3.1 - Introduction

The Dead Sea in Israel provides the raw materials for a varied and diverse chemical industry, in which bromine and its compounds, to which this book is dedicated, play a significant role. These resources can be exploited for many purposes and there is virtually no limit to the development of new products for a wide diversity of uses. The route from the Dead Sea waters to bromine and bromine compounds is illustrated in the scheme below:

Look at the scheme and the Table No. 2.2 of ion concentrations in the Dead Sea on Page 42 and answer the following questions:
- Why are the only products manufactured from Dead Sea water obtained from evaporation pools?
- Which materials are separated from the water of the evaporation pools before it is conveyed to the bromine plant?
- On what does the order in which salts are precipitated in the evaporation pools depend?
How is bromine produced? How is bromine produced?

Evaporation pools at the Dead Sea Works

The total surface of the evaporation pools is approximately 150 km² and the average amount of water evaporating annually is 135 million m³.
The annual (1997) amount of common salt produced: 700,000 ton.
The annual (1997) amount of potash produced: 2.5 million ton.

As the scheme on the previous page illustrates, bromine is produced from brine present in the evaporation pools after separation of most of the sodium chloride and potash. The concentration of bromine ions in these solutions reaches 10-12 gr/l, which guarantees an extremely efficient and profitable production process compared with other sources in the world containing much lower concentrations of bromine ions.

To obtain bromine from a solution containing bromide ions, a suitable oxidant is needed and there are many oxidants that can be used to produce bromine.

- Which substances would be suitable oxidants for obtaining bromine from bromide solutions?
- Give their formulas and, if possible, the reaction equation.
How is bromine produced?

- What is required of the substances you found to make useful bromide oxidizers for industrial production of bromine?
- Suggest other methods to oxidize bromide to bromine. Give details.

The bromine production process in Israel is based on the reaction of bromide ions with chlorine, precisely as discovered at the beginning of the 19th century. It is an oxidation-reduction reaction in which the bromide ions in aqueous solution are oxidized to produce elementary bromine:

$$ \text{Cl}_2(g) + 2\text{Br}^-(aq) \rightarrow \text{Br}_2(l) + 2\text{Cl}^-(aq) $$

- Examine the use of chlorine as oxidizing agent in view of the requirements you specified above.
- Calculate the chlorine volume under standard conditions needed to produce 160 kg of bromine, based on the reaction equation and assuming no losses occur.

Chlorine meets most of the requirements.

**Properties**

**Name of substance: Chlorine, Cl₂**

Greenish colored gas  
Melting point: -100°C  
Boiling point: -35°C  
Density: 2.99 gram/liter  
Solubility in water: Slight (with reaction). 0.63 gram in 100 cm³ water (at 25°C).  
Solubility in other solvents: Dissolves well in CCl₄, heptane, benzene, etc.  
Flammability: Non-flammable  
Toxicity: Very toxic. Causes skin irritation and burns. Dangerous on inhaling and for eyes  
Typical reactions:  
  - Strong oxidizing agent  
  - Substitution reaction with alkanes and addition reactions with alkenes.  
  - Reacts easily with most elements.  
Bonding enthalpy: 242 kJ/Mol.

---

1 Please remember that these substances should not be used in the school laboratory.
3.2 - How is chlorine produced in the laboratory?

In the previous chapters we discussed processes for the production of chlorine in the laboratory:
- Direct oxidation-reduction reactions between reactants with formation of chlorine as one of the products.
- Electrolysis of a concentrated aqueous salt solution containing chloride ions.

A typical example of a direct oxidation-reduction reaction frequently used to produce chlorine in the laboratory is the reaction between a concentrated hydrochloride solution and potassium permanganate crystals:

\[
\text{KMnO}_4(s) + 4 \text{H}_3\text{O}_\text{aq}^+ + 3 \text{Cl}_\text{aq}^- \rightarrow \text{K}^+ + \text{MnO}_2(s) + 6 \text{H}_2\text{O}(l) + 1\frac{1}{2}\text{Cl}_2(g)
\]

Chlorine can be obtained by the electrolysis of aqueous solutions containing chlorine ions as well as from molten chlorine salts.

- **Give examples and write the equations for the reactions occurring at the anode and the cathode.**
- **Compare the possibilities of producing chlorine by the direct oxidation-reduction method with producing it by electrolysis?**
  a. In the laboratory
  b. In industry?
- **Give details and explanations for each case.**

Hoffman instrument for electrolysis in the laboratory
3.3 - How is bromine produced in the laboratory?

When a chemist discovers a certain laboratory process that may be applicable to large-scale industrial production, he first has to perform laboratory tests. He does this by building an experimental set-up that closely resembles a production process and by testing the different steps of the process as accurately as possible. The test tube reaction that yielded bromine is only the beginning of a complicated process of transforming the idea into practice, with the aim of commercially obtaining bromine of the desired purity and quantity. To make bromine in the laboratory we need to find a chlorine source and react it with a solution of bromide ions. After formation of the bromine it must be separated from the solution in a suitable way. All this requires thinking and planning which, besides the procedural aspects involves other questions that will be discussed later.

Let us now examine how such a system can be built to include all the previously mentioned necessary components. The three main steps of such a system are:

a. Preparation of chlorine
b. Reaction to form bromine
c. Separation of the bromine

**Step A: Preparation of chlorine**

In the scheme depicted below chlorine is obtained by the earlier mentioned laboratory process, in which a concentrated solution of hydrochloric acid reacts with crystals of potassium permanganate:

$$\text{KMnO}_4(s) + 4 \text{H}_3\text{O}^+ + 3 \text{Cl}^- \rightarrow \text{K}^+ + \text{MnO}_2(s) + 6 \text{H}_2\text{O}(l) + \frac{1}{2}\text{Cl}_2(g)$$

Concentrated aqueous solution of HCl
How is bromine produced?

The chlorine produced by the reaction can be carried directly through the bromide solution. What are the advantages and disadvantages of this method compared with preparing a preset quantity of chlorine that is subsequently stored and transferred to the bromide solution?

Step B: Reaction to form bromine

In the first step a certain amount of chlorine is prepared. This reacts with a certain amount of a magnesium bromide solution. Basically this procedure can also be carried out on a larger scale to produce a large amount of bromine.

By directly passing chlorine through the bromide solution an easy and efficient reaction is obtained. Based on this we can now build an integrated system in the laboratory:

```
- What will happen to the bromine produced as a result of passing chlorine through the bromide solution? Elaborate.
```

As we watch what is happening, we observe that the color of the magnesium bromide solution gets stronger and changes to orange-brown, while very little bromine gas goes over to the gaseous phase. The solubility of the bromine in the aqueous solution is explained by the equilibrium reaction in which a complex ion is produced, \( \text{Br}_3^{-(aq)} \), which is highly soluble in water: \( \text{Br}^-_{2(aq)} + \text{Br}^-_{(aq)} \rightleftharpoons \text{Br}_3^{-(aq)} \). For the direct reaction: \( \Delta H < 0 \)

The bromine ions actually bind to the bromine molecules and keep them in solution.
How is bromine produced?

- In which direction must the process be moved to release the bromine from the solution?
- Can you suggest a method for removing the bromine from the solution?

**Step C: Separation of the bromine**

The direct reaction leading to the formation of the Br\(_3\)\(^{(aq)}\) ion is, as already mentioned, exothermic. Therefore, the bromine can be released from the solution by heating.

One way to perform the reaction is to pass the entire amount of prepared chlorine through the bromide solution and, after termination of the reaction, to heat it to the temperature at which bromine vapors are released. Another possibility is gassing with chlorine and heating the solution simultaneously.

The bromine vapors are condensed and collected in a cooled vessel. Condensation can be achieved by collecting the bromine vapors in a test tube placed in ice (or an ice-salt mixture, to attain even lower temperatures).

Another way to condense the bromine is by using a **condenser**.

**Condenser:** A device with a double-walled jacket, through which the cooled off gases flow. Cold water for absorbing the energy runs through the jacket causing condensation.
How is bromine produced?

Condenser

Explain how a condenser works:
- What is its advantage compared with a refrigerated test tube?
- What is its disadvantage compared with a refrigerated test tube?

The industrial term for a process carried out in steps is a batch or discontinuous process.

**Batch process:** A process in which the reactor is supplied with a certain amount of raw material (reactant/s auxiliary substance/s). The reaction mixture is treated to get the desired product/s. After obtaining the product/s and removal of the reaction mixture from the reactor the next portion of raw material is added and treated identically to get an additional quantity of the product/s.

Most laboratory experiments are performed batchwise, but stepwise processes are also used industrially in which case they are called batch processes.

Industrial processes may be carried out as batch processes if there is a request for relatively small amounts of products whose production does not require continuous operation of the installation.

If we incorporate all the previously described components in an integrated system for carrying out a continuous reaction, from the chlorine preparation step to the formation of liquid bromine, we have a procedure that is easier to control and is more efficient. In such an integrated system the products of each step are passed on directly to the next step.
Answer the following questions:

- Can this type of method be used for industrial production of bromine? Explain.
- What other laboratory methods are there for producing bromine? Give the reaction equations and explain.
- How can these laboratory methods be applied to the industrial production of bromine? Explain.
- What should be the characteristics of an industrial manufacturing process in comparison with a laboratory-scale synthetic procedure?

Let us now examine the reaction product, i.e. the bromine, formed in the refrigerated test tube or in another closed container. If we leave the test tube standing for a while, we see that, after condensation, a brown layer containing bromine is formed with a lighter, aqueous layer.

- Why are there two layers?
- What does each layer contain?
- Can the bromine formed in the experiment be used for different purposes?
- Are there cases in which we need dry, water-free bromine?
- Are there other impurities in the bromine?
- If so, what are these impurities and how can we separate them and prepare pure bromine?
- Do we need bromine of identical purity for each purpose and use?
We shall deal with some of these questions and give possible answers in the section discussing the industrial production of bromine.

- *Use your knowledge to suggest methods for obtaining bromine free of water and other impurities.*

A block diagram depicting different processing steps may provide an overview of the complete process. The term used in industry for such a block diagram is flowchart, and its purpose is to show the sequence of operations performed in the process. Each step in the flowchart is represented by a square. The incoming arrows signify the materials entering the process, while the outgoing arrows signify the materials leaving the process, i.e., the products.

The entire process can be described by a row of such squares.

**Flowchart:** Block diagram describing the sequence of steps in a process

*Sketch a flowchart for the laboratory production of bromine.*
3.4 - Safety in the laboratory

In the first chapter we learned that bromine is a toxic and corrosive material. It can therefore be dangerous to handle without taking appropriate precautions. Observing the safety rules is of the utmost importance, being the primary and essential condition for the performance of any experiment, and especially when dealing with dangerous materials and processes.

Because of the strong corrosive action of bromine it is important to choose the reaction vessels, stoppers, tubing or any other part of the system that may come in contact with bromine carefully. All these parts must be made from bromine-resistant materials under the given reactions conditions. The resistance of glass to bromine allows the use of regular laboratory glassware. The question of selection of resistant construction materials for different equipment parts is typical not only of bromine production, but also of many chemical reactions and of crucial importance for system design.

**Construction materials:** Materials used for construction of equipment parts involved in chemical processing storage or transporting.

Because of the toxicity of bromine, any experiment in which it is involved must be performed in a fume cupboard and precautions must be taken, such as wearing gloves and safety glasses to protect hands and eyes. Furthermore it is very important, before starting the experiment, to be aware of the expected dangers and to take preparatory action in case of an accident. When dealing with toxic substances, suitable means or materials must be prepared that react with these substances and eliminate their harmful effects in case of a leakage or spillage. The industrial term for these materials is neutralizers or neutralizing agents.

**Neutralizing agents:** Materials that react with a hazardous substance in a reaction that does not generate other hazardous substances or cause any other hazards. These materials are used for safety reasons in case of leakage of a dangerous substance or any other accident – and their purpose is to prevent possible danger to people or to the environment.

- What are the properties required of a good neutralizing agent? Explain.
- Look at the list of reactions of bromine appearing on Pages 14-15 and suggest suitable neutralizing agents for bromine.
- Try to assess the advantages and disadvantages of each of the materials you
suggested. If you need more data, define them and explain why they are important. Try to find these data in handbooks or databases.

- In certain reactions bromine gas is formed and in other cases liquid bromine is obtained. Suggest suitable neutralizing agents for: gaseous bromine; liquid bromine.

For many years the most common suitable neutralizing agent for laboratory use was sodium thiosulfate, Na$_2$S$_2$O$_3$. If a reaction runs out of control or, after its termination, we want to neutralize the excess bromine, the bromine can be allowed to flow directly into the thiosulfate solution.

**Experiment: How to choose a neutralizing agent? (The experiment must be performed in a fume cupboard!)**

a. In a chemical beaker, insulated with Styrofoam, the teacher puts 50 cm$^3$ of a 1M thiosulfate solution and then measures the temperature.

b. The teacher adds 1 cm$^3$ of bromine (small ampoule) to the thiosulfate solution, while stirring gently and monitoring temperature.

c. Watch the procedure and record the change in temperature.

- Upon passing bromine through the thiosulfate solution the brown color disappears. Why?

- Calculate the change in energy accompanying the reaction.

- Calculate the change in energy when adding 10 cm$^3$ of bromine instead of 1 cm$^3$ of bromine.

- Calculate what the change in temperature would be after addition of 10 cm$^3$ of bromine.

- What can be learned from this experiment?

The reaction between bromine and thiosulfate is exothermic and therefore not suitable for all cases where leakage of bromine occurs.

- What are the dangers of neutralizing bromine with thiosulfate?

- In case bromine spills on a person, do you think it would be a good idea to neutralize with thiosulfate solution? Explain.

- In case bromine spills on a person, the affected area should be thoroughly washed with large amounts of water. Explain.

- Suggest other neutralizing agents for bromine. Give the formulas and explain.

- What factors are involved in choosing the most suitable bromine neutralizing agent?
3.5 - From laboratory to industrial production of bromine

The concept behind the industrial production of bromine resembles the one presented in the experimental set-up described in Section 3.3. Nevertheless it is important to note that converting the process from the laboratory to a plant poses many problems that do not arise when planning a laboratory experiment. In this section we shall present some of these problems. There are of course several solutions for each problem. Even if identical products or similar production methods are involved, different plants or countries may offer different solutions to these problems. Remember that economic considerations tip the balance and that non-profit solutions are unacceptable.

Choosing raw materials

Bromine is produced both in the laboratory and industry by the reaction between a solution containing bromide ions and chlorine. In the laboratory, chlorine is prepared by the reaction between potassium permanganate and a solution of hydrochloric acid. Both are regular laboratory reagents, but too expensive for industrial use. To produce industrial chlorine, cheaper raw materials must be found, even if this entails a change in production methods.

Considerations as to what is a suitable raw material for a certain product may change over the years, if more suitable, more readily available or cheaper sources are found.

Try to suggest cheap sources for chlorine. How can you compare the profitability of different sources for chlorine?

Choosing construction materials

The problem of construction materials is relevant throughout the production process. Any part of the system that comes in contact with the reactants must be resistant under the existing conditions. The problem of resistance to reactants does not end with the production installation itself, but applies also to the pipe system carrying chlorine and brine, storage tanks, transportation of bromine etc.

The equipment and vessels used in the laboratory are made of glass, which is resistant to high temperatures and highly corrosive materials. Laboratory equipment is, however, breakable and relatively expensive, and appropriate only for the preparation of small amounts of material. And, although glass is suitable for carrying out processes in which materials such as chlorine and bromine are involved, the use of all-glass equipment for pipes and industrial installations is not always practicable.
In the case of bromine, the problem is especially difficult. In the first chapter you learned about the diversity of reactions of bromine with different materials among them many metals. This demonstrates the great difficulty in choosing suitable construction materials.

- **Is it possible to store bromine in an aluminum container? Iron? Stainless steel containing iron and nickel and chromium? Explain.**

**Quantitative aspects of the process**
The yield of a laboratory experiment usually has no special significance. Rather the purpose is to evaluate the principle aspects of the process. Is it feasible? And under what conditions?
In most cases costs do not pose a problem in laboratory experiments and neither are yields of crucial importance. In contrast, in a large-scale industrial process it is important that the conversion of raw materials to products proceeds with maximum efficiency.

*In the experimental set-up for producing bromine we did not relate to the residual non-reacted chlorine.*
- **What is the significance of this regarding the quantitative aspect?**
- **Try to examine this question from those aspects that may influence the industrial process.**

**Degree of product purity**

In the experiment on Page 70, we succeeded in producing bromine, but we did not relate to the presence of impurities, such as water and chlorine, which to some extent dissolve in the bromine. It should be noted that for most purposes pure bromine is required, necessitating several purification steps.

Various purification methods exist, and their choice depends on the materials and their properties, the desired degree of purity and how much it costs to separate the different impurities. Such considerations constitute an inseparable and often major part of process design.

- **Suggest methods for the separation of chlorine and water from the bromine in which they are dissolved.**
- **Try to compare the relative costs of these methods. Take into account such factors as investment of energy, materials needed, etc.**
Energy costs
One question that concerns designers of production plants is how to economize on energy costs?

- In the laboratory experiment we used an electrical plate for heating. How do we heat in industry?

- Do you know other means of heating? Specify.

- The bromine condensation step can also significantly influence industrial process costs. What are the variables to be reckoned with? Explain.

In the next section we shall deal with solutions for the energy problem in bromine production.

- What other factors must be taken into account during the transition from laboratory to industrial production of bromine?
3.6 - How is chlorine produced industrially?

You have probably studied electrolytic processes in aqueous solutions in the past, and most probably conducted experiments in which you passed an electric current through a solution of chlorine salts. The same method was selected to produce the chlorine needed to form bromine. It would appear that an electrolytic process requiring electric energy would not be profitable.

- *Give the reasons for choosing this process?*

Chlorine has been produced in the chlorine plant in Sdom since 1977. As mentioned before, the raw material used for many years is common salt, NaCl. After the salt is purified, it is dissolved in water and the brine thus obtained is transferred to the electrolytic cells. During electrolysis chlorine gas is formed at the anode:

\[
2\text{Cl}^-_{(aq)} \rightarrow \text{Cl}_2_{(g)} + 2\text{e}^-
\]

Close to the cathode, hydrogen gas is formed:

\[
2\text{H}_2\text{O}_{(l)} + 2\text{e}^- \rightarrow 2\text{OH}^-_{(aq)} + \text{H}_2_{(g)}
\]

Sufficient voltage must be applied in the electrolytic cells to oxidize the chlorine at the anode and reduce the water to hydrogen at the cathode. This voltage is generated by the Dead Sea Works power station built close to the plants specifically for this purpose.

- *What is the minimum voltage required for electrolysis?*
- *Can the common salt generated in the evaporation pools be used directly for the electrolytic process?*
- *Is it possible to use regular water for the electrolytic process? Explain.*
- *What is the amount of chlorine needed to produce one ton of bromine? Show your calculations. Assume that the reaction goes to completion without loss of material.*

2 Common salt obtained after separation of potash from carnallite is used. Carnallite is the hydrated salt of magnesium chloride and potassium chloride.

3 In practice, it is necessary to increase the actual voltage above the calculated minimum. The difference between the actual and calculated voltage is called overvoltage. The overvoltage represents the activation energy to be invested in the process.
How is bromine produced? How is bromine produced?

In contrast, industrial bromine production resembles laboratory production by direct reaction with chlorine. This is a rapid, relatively easy and economic process. On the face of it, one could consider using a similar electrolytic method to produce bromine from Dead Sea water, because bromine ions too can be oxidized by means of an electric current. (See reduction potentials in any available handbook).

- What is the minimum voltage needed to produce bromine?

- What are the advantages of bromine ion oxidation by an electric current?

Unfortunately this idea, which would have saved the chlorine preparation step, is impracticable. Despite numerous experiments and investigations conducted on the subject, the reaction poses technological problems that as yet remain unresolved.

Electrolytic cell in the chlorine plant (membrane system)

The chlorine and bromine plants are located close to each other and adjacent to their common raw material source – the Dead Sea. A continuous flow of chlorine generated by the electric cells is supplied directly to the bromine plant via a pipeline.

- What are the advantages of building the chlorine plant next to the bromine plant?
How is bromine produced?

- What are the reasons for building the two plants near to the Dead Sea?

- Do you think there are disadvantages connected to the location of the two plants near the Dead Sea?

In the first two years of the bromine plant’s existence no chlorine was produced in Sdom. The chlorine was brought in containers from the Frutarom Company located in the Acre industrial area in northern Israel. At a later stage two chlorine plants were built; the first with a production capacity of 45,000 tons per year, was built in 1976 and is based on an electrolytic process in diaphragm cells. The second, also with a production capacity of 45,000 tons per year, was built in 1987 and is based on an electrolytic process in membrane cells.

“The amount of chlorine that can be produced determines the extent of bromine production”. Please comment.

- How many tons of bromine per year can be obtained from the chlorine produced in the two chlorine plants? Assume that the process goes to completion and that there are no losses.

- Try to explain the data on the amount of bromine produced in Israel starting from the year 1975. (See Table No. 1.3 on Page 34).

In December 1996 the magnesium plant, which produces magnesium by electrolysis of carnallite (hydrated salt of magnesium chloride and potassium chloride) after dehydration and melting, became operative. In addition to magnesium this process also generates chlorine.

- How can the foundation of the magnesium plant influence bromine production?

- How can the foundation of the magnesium plant influence production in the chlorine plant?

- What problems may arise as a result of using chlorine from the magnesium plant?

- What is the advantage using the chlorine produced in the magnesium plant?
Graph No 3.1. Growth in chlorine production over the years

Today the magnesium plant supplies 45,000 ton of chlorine per year. For this reason the first chlorine plant stopped operating in mid 1998 and the second plant produces chlorine according to demand.

- Calculate how much chlorine is needed to produce 185,000 tons of bromine (annual production in 1998)
3.7 - Bromine production at Sdom - How is bromine produced industrially?

The industrial production process of bromine resembles the laboratory process, in principle, and involves the direct reaction of chlorine with brine rich in bromine ions. The process is fast, simple and relatively economical. Bromine production in Sdom employs the “hot” process, based on the direct feed of chlorine and steam (produced by the power station of the Dead Sea Works), as well as Dead Sea brine rich in bromine ions, into the reaction tower. The following general scheme illustrates the bromine production process.

In this section we shall describe the different steps of the bromine production process in Sdom and present its main scientific and technological aspects.

---

4 For the sake of simplicity, certain details not directly connected to the production process proper, but concerning increasing the system’s yield, have been omitted.
**How is bromine produced?**

**The bromine-generating step**

Input to the reaction tower:
From above – hot brine rich in bromine ions
From below – chlorine and water.

- *Why is the brine in the reaction tower fed from above and the chlorine from below?*

In the reaction tower an oxidation-reduction reaction takes place, generating bromine:

\[ 2\text{Br}^- (\text{aq}) + \text{Cl}_2 (\text{g}) \rightarrow \text{Br}_2 (\text{g}) + 2\text{Cl}^- (\text{aq}) \]

We saw that it is necessary to heat the system to prevent the bromine from remaining in solution, as happened during the first stages of the lab experiment.

Heating is provided by steam, which actually serves two purposes:
- Heating of the reaction tower above 100°C (100°C – 120°C).
- Removal of the bromine from the solution (the steam\(^5\) carries the bromine vapors with it).

The gas mixture containing the bromine vapors, residual chlorine and steam rises to the top of the tower, while the liquid brine accumulates at the bottom of the tower. To improve the efficiency of the reaction in the gas-liquid system (two phase), measures have to be taken to optimize the contact between the reactants. The tower is filled with suitable filling materials (rings or disks made from resistant materials) to increase the contact area and the reaction time between the gases and the solution. The gases as well as the solution must pass between the gaps of the filling material, which improves the efficiency of the reaction. This type of tower is called a **packed tower**.

**Packed tower:** A tower with filling material (rings, disks etc.) in which a reaction takes place between gases and liquid or solution. The purpose of the filling material is to increase the contact area between the reactants in the tower.

---

\(^5\) Steam – water vapors above 100°C.
How is bromine produced?

The reaction conditions, quantitative ratios and flow rates determine the efficiency of the reaction, requiring the establishment of optimal conditions to obtain the maximum amount of bromine. This is an engineering-technological problem going beyond pure chemical expertise and is referred to the chemical engineers. The maximum theoretical yield of bromine according to the reaction equation (molar ratios), assuming the reaction goes to completion, is 2.2 tons of bromine for each ton of chlorine (see question on Page 74), providing that the process is designed in such a way that all available chlorine reacts.

Actually two conditions must be fulfilled to obtain optimal process efficiency:
- All bromine ions in the brine react
- The only reaction product is bromine.

When both conditions are fulfilled the implication is that all the bromine ions in the brine have reacted to form bromine. We must of course try to approach this ideal situation as closely as possible, but in most cases we need to find a realistic compromise if we wish to keep costs and reaction times within reasonable boundaries.

In practice, some of the bromine ions in solution do not react and, together with the residual brine, are carried back to the Dead Sea. This means of course that the brine has not been fully depleted and the production potential of bromine has been partly wasted. More waste may occur if process conditions are not optimized but, by applying suitable flow rates and excess chlorine, conditions can be established so that most bromine ions react to form bromine.

_The concentration of bromine ions in the diluted brine carried back to the Dead Sea is 1-2 gram/liter. Reviewing Table No. 1.2 on Page 32 once more confirms the advantage of the Dead Sea as a source for extracting bromine._

One of the parameters for reaction efficiency is the relative amount of reactants that react. People in industry use the term _conversion_ or percentage conversion⁶.

**Conversion:** Ratio expressed in percentages between the amount of reactant reacted and the amount of reactant introduced in the reaction vessel.

For example: If only 80% of the bromine ions reacts and the rest remains in the brine carried back to the Dead Sea, the conversion percentage of the bromine ions is 80%.

⁶ For further examples see Appendix A.
It is possible to measure the conversion of each reactant in the system and therefore it is, of course, also possible to calculate the percentage of conversion with respect to chlorine at the same time.

**Is conversion always an accurate measure for reaction efficiency? Explain.**

In reversible reactions, which may reach equilibrium, the conversion percentage depends on the equilibrium constant. If the equilibrium constant of the reaction is very low, the conversion percentage is very low. If the equilibrium constant of the reaction is very high the conversion percentage is also very high and can reach 100%, which implies that the reaction proceeds practically to completion.

The conversion percentage, like the equilibrium constant, is unique for each reaction and is influenced by reaction conditions, such as: temperature, pressure (in a gas reaction) and concentrations.

Industrial processes are not usually carried out under equilibrium conditions, even if the reaction is reversible and if, given enough time, equilibrium attainable. Nevertheless, for process planning and determining reaction conditions, general knowledge of reversible reactions as formulated in Le Châtelier’s principle is applied.

An additional factor that process designers must take into account is the prevention of competitive reactions of bromine or chlorine that may yield undesirable byproducts.

**Does the formation of a byproduct influence the conversion percentage? Explain.**

**How can the conversion percentage be increased?**

The formation of byproducts lowers process efficiency and prevents maximum product yield. This entails extra investment in product purification, to separate the product from the reaction mixture.

The latter factor influences a more accurate measure for efficiency, which in industry is called reaction yield. The reaction yield relates to the amount of desired product obtained in the reaction.

---

7 For other examples see Appendix A.
How is bromine produced?

**Reaction yield:** The ratio, expressed in percentages, between the amount of desired product obtained in the reaction and the amount that should have been obtained according to the reaction equation, the starting amount of reactants and the conversion percentage.

For example: If the conversion percentage is 100%, but only 80% of the reactant was converted to the desired product, the reaction yield is 80%. This is true of course on the assumption that there were no losses due to other causes.

- **What else can cause a decrease in reaction yield?**

Unfortunately, in the bromine production process too there are a number of obstacles that may have a negative influence on conversion and yield percentages. These factors must be taken into account when designing the process.

**Residual organic matter found in Dead Sea water**

If the brine contains residual organic matter the amount of bromine produced can drop very significantly, because some of the chlorine oxidizes the organic compounds instead of the bromine ions and, likewise, the bromine itself can react with the organic matter. On the other hand, the organic compounds may contaminate the product, necessitating extra purification steps and causing decreased yields as a result of loss of material.

In the USA bromine is produced from underground brine that is pumped from wells also containing oil. As a result, bromine produced from such brine sources contains organic contaminants, which can be separated from the bromine by distillation.

- **What is the principle of the distillation process?**
- **How is a distillation system built?**
- **How can the distillation process influence the yield of bromine production?**
- **What is the advantage of producing bromine from Dead Sea water as compared to its production from brine obtained from oil-containing wells?**

---

Separation by distillation can be achieved if the mixture contains a number of components each with its own different boiling temperature. Each component is converted to gas when the appropriate temperature is reached. The temperature is raised gradually to enable separation of the different compounds.
How is bromine produced? How is bromine produced?

**Distillation:** Process by which liquid components are separated from a solution by evaporation and condensation.

**Side-reactions occurring in the reaction tower**

In a mixture containing chlorine and bromine as well as bromine and chlorine ions, a number of competitive reactions may occur, one being the following equilibrium reaction: \( \text{Br}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{BrCl}(\text{g}) \)

*It is a given that the bonding energy of Br-Cl is 215.1 kJ/mol.*

- **Consult a handbook and calculate the enthalpy of the above reaction. Suggest ways to force the reaction to yield the maximal amount of bromine (minimal amount of bromine chloride)?**

Competitive reactions such as these may decrease the yield of bromine and therefore their conversion percentages should be kept as low as possible. The formation of \( \text{BrCl}_{(\text{g})} \) is an endothermic reaction and thus an elevated temperature is needed to lower the conversion percentage and prevent the formation of bromine chloride. Too low a temperature will result in a high conversion rate of the above reaction and formation of a relatively large amount of bromine chloride. A high temperature will also prevent condensation of the steam carrying the bromine and of course will keep the bromine itself in the gas phase. Using excess chlorine leads to the presence of \( \text{BrCl} \) in the product. Actually this reaction can interfere only if a large excess of chlorine is used. Another problem is the formation of the complex ions \( \text{Br}_3\text{Cl}_{(\text{aq})}^- \) which are very soluble in water. We have seen that these complex ions are unstable at high temperatures and so maintaining an adequate reaction temperature is very important.

Thus we are presented here with a number of considerations for finding optimal conditions to get the best results. On the one hand we want to get maximum yield and on the other hand, the purest possible product. All this should be achieved without excessive costs. Accordingly, care must be taken to have enough available chlorine, so as not to leave bromine ions in the solution, but on the other hand supplying too much chlorine to the reaction tower must be avoided. We have shown here an example of how the various requirements demand a thorough examination to select the best possible conditions. An optimal temperature of 100°C-120°C was chosen for the reaction tower, while chlorine is added at the smallest possible excess.
How is bromine produced?

- Why is excess chlorine used?
- Why should a too large excess of chlorine be avoided?

The depleted brine is returned to the Dead Sea, containing slightly more chlorine ions than the original amount and a small amount of bromine ions that did not react with the chlorine. Returning bromine ions to the original reservoir prevents waste.

- Do you think that returning this brine to the Dead Sea presents an ecological problem? Explain.
- The brine leaves the bottom of the reaction tower when it is hot. Do you think there is any justification for letting the hot solution flow directly in the Dead Sea? Explain

The brine is returned to the Dead Sea only after the energy it contains has been exploited by an energy exchange system between the cold solution entering the reaction tower and the hot solution being returned to the sea. The energy is exchanged via heat **exchangers**, a pipeline system with a large contact surface area.

**Heat exchanger:** A device in which indirect energy transfer takes place between fluids flowing at different temperatures in order to save energy.
How is bromine produced?

The untreated brine being carried to the reaction tower passes through these heat exchangers and is heated by the hot depleted brine that leaves the reaction tower.

- What is the thermodynamic principle underlying the action of heat exchangers?
- How do heat exchangers contribute to energy saving?

If we preserve optimal reaction conditions as described above, the brine returned to the Dead Sea still contains a relatively small amount of bromine ions. This amount ought to be as small as possible to optimally exploit the bromine ion content of the brine entering the reaction.

**Bromine separation steps**

A mixture of hot gases containing bromine, chlorine and water vapor leaves the top of the tower. This mixture undergoes a number of work-up steps, some of which resemble those carried out in the previously described laboratory experiment.

In the experiment we saw that to obtain liquid bromine, the first step is to cool the gas mixture.

1. **Condensation**

The hot gas mixture arrives in the condenser, which has a temperature at which bromine, but not chlorine, condenses.

- To which temperature it is necessary to cool down the gas mixture to get liquid bromine?
- What is the physical state of water at this temperature?
- What is the physical state of chlorine at this temperature?
- What is the temperature range suitable for condensation of bromine but not of chlorine?
- What happens to the water vapor at these temperatures?
- Do you think the bromine is pure?
- If not, which impurities do you think it contains?
- Do you think the chlorine is pure?
- If not which impurities do you think it contains?
- What are the next steps to be taken with the bromine?
How is bromine produced?

- What are the next steps to be taken with the chlorine?
- What are the next steps to be taken with the water?

At the temperature conditions in the condenser, the chlorine gas is separated from the liquid and after leaving the bromine and water-rich condenser it is returned to the reaction tower. Efficient use is thus made of expensive raw materials and, in addition, we do not need to find an ecological solution for hazardous materials, because such materials cannot be allowed to escape to the atmosphere without appropriate treatment.

Returning non-reacted raw materials to the reaction is called recycling.

**Recycling:** Returning non-reacted reactants to the reaction container.

The liquid phase containing chlorine and water-containing bromine is transferred to the next separation step by means of a special container, called a separator.

### 2. Separation

Two layers are formed in the separator:
- What does each layer contain?
- Why do we get two layers?
- Which layer will be the lower one and which the upper one?

The bromine plant at Sdom
The heavy, lower layer is the bromine. The lighter, upper layer is the aqueous layer.

The separation method (which is called phase separation) is based on a property of bromine. You are already familiar with:
- The low solubility of bromine in water
- The relative high density of bromine compared to water

- What should be the next steps in the treatment of the bromine layer?
- What should be the next steps in the treatment of the aqueous layer?

The aqueous layer contains bromine and chlorine, which are slightly soluble in water (see Properties on Pages 13, 61). After separation, this layer is recycled to the reaction tower. The bromine layer, which contains chlorine and water as impurities, is further purified as necessary.

3. Purification
As mentioned earlier, the bromine obtained after the separation step is not completely pure and contains chlorine and water. Explain:
- How chlorine is dissolved in the bromine
- How water is dissolved in the bromine?
- How can the chlorine can be separated from the bromine?
- How can the water can be separated from the bromine?

The chlorine and most of the water are separated by distillation and recycled to the reaction tower. To get dry bromine, the residual water is removed by a drying process. This last step of drying the bromine from the residual water is performed only if necessary. Certain applications allow the use of wet bromine, i.e. bromine that has not been dried, while other processes require the use of dry bromine.
- Which principles must be followed in choosing a drying method?

Drying: Removal of water from material.

Steps in the production process are subjected to strict in-process control and samples are taken to monitor the quality of the bromine. The bromine obtained is collected in storage tanks close to the plant and from
How is bromine produced?

there, transferred to the transport vehicles. The whole process consists of a number of steps carried out in a series of different containers. Such a process is called a continuous process. The raw materials are fed continuously into the first reaction container in which the first reaction step takes place. The containers are connected by pipes, pumps and other equipment that allow the uninterrupted flow of the reaction mixture from container to container. Care is taken that in each step optimal reaction conditions exist in terms of temperature, pressure, catalyst, etc. After the last step the desired product is obtained. Thus a continuous flow of raw material is sustained while at the same time the product is formed uninterruptedly.

Continuous process: A process in which raw materials are fed continuously to the system, while simultaneously products are continuously removed. In each part of this uninterrupted operating system, preset operations are carried out, keeping the concentration of reactants and products constant in each part of the system, so that the process is kept under control.

A continuous production process is applied when the product is in constant demand and must be produced in large quantities. Technologically a continuous process is far more complicated than a batch process, demanding a much more intricate control mechanism, but it also has advantages. In a continuous process it is possible to produce large quantities without the need for large containers, since the reaction mixture is not kept in one stage of the process for a long time, but continuously flows from one container to the other. The saving made by building small containers, and as a result also in space, compensates for investments made in automation and control systems. Likewise, if the process is correct and reaction conditions remain constant during all the stages, product quality remains essentially unchanged and stable.

There are different industrial systems, starting from fully continuous systems to partly continuous and partly batch systems. Each step and each process is designed in accordance with its specific requirements. In the next chapter we shall give a few more examples of batch and continuous processes.

- Which changes have to be made to convert the laboratory system described on Page 67 to a continuous system? Do you think it would be profitable to do this in this lab system?
Indicate other possible reasons for designing a continuous process and likewise for designing a batch process.

- Give the advantages and disadvantages of a batch process and the advantages and disadvantages of a continuous process.

In an industrial process the amount of product obtained from a given amount of raw material must be measured and this data defines process efficiency. Reducing losses of raw materials or products during the manufacturing process is of crucial importance. In a batch process, the yield of the reaction can be calculated for each separate step.

- What can cause decreases in yields in each individual bromine separation step?

In industry we are interested in the final amount of product obtained from a specific amount of reactants entering the process, and how to improve process efficiency in order to obtain the optimal amount of this product. To this end we often look at the overall efficiency of the process in all its different stages from beginning to end. This concept is called overall yield\(^9\). The overall yield is calculated according to the amount of product obtained from a given amount of reactants.

**Overall yield:** Amount of product, expressed in percentages, actually obtained relative to the maximum amount obtainable, based on the reaction equation and starting concentrations of reactants.

In the case of bromine production, the overall yield is calculated relative to the amount of chlorine (or concentrated brine) introduced in the process and the final amount of pure bromine obtained and stored in the various storage tanks. The overall yield is generally calculated relative to the most expensive component participating in the process. In this calculation the different steps of the process are not taken into account, but only the starting point and the endpoint of the process.

\(^9\) For examples see Appendix A.
- Recycling the chlorine to the reaction tower increases the overall yield of the process. Explain.
- Does recycling the chlorine change the yield of the reaction taking place in the tower? Explain.

In a batch process, the overall yield of each step can be calculated. In a continuous process, in contrast, the overall yield per time unit must be calculated. This time unit may be 24 hours, a week, a month, a year, etc.
To summarize:

If we review the overall bromine production process we can simplify the diagram by drawing the following general flowchart:

```
Flowchart of operations in a chemical industry production unit

Raw materials

Preparation of raw material(s)

Process

Recycling of non-reacted material(s)

Separation

Byproduct(s) if present

Storage and/or repacking

End product(s) for marketing
```

This type of diagram can make it easier to analyze the bromine production process or any other process. Each box may relate to one step or a number of steps, dependent on the process under discussion.

- Which steps of the bromine production process discussed in this chapter relate to which boxes in the general flowchart?
- For each step in the general flowchart compare the laboratory production of bromine with industrial bromine production.
3.8 - Construction materials in the bromine plant

Both bromine and chlorine are highly corrosive materials, especially in the presence of water. In certain steps of the bromine production process other factors also play a role, such as high temperature, presence of gases, etc. This makes it necessary to use special construction materials for all system components, which must be designed to meet the conditions.

During the initial days of the bromine plant, construction materials available were found to be usable, if not always ideal. The reaction tower and other parts of the plant were built from silicates, and clay pots served as storage containers. Along with technological developments in glass processing, the reaction tower and other parts of the plants were gradually constructed from glass resistant to bromine and other reactants. Today, glass is the most common construction material used for equipment in the bromine industry. At a later stage the reaction tower and other pieces of equipment were built from glass-coated iron, which is of course mechanically stronger. Today there are even towers and equipment built from rare metals such as tantalum, which is resistant to bromine. Although such towers are more expensive, their clear advantage lies in their strength and sturdiness.

All other parts of the installation, such as pipes, pumps, faucets, valves and heat exchangers must also be constructed from suitably resistant materials. Along with technological developments and the development of plastic materials, parts of the pipelines made from lead or glass were exchanged for highly resistant, fluorocarbon plastic pipes such as polyvinylidifluoride (PVDF), Teflon and others. The pumps are made from iron, coated with one of the compatible plastic materials. In cases where heat conductance is required, such as for condensers and heat exchangers, the equipment is constructed from special bromine-resistant metals.
3.9 - Production safety, storage, transportation and use of bromine

General
Bromine has very few applications as an element and therefore most of the bromine produced in the world is used for synthesizing bromine compounds. Bromine compounds have diverse applications, the most important of which will be discussed in Chapter 6.

The global production of bromine in the year 1998 was about 470,000 tons. Three companies jointly produce approximately 75% of the total amount of bromine: Two companies in the USA produce about 50% Dead Sea Bromine in Israel produces about 30%. These three companies are also the biggest producers of bromine compounds, although many other companies, spread over different countries and continents, also produce bromine compounds (see Table 1.3 on Page 34). This implies that bromine has to be transported to bromine-consuming plants around the world. Both to the plants producing bromine itself and to those producing bromine compounds, the bromine must be handled correctly and safely, so that all functions can be carried out efficiently and smoothly, without endangering employees or damaging the environment.

Looking once more at the properties of bromine,

- it is a Volatile liquid
- has High density
- is Non-flammable
- is Toxic
- is Corrosive

These properties must be kept in mind all the time: during production, storage, transportation and use. In this chapter we shall discuss the complete range of safety aspects.

Hazards of bromine
An exhaustive survey and awareness of safety hazards are among the basic and primary conditions for the safe handling of materials at all stages, including: production, storage, transportation and use. Let us therefore review the properties of bromine:
How is bromine produced? How is bromine produced?

- In the gas phase bromine has an orange-brown color and an irritating and suffocating odor. This odor makes it easily identifiable in air, even at concentrations as low as 0.05-3.5 ppm.
- Bromine is a liquid at room temperature, but because it has a relatively low boiling point it is considered a volatile liquid and its vapor may spread if liquid bromine is spilled.
- The high density of bromine vapor relative to air, causes accumulation in low places. This must be taken into account in case of accident, because the vapor may remain close to the ground for a relatively long time without dispersing.
- Bromine is defined as incombustible in air, but because it is a strong oxidant ignition may occur on contact with organic materials or combustible gases.
- The high toxicity of bromine may cause temporary or permanent damage even after short exposure to bromine vapor.
- Following are exposure limits for bromine:

  Threshold Limit Value – Time Weighted Average (TLV-TWA): 0.10 ppm
  Short-Term Exposure Limit (TLV – STEL): 0.2 ppm

- Bromine is a corrosive material especially in the presence of water. Dry bromine is not corrosive, but wet bromine is a very corrosive material.

In the UN international regulations, bromine is defined as a material that is:

- A corrosive substance:
  Belongs to the group of corrosive materials whose chemical action may cause extensive damage to living tissue, packing materials or means of transportation.

- Toxic:
  Belongs to the group of toxic materials that may harm human health or cause death.

---

10 Two accepted ways to define permitted/prohibited exposure limits of dangerous materials are:
- Threshold Limit Value – Time Weighted Average (TLV – TWA): Permitted average upper concentration limit (weighted with respect to eight hours exposure on a workday, in a 40 h workweek, in which almost all employees may be repeatedly exposed, day after day, with no apparent negative effects to their health.
- Threshold Limit Value – Short Term Exposure Limit (TLV – STEL): Permitted short-term exposure level for a duration of 15 minutes
Consider the properties of bromine and:
- Pinpoint problems with production, storage, transportation and use, due to these properties.
- Suggest ways to overcome these problems.

Any use or handling of bromine requires that these stringent safety regulations be strictly obeyed to prevent harm to people and the environment. The unbreakable rule to be observed for each dangerous material is preserving absolute safety.

Safe production of bromine
In bromine production, as in any other production process in which bromine is involved strict safety rules have to be observed\(^\text{11}\), based on a thorough understanding of the hazards inherent in each of the processes, raw materials, intermediate products and products.

The following precautions should be taken:

- All the production systems should be hermetically sealed
- All outputs of the system should be treated appropriately (products, byproducts, exhaust fumes, sewage and solid waste) to prevent compromising safety and endangering the environment.
- Appropriate steps must be taken to prevent emission of toxic gases.
- All parts of the installation must be constructed from bromine-resistant materials.

\(^{11}\)Obeying the safety rules is important during production of materials in general and production of dangerous materials in particular. Of course, special safety rules must be established for each individual process or material, dependent on the type of process or the properties of the material.
How is bromine produced?

The following equipment should be permanently present in the immediate vicinity of the installations:

- Gas monitors
- Detectors for dangerous materials in all liquid and gas flow outlets
- Alarm systems
- Neutralizing agents
- Protective clothing and equipment

Likewise, detailed standard operating procedures and procedures for handling accidents and failures must be recorded and all employees required to be completely familiar with these procedures.

Among the most important means for the prevention of bromine leakage into the environment are the absorption towers, which function by absorbing any emission of bromine to the surroundings.

**Absorption**: Dissolution of gas in liquid under reaction.

**Absorption tower**: Glass container filled with glass rings, ceramic disks or other filling material, in which the neutralizing solution is introduced from above, while the gases to be absorbed enter from below.

Each part of the production system from which bromine vapors might be able to escape is closed with a special pressure-sensitive plug and connected to the absorption tower. Emission of the bromine vapors exerts pressure, which releases the plug as a result of which the vapors flow to the lower part of the absorption tower. A reaction takes place, which neutralizes the bromine, preventing the danger of leakage to the surroundings.

The bromine-neutralizing solution consists of a diluted (10%) solution of sodium hydroxide. In principle it would be possible to use another, cheaper base, such as calcium hydroxide, but the choice is dependent not only on the price of the neutralizing material but on other factors as well, such as the need for constant mixing when using an insoluble material and the ability to recycle the absorption solution, or to use it for other purposes in the plant.
How is bromine produced?

- What reaction takes place in the tower?
- Why are the vapors introduced from below and the solution from above?
- Why is the absorption tower filled with glass rings?
- What other factors are important in choosing a neutralizer?

For in-process and product quality control, samples are taken from different stages of the production process. The sampling procedure is planned in such a way as to prevent the danger of bromine leakage and to protect the employees. In addition, the bromine plant employees wear protective suits, gloves, masks, and closed respiratory systems when necessary.

Central containers for the storage of neutralizing materials are situated in the bromine plant. Pipes leading from these containers convey neutralizing agents when needed to different areas in the plant. Ammonium containers located at a distance from the plant are activated in case of bromine gas alert. In certain areas of the plant there are containers with diluted thiosulfate solutions and sodium bicarbonate, which are activated in cases of liquid bromine alert. There are also containers with calcium hydroxide solutions. All neutralizing agents are applied under strict flow-rate control, to prevent the neutralizing reaction itself, which is exothermic, from developing into a dangerous and harmful occurrence. The neutralizing action must be carried out under controlled dosing and flow-rates, using diluted solutions and strictly observing the safety rules.

The depleted brine leaving the reaction tower may contain residual bromine or chlorine. Even if the bromine and chlorine concentrations are very low, they must be neutralized before allowing the brine to flow back to the Dead Sea.
To accomplish this, a control system is installed with continuously operating detectors for monitoring the brine composition. If the bromine or chlorine concentrations in the brine are found to be above the accepted level, they are neutralized by appropriate amounts of ammonia or other neutralizing solutions.

**Safe handling of bromine leakage**

If an accident occurs and there is a bromine leakage, it is important to deal with the leakage immediately in such a way as to limit the harm done to people and the environment as much as possible. We saw how bromine is neutralized in the laboratory. Different considerations may be put forward for the establishment of suitable industrial bromine-neutralizing methods, adapted to large-scale processes. The use of larger quantities of material requires that serious thought be given to such questions as:

- Ease of handling
- Availability of neutralizing agents
- Costs
- Reaction enthalpy
The handling of a bromine leakage depends upon the physical state of the bromine.

**Gaseous bromine** is neutralized by reaction with ammonia. The two gases react with each other in an exothermic reaction with the formation of ammonium bromide. Accordingly, if ammonia is released in an area with bromine leakage, we see the appearance of a white cloud of ammonium bromide.

- Which reaction is taking place? Give the reaction equation.
- Why is this method only suitable for treating a leakage of bromine gas?
- Although this is an exothermic reaction, it does not pose a problem for the neutralization of bromine gas. Why?

**Liquid bromine** can be neutralized by direct reaction with a thiosulfate solution as described in the first chapter, but this being a highly exothermic reaction, it can cause evaporation or spraying of bromine and therefore is not recommended. The best way to neutralize liquid bromine is by absorption of the liquid by a suitable solid material, followed by washing or reaction with a neutralizing agent. For this purpose lime powder, Ca(OH)₂, is generally applied in the plant. After the lime has absorbed the bromine, it is washed with enough water to allow the neutralizing reaction to take place. The disadvantage of this reaction is that it is relatively slow.

- Give the equation for the reaction between liquid bromine and lime in the presence of water (make use of the reactions described on Pages 14-15)
- What is the role of the absorption?
- Why is the absorption reaction carried out before the washing and not vice versa?
- If no other material is available, it is also possible to use sand to neutralize liquid bromine. Explain
- Liquid bromine can also be neutralized with a 10% sodium hydroxide solution. Give the reaction equation and explain.
- If no ammonia is available, bromine can be dealt with by spraying with water. Explain.
- The reaction between liquid bromine and sodium carbonate Na₂CO₃ is less exothermic. Nevertheless, in industry we use lime and not sodium carbonate. Why?
Safe storage of bromine

Safe storage of materials is an important issue, which over the years has itself become a special expertise. Storage rules and methods must comply with the particular properties of each material, its reactions with other materials and the different hazards involved.

The properties of bromine also have an important bearing on its storage:
- **The volatility of bromine** dictates the need to store it in a place protected from external damage.
- **Its oxidizing capacity** dictates the need to avoid contact with reducing agents, organic compounds and combustible materials.
- **Its highly corrosive action** in the presence of water dictates the need to store it in a dry place and to build storage tanks with suitable resistant coating.
- **Its ability to form light-induced free radicals** requires storage in a dark place.
- In addition there are other requirements, such as: protection against static electricity, etc.

*The storage of bromine near ammonia, phosphorus and metals is forbidden. Explain why.*

After production, the bromine is conveyed to large storage tanks located close to the plant and from which it is pumped to fill the transporters. These storage tanks are made from iron with an interior glass coating and they are protected by absorption systems for the neutralization of excess bromine if the need arises. Low concrete walls are built around them to prevent accidental overflow of liquid bromine to the surroundings.

Storage area for bromine (storage tanks)
Safe transportation of bromine

Accidents in which toxic materials are involved, and plants producing such materials, quickly make headlines and are widely publicized. Usually these accidents are caused by carelessness, negligence or human error. Many accidents during transportation of hazardous materials occur as a result of speeding. These accidents could have been prevented if everybody involved in the transportation of materials in general, and hazardous materials in particular, had obeyed the rules that apply to them.

Transportation of hazardous materials requires particular expertise and bromine is no exception. International and local transportation of bromine is subject to international control and regulations on transportation of hazardous materials. Bromine is transported in liquid form, but its volatility and toxicity demand that it be transported in the safest possible way, with complete sealing of the transporters and precautions against the danger of bromine leakage to the air.

- What is the advantage of transporting liquids instead of gases?
- Is it necessary to take special measures to keep the bromine in liquid form?

To cope with the dangers discussed in the previous paragraph the Bromine Company developed special isotanks\textsuperscript{12} for bromine, in compliance with international UN regulations. 1250-liter and 8000-liter isotanks were constructed for this purpose made from steel coated internally with a layer of lead (for dry bromine) or glass (for wet bromine)\textsuperscript{13}. The steel imparts strong mechanical properties and the interior coating provides resistance to the strong corrosive action of the bromine.

- Transportation in lead-coated isotanks is suitable for dry bromine, but not for wet bromine. Explain.
- What is the weight of bromine in an isotank with a capacity of 8,000 liter?

A framework equipped with four special corner locks supports the isotank. These units allow the isotank to be lowered by means of a conveyor. This ensures that the isotank remains stable during transportation and also makes it possible to lift it from the truck and use it for storage.

\textsuperscript{12}Special containers carried by heavy trucks used for transport of hazardous materials.
\textsuperscript{13}Today most isotanks are coated with lead. All shipments abroad employ lead-coated isotanks, while glass-coated isotanks are used only for local transport.
The isotanks are equipped with safety and control systems for maximum safety during filling, transportation and emptying. All isotanks meet international standards for transportation of hazardous materials. After each usage the condition of all the accessories is checked. Furthermore, in compliance with hazardous materials regulations, the condition of the internal coating is examined once a year. This examination is of course only done after the containers have been completely emptied, which is accomplished by blowing air through for several days under strict safety precautions to protect both the environment and the employees.

Customers who need smaller quantities of bromine are supplied with glass bottles (containing 1 liter of bromine) or iron, lead-coated, containers, containing about 140 liters of bromine. The bottles are packed and transported with strict observation of safety regulations and in compliance with international transportation regulations. Each box contains six bottles, with the space between the individual bottles and between the bottles and the box being filled with vermiculite. The latter is an ore with special properties used as a shock absorber during transportation and capable of completely absorbing the bromine. The amount of material is sufficient to absorb the bromine in the extreme case that all the bottles break and the bromine escapes. Each box is fastened to a pallet holding a group of boxes and is put in a closed container.

The American National Fire Protection Association (NFPA) has developed a simple method to identify hazards during transportation and storage of dangerous materials, which has also been adopted in Israel. According to this method, all storage tanks and transport vehicles carry a special sign warning of the dangers. The storage tanks of all hazardous materials contain a standardized sign describing the chemical activity of the material, its flammability, health hazards and other specific hazards. The NFPA system defines bromine as incombustible and stable, but as a very toxic and oxidizing material.

The bromine storage tank sign is as follows:
How is bromine produced?

The transport vehicle signs carry a UN Number, which is the international identification number of the transported material, and an additional code indicating the action to be taken in case of an accident or emergency. The driver must have a license to transport hazardous materials and a list of instructions (safety manual) specifying how to act in case of emergency. There are special signs for transportation by sea, land (roads and trains) and air.

**UN Number:** International identification number for transported material

---

**Safe use of bromine**

Bromine is used for many purposes in research and industry. All safety rules observed during the production, storage and transportation of bromine must also be obeyed during its handling and use. Every customer who uses large amounts of bromine must have an unloading station. The bromine is unloaded while connected to the isotank or the container of the absorption tower to prevent bromine vapors escaping into the air. Emptying of the isotank is monitored by weighing or by watching through a glass window. When all the bromine is removed, the color of the windows changes from brownish-red to a light hue. At any such unloading station suitable neutralizing materials and protective equipment must be available.
How is bromine produced?

Safe use requires:

- Development of application technologies
- Customer guidance
- Preparation of safety manuals or Material Safety Data Sheets (MSDS) - see details on Page 148.
- Signs and labels

**Material Data Safety Sheet**: An information sheet summarizing all information on the properties of the material, its toxicity, different kinds of exposure hazards to the material and correct ways of treatment.

Bromine unloading station at Bromine Compounds Ltd.
**Concepts studied in Chapter 3**

**Absorption:** Dissolution of gas in liquid under reaction.

**Absorption tower:** Glass container filled with glass rings, ceramic disks or other filling material, in which the neutralizing solution is introduced from above, while the gases to be absorbed enter from below.

**Batch process:** A process in which the reactor is supplied with a certain amount of raw material (reactant/s, auxiliary substance/s). The reaction mixture is treated to get the desired product/s. After obtaining the product/s and removal of the reaction mixture from the reactor, the next portion of raw material is added and treated identically to get an additional quantity of the product.

**Condenser:** A device with a double-walled jacket, through which the cooled-off gases flow. Cold (salt)-water for absorbing the energy runs through the jacket causing the required condensation.

**Construction materials:** Materials used for construction of equipment parts involved in chemical processing storage or transporting.

**Continuous process:** A process in which raw material are fed continuously to the system, while simultaneously products are removed continuously. In each part of this uninterrupted operating system, preset operations are carried out, keeping the concentration of reactants and products constant in each part of the system, so that the process is kept under control.

**Conversion:** Ratio, expressed in percentages, between the amounts of reactant that reacted and the amount of reactant introduced in the reaction vessel.

**Distillation:** Process by which liquid components are separated from a solution by heating to a suitable temperature.

**Drying:** Removal of water from material.

**Flowchart:** Block diagram describing the sequence of steps in a process.
How is bromine produced?

**Heat exchanger:** A device in which indirect energy transfer takes place between fluids flowing at different temperatures in order to save energy.

**Neutralizing agents:** Materials that react with a hazardous substance in a reaction that does not generate other hazardous substances or cause any other hazards. These materials are used for safety reasons - in case of leakage of a dangerous substance or any other accident - by preventing possible dangers to humans or to the environment.

**Overall yield:** Amount of product, expressed in percentages, actually obtained relative to the maximum amount obtainable based on the reaction equation and starting concentrations of reactants.

**Packed tower:** A tower with filling material (rings, disks etc.) in which a reaction takes place between gases and liquid or solution. The purpose of the filling material is to increase the contact area between the reactants in the tower.

**Reaction yield:** The ratio, expressed in percentages, between the amount of desired product obtained in the reaction and the amount that should have been obtained according to the reaction equation, the starting amount of reactants and the conversion percentage.

**Recycling:** Returning non-reacted reactants to the reaction container.

**Safety manual:** An information sheet summarizing all information on the properties of the material, its toxicity, different kinds of exposure hazards to the material and correct ways of treatment.

**Short Term Exposure Limit** (TLV – STEL): Permitted short-term exposure time of 15 minutes.

**Threshold Limit Value – Time Weighted Average** (TLV – TWA): Permitted average upper concentration limit (weighted with respect to eight hours exposure on a workday, in a 40 h workweek, in which almost all employees may be repeatedly exposed, day after day, with no apparent negative effects to their health.

**UN Number:** International identification number for transported material.
Questions about Chapter 3

1. “The amount of bromine that can be produced depends on the chlorine sources”. Explain this statement and give examples.

2. Which properties of bromine are used in the various stages of its industrial production?

3. In the next table the main problems concerning the industrial production of bromine are listed. Indicate what suitable solutions have been found for each of them.

<table>
<thead>
<tr>
<th>Problem</th>
<th>Solutions in industry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suitable raw materials</td>
<td></td>
</tr>
<tr>
<td>Suitable construction materials</td>
<td></td>
</tr>
<tr>
<td>Energy saving</td>
<td></td>
</tr>
<tr>
<td>Large-scale production</td>
<td></td>
</tr>
<tr>
<td>Increased reaction time</td>
<td></td>
</tr>
<tr>
<td>High yield</td>
<td></td>
</tr>
<tr>
<td>Storage and transportation</td>
<td></td>
</tr>
<tr>
<td>Safety measures</td>
<td></td>
</tr>
</tbody>
</table>

4. Several technologies are used for the production, storage and transportation of bromine. What are the scientific principles guiding these technologies? Give examples.

5 a. How many tons of bromine are obtained in the reaction between 18.2 ton of magnesium bromide with chlorine (in sufficient quantity), assuming that the conversion percentage is 98%, and the yield 95%? Detail your calculations.

b. What is the volume of the magnesium bromide solution assuming that the bromide concentration of the solution is 12 gram/liter?

c. In this reaction what are the factors that can influence the: conversion percentage: the percentage yield
6. Read the following newspaper excerpt and answer the questions:

**Accident with bromine transporter apparently caused by driver’s negligence**
By Eitan Rabin, Ha’Aretz, 5.3.1989

The first findings of the investigation into the reasons for the overturning of the bromine truck in the Dimona industrial area the day before yesterday indicate that because of the truck driver’s negligence the trailer became detached, causing the truck to overturn. According to an eyewitness report, the bromine continued to flow from the overturned truck. A large number of IDF troops arrived at the site, joined by fire department crews with special equipment for neutralizing bromine with lime, water and foam. Also called in were specialist teams from the bromine plant, who for hours contemplated how to put the truck back on its wheels without causing more bromine to leak out. Eventually a crane brought from the Dead Sea was used to lift up the truck. A special army and police control unit was established on the spot, including the General Manager of Israel Chemicals and officials from the Ministry of Health, who checked the wind directions. At a certain point the possibility was even considered of evacuating all the inhabitants of Dimona…”

a. How did the accident happen?

b. Every driver transporting hazardous material must carry a safety manual with him. Use the bromine property chart and the information sheet in Appendix B to indicate the dangers involved in such a type of accident and how to cope with this dangerous situation.

c. According to the newspaper report what actions did the teams arriving at the accident take, and what was the purpose of each of these actions?

d. According to the fire department report the fire brigade took a number of steps in the following order:
   - Covering the spill with extinguishing foam
   - Putting up sand walls around the container truck
   - Pouring first lime then water on the liquid bromine
   - Lifting the truck and putting it back on its wheel while spraying foam jets.

What was the purpose of each of these actions? Why were they carried out in this order? Make use of the bromine properties and explain.

7. Read the following newspaper excerpt, which discusses accidents that happened in another plant, and then answer the questions.
A leakage of acid used for waste processing was discovered in the backyard of the Coca Cola plant. A chain of errors made during the attempts to neutralize the leakage caused a huge explosion. A 35-year old firefighter was killed and 40 others were slightly injured.

By Adar Avishar, Adi Katz and Kobi Gleich
“Ma’ariv”, 29.10.1993

One firefighter was killed and 40 others were slightly injured during an explosion in a hydrochloric acid storage pit at the “Coca-Cola” plant in Bene Beraq.

Yesterday morning at 9.30 a.m. the fire brigade from Bene Beraq received an alarm call from the Coca-Cola plant, reporting a leakage of acid used for waste processing. Moments later there was a loud explosion.

An early investigation showed that the disaster was due to a combination of bad judgment and human errors. A senior official told Ma’ariv yesterday that contact between the acid and caustic soda crystals caused the explosion.

Unfortunate coincidence
“From initial evidence”, the senior official said, “it appears that when the plant employees, including the chemist, first noticed the leakage, they took action to start neutralizing the acid. The standard procedure in case of a leakage is that first the plant teams take care of it and after that, when the emergency teams arrive, the latter take responsibility. The employees brought sacks of caustic soda crystals, which is an acid-neutralizing material, to the site of the leakage. According to instructions the acid must be neutralized with caustic soda diluted with water to 10 percent.”

By an unfortunate coincidence the first firemen arrived at the spot precisely after the sacks of caustic soda were placed near the opening of the pit. Apparently the firemen, for some reason, failed to read the instructions and the identification tables specifying the required dilution. As a result they poured the concentrated (almost 100%) caustic soda crystals into the hydrochloric acid pit. The resulting chemical reaction between the two concentrated materials caused the explosion. Apparently the shock wave following the explosion threw the fireman who was standing near the opening into the dangerous chemical material causing his death.

What happened actually?
The hydrochloric acid leaked from a big container with a capacity of hundreds of liters in an underground waste-processing device. Because of its high concentration the hydrochloric acid digests the waste and during the process acrid vapors are released. To neutralize the acid leakage it must be mixed with sand and sodium carbonate. This mixture must be neutralized with a highly diluted (10%) solution of caustic soda. Instead highly concentrated caustic soda (98%) was poured on the mixture, causing the explosion.

Alex Doron

---

a. What was the reason for the disaster that took place in the backyard of the Coca Cola plant?
b. What was the material they wanted to neutralize in the plant?
c. What was the neutralizing material?
d. Give the reaction equation.
How is bromine produced?

- What was the mistake that was made?
- How could the disaster have been avoided?
- What actions ought to have been taken to handle the leakage of materials safely and to prevent disaster? Explain.

8. As neutralizing agents for bromine several bases, such as Ca(OH)$_2$(s) and Na$_2$CO$_3$(s) can be used.
   a. Are these bases useful for neutralizing bromine gas? Explain.
   b. Are these bases useful for neutralizing liquid bromine? Explain.
   c. How do Ca(OH)$_2$(s) or Na$_2$CO$_3$(s) exert their neutralizing action? Explain.
   d. What are the arguments for choosing Ca(OH)$_2$(s) or Na$_2$CO$_3$(s) for neutralization? Explain.
   e. Give the reaction equations for the neutralizing reactions with Ca(OH)$_2$(s) and Na$_2$CO$_3$(s).

9. Give examples of materials that may be suitable neutralizers for:
   a. Chlorine gas
   b. An aqueous solution of HBr$_{(aq)}$. 
   c. Hydrogen bromide gas HBr$_{(g)}$. 
   d. An aqueous solution of sulfuric acid H$_2$SO$_4(aq)$. 
   e. An aqueous solution of NaOH$_{(aq)}$. 
   Give reaction equations and describe what you consider to be the recommended method of neutralization.