be both a decreased yield and environmental damage. Absorbing the carbon dioxide can solve these problems.

- Which of the following materials could be successfully used as absorbents:
  - Water?
  - Sodium hydroxide solution?
  - Calcium hydroxide solution?
  - How would you prevent a decrease in yield?

Recently the procedure has been changed and instead of Ca(OH)$_2$(s), which costs about $80/ton, CaCO$_3$(s) (limestone) is being used, which costs only $40/ton.

- What are the advantages of this change?
- What are the disadvantages of this change?
- Suggest methods to overcome the disadvantages.
- Why was the process developed initially with the more expensive calcium hydroxide rather than with calcium carbonate which is cheaper?

This plant produces an average of 150,000 liter calcium bromide at a concentration of 52% per 24 h.

- Calculate how much CO$_2$(g) is liberated in 24 hours. Give your calculation.

The Dead Sea Bromine Group now applies a new, batchwise method, which is outlined in the following scheme:
Is this an exothermic or endothermic reaction?

How can the reaction be controlled and its completion verified?

What kind of construction materials should be used for the reactor? Suggest suitable material.

Is the order in which the reactants are added to the reactor of any importance?

**Stage A: Reaction**

First aqueous hydrogen bromide is added to the reactor, followed by calcium carbonate with stirring.

The order in which the reactants are added actually dictates the materials from which the reactor is constructed. In this case aqueous hydrogen bromide is added first and therefore both the reactor and the stirrer are glass-coated.

Can glass be used for a basic solution?

Why can glass be used despite the fact that base is added?

In this case too (as in the process based on slaked lime) the CO$_2$(g) formed is absorbed in water. There is no need to use a base solution, since the slaked
Production of bromine compounds

lime particles and the hydrogen bromide, which actually are raw materials, are absorbed together with the gas and dissolve in water. The resulting acid-base reaction generates the product, a calcium bromide solution. This solution is recycled to the reactor, preventing waste of raw material, and pollution. Although the reaction between aqueous hydrogen bromide and calcium carbonate is exothermic, it is much less so than the reaction between aqueous hydrogen bromide and slaked lime (calcium hydroxide). This is an additional advantage of the new process, because no special cooling of the reactor is needed.

- The endpoint of the reaction can be determined by measuring the pH or the temperature of the solution. Explain.

- What are the disadvantages of an exothermic reaction?
- How can the reactor be cooled in the case of an exothermic reaction?

Stage B: Filtration
After its formation, the calcium bromide solution must be filtered. The solution is filtered through a solid, quarried material, called Dakelite. A thick layer of this material is placed on the surface of a rotating, perforated drum. The calcium bromide solution is drawn by vacuum into the hollow space of the drum. The drum rotates while immersed in the calcium bromide solution. The solution is drawn inside through the Dakelite layer, purified and continues to the next stage. Most impurities accumulate on the outer surface of the Dakelite, which is slowly and continuously removed with a scraper. The impurities stick to the Dakelite, while the clear and pure solution flows through the holes and is collected in storage tanks. The Dakelite waste is sent to the industrial hazardous waste processing plant at Ramat Hovav. Reactivation of the Dakelite by purification has been considered, but was rejected for technical and economic reasons.

Recovery: Process of renewing a material and restoring its active state. In many cases reactivation involves distillation, washing, etc., to remove impurities adsorbed to the material.

Stage C: Evaporation
A 48% calcium bromide solution is usually obtained. Since most calcium bromide is supplied as a 52% solution, an evaporation stage must be added to increase the concentration.
Production of bromine compounds

Due to the exothermic reaction, the calcium bromide solution formed is still warm (50°C), and this saves energy needed for the evaporation stage. The solution is put in the evaporator, which functions as a heat exchanger, and the water evaporates by the action of steam introduced in the evaporator. An extremely dense solution is obtained (about 1.7 gram/cm³), the use of which will be discussed in the next chapter.

Stage D: Filtration
Additional filtration is needed to achieve the required purity.

Stage E: Drying
Some of the solution is dried to generate solid calcium bromide, which is most often used to make dilute calcium bromide solutions more concentrated (e.g., during recycling of solutions after their use).

Calcium bromide solution storage tanks

Calcium bromide solutions are stored in iron tanks coated with an internal epoxy layer. Such storage tanks can be found both in the plant and in the ports. The calcium bromide solutions are transported from the plant to the containers in the port by container trucks and to the countries of destination abroad in container ships. These ships empty their contents into enormous storage tanks located in the ports, and the product is transported to the customers by container trucks.

Safety
As in any other production facility, here too we need to take appropriate safety measures.
To prevent pressure from building up in the reactor as a result of the release of carbon dioxide, CO\(_{2(g)}\), a number of precautions are taken:

- Computerized control of the molar ratios in the reaction. The molar concentration of the acid (introduced, in its entirety, at the start of the reaction) is calculated by measuring its volume and density, and weighed portions of limestone are added accordingly. At the start of the reaction, most of the material is added quickly and towards the end of the reaction the remainder is added slowly and gradually, until the correct p\(\text{H}\) is obtained.

- Extra process control by measuring the p\(\text{H}\) to determine the endpoint of the reaction.

- The CO\(_{2(g)}\) is removed from the reactor by bellows that blow the gas into the absorption tower, which contains water (as described on Page 96).

- Safety seals are placed at critical points in the system, which are broken if the pressure exceeds a certain value, causing the gas to pass into an absorption vessel. Breaking the seals automatically shuts off the limestone feed.

- Process control by a pressure gauge, which monitors the pressure caused by release of CO\(_{2(g)}\). When the pressure exceeds a certain threshold value, the limestone feed is shut off.
5.3 - Production of sodium bromate, NaBrO₃, and potassium bromate, KBrO₃

**Properties**

**Name of material: Sodium bromate, NaBrO₃**

- White, odorless material (powder or crystals)
- Molar mass: 150.9 g/mol
- Melting point: 381°C
- Boiling point: decomposes
- Density: 3.34 g/cm³ at 20°C
- Solubility in water: Dissolves well in water: 28.3 g in 100 g water at 25°C
  90.9 g in 100 ml water at 100°C
- Solubility in other solvents: Dissolves well in alcohol
- Flammability: May form flammable and explosive mixtures in the presence of reducing agents, sulfuric acid, ammonium salts or metal powder. Decomposes if involved in a fire or at temperatures above 380°C with release of toxic gases.
- Toxicity: Toxic on swallowing or inhalation. Causes respiratory problems, abdominal pain, vomiting and irritation of skin, eyes and mucous tissues.

**Typical reactions:**
- Strong oxidant
- Reacts with strong acids under heat development and release of bromine.

**Applications:** hair dressing, dyeing of textiles (bleaching of fabrics, initial treatment of wool) and distillation of precious metals.

**Sodium bromate** can be produced by reacting liquid bromine with a solution of sodium hydroxide:

\[
3\text{Br}_2(l) + 6\text{Na}^+(aq) + 6\text{OH}^-(aq) \rightleftharpoons 6\text{Na}^+(aq) + \text{BrO}_3^-(aq) + 5\text{Br}^-(aq) + 3\text{H}_2\text{O}(l)
\]

For the forward reaction: \(\Delta H < 0\)

According to the reaction equation most of the bromine is converted to bromine ions: from every three moles of bromine, five moles of bromine ions are formed and only one mole of bromate ions.

To improve the efficiency of the process, an electrolysis stage is added, in which the bromine ions are oxidized at the anode and reconverted to bromine:

\[
2\text{Br}^-(aq) \rightleftharpoons \text{Br}_2(l) + 2e^-
\]

This way the bromine that was not converted is recycled and the bromine obtained in Reaction (2) can react again in Reaction (1), etc. The addition of the electrolysis stage increases the conversion efficiency of bromine to bromate.
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Parallel to the oxidation of the bromine ions at the anode, hydrogen is formed at the cathode:

\[ 2\text{H}_2\text{O} + 2e^- \rightleftharpoons \text{H}_2\text{O}_2 + 2\text{OH}^- \]

The hydrogen is used for the production of hydrogen bromide as discussed in Section 5.1.

The production process of sodium bromate is quite complicated and to carry it out efficiently a number of chemical and technological problems must be solved. In the first chapter we encountered a few reactions that can take place in a solution containing bromine and sodium hydroxide at different concentrations (see Page 15). Some of the reactions are desirable since they contribute to the yield of the required product, but some are undesirable and conditions should be adjusted to minimize them:

\[ \text{H}_2\text{O}(l) + \text{Br}_2(aq) \rightleftharpoons \text{H}_3\text{O}^+ + \text{Br}^- + \text{HOBr} \]
\[ \text{H}_2\text{O}(l) + \text{HBrO}(aq) \rightleftharpoons \text{H}_3\text{O}^+ + \text{BrO}^- \]
\[ \text{H}_2\text{O}(l) + 2\text{HOBr}(aq) + \text{BrO}_3^- \rightleftharpoons 2\text{H}_2\text{O}^+ + 2\text{Br}^- + \text{BrO}_3^- \]

When base conditions are too strong a competitive reaction can occur at the anode generating oxygen:

\[ 4\text{OH}^- \rightleftharpoons 2\text{H}_2\text{O} + \text{O}_2 + 4e^- \]

- In which direction will the reaction move at very high pH?
- In which direction will the reaction moves at very low pH?
- How can the reaction be influenced so that it will proceed in the right direction?

This is a complex situation, which requires strict control of the pH. On the one hand the pH is basic (due to the sodium hydroxide), and on the other hand a too high pH is not permissible because of the formation of undesirable competitive reactions. If the pH is too high too much BrO$_3^-$ and oxygen are formed. If, by contrast, the pH is too low, the main reaction products are hypobromite acid, HOBr and bromine. To obtain the highest yield of sodium bromate the reaction should be carried out under mildly basic conditions (pH 8-9). In addition, before the solution is transferred to the crystallization stage, small amounts of ammonium bromide are added to reaction II (see general scheme of production process on Page 188).
Production of bromine compounds

- Which reactions can take place between ammonium bromide and a basic solution?
- What determines which reaction will take place?
- What is the importance of adding ammonium bromide?

The dependence of the various stages of the process on the concentration of base requires continuous and strict pH control.

To accomplish this, samples used to be taken regularly from the solution entering the electrolysis cell and the ratio of the bromine and bromate ions measured. To improve monitoring efficiency and reduce the number of samples necessary, a mathematical model was built, based on previous experience, which is now used to calculate the concentrations projected in the system. About once a day a sample is taken and appropriate corrections made if the results differ from the model.

Stage A: Reaction

Reaction takes place in two successive reactors (I, II). Liquid bromine and sodium hydroxide solution are allowed to flow into reactor I (which is kept at fixed pH). The resulting mixture is passed on to reactor II (also kept at fixed pH). To this reactor a solution of ammonium bromide is added to eliminate the residual \( \text{BrO}^- \) ions:

\[
2\text{NH}_4\text{Br}_{(s)} + 3\text{BrO}^-_{(aq)} + 2\text{OH}^-_{(aq)} \rightleftharpoons 5\text{Br}^-_{(aq)} + \text{N}_2_{(g)} + 5\text{H}_2\text{O}_{(l)}
\]

This reaction results in a decrease in the concentration of \( \text{OH}^-_{(aq)} \).
- What are the other advantages of this reaction? Give a detailed explanation.

The reaction generates nitrogen.
- What problems may arise as a result of the nitrogen formation?
- How can they be solved?
- Can the formation of nitrogen cause environmental pollution?

The nitrogen released in the reaction is led into an absorption tower containing sodium hydroxide.
- Why is the nitrogen led into an absorption column?
- Why does the absorption column contain sodium hydroxide?
- What can be done with the solution obtained in the column?
Production of bromine compounds

Stage B: Separation of crystals from solution (and treatment of crystals)
The solution obtained in reactor II is filtered and subsequently transferred to a crystallizer in which the water is partly evaporated, until the solution is oversaturated and sodium bromate crystals, the desired product, start to precipitate.

Crystallization: Precipitation of solid crystals from a saturated solution.

In fact, a thick slurry is obtained, which is transferred to a special system (multipurpose centrifuge) to carry out the following operations:
- filtration
- washings with water
- additional filtration
- hot air drying

After finishing these operations, the product is obtained in the form of white sodium bromate crystals, and in addition a saturated solution of sodium bromate containing a high concentration of bromine ions, is obtained. The solid crystals are further worked up as described below, while the filtrate is transferred to the electrolysis installation.
- What is required of the construction materials of the electrolysis installation?

- Prepare a list of factors that can influence the efficiency of the electrolytic reaction.

Stage C: Electrolysis

Electrolysis is performed in a device composed of a number of parallel-coupled electrolytic cells, whose anodes are coated with noble metals and whose cathodes are made from steel. To increase the electric yield and conserve energy, it is best to perform the electrolysis at the lowest possible voltage. It was found that it is possible to decrease the voltage by increasing the temperature. This is another example of balancing advantages and disadvantages. On the one hand it is worthwhile increasing the temperature to save electrical energy, but on the other hand increasing the temperature may cause procedural problems and have technological limitations. All these aspects depend, among others, on:
- Resistance of the construction materials used for the electrodes and the cells
- The boiling point of the solution
- The effect of the temperature on the electrical resistance of the solution

As in many other instances, the solution to the dilemma is to compromise, by applying a temperature that fulfills all the requirements in the best possible way. The hydrogen released during electrolysis is led to the absorption tower to
Production of bromine compounds

separate it from residual bromine, which is used (as mentioned in Section 5.1) for production of hydrogen bromide.

**Stage D: Grading the crystals**
The sodium bromate crystals are obtained in different sizes: large, medium and small. Although it may seem that the main objective is to get the product, this is not the only goal. The size of the crystals is also of major, and sometimes crucial, importance. The final product should consist only of medium-sized crystals, because the fine and large crystals have a tendency to form aggregates. This phenomenon is called **aggregation**.

**Aggregation**: Formation of aggregates of material

Aggregation is detrimental to the quality of the product and causes problems for the user. Therefore, the final product should only contain medium-sized crystals.

- **What problems could arise as a result of aggregation? Explain.**

All crystals are sorted out and the medium-sized ones are separated. The large and small crystals are collected and used, after recrystallization, for the production of potassium bromate, as described later in this chapter.

- **Suggest a method for recrystallization of the crystals**
- **Does the formation of different sized sodium bromate crystals have an effect on the yield of the process?**
Although it may appear that potassium bromate can be produced in a similar way to that described earlier for sodium bromate, this is not the case. Looking at the properties of potassium bromate, we immediately see that potassium bromate is much less soluble in water than sodium bromate.
Properties

Name of material: Potassium bromate, KBrO₃
White, odorless material (powder or crystals)
Molar mass: 167.0 g/mol
Melting point: decomposes at 370°C
Solubility in water: 13.3 g in 100 g water at 25°C
49.75 g in 100 ml water at 100°C
Solubility in other solvents: Dissolves well in alcohol
Flammability: Can form flammable and explosive mixtures in the presence of reducing agents, combustibles, sulfuric acid and ammonium salts.
Toxicity: Toxic upon swallowing or inhalation. Causes irritation of skin, eyes and mucous tissues.
Concentration permitted in food up to 30-40 ppb.

Typical reactions:
- Strong oxidant
- Decomposes at very high temperature into potassium bromide, oxygen and bromine.
- Reacts vigorously with textile, oil, fat, sugar, and phosphorus and ammonium compounds.
- Strong exothermic reaction with acids with release of bromine.

Applications: Food additive³ (for rising of dough⁴, beer and cheese industry), oxidant in chemical industry, cosmetics industry and in the explosives industry.

Because of its low solubility, potassium bromate has a tendency to precipitate in electrolytic cells and on electrode surfaces, making these methods inappropriate and necessitating alternative ways to produce potassium bromate.
- Suggest alternative routes to produce potassium bromate and give the reaction equations.

To get potassium bromate from sodium bromate, a compound containing potassium ions must be added.
- What is required of a potassium ion containing material to be of use for this purpose?
- Do you have any suggestions? Give details.

³ In certain countries its use is prohibited.
⁴ In combination with magnesium carbonate used for improvement of baking process.
In the second chapter we saw that one of the more important materials obtained from the Dead Sea is KCl. This is a relatively cheap and extremely pure raw material. It is used together with sodium bromate (produced in the plant as described earlier) for the production of potassium bromate.

The following graph shows the solubility of the different substances involved in the process:

- How does the solubility of sodium bromate depend on temperature?
- How does the solubility of potassium bromate depend on temperature?
- At which temperatures is there a significant difference between the solubility of sodium and potassium bromate?
- How can these differences in solubility be used to produce potassium bromate?
- Give the reaction equations for the process you suggest.

Sodium bromate and potassium chloride are dissolved in water while heating the mixture to 70°C-80°C. After filtration to remove impurities, the solution is cooled to 5°C-10°C. At this temperature the potassium bromate precipitates and the sodium bromate remains in solution:

\[
\text{K}^+_{(aq)} + \text{Cl}^-_{(aq)} + \text{Na}^+_{(aq)} + \text{BrO}_3^-_{(aq)} \rightarrow \text{KBrO}_3_{(s)} + \text{Na}^+_{(aq)} + \text{Cl}^-_{(aq)}
\]
Production of bromine compounds

After drying the potassium bromate, the final product is obtained as a white crystalline material.

- How can the potassium bromate be purified?
- How can the potassium bromate be dried?
- Draw a general flowchart for the production of potassium bromate.

Sodium bromate and potassium bromate, which are both solid crystalline materials, are packaged in polyethylene sacks and stored in containers made from compressed cardboard. The different sized containers are stacked in groups on wooden platforms.

Storage of the products is strictly supervised, keeping them away from reducing agents because both products are strong oxidants.

Based on the properties of sodium bromate and potassium bromate, can you indicate:
- What are the requirements for storage of these products?
- What are the requirements for transporting these products?
Production of bromine compounds

5.4 - Production of bromomethane, CH₃Br (methyl bromide)

Properties

Name of material: Bromomethane (methyl bromide), CH₃Br
Toxic, colorless and odorless gas at low concentrations
Molar mass: 95.0 g/mol
Melting point: -94°C
Boiling point: 3.5°C
Density: Gas is 3 times heavier than air
  Liquid is 1.73 times heavier than water
Solubility in water: Very low. 1.34 g in 100 g water at 25°C
Solubility in other solvents: Very soluble in non-polar solvents, ethanol, diethyl ether and acetone.
Flammability: Non-flammable except at high temperature
Toxicity: Highly toxic, especially on inhalation and skin absorption. Causes severe skin burns. May cause damage to lungs, nervous system and kidneys. Decomposes above 400°C while releasing toxic gases.

Typical reactions:
- Reacts with SH-groups in proteins while releasing HBr
- Corrosive for magnesium and aluminum
- Suspected of causing harm to the stratospheric ozone layer⁵

Applications:
- Soil pest control
- Agricultural pest control (silos)
- Methylation of organic compounds

There are a number of ways to produce bromomethane, CH₃Br, which are based on the classic reactions of carbon compounds.
- Which raw materials can be used for the production of bromomethane? Give examples.
- Give reaction equations for the different reactions.
- Under which conditions will the reactions you suggested take place?
- Try to compare the different methods you suggested by applying as many parameters as possible (e.g., costs of reactants, energy costs, expected yield, etc.)

⁵ In certain countries its use is prohibited.
Production of bromine compounds

- What are the advantages and disadvantages of each of the methods you suggested?
- What is the preferred method? Elaborate.

Although methane is a relatively cheap material compared to methanol, and bromine is cheaper than hydrogen bromide, the Dead Sea Bromine Group nevertheless decided to produce bromomethane from methanol. Producing bromomethane from methanol is the preferred method because it involves lower energy costs and better control of the substitution process (proceeding by ionic mechanism) with hydrogen bromide, yielding a single compound, as compared to a substitution process (proceeding by radical mechanism) generating different products that later have to be separated.

Substitution of the OH-group in methanol by a bromine atom occurs in the presence of an acid catalyst:

\[
\text{concentrated } H_2SO_4 \\
\text{CH}_3\text{OH}(l) + HBr(g) \rightleftharpoons \text{CH}_3\text{Br}(g) + H_2O(l)
\]

For the forward reaction: \( \Delta H < 0 \)

- What are the best temperature conditions to obtain bromomethane? Explain.
- Under what conditions can the conversion percentage of the reaction be increased? Elaborate.

Once more we see that the choice between the different possibilities is a complicated one, involving different aspects and weighing advantages against disadvantages. Although under the prevailing reaction conditions more than 95% of the raw material is converted to product, the critical stage of the process is the separation of the crude bromomethane from the starting materials and other byproducts (to be described later) formed during the reaction. During the entire process the bromomethane is in gas form and only when stored is it kept as a liquid.

Consult the bromomethane properties on Page 192 and answer the following questions:
- Why is the material in gas form during the entire process?
- Why is it liquefied for storage?

This is a continuous process with the complete system operating at sub-atmospheric pressure.
- What are the reasons for a continuous process?
- Why does the system operate at low pressure?
Production of bromine compounds

A bromomethane production facility

The following are the reasons for designing a continuous process:
- Very large quantities are needed
- During the process bromomethane is in gas form and therefore moves easily through the entire production system.

Keeping the system under low pressure is a necessary safety measure because bromomethane is an extremely toxic substance, which attacks the respiratory system even at very low concentrations. Because it exists as a gas during the entire production process, special measures have to be taken to safeguard the hermetic sealing of the system. Any leakage can cause extensive damage to the environment. By contrast, any leakage or damage occurring in a system operating at sub-pressure (vacuum) causes air to be drawn inside, preventing the leakage of the poisonous gas itself. The in-process control of the system is designed so that it immediately flashes a warning in case of overpressure in the system, allowing quick identification and attention.

Storage place of bromomethane containers
Production of bromine compounds

The entire process can be illustrated in the following general scheme:

General flowchart of production process of methyl bromide
As illustrated in the flowchart, we can divide the production process of bromomethane into four main stages:
- Reaction
- Purification
- Condensation
- Storage and packaging

**Stage A: Reaction**
Methanol, hydrogen bromide and sulfuric acid, the latter functioning as catalyst, are the constituents needed for the substitution reaction, in which the alcoholic group in methanol is replaced by a bromine ion:

\[
\text{concentrated } \text{H}_2\text{SO}_4(l) \quad \text{CH}_3\text{OH}(l) + \text{H}_3\text{O}^+(aq) + \text{Br}^-(aq) \rightleftharpoons \text{CH}_3\text{Br}(g) + 2\text{H}_2\text{O}(l)
\]

As mentioned before, this is an exothermic reaction and hence the reactor must be cooled. The Dead Sea Bromine Group does not use a ready-made hydrogen bromide solution, but controls the supply of hydrogen bromide during the reaction by means of a reaction between sulfur and bromine, as shown in the first chapter:

\[
3\text{Br}_2(g) + \frac{1}{8}\text{S}_8(s) + 11 \text{H}_2\text{O}(l) \rightarrow 7\text{H}_3\text{O}^+(aq) + 6\text{Br}^-(aq) + \text{HSO}_4^-(aq)
\]

This reaction also generates sulfuric acid.

- **What is the reason for using bromine and sulfur instead of hydrogen bromide and sulfuric acid?**

Parallel to the desired main reaction, a chain of partly unidentified, competing side reactions occurs, generating various organic compounds that contaminate the product.

- **What side reactions can occur?**

Since the reaction does not go to completion and, as said before, some byproducts are formed, the bromomethane must be separated from the starting materials as well as from the byproducts.

- **How can the product be separated from the contaminating organic compounds?**

- **Which starting materials may be found in the reaction mixture and how can they be separated from the product?**
Production of bromine compounds

Stage B: Purification
Due to the fact that it exists as a gas, the bromomethane is separated from the solution and continues flowing to the next stages of the process. Along with it, it carries bromine, hydrogen bromide and organic impurities and therefore is termed a crude product. To get pure bromomethane the crude product must be treated to remove the starting materials, and extensively purified by washings, distillations and extractions.

For example:
Washing with a sodium hydroxide solution, as shown in the scheme, to neutralize the hydrogen bromide and remove excess bromine:

\[
\begin{align*}
HBr_{(g)} + OH_{(aq)}^{-} & \rightarrow Br_{(aq)}^{-} + H_{2}O_{(l)} \\
3Br_{2(g)} + 6OH_{(aq)}^{-} & \rightarrow 5Br_{(aq)}^{-} + BrO_{3(aq)}^{-} + 3H_{2}O_{(l)}
\end{align*}
\]

Although this washing removes all traces of hydrogen bromide and bromine, it generates water vapors in the product. To obtain an anhydrous, pure product, it has to be dried.

Look at the properties of bromomethane given on Page 192.
- Which desiccants can be used to remove the remaining traces of water from the final product?
- How can the organic impurities be removed?

The solution containing sulfuric acid and starting materials is transferred to the distillation tower. The starting materials are separated from the sulfuric acid and recycled to the reaction. The acid obtained is actually a byproduct that can be used for different purposes, both in-house and elsewhere.
Production of bromine compounds

Stage C: Condensation
After the washings and various other work-up procedures pure bromomethane is obtained, but to be able to store it effectively and to limit storage space it is necessary to liquefy it.
The bromomethane is therefore cooled in a condenser in a two-stage procedure. The first stage consists of cooling to –20°C by cold brine, and in the second stage further cooling to –40°C is achieved by means of ammonia cooling units. This way the gas becomes almost completely liquefied with a very low vapor pressure. To absolutely safeguard the environment against leakage of bromomethane, the deep cooling system is connected with an absorption column to trap any gas that is not liquefied. The sophisticated and efficiently designed absorption column uses methanol, which actually is the raw material, as the absorbent. The methanol flows to the top of the column and the gas flows to the bottom of the column.
- Name two advantages of an absorption column containing methanol.
- Why does the methanol flow from above and the gas from below?

Stage D: Storage and packaging
After condensation the liquid bromomethane flows to double-walled storage tanks cooled to –20°C by circulating cold brine. An insulating layer covering the tanks keeps the temperature down and protects the brine against warming by ambient heat. These precautions are taken to avoid any danger of leakage of the toxic material to the outside in case there is a defect in one of the storage tanks. Bromomethane is prepared for shipment by storing the product under pressure in isotanks and containers of different sizes (custom-built), while ensuring that the material is kept in liquid form until use. The isotanks and the containers are constructed to resist pressures of 15 atmospheres and more, but for safety reasons they are filled at a pressure of only about 6 atmospheres.
- The gas pressure in the containers depends on the temperature. Explain.
- Explain why the containers are not filled up to a pressure of 15 atmospheres.
Bromomethane is a colorless and odorless gas and therefore chloropicrin which even at very low concentrations is easily detectable by its pungent odor is often added to it. Chloropicrin is also added to cooking gas, giving the latter its familiar intense odor. In case of a leakage this material functions as an alarm signal, enabling the user to protect himself and the environment.
Special, continuously active detectors sensitive to bromomethane are placed all around the production and filling facilities to detect leakages. These detectors are linked to alarm systems and other protective devices that prevent spreading of bromomethane to the surroundings.
Production of bromine compounds

Summary
As opposed to all inorganic compounds whose production processes we have described in this chapter, bromomethane (methyl bromide) is the only example given of a carbon compound produced in the plant. The Dead Sea Bromine Group produces many other organic compounds for various uses, but most involve complicated processes and are not discussed in this chapter. Most cases involve substitution reactions, like the one described for the production of bromomethane, and some of them are based on addition reactions of bromine to double bonds. One example is the production of 1,2,5,6,9,10 hexabromocyclododecane, HBCD, which we met in the first chapter. This material is obtained by addition of 3 molecules of bromine to 1,5,9-cyclododecatriene:

\[ \text{1,5,9–cyclododecatriene} \]

- Give the reaction equation for the formation of HBCD
- Are special reaction conditions required for the formation of HBCD?
- How can you verify that the reaction is completed?
- What safety measures have to be taken?

At the Dead Sea Bromine Group many more compounds are produced via interesting synthetic pathways. Altogether the Group produces about 70 compounds, some at Ramat Hovav and others in the plant in Holland and in other subsidiary companies.
Some of these compounds are consumer products and some of them serve as raw material for the production of more complicated compounds. Other products manufactured by the company do not contain bromine, but bromine is often used to produce them.

---

6 Other examples of compounds and their properties are displayed on the Dead Sea Bromine Group website: http://www.DSBG.com (“Our Products”)
In this chapter we have tried to describe a number of processes (relating to both inorganic and organic compounds) and to review the major principles supporting the bromine industry. These examples illustrate:

- General principles of design, building and operation of a chemical plant or any chemical installation
- Problems associated with various production processes.
- Methods of safeguarding efficiency, safety and environment

The toxicity of bromine and some of the bromine compounds poses a problem for the production, storage, transport and use of these compounds, and other properties can add to the problems, such as corrosiveness, strong oxidative capacity, sensitivity to light or heat, hygroscopicity, etc. For all these problems suitable solutions must be found, starting from storage of raw materials to shipment of the final product to the customer, and sometimes even after the product is no longer in use.

The following table lists a number of problems concerning processes or materials in the bromine and other industries. Give examples of problematic materials in the sense described in the table and frequently applied, industrial solutions to overcome these problems.

<table>
<thead>
<tr>
<th>Problems</th>
<th>Solutions</th>
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<tbody>
<tr>
<td>Toxic materials</td>
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<tr>
<td>Examples:</td>
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<tr>
<td>Corrosive materials</td>
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<tr>
<td>Examples:</td>
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<tr>
<td>Explosive materials</td>
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<tr>
<td>Examples:</td>
<td></td>
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<tr>
<td>Light or heat sensitive (unstable) materials</td>
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<tr>
<td>Examples:</td>
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<td>Hygroscopic materials</td>
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<tr>
<td>Examples:</td>
<td></td>
</tr>
</tbody>
</table>

- *Can you give other examples of problems and suggest solutions?*
Production of bromine compounds

Concepts studied in Chapter 5

Aggregation: Formation of aggregates of material.

Crystallization: Precipitation of solid crystals from a saturated solution.

Economic added value of product: Price of product relative to price of raw materials. The price of advanced products, whose production requires much know-how, is high relative to the price of raw materials. In such cases the products have a high added value.

Recovery: Process of renewing a material and restoring its active state. In many cases reactivation involves distillation, washing, etc, to remove impurities adsorbed to the material.

Questions about Chapter 5

1. The production of hydrogen bromide, HBr (aq), at Bromine Compounds Ltd is based on the following reaction:

\[
\text{H}_2(g) + \text{Br}_2(g) \rightleftharpoons 2\text{HBr}(g)
\]

The hydrogen bromide is supplied as an aqueous solution of 48% or 62%. Refer to the flowchart on Page 167 and answer the following questions:

a. What are the raw materials for the production of hydrogen bromide and what is their sources? Are there any processes preceding this one? Give details.

b. What are the conditions in the reactor (Stage A)? Relate to pressure and temperature conditions, and concentrations of reactants. Detail and explain why these particular conditions were chosen.

c. What products leave the reactor? Explain.

d. In Stage C the gases leaving the previous stage enter a double-walled pipeline system with circulating water. Which process is carried out and why?

e. Why is a double-walled pipeline system used instead of a large container with water?

f. Is it possible to keep a hydrogen bromide solution in a steel container? Explain.
Production of bromine compounds

2. This question relates to the production of lithium bromide used as a coolant in air conditioning systems. It is recommended to hold a group discussion on this question.
   a. Suggest at least three routes, based on different raw materials, to prepare a lithium bromide solution. Give the reaction equation.
   b. Suggest criteria for the selection of the preferred method of those you suggested.
   c. Compare the three methods with the criteria you suggested.
   d. If you are studying in a group or in the classroom, compare your answer with the answers of other students or groups of students and together try to choose the best method suggested.
   e. Draw a flowchart of the method chosen to produce a lithium bromide solution.
   f. What is required of the construction materials used for different parts of the installation and product containers?
   g. Which safety measures should be taken in the production of the lithium bromide solution?
   h. Does the process cause environmental problems? If so, what problems and how can they be solved?
   i. How can the total yield from the production of lithium bromide be increased?

3. Calcium bromide is marketed in two forms: as a 52% aqueous solution and as a solid. In Section 5.2, Page 174, two methods are described to produce calcium bromide, CaBr₂. In both methods hydrogen bromide, HBrₐq is used, but the second starting material is different for each method:
   In Method I slaked lime, Ca(OH)₂(s), is used.
   In Method II limestone, CaCO₃(s) is used.
   a. Write down the reaction equations for both processes.
   b. Indicate the advantages and disadvantages of preparing a CaBr₂ₐq solution by method I as compared to Method II.
   c. What are the advantages and disadvantages of marketing calcium bromide in solution compared to marketing it as solid material.
   d. How many tons of limestone, CaCO₃(s), are needed to obtain 1 ton of a 52% CaBr₂ₐq solution? Assume that the conversion rate is 100% and the yield 95%.
   e. Suggest two possible reasons for the fact that the yield is less than 100%.
   f. The first chapter (Page 22) tells the story of transporting bromine in
Production of bromine compounds

the form of a calcium bromide solution during the Second World War. Suggest a reaction for producing bromine, Br\(_2\), from a calcium bromide solution, CaBr\(_2\)\(\text{aq}\).

**4.** At Bromine Compounds Ltd. 1-bromobutane, an intermediate product for the synthesis of different compounds, is produced. Two possible methods exist for its production:

I from the corresponding alcohol
II from the corresponding alkane

a. Give reaction equations for Methods I and II and describe the reaction conditions.
b. Which of the two methods is the preferred one for industrial production of 1-bromobutane? Explain.
c. In Method I, 1-bromobutane is obtained at a conversion rate of 90% and a yield of 85%. Calculate how many tons of material would be obtained if 226 tons of alcohol were added to the reactor (the other ingredients being added in excess).
d. Why is the conversion less than 100%?
e. Why is the yield less than 100%?

**5.** Sodium bromate is produced by a combination of the reaction between bromine, Br\(_2\), and a sodium hydroxide solution, NaOH(s), and electrolysis.

a. What is the purpose of the electrolysis?
b. Does the electrolysis have an effect on the conversion rate? Explain.
c. Does the electrolysis have an effect on the overall yield of the process? Explain.
d. Why is this method impracticable for the production of potassium bromate?

**6.** At Bromine Compounds Ltd. ammonium bromide is produced as solid material and as solution in a continuous process by reacting bromine with ammonia.

a. Give the reaction equation.
b. By what other methods can ammonium bromide be produced? Give the reaction equations.
c. Why do you think the method described in a. above was chosen?
d. Draw a flowchart for the production of ammonium bromide.
e. What is required of the construction materials used for different parts
Production of bromine compounds

of this installation? Give details.

f. Suggest ways to maintain industrial safety and to use suitable neutralizing agents.

g. What is required of the construction materials for suitable storage facilities for the product?

7. In the production processes described in this chapter different separation methods are used. Summarize these separation methods in the following table:

<table>
<thead>
<tr>
<th>Production process</th>
<th>Separated material and composition of mixture from which it was separated</th>
<th>Separation method</th>
<th>Principles of separation method</th>
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8. The installations used for the production processes described in this chapter are built from different construction materials. Summarize the individual materials in the following table and indicate the reasons for their choice:

<table>
<thead>
<tr>
<th>Production process</th>
<th>Process stage</th>
<th>Construction material</th>
<th>Reasons for choosing construction material</th>
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9. In the vicinity of the Bromine Compounds Ltd. production plant various neutralizing agents are kept for emergency cases. Summarize the neutralizing agents in the following table and indicate which materials they are intended to neutralize and the reasons for their choice as neutralizing agent:

<table>
<thead>
<tr>
<th>Production process</th>
<th>Neutralizing agent</th>
<th>Neutralized material</th>
<th>Reasons for choosing neutralizing agent</th>
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Production of bromine compounds

10. In the different production plants various precautions are taken to prevent faults, injury, and environmental damage. For each process, indicate the hazards and precautions taken:

<table>
<thead>
<tr>
<th>Production process</th>
<th>Process stage</th>
<th>Hazard</th>
<th>Precautions taken in plant</th>
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</table>

11. For product storage at the Bromine Compounds Ltd. containers or other means made from different construction materials are used. Summarize the individual materials in the following table and indicate the reasons for their choice:

<table>
<thead>
<tr>
<th>Stored material</th>
<th>Storage method</th>
<th>Construction material</th>
<th>Reasons for choosing construction material and method of storage</th>
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12. In the ports, on important transport routes and at other strategic places in the country neutralizing stations have been established containing ammonium and lime.
   a. What is the purpose of these stations?
   b. Prepare a list of all the substances that these materials can neutralize.