5.13: Industrial Chemical Reactions - The Solvay Process

Literally thousands of chemical reactions are used to make important industrial products. Most of these involve organic chemicals, which are addressed in Chapter 9 and later chapters of this book. Some are used to make inorganic chemicals in large quantities. One such synthesis operation is the **Solvay process**, long used to make sodium bicarbonate and sodium carbonate, industrial chemicals required for glass making, cleaning formulations, and many other applications. The Solvay process is examined in some detail in this section because it illustrates some important inorganic chemical reactions and can be used for the discussion of green chemistry in industry.

The key reaction in Solvay synthesis is,

$$\mathrm{NaCl + NH_3 + Co_2 + H_2O \rightarrow NaHCO_3(s) + NH_4Cl} \tag{5.13.1}$$

in which a sodium chloride solution (brine) is saturated with ammonia gas (NH_3), then with carbon dioxide, and finally cooled. This is a precipitation reaction in which solid sodium bicarbonate, $NaHCO_3$, comes out of solution. When heated, the solid $NaHCO_3$ yields solid sodium carbonate, Na_2CO_3, water vapor, and carbon dioxide gas:

$$\mathrm{2\,NaHCO_3 + heat \rightarrow Na_2CO_3 + H_2O(g) + CO_2(g)} \tag{5.13.2}$$

In keeping with the practice of green chemistry (although Solvay developed the process long before anyone ever thought of green chemistry), the CO_2 from Reaction 5.13.2 is recycled back into Reaction 5.13.1

The raw materials for the Solvay process are cheap. The NaCl solution can be pumped from the ground from brine deposits in some locations, or fresh water can be pumped into a salt formation to dissolve NaCl and the resulting brine pumped to the surface. The most expensive raw material is ammonia, which is made by the reaction of elemental hydrogen and nitrogen over an iron-based catalyst,

$$\mathrm{3\,H_2 + N_2 \rightarrow 2\,NH_3} \tag{5.13.3}$$

a means of making ammonia developed by Haber and Bosch in Germany in 1913. However, as shown below, the ammonia is recycled, so only relatively small quantities of additional makeup NH_3 are required.

In addition to NaCl, the major consumable raw material in the Solvay process is calcium carbonate, $CaCO_3$, which is abundantly available from deposits of limestone. It is heated (calcined)

$$\mathrm{CaCO_3 + heat \rightarrow CaO + CO_2} \tag{5.13.4}$$

to produce calcium oxide and carbon dioxide gas. The carbon dioxide gas is used in Reaction 5.13.1, another green chemical aspect of the process. The calcium oxide is reacted with water (it is said to be slaked),

$$\mathrm{CaO + H_2O \rightarrow Ca(OH)_2} \tag{5.13.5}$$

to produce basic calcium hydroxide. This base is then reacted with the solution from which solid $NaHCO_3$ has been precipitated (Reaction 5.13.1) and that contains dissolved ammonium chloride,

$$\mathrm{Ca(OH)_2(s) + 2\,NH_4Cl(aq) \rightarrow 2\,NH_3(g) + CaCl_2(aq) + 2\,H_2O(l)} \tag{5.13.6}$$

releasing ammonia gas that is recycled back into Reaction 5.13.1 for $NaHCO_3$ synthesis. This has the advantage of recycling ammonia, which is essential for the process to be economical. It has the disadvantage of generating a solution of calcium chloride, $CaCl_2$. The commercial demand for this salt is limited, although concentrated solutions of it are used for de-icing ice-covered roads. It has such a voracious appetite for water that it cannot be dried economically for storage in a dry form.

Does the Solvay process meet the criteria for a green chemical synthesis? There is not a simple answer to that question. There are two respects in which it does meet green chemical criteria:

1. It uses inexpensive, abundantly available raw materials in the form of NaCl brine and limestone ($CaCO_3$). A significant amount of NH_3 is required to initiate the process with relatively small quantities to keep it going.

2. It maximizes recycle of two major reactants, ammonia and carbon dioxide. The calcination of limestone (Reaction 5.13.4) provides ample carbon dioxide to make up for inevitable losses from the process, but some additional ammonia has to be added to compensate for any leakage.

What about the percent yield and atom economy of the Solvay process? The percent yield of reaction generating the product, Reaction 5.13.1, can be expected to be significantly less than 100% in large part because the stoichiometric amount of $NaHCO_3$ cannot be expected to precipitate from the reaction mixture. To calculate the maximum atom economy for Na_2CO_3 production, it must be assumed that all reactions go to completion without any losses. In such an ideal case, the overall reaction for the process is

$$\mathrm{CaCO_3 + 2\,NaCl \rightarrow Na_2CO_3 + CaCl_2} \tag{5.13.7}$$

Using the atomic masses Ca 40.0, C 12.0, O 16.0, and Cl 35.5 gives the molar masses of $CaCO_3$, 100 g/mol; NaCl, 58.5 g/mol; Na_2CO_3, 106 g/mol; and $CaCl_2$, 111 g/mol. If the minimum whole number of moles of reactants were to react, 100 g of $CaCO_3$ would react with 2×58.5 = 117 g of NaCl to produce 106 g of Na_2CO_3 and 111 g of $CaCl_2$. Note that the mass of NaCl reacting is 2 times the molar mass because 2 moles of NaCl are reacting. So, for these amounts of materials inthe reaction, a total mass of 100 + 117 = 217 g of reactants produces 106 g of the Na_2CO_3 product. Therefore, the percent atom economy is

$$\text{Percent atom economy} = \frac{\text{Mass of desired product}}{\text{Total mass of reactants}} \times 100 = \frac{106g}{217g} \times 100 = 48.8\% \tag{5.13.8}$$

This is the maximum possible value assuming complete reactions and no losses. If the CaCl2byproduct is considered to be a useful product, the atom economy can be regarded as being higher.

Is the Solvay process green with respect to environmental impact? Again, the answer to this question is mixed. Extraction of the two major raw materials, limestone and NaCl, normally can be accomplished with minimal adverse effects on the environment. Quarrying of limestone in open pits results in dust production and blasting of the rock, which is usually carried out with an explosive mixture of fuel oil mixed with ammonium nitrate, NH_4NO_3, causes some disturbance. Open-pit lime stone quarries can be unsightly, but can also serve as artificial lakes. In some places the underground spaces left from the underground quarrying of limestone have found excellent commercial use as low-cost warehouses that largely provide their own climate control. Truck transport of quarried lime definitely has negative environmental impacts. Extraction of liquid NaCl brine usually has minimal environmental impact. The Solvay process, itself, releases significant quantities of greenhouse gas CO_2 and some gaseous ammonia to the atmosphere. Solvay production of sodium carbonate requires significant amounts of energy.

There are numerous natural deposits of sodium bicarbonate and sodium carbonate. The most common source of these salts is a mineral called **trona**, for which the chemical formula is Na_2CO_3•$NaHCO_3$•$2H_2O$. (This formula shows that a formula unit of trona mineral consists of 1 formula unit of ionic Na_2CO_3, 1 formula unit of ionic $NaHCO_3$ and 2 molecules of H_2O). The development of huge deposits of trona in the state of Wyoming and elsewhere in the world has lowered dependence on the Solvay process for sources of sodium bicarbonate and sodium carbonate and the process is no longer used in the United States.