

Year 12 Chemistry Depth Study

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1 Equilibrium Systems: Contact Process

The Contact Process is a multi-step industrial process used to produce concentrated sulfuric acid.

1. Produce sulfur dioxide from sulfur and excess oxygen
2. Convert sulfur dioxide to sulfur trioxide
3. Produce oleum (fuming sulfuric acid) from sulfur trioxide
4. React oleum with water to produce concentrated sulfuric acid

1.1 Exploring the Contact Process

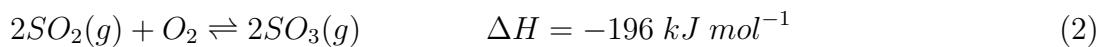
1.1.1 Producing sulfur dioxide

To produce sulfur dioxide, an irreversible exothermic combustion reaction between sulfur and oxygen is used to produce sulfur dioxide.



1.1.2 Sulfur dioxide to sulfur trioxide

The conversion of sulfur dioxide to sulfur trioxide is an exothermic reversible reaction, generally performed in a contact tower or oxidation chamber.

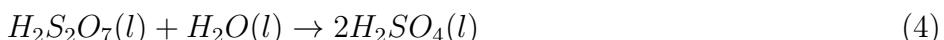


1.1.3 Producing concentrated sulfuric acid

After the production of sulfur trioxide, sulfuric acid is produced in an absorption tower. For a more stable reaction, sulfur trioxide is first dissolved in concentrated sulfuric acid, to produce **oleum** (or fuming sulfuric acid). Without this initial step, the reaction would produce sulfuric acid gas (as a mist or vapor) as the reaction would be highly exothermic.



Once oleum is produced, it is safely reacted with water to produce concentrated sulfuric acid, in a dilution tank.



As indicated by the molar ratio in reactions (3) and (4), the production of concentrated sulfuric acid from oleum produces twice as much concentrated sulfuric acid, as what was originally used to produce oleum.

1.2 The importance and uses of sulfuric acid

Sulfuric acid is a key primary product used to produce a number of other chemical compounds, and the Contact Process allows them to be produced efficiently in high concentrations at industrial scales.

1.2.1 Fertilisers

Sulfuric acid is a key reactant for the production of phosphate-based fertilisers. For example, calcium phosphates are often used as fertiliser and is produced by reacting phosphorite with sulfuric acid.



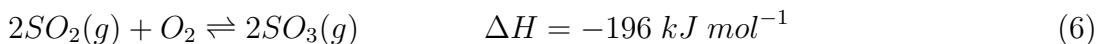
Phosphate-based fertilisers are critical to the world's food supply, in ensuring that there is enough food production to sustain a growing world population. According to researchers, without phosphate and nitrogen-based fertilisers, humanity would only be able to produce half its current food production.¹

1.2.2 Cleaning agents

Outside of fertiliser, sulfuric acid is also used as an industrial cleaning agent. It helps to remove oxidation and rust from iron and steel-based components in the passenger motor vehicles (PMV) and major appliances industries, while also featuring as an ingredient in some household cleaning agents such as drain cleaners.

1.3 Factors affecting equilibrium

Le Chatelier's Principle states that within equilibrium, a disturbance caused by changing conditions (such as temperature, pressure and concentration) will result in an **equilibrium shift** to counteract and re-establish the equilibrium. In the case of the Contact Process, it features one **equilibrium reaction**: the conversion of sulfur dioxide to sulfur trioxide.



¹Faradji & de Boer, 2016.

1.3.1 Temperature

The forward reaction is **exothermic** ($\Delta H = -196 \text{ kJ mol}^{-1}$). By **Le Chatelier's Principle**, lowering temperature will favour the exothermic side of the reaction. Hence, as temperature decreases, the equilibrium shifts right and the disturbance of the equilibrium is counteracted by an increase in the production of sulfur trioxide.

However, as temperature decreases, there is less kinetic energy and less frequent successful collisions, hence the rate of reaction decreases (as increased energy is required to break bonds). Therefore, to produce a reasonably high yield at a fast rate, a higher compromise temperature of 400°C to 450°C is often used in industrial applications. As seen in the provided graph, this temperature will gain 80% (at 450°C) to 90% (at 400°C) yield, with minimal yield increases as temperature approaches zero.

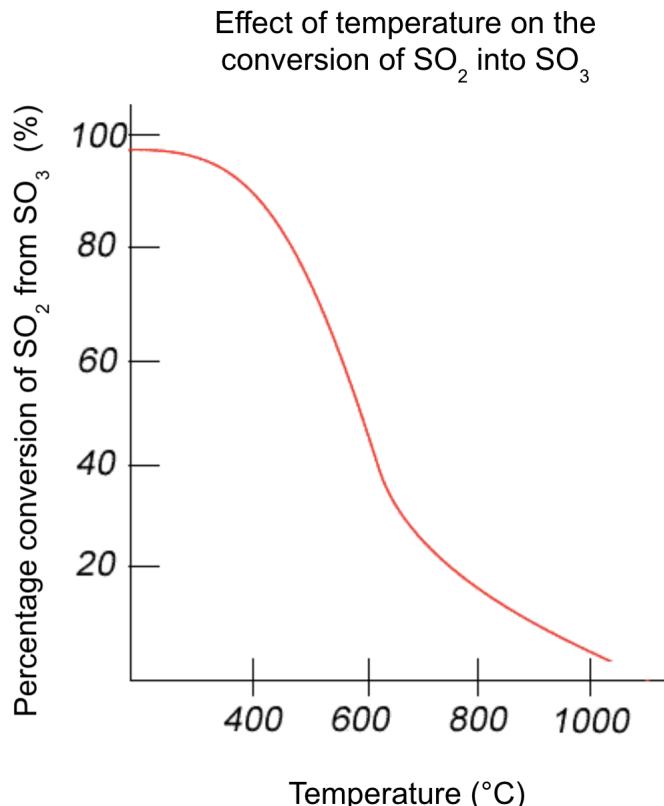


Figure 1: Temperature/yield graph for the conversion of SO_2 into SO_3

1.3.2 Pressure

By **Le Chatelier's Principle**, an increase in pressure will favour the side with fewer number of moles. In this case, this is the products side, and the equilibrium shifts right. The system will then counteract the disturbance by decreasing pressure, both increasing the rate of reaction, as well as producing more sulfur trioxide.

However, low pressure can still garner an extremely high rate of sulfur dioxide to sulfur trioxide. In industrial applications, lower pressures are used, as they still generate high yield (99.5%) and often it is economically not justifiable to invest in substantially higher pressures for minimal yield gain.

1.3.3 Concentration

By **Le Chatelier's Principle**, an increase in reactants will disturb equilibrium. This will cause increased collisions, and hence an increased rate of the forward reaction. Initially, the rate of the reverse reaction remains unchanged but eventually the two rate of reactions will approach equilibrium and become constant once more, causing a shift to the right and producing more sulfur trioxide.

1.3.4 Catalyst

Catalysts lower the activation energy required for the reaction to take place, increasing the rate of reaction. By lowering the activation energy, the bonds in the reactants weaken, thereby increasing the rate of reaction, and eliminating the need for otherwise-needed expensive high-pressure systems.

Within the equilibrium reaction, a catalyst of vanadium(V) oxide (V_2O_5) is used for a reversible reaction, enabling a dynamic equilibrium to be established. Without a catalyst, the reaction would virtually remain at a static equilibrium.

2 Industrial Design: Solvay Process

The Solvay Process is a synthesis reaction which reacts carbon dioxide (produced from limestone), ammonia and brine to produce sodium carbonate.

2.1 Exploring the Solvay Process

The process can be illustrated in the following flowchart:

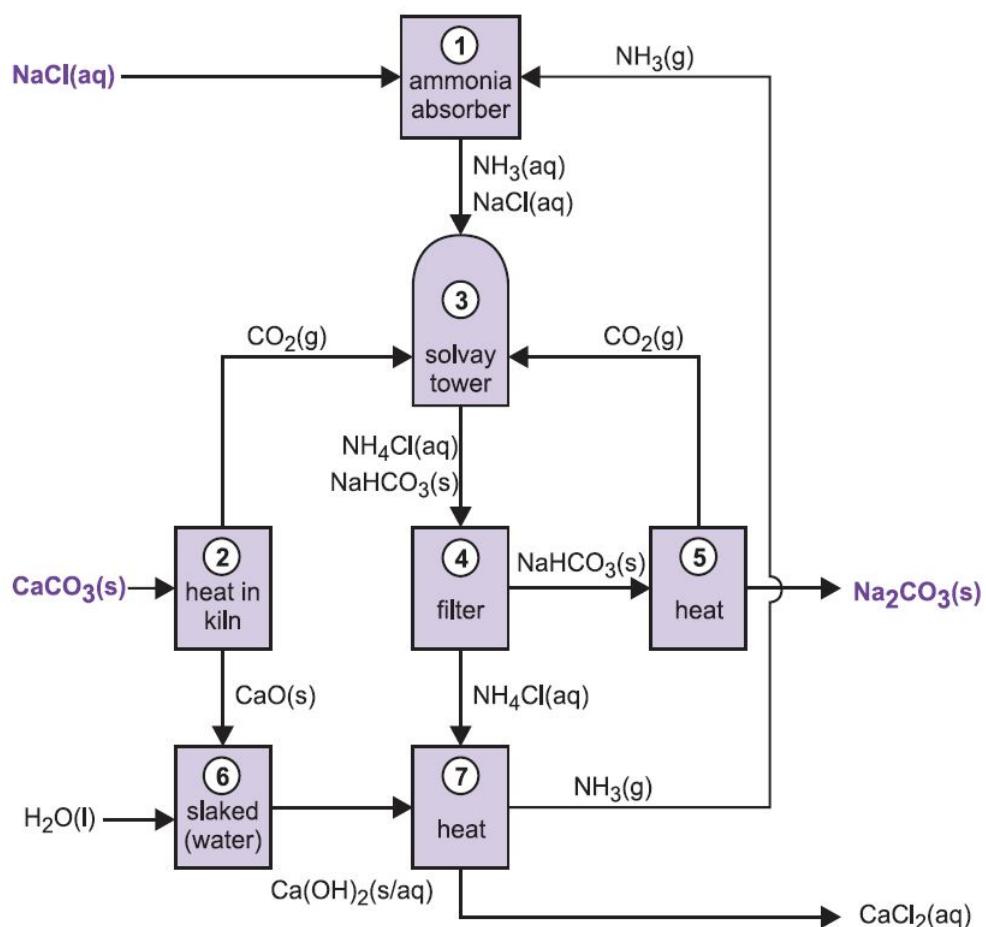
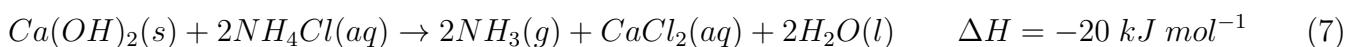


Figure 2: Flowchart of the Solvay Process

2.1.1 Ammonia gas as a reactant

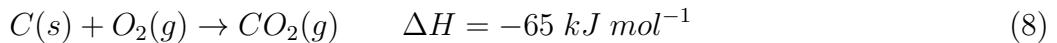
Brine (NaCl(aq)) is fed through an ammonia absorber at (1), where $\text{NH}_3(\text{aq})$ is added to the reactants. The $\text{NH}_3(\text{aq})$ used is often recycled in high proportions in later stages at (7).



2.1.2 The effect of heating calcium carbonate

Large amounts of carbon dioxide gas are produced by the calcination of calcium carbonate (limestone) in a kiln, depicted at (2).

Coke burns in a counter-current of pre-heated oxygen gas, heating the kiln to at least 840°C². This process is **exothermic** (with a negative enthalpy change).

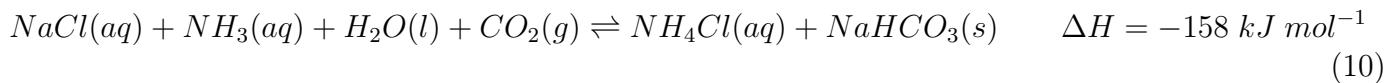


Hence, there will be enough energy to establish a dynamic equilibrium for the calcination (thermal decomposition) of calcium carbonate (an endothermic process with positive enthalpy change).



2.1.3 Solvay tower

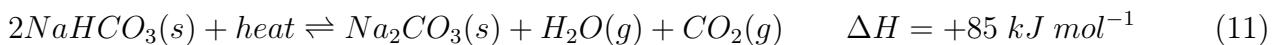
The key equilibrium reaction involves saturating brine (sodium chloride solution) with ammonia gas and carbon dioxide to form ammonium chloride and sodium bicarbonate. It occurs at the Solvay tower at (3) in the flowchart. At low temperatures, the reaction shifts right towards the exothermic products side of the reaction.



2.1.4 Forming sodium carbonate

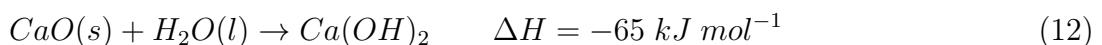
At (4), aqueous ammonia chloride is filtered from solid sodium bicarbonate.

Sodium bicarbonate is then heated (and hence dehydrated) at (5) in order to produce sodium carbonate, and will begin to thermally decompose at around 100°C, with complete conversion at 200°C³.



2.1.5 Recycling calcium oxide to form ammonia gas

In the calcination reaction, calcium oxide is also produced alongside carbon dioxide. This can be used to form and hence recycle ammonia gas. It is first reacted with water to form calcium hydroxide in a process known as **slaking**, located at (6).



Calcium hydroxide is then reacted and heated with the produced ammonium chloride NH_4Cl from the Solvay equilibrium reaction, to form ammonia gas, calcium chloride and water at (7).

²Science Learning Hub, 2021

³Senese, 2010

2.2 Risk assessment

Hazard	Risk
Heating of calcium carbonate	Calcium carbonate is heated to upwards 600-800°C. There is a fire hazard given the presence of flammable material.
Corrosiveness, flammability and toxicity of ammonia gas	If it were to be inhaled, it could cause death, life-threatening pulmonary edema (fluid in the lungs) or breathing difficulties. Contact with skin or eyes could cause irritation or eye damage respectively.
Carbon dioxide gas	Exposure to high concentrations of carbon dioxide gas can lead to drowsiness, headaches, dizziness, increased heart rate, or nausea. At 5000 ppm and above, this could lead to oxygen deprivation.
Calcium oxide as an irritant and corrosive waste product	Contact with skin or eyes could cause irritation or eye damage respectively. Inhalation of calcium oxide could cause coughing or breathing difficulties. In more severe cases, it could cause life-threatening pulmonary edema (fluid in the lungs). Long-term exposure may result in a hole within the inner nose bone. It can cause brittle nails or thicken/cracken skin.
Calcium hydroxide	Skin contact could cause irritation or burning. Eye damage could occur upon eye contact.
Ammonium chloride as an irritant	Contact with skin or eyes could cause irritation or eye damage respectively. Inhaling ammonium chloride fumes may also induce coughing or breathing difficulties.

2.3 Assessment of key considerations

This section assesses the relevant key economical, environmental and social considerations applicable to the Solvay Process at Penrice Factory, Osbourne SA, operational from 1935 to 2014.

2.3.1 Economical

Advantages Penrice Factory is in close proximity to raw materials and environmental features, including the Port River, the St Kilda salt lagoons, the Osborne Power Station (which was utilised as a cogeneration facility for Penrice) and the Penrice limestone quarry in the Barossa Valley (where limestone was transported to the factory by the Penrice Stone Train). Being located in Adelaide, it could take advantage of a large local supply of labour, with sufficient housing and access to public services and railway lines.

Disadvantages Being located within Australia, Penrice Factory was vulnerable to foreign imports, over-reliance on the Australian dollar, increased regulation, and increased taxes, in particular, the carbon tax in effect from 2011 to 2014. In 2011, Penrice Factory requested carbon compensation from the federal government, running it would be forced out of business otherwise. It, and many of its client base (including glass and detergent manufacturers) were unable to compete against foreign imports with the added cost of the carbon tax and complying with new legislation. This was exacerbated by limited protectionist trade barriers and the lowering cost of international transportation. Hence, with both a reduction in domestic demand and an increase in foreign imports, Penrice Factory was not economically viable and its operator switched to a import and marketing role after closing the factory in 2014.

2.3.2 Environmental

Advantages Penrice Factory recycles ammonia and carbon dioxide, such that only small amounts of ammonia need to be refilled at intervals. This somewhat mitigates the impact on the local environment by reusing waste products, particularly for the nearby Port River Estuary. Obtaining reactants has minimal environmental impact, given that brine is easily sourced from the nearby St Kilda salt lagoons. Limestone is naturally abundant and easily obtained from nearby Penrice quarry.

Disadvantages In 2003, the South Australia Environment Protection Authority (EPA) cited Penrice Factory as being one of the main sources of oxidised nitrogen and ammonia being present within the Port River Estuary. Other outflow includes calcium chloride and nitrogen. High nutrient concentrations leads to excessive algae and plant growth (which in turn can produce toxins and make shellfish unsafe for human consumption), cause fish deaths, or suffocate seagrass. Furthermore, outflow from the factory is responsible for thermal pollution (the discharge of heated water) of the estuary, given that the Solvay process is largely exothermic.

2.3.3 Social

Advantages Penrice Factory has been operating for 80 years. At the time of its closure, there were 95 employees at the plant. It also acted as major demand source for the nearby Penrice quarry, with 180 employees across the former Penrice Soda Products corporation. It was important for local jobs in the community and the economy in north-western Adelaide, was the only soda ash plant in Australia.



Figure 3: Google Earth satellite imagery showing calcium carbonate mounds at Penrice Factory, dated 2014.

Disadvantages The Penrice Factory stockpiled large amounts of calcium carbonate after EPA action against their dumping in the Port River. According to a Port Adelaide Residents Environment Protection Group submission to Parliament, these large mounds of calcium carbonate were considered to be an eyesore and blocked views of the Port River.

Penrice Factory was also responsible for a considerable number of noise complaints, which increased during plant slowdowns, startups, and maintenance exercises. This was mitigated through environmental mounding and plant boundaries.

2.3.4 Justification for location suitability

The Penrice Factory is located in a largely unsuitable location. Although there are many economic advantages of the site, including its close proximity to key resources, transportation hubs, and labour resources, its impact on the environment and surrounding community has largely been devastating. This includes being cited by the EPA as a major factor towards the Port River Estuary's poor to moderate water quality, a result of decades of nutrient pollution, thermal pollution and human impact. Furthermore, while it contributed to local jobs, it had a largely negative impact for urban areas of metropolitan Adelaide, in the form of noise & dust pollution, and visually undesirable calcium carbonate waste product which had accumulated over the years. These factors considerably outweigh its economic opportunity, given that despite the location's advantages, the business would be unable to compete against more economically-efficient foreign firms, and as the only remaining soda ash producer in Australia, the factory's ongoing operation would be a misallocation towards less-efficient resources within the local and nationwide economy.

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