

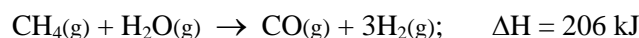
Elements of Industrial Importance

The Production and Uses of Hydrogen

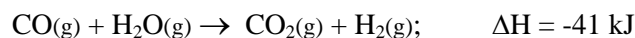
Hydrogen is the most abundant element in the universe, but in the Earth's crust it accounts for less than 1% (by mass); it is the third most abundant element in the human body. Virtually all of the hydrogen found on Earth is in the form of compounds, mainly as water and hydrocarbon compounds.

Industrial Production of Hydrogen

In the U.S. hydrogen gas is produced at an annual rate of 2.5×10^5 metric tons (2.5×10^8 kg or 3×10^9 m³ at STP). The most important industrial method for the production of hydrogen is the *steam-reformation process*, which involves three steps. The first step is the reaction of methane gas and steam that produces a mixture of CO and H₂ and is called *synthesis gas*. The reaction is endothermic, normally carried out at around 1100°C over a *nickel-based catalyst*.

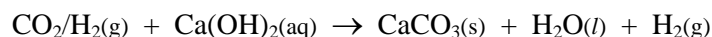


In the next step, the *synthesis gas* mixture and an additional steam are passed over a metal oxide catalyst (such as Fe₂O₃ or CoO) at about 400°C. Under this condition, the carbon monoxide in the mixture reacts with steam to produce CO₂ and more hydrogen. The reaction is called *water-gas shift reaction*.

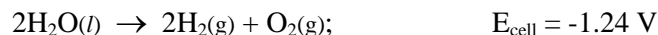


This second reaction is exothermic and the energy produced is channeled to the first reaction, which helps to drive the endothermic reaction forward and at the same time reduces the fuel consumption.

In the third step, CO₂ is removed by passing the CO₂-H₂ mixture through lime-water, Ca(OH)₂, or other basic solution. This treatment converts the carbon dioxide to the carbonate ion, which remains in the aqueous phase.



By removing the CO₂ gas, the equilibrium shifts to the right and produce H₂ that is about 98% pure. Hydrogen of higher purity (~99.9%) is obtained by passing the gas through *synthetic zeolite* that filter out other molecules greater than H₂. In countries where electricity is cheap, hydrogen is prepared by electrolysis of water using Pt or Ni-electrodes:

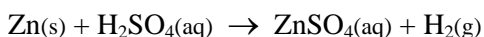
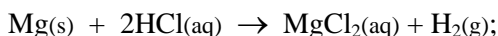


Over-potential increases the voltage requirement to about 2V. Under typical operating conditions, the energy rate in hydrogen production by electrolysis is about 400 kJ per mole of H₂ produced.

$$(\Delta G = -nFE = -(2 \text{ mol e}^-/\text{mol H}_2)(9.65 \times 10^4 \text{ C/mol e}^-)(-2 \text{ V}) = 400 \text{ kJ/mol H}_2)$$

Laboratory Preparation of H₂

Small amount of hydrogen gas can be prepared in the laboratory by reaction of some metals with dilute hydrochloric or sulfuric acid, and the hydrogen gas produced is collected over water:

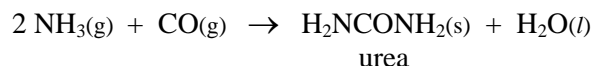
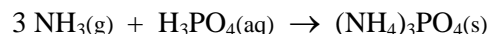
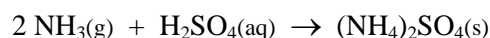
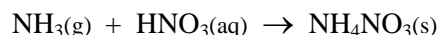


Industrial Uses of Hydrogen

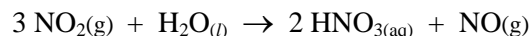
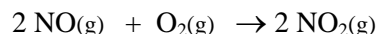
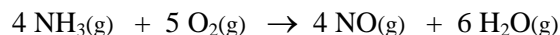
Most (~95%) of the hydrogen produced in industry is consumed on-site for the manufacture of other chemicals. The largest consumer of hydrogen is the *Haber process* for synthesizing ammonia, which uses nearly 70% of the hydrogen produced. The reaction is carried at about 250°C and 200 atm, using iron as catalyst.



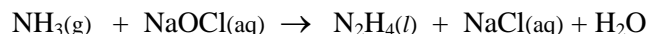
Because of its many uses, ammonia is one of the most highly produced inorganic chemicals. The annual global production is about 1.1×10^8 metric tons, with China being the major producer. U.S alone produces about 9 millions metric tons (almost 20 billions pounds). About 70% of the ammonia produced is converted into inorganic and organic fertilizers, such as ammonium nitrate (NH_4NO_3), ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$), ammonium phosphate ($(\text{NH}_4)_3\text{PO}_4$), and urea ($\text{CO}(\text{NH}_2)_2$).



About 20% is used in the Oswald process to manufacture nitric acid.

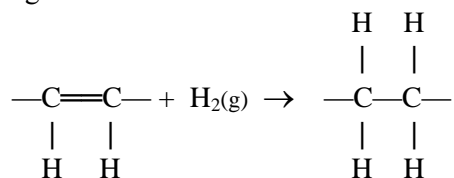


Ammonia is also used in the production hydrazine, N_2H_4 , which is used to make rocket fuel:



Ammonia is also a precursor in the syntheses of monomers for making nylons and other synthetic polymers.

The second major use of hydrogen is the *hydrogenation* of vegetable oils to make solid shortenings such as “Crisco” and margarine.



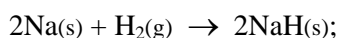
Large amounts of hydrogen are also used for the manufacture of methanol:

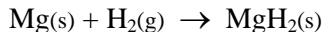


The reaction is exothermic and carried out over a cobalt or copper-zinc oxide catalyst. Methanol is an industrial solvent, a precursor to additives in unleaded gasoline, and a starting material for the manufacture of formaldehyde, HCHO , used in making plastics. U.S. produces about 1.7 billion gallons of methanol, which consumes about 700,000 tons of hydrogen.

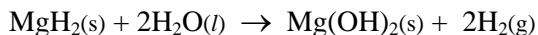
Chemical Properties

Hydrogen reacts with reactive metals to form hydrides and with most nonmetals;

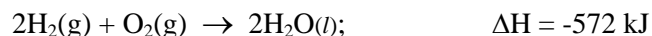




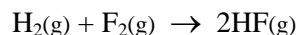
Metal hydrides react with water very readily to produce hydroxides and hydrogen gas:



Reactions of hydrogen with nonmetals are very exothermic, but with high activation energy. For example, a mixture of hydrogen and oxygen can stand for a long time without reacting, but if ignited, the reaction will take place with an explosive force:



Fluorine is the only gas that reacts with hydrogen at room temperature (even in the dark):

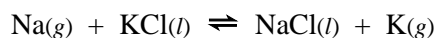


Industrial Production of Sodium and Potassium

The sodium ore is called *halite*, mainly NaCl, which is obtained by evaporation of concentrated salt solution (brines) or by mining vast salt deposits that are formed from the evaporation of prehistoric seas. Some of these salt deposits are found in Cheshire GB, NM, Michigan, NY, and Kansas.

The brine is evaporated to dryness, the solid crushed, and melted. CaCl₂ is added to form a mixture that has lower melting temperature (about 600°C as compared to 801°C for pure NaCl). The molten mixture is then electrolyzed in the **Down cell**. Molten sodium formed at a cylindrical stainless steel cathode is lighter than the molten NaCl/CaCl₂ mixture; it floats on the top layer and is easily siphoned off. Chlorine gas is formed at stainless steel anode enclosed within an inverted cone-shaped stainless steel screen that prevents explosive contact with the molten sodium. The chlorine gas is an important commercial by-product in this process.

The major ore for potassium is called *sylvite*, which contains mainly KCl. Unlike sodium, potassium is not produced by electrolysis of molten KCl because the molten potassium is soluble in the salt. Instead, potassium is produced by reduction of molten KCl with liquid sodium:



The reaction is carried out at about 850°C, which is above the boiling point of potassium. The potassium vapor is continuously removed and this shifts the equilibrium to the right.

Properties of Sodium and Potassium

- Silvery metals, soft, low melting points (93.5°C for Na and 65.7°C for K);
- Highly reactive – react violently with water, O₂ and halogens:
 - $2\text{Na(s)} + 2\text{H}_2\text{O(l)} \rightarrow 2\text{NaOH(aq)} + \text{H}_2\text{(g)} + \text{Heat};$
 - $2\text{K(s)} + 2\text{H}_2\text{O(l)} \rightarrow 2\text{KOH(aq)} + \text{H}_2\text{(g)} + \text{Heat};$
 - $2\text{Na(s)} + \text{O}_2\text{(g)} \rightarrow \text{Na}_2\text{O}_2\text{(s)};$
 - $\text{K(s)} + \text{O}_2\text{(g)} \rightarrow \text{KO}_2\text{(s)}$
 - $2\text{Na(s)} + \text{Cl}_2\text{(g)} \rightarrow 2\text{NaCl(s)};$
 - $2\text{K(s)} + \text{Br}_2\text{(l)} \rightarrow 2\text{KBr(s)}$

Uses of Sodium, Potassium and Their Compounds

The elemental forms of sodium and potassium have limited uses. Sodium is used as reducing agent in the production of potassium, titanium, zirconium, and others; liquid sodium is used as heat exchanger in nuclear reactors (including breeder reactors). Sodium and potassium are mainly used as their compounds.

- NaCl – main source for electrolytic production of sodium metal and chlorine gas;
Important ingredient in food – needed to maintain electrolyte balance in the human body fluid;
- NaOH – is produced by electrolysis of brine (concentrated NaCl solution) in the Chlor-alkali process – H₂ and Cl₂ gases are important by-products. More than 11 billions of NaOH are produced annually. It is an important starting material for the production of other sodium salts. NaOH is a strong base and used widely in industry to neutralize acid and in the production of soaps and detergents as well as other compounds.
- Na₂CO₃ – also called *soda ash* or *washing soda*; obtained from natural deposits of Na₂CO₃·10H₂O. Na₂CO₃ is used in the manufacture of glass, for water treatment, and as dishwashing detergent;
- NaHCO₃ – baking soda, used in cooking as the rising agent in bread and cake (baking powder is a mixture of NaHCO₃ and NaH₂PO₄ (or KH₂PO₄), dry fire extinguisher, antacid (eg. Alka-Seltzer).
- NaN₃ – sodium azide, is used in airbag – it decomposes when ignited, producing N₂ gas which inflates the airbag: $2\text{NaN}_3(\text{s}) \rightarrow 2\text{Na}(\text{s}) + 3\text{N}_2(\text{g})$
- KO₂ – potassium superoxide is an air purifier, used to remove CO₂ and re-generate oxygen in confined areas, such as submarines, spacecrafts and aircrafts:
 - $4\text{KO}_2(\text{s}) + 2\text{CO}_2(\text{g}) \rightarrow 2\text{K}_2\text{CO}_3(\text{s}) + 3\text{O}_2(\text{g})$;
- K₂O – an ingredient in plant fertilizers (5-10-5 fertilizer contains, by mass, the equivalent of 5% N, 10% P₂O₅, and 5% K₂O)
- KNO₃ – used in matches, black gunpowder mixture;
- KClO₃ – as an oxidizing agent in matches and fireworks;
- KMnO₄ & K₂Cr₂O₇ are strong oxidizing agents used in syntheses of organic compounds. They are also used as a mild disinfectant.

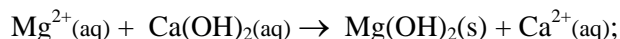
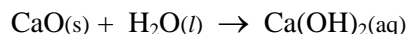
Isolation and Uses of Magnesium

- Sources of Magnesium:
 - The ocean and dolomite (which contains mainly MgCO₃ and CaCO₃).
- The *Dow process* for the isolation of Mg from the sea involves the following steps:

1. **Mining** – intake of seawater and straining the debris.

2. **Converting to Mineral** –

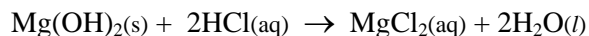
CaO is added to the seawater to precipitate Mg²⁺ as Mg(OH)₂:



3. **Converting to compound** –

Mg(OH)₂ goes into settling tank, concentrated and filtered.

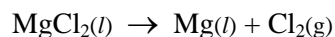
Solid Mg(OH)₂ is reacted with HCl(aq) to form MgCl₂(aq):



Water is evaporated to give a hydrated solid MgCl₂·nH₂O.

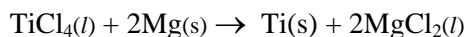
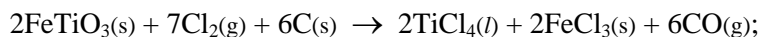
4. **Extraction of metal by electrolysis.**

MgCl₂·nH₂O is heated to above 700 °C to remove water of hydration and produce molten MgCl₂, which is electrolyzed to produce Mg and Cl₂ as by-product.

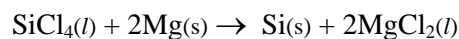
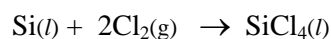
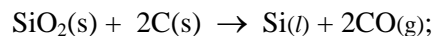


Properties and Uses of Magnesium

- Magnesium is the lightest structural metal.
- Magnesium containing alloys are light but tough. They are used for aircraft bodies, engine blocks, and cameras.
- The pure metal is a strong reducing agent,
- It is widely used in the extraction of other metals, such as Be, Ti, Zr, Hf, and U.
- Example: titanium is extracted from its ore, *ilmenite*, in two steps:

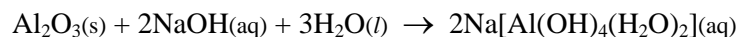
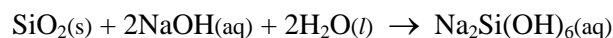


- Magnesium is also used in the final extraction process of silicon:

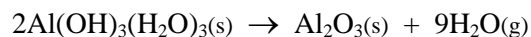


Isolation, Uses, and Recycling of Aluminum

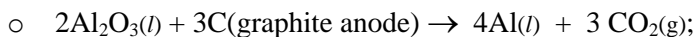
- Aluminum is the most abundant metal in the Earth's crust,.
- Found in numerous *aluminosilicate* minerals, such as feldspar, micas, and clays, and in rare gems garnet, beryl, and turquoise;
- Corundum is pure Al_2O_3 , which is very hard; it exists as ruby and sapphire;
- Bauxite, $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$, is the industrial source of Aluminum
- The extraction of aluminum from the ore involves two processes:
 - Pretreatment of the ore to obtain Al_2O_3 ,
 - The electrolysis of molten Al_2O_3 in Na_3AlF_6 .
- Al_2O_3 is separated from the ore by boiling in 30% NaOH (Bayer process), - acidic SiO_2 and amphoteric Al_2O_3 dissolve as sodium silicate and aluminate, respectively:



- Basic oxides such as Fe_2O_3 do not react with NaOH.
- Heating causes $\text{Na}_2\text{Si}(\text{OH})_6$ to precipitate, which is filtered out with the insoluble Fe_2O_3 and TiO_2 .
- The filtrate contains $\text{Na}[\text{Al}(\text{OH})_4(\text{H}_2\text{O})_2]$, when acidified causes $\text{Al}(\text{OH})_3(\text{H}_2\text{O})_3$ to precipitate.
- $\text{Al}(\text{OH})_3(\text{H}_2\text{O})_3$ is dehydrated to produce Al_2O_3 :



- Al_2O_3 is dissolved in molten cryolite, Na_3AlF_6 , and electrolyzed using *Hall-Heroult process* at about 1000 °C.
- The cell operates at about 4.5 V, but uses $> 1.0 \times 10^6$ A. of current.
- The overall reaction in the electrolysis of molten Al_2O_3 is,



Properties and Uses:

- Aluminum is a reactive metal and is readily oxidized by air.
- Al_2O_3 forms a continuous thin layer of protective coating that prevents further oxidation.
- This makes aluminum resistant to corrosion.
- Aluminum is extensively used in production of household appliances and as power lines.

- It forms light but strong alloys with Mg, used to make the body and engine parts of aircrafts.

Energy Consumption:

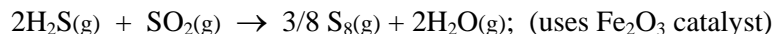
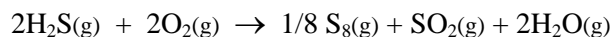
- Production of Al by electrolysis of molten Al_2O_3 -cryolite mixture consumes a large amount of energy.
- The Hall-Heroult process is estimated to consume about 14 kJ/g Al.
- The entire manufacturing process (including mining, pre-treatment, maintaining operating conditions, electrolysis, and so forth) is estimated to consume about 220 kJ/g Al.
- Energy needed for recycling is only about 1 kJ/g Al, which is about 7% of the energy consumed during electrolysis, or less than 1% of the energy consumed in the manufacturing process.

Production of Sulfuric Acid

Sulfuric acid is produced worldwide in a gigantic scale – more 150 million tons annually. The annual production in the USA alone is nearing 50 million metric tons. The modern method in the manufacture of sulfuric acid is the **contact process**, in which sulfur dioxide is oxidized to sulfur trioxide which, in turn, is converted to sulfuric acid. The key steps in this process are:

1. Extraction of Sulfur

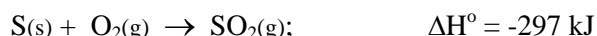
- from H_2S found in natural gas:



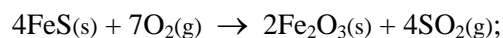
- The mining of sulfur from underground sulfur deposit uses the *Frasch process*, in which a three-concentric ring steel pipe is drilled to the deposit. Superheated water (about 160°C) is pumped through the outer pipes to melt the sulfur and a hot, compressed air is forced through a narrow innermost pipe. The hydraulic pressure in the outer pipe and the air pressure in the innermost pipe force the molten sulfur up to the surface through the middle concentric pipe. Sulfur produced by this process is about 99.7% pure.

2. From Sulfur to Sulfur Dioxide

- Sulfur burns in air to form sulfur dioxide:



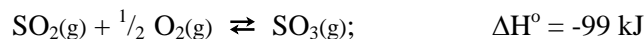
- Sulfur dioxide is also produced during the roasting of metal sulfide, such as FeS and CuFeS_2 :



- About 90% of processed sulfur is used to make SO_2 for the manufacture of sulfuric acid.

3. Conversion of SO_2 to SO_3 in the Contact Process

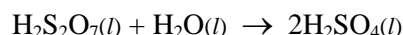
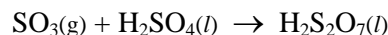
The key step in the production of sulfuric acid is the contact process, which convert SO_2 to SO_3 :



This reaction, although spontaneous, is very slow due to high activation energy. Increasing the temperature will speed up the reaction, but too high a temperature will result in poor yields. Therefore, the reaction is normally carried out at temperatures between 400°C and 600°C . Normally, a mixture consisting 5 parts air and 1 part SO_2 is passed over catalyst beds, which consists of V_2O_5 on inert silica, in four stages; the SO_3 is removed at several points in order to shift the equilibrium in favor of SO_3 . This process gives an overall yield of 99.5%.

4. From SO_3 to H_2SO_4

At low temperature ($< 100^\circ\text{C}$) SO_3 may be passed into water to form H_2SO_4 . However, at the industrial operating temperature ($> 400^\circ\text{C}$), it will cause water to vaporize and the steam will catalyze the polymerization of SO_3 , resulting in a smoke of solid particles that do not dissolve in water. Under the industrial condition, SO_3 is absorbed into concentrated H_2SO_4 to form *disulfuric acid*, $\text{H}_2\text{S}_2\text{O}_7$, which is then hydrolyzed to sulfuric acid by adding water when the liquid has sufficiently cooled down.

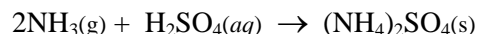


This process yield sulfuric acid that is 98% by mass in H_2SO_4 .

The production of sulfuric acid is an exothermic process. Three-quarters of the heat produced is sold as steam, and the rest is used to pumped gases through the plant. A typical plant produces about 825 tons of H_2SO_4 per day and enough steam to generate 7×10^6 watts of electricity.

Uses of Sulfuric Acid

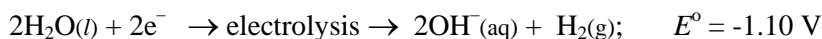
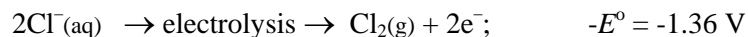
About two-third of the sulfuric acid produced is used in the manufacture of fertilizers such as ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$, which is formed by reaction with ammonia,



Another important chemical that uses sulfuric acid is aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$, which is produced by treating bauxite, $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$, with sulfuric acid. Sulfuric acid is also used in the manufacture of various products such as detergents, resins, coatings, pharmaceutical products, plastics, etc. A large quantity of sulfuric acid is used for making lead storage batteries.

The Chlor-Alkali Process

The *chlor-alkali process* electrolyzes concentrated aqueous NaCl solution (brine) to produce NaOH ; Cl_2 and H_2 are by-products.



Chlorine is formed at the anode and hydrogen at the cathode. A diaphragm separates the anode and cathode half-cells to prevent an explosive contact between chlorine and hydrogen gases. Brine solution is continuously pumped into the anode half-cell and aqueous NaOH formed removed from the cathode side. This prevents the back flow of OH^- into the anode side that would cause a reaction between OH^- and Cl_2 , producing a bleach solution:



NaOH is obtained by evaporating and drying the aqueous NaOH formed in the chlor-alkali process. NaOH is a very important base. It is used in large quantities as drain cleaning solution and in the manufacture of bleach solution and soap making.