The design of a chemical process requires a detailed knowledge and understanding of the physical and chemical properties of all the components of the process – reactants, products, solvents, catalysts, co-products and so on. The chemical properties of the substances involved in the reaction will influence the reaction mechanism and hence the equilibrium and kinetic features of the reaction; the physical properties will be particularly important for the separation and purification processes.

In this topic guide, you will look at an industrial process in some detail to see how the properties of the substances involved are used in the design of the process.

On successful completion of this topic you will:
- understand the physico-chemical aspects of an industrial process (LO3).

To achieve a Pass in this unit you need to show that you can:
- explain how energetic, equilibrium and kinetic factors influence the selected industrial process (3.1)
- explain the principles of separation and purification used in the process (3.2)
- explain the impact of the transfer of materials used in the process (3.3).
1 Energetic factors

The need for energy

Energy is required in an industrial process for a variety of reasons:

• heating reactants to a suitable temperature to ensure an economic rate of reaction and/or yield
• to compress gases to create conditions of pressure needed for an economic rate and/or yield
• energy required in purification and separation processes (for example, distillation).

The majority of energy used in industrial processes is supplied in the form of heat from burning fuel, although processes such as electrolysis obviously require large amounts of electrical energy.

Rising fuel costs and greater emphasis on sustainability have led to the introduction of more energy-efficient processes. Much heat energy is also transferred between different parts of the process.

Case study: Contact process

Sulfuric acid is manufactured by a process that uses sulfur, air and water as the raw materials. The process involves three stages:

Stage 1: Burning of sulfur in air to form sulfur dioxide: \( S(l) + O_2(g) \rightarrow SO_2(g) \)

Stage 2: Catalytic oxidation of sulfur dioxide to sulfur trioxide: \( SO_2(g) + O_2(g) \rightarrow SO_3(g) \)
\( \Delta H = -196 \text{ kJ mol}^{-1} \)

Stage 3: Absorption of water by sulfur trioxide to form sulfuric acid.

Equilibrium factors

Many reactions used in industry are reversible, for example, the second stage in the formation of sulfuric acid (see Case study: Contact process). Conditions are chosen to favour the forward reaction as far as possible, by applying Le Chatelier’s principle. Strictly speaking, most reactions in industry will not reach equilibrium as the system is not closed but the broad principles of Le Chatelier’s principle can be used to maximise the percentage conversion of reactants to products.

Le Chatelier’s principle states that ‘when a system at equilibrium is subject to a change, the position of equilibrium will shift in such a way as to oppose the change, as far as possible.’

Temperature

For an exothermic reaction, Le Chatelier predicts that the forward reaction is favoured by a low temperature.

For an endothermic reaction, Le Chatelier predicts that the forward reaction is favoured by a high temperature.

In practice, the actual temperature chosen will be a compromise between the requirement for high yield, and other factors, such as the requirement for a high rate or the need to keep energy costs to a minimum.
Activity
Predict the changes in temperature conditions (if any) which will favour the forward reaction in these processes:

\[ C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g) \quad \Delta H = -87.5 \text{ kJ mol}^{-1} \]
\[ CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \quad \Delta H = +206.1 \text{ kJ mol}^{-1} \]

Case study: Temperature conditions in the sulfur dioxide oxidation

Figure 13.3.1 shows the way in which the percentage conversion of sulfur dioxide to sulfur trioxide is affected by temperature.

- Use Le Chatelier’s principle to explain the pattern shown in this graph.

Pressure

The percentage conversion of reactants to products can be affected by the pressure in the reactor:

- if the reaction results in a reduction in gaseous volume, Le Chatelier’s principle predicts that an increase in pressure will favour the forward reaction
- if the reaction results in an increase in gaseous volume, Le Chatelier’s principle predicts that a decrease in pressure will favour the forward reaction
- changes in pressure will have no effect on the percentage conversion if there is no change in gaseous volume as a result of the reaction.

In practice, the actual pressure chosen will be a compromise between the requirement for high yield and other factors, such as the requirement for a high rate or the need to keep plant or energy costs to a minimum.
Activity
Predict the changes in pressure conditions (if any) which will favour the forward reaction in these processes:
1. \[ \text{C}_2\text{H}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{g}) \]
2. \[ \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}(\text{g}) + 3\text{H}_2(\text{g}) \]
3. \[ \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \]

Case study: Effect of pressure
The oxidation of sulfur dioxide to sulfur trioxide is carried out at atmospheric pressure (or just above) and a temperature of around 650–700K. The use of atmospheric pressure can be explained by considering the factors involved.

Questions:
1. Use Le Chatelier's principle to predict the effect of increasing pressure on the percentage conversion.
2. Discuss the general reasons why high pressure may be undesirable in industrial processes.
3. With reference to the percentage conversion achieved at 1 bar pressure and 650–700K, explain why pressures above 1 bar are not used in this process.

Activity
Find out whether any reversible processes are involved in your chosen reaction. Use Le Chatelier's principle to predict conditions that favour the conversion of reactants to products.

Kinetic factors
The kinetics of a reaction – the rate at which reactants are converted to products – also depend on a variety of conditions:
- the temperature of the reactants: generally rate is increased by high temperature
- the pressure of the gaseous reactants: generally rate is increased by high pressures
- the concentration of any reactant solutions: generally rate is increased by high concentrations
- the presence and efficiency of a catalyst: catalysts may have optimum temperature ranges at which they work most effectively; very high concentrations of reactant solutions or gases may saturate the catalyst surface and so the rate may reach a maximum
- the effective surface area of the catalyst or of any solid reactants.

Catalysts and catalyst choice
Most catalysts used in industry are heterogeneous catalysts in which the catalyst is in a different phase – usually solid – from the reactants and products (which are usually gases, liquids or solutions).

In heterogeneous catalysis, a stream of reactants is passed over a heated solid catalyst. This means that there is no problem with separation of the catalyst from products (and any unreacted reactants). Commonly, a fluidised bed system is used, in which the finely divided catalyst particles are suspended in a fluid (usually a gas) to give them fluid-like properties, as shown in Figure 13.3.2.
The advantage of this design is that the surface area of the catalyst in contact with the reactants is very high and very effective mixing of the catalyst with the reactants is obtained.

In some cases, a soluble catalyst may be immobilised by attaching it to a solid support.

**Figure 13.3.2:** The design of a fluidised bed reactor.

**Take it further**

*The Essential Chemical Industry* (Allan Clements et al., 2010) has an excellent general discussion of the use of catalysts in industrial processes (p11–20) and details of the specific catalysts used in a range of processes.

**The mechanism of heterogeneous catalysis**

The mechanism of heterogeneous catalysis involves the formation of bonds between the reactants and the surface of the catalyst. The strength of the bond formed between catalysts and reactants is critical – if the bond is too strong then the product molecules may not be easily released from the catalyst surface.

Metal oxides, such as aluminium oxide and aluminosilicates, often make good catalysts because the oxygen atoms on the surface are converted into hydroxyl groups, allowing them to bond to H\(^+\) ions that may be involved in the catalytic mechanism.

Transition metal compounds often show catalytic activity due to the ability of the transition metal to exist in a range of stable oxidation states. The mechanism for the process then involves a series of redox reactions.

In order to be effective, catalysts need to have a high surface area. This can be achieved by using the catalyst in a finely powdered form in a fluidised bed (see above) or, in the case of aluminosilicates, using the catalyst in the form of a zeolite (a honeycomb-like structure with a large internal surface area) (see **Figure 13.3.3**).
Case study: Catalyst in the oxidation of sulfur dioxide

The catalyst used in this process is vanadium(V) oxide on a silica support. A small amount of potassium sulfate is also present as a promoter (a substance that increases the activity of a catalyst).

The silica support has a porous structure, and it is thought that at the conditions in the reactor, the vanadium(V) oxide melts and covers the pores of the silica support.

The solid catalyst is divided into cylindrical pellets with a volume of about 0.5 cm³. These pellets are packed into a cylindrical vessel in four separate ‘beds’, as shown in Figure 13.3.4, with a layer of catalyst supported by a perforated plate.

The mechanism for the reaction is based on a redox process involving the vanadium atoms:

Step 1: \( V_2O_5 + SO_2 \rightleftharpoons V_2O_4 + SO_3 \)
Step 2: \( V_2O_4 + \frac{1}{2}O_2 \rightleftharpoons V_2O_5 \)

Questions:
1. Write out an equation to describe the overall effect of the two steps in this process.
2. Describe what happens to the oxidation state of vanadium during the two steps. Suggest why vanadium oxide was chosen as a catalyst in this process rather than, for example, aluminium oxide.
2 Separation and purification

A range of techniques exists for the separation of the product from other components of the reaction mixture, and for the final purification of the product. Among the most common are:

- distillation
- solvent extraction
- crystallisation and evaporation
- chromatography
- filtration
- decanting
- calcination.

Distillation

Distillation is used to separate liquid components of a system with different boiling points.

Simple distillation

In simple distillation, a mixture of the two liquids is boiled and the vapour is then condensed and collected. The process can easily be explained using a boiling point composition diagram, such as that displayed in Figure 13.3.5. These diagrams show the boiling point of mixtures with different compositions, and the composition of the vapour in equilibrium with this liquid. Notice how the composition of the vapour in equilibrium with a boiling liquid is different from that of the liquid. This is the principle upon which the process of distillation relies.

Figure 13.3.5 illustrates how pentane can be distilled from a mixture of pentane and octane (point A on the graph). The vapour that boils off from this mixture is shown by point B on the graph, and has a composition that is much richer in pentane than in the original liquid. When this is condensed, the distillate obtained has this same composition.

Link

Boiling point composition diagrams and their application in distillation were explained in Unit 6, Topic guide 6.2.
Fractional distillation involves repeated cycles of distillation, and is necessary when the boiling points of the two components are closer than the octane and pentane example shown in Figure 13.3.5.

As noted in Topic guide 13.2, some systems form azeotropic mixtures, where the minimum (or maximum) boiling point occurs at a specific composition of the two liquids. This creates particular problems for separating the two components, as discussed in the earlier topic guide.

**Solvent extraction**

Solvent extraction (sometimes called liquid-liquid extraction) uses the idea that a solute in contact with two different solvents will partition between the two.

This idea is often used to extract organic substances from aqueous solutions in the laboratory as the partition coefficient for these substances is very high. The process is carried out in a separating funnel, which allows the two layers to be run off separately.

In some cases, where the partition coefficient between the two solvents is not very great, the process may need to be repeated many times to obtain satisfactory separation.

**Activity**

The partition coefficient for ammonia partitioning between trichloromethane and water is 0.4.

\[
\frac{[\text{NH}_3 \text{ (trichloromethane)}]}{[\text{NH}_3 \text{ (aq)}]} = 0.4
\]

1. Starting with a solution containing 2 moles of ammonia dissolved in 0.25 dm³ of trichloromethane, calculate the number of moles of ammonia extracted into the aqueous layer when this solution is shaken with 0.5 dm³ of water.
   (Hint: represent the number of moles extracted by \(x\); the number of moles remaining in the trichloromethane layer will be \(2 - x\). These numbers and the volumes of the two solvents can then be substituted into the equation for the partition coefficient above, which will enable you to solve for \(x\).)

2. Carry out the same calculation, but this time calculate the total amount of ammonia extracted when the trichloromethane layer is shaken with two separate 0.25 dm³ portions of water.

3. Comment on the difference between the two results — what does that suggest about the most effective way of carrying out solvent extraction?
In industry, a similar procedure can be carried out as a continuous process, often using countercurrent distribution (see Figure 13.3.6).

**Figure 13.3.6:** The principles of countercurrent solvent extraction. The two solvents flow through the vessel in opposite directions and there is transfer of solute from solvent 1 to solvent 2.

### Case study: Processing of naphtha

Naphtha is a fraction of crude oil consisting of molecules with between six and eight carbon atoms. It is the main feedstock used in the production of benzene and other aromatic compounds. The naphtha fraction undergoes a process known as reforming in which straight chain hydrocarbons are converted into a variety of cyclic and aromatic hydrocarbons. The aromatic hydrocarbons can be separated from this mixture using solvent extraction. The solvent used is often sulfolane (b.p. 285 °C), whose structure is shown in Figure 13.3.7.

**Figure 13.3.7:** The structure of sulfolane.

**Questions:**

1. Sulfolane is used to extract the aromatic compounds from a mixture of aliphatic and aromatic hydrocarbons. What does this tell you about the relative solubilities of aromatic and aliphatic hydrocarbons in this solvent?

2. How do you think benzene (and other related aromatic compounds) will be separated from the sulfolane solution?

### Crystallisation and evaporation

Many products of industrial processes are solid and will probably be formed in solution. The solute can be obtained by a process of crystallisation – the slow precipitation of crystals from a solution (or, in some cases, liquid or vapour phases). Crystallisation involves lowering the solubility of the solute by processes such as:

- cooling
- adjusting the pH
- adding ionic salts.

Once the solubility falls below the concentration of the solute, the solution becomes supersaturated. Crystallisation may then occur spontaneously or on the addition of a small number of ‘seed’ crystals.

In addition, the concentration of the solution can be increased by partial evaporation of the solvent.

Crystal size in the precipitated solid is affected by the rate of crystallisation, and so the rate is usually carefully controlled to obtain crystals of the required size. Rapid cooling results in solutions in which there is a big difference between the

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**Key terms**

- **Aromatic:** Hydrocarbon molecules which contain one or more benzene rings.
- **Aliphatic:** Hydrocarbon molecules which do not contain a benzene ring.
- **Supersaturated:** A solution is supersaturated under a given set of conditions if it contains more solute than can usually be dissolved in a certain volume of solvent.
concentration of the supersaturated solution and the solubility of the solute. As a result, crystal formation, once it starts, is rapid and produces small crystals. This rapid crystal formation can also trap soluble impurities within the crystal mass. Conversely, slow cooling produces slower crystal growth and larger crystals.

**Fractional crystallisation**

If several solutes are present in a solution, with differing solubilities, fractional crystallisation can be used to separate them. In this process, solvent is evaporated until the least soluble solute begins to precipitate out. On further evaporation of solute, the next least soluble solute precipitates out and so on. Alternatively, the temperature of the solution is gradually lowered to achieve a similar result.

Fractional crystallisation from melts is also frequently carried out in industry, although obviously this usually occurs at higher temperatures.

This technique has applications in the pharmaceutical industry, where it can be used in a procedure that enables the separation of enantiomers.

**Case study: Separation of enantiomers**

Many biologically active molecules, including most drug molecules, are enantiomeric – that is, they can exist in two non-superimposable mirror image forms, known as enantiomers.

Synthesis of drug molecules often produces a mixture of the two enantiomers, known as a racemic mixture. Properties such as solubility, melting point, etc. are identical in these two molecules, so they can be very difficult to separate.

However, if these enantiomers are chemically combined with another chiral molecule, then the two products are then described as diastereomers (sometimes called diastereoisomers). Although they remain isomers of one another, they are no longer mirror images and have slightly different three-dimensional structures, which means that their properties, such as solubility, will differ from one another.

**Figure 13.3.8** shows how this could be done to separate a racemic mixture containing the two enantiomers of a carboxylic acid.

![Diagram](image)

**Figure 13.3.8:** The formation of diastereomeric (diastereoisomeric) salts from two enantiomers of an organic acid.

The two diastereomers (diastereoisomers) can be separated by repeated fractional crystallisation from solution and then broken down to regenerate the original enantiomers.

**Question:**

Suggest another physical property that will be different for the two diastereomers (diastereoisomers) shown in **Figure 13.3.8**. Could this property be used as the basis of an alternative separation method?
Chromatography

Chromatography is a technique used both for analysis of substances at a laboratory scale and separation of substances on an industrial scale.

In all chromatographic techniques, a mobile phase (such as a solvent) is passed through a stationary phase (such as an absorbent solid). Separation or identification of the components is based on the principle that the different components of a mixture will display different affinities for the mobile and stationary phase.

Analytical techniques include thin layer chromatography (TLC), gas-liquid chromatography (GLC) and high-performance liquid chromatography (HPLC).

Take it further

More details about analytical chromatography can be found in the RSC publication, Modern Chemical Techniques (Ben Faust, 1997), Chapter 5.

Chromatography in industry

In industry, the separation of different components of a mixture is carried out using a column packed with absorbent material along with a liquid solvent, known as the desorbent.

Fixed-bed chromatography

This is the simplest way of carrying out chromatography but it has the disadvantage of being a batch process.

A sample is introduced at one end of the column and desorbent liquid is continuously fed in at the same end. The different components of the mixture will pass through the adsorbent material at different rates, and hence will emerge from the column at different times, enabling them to be collected separately, as shown in Figure 13.3.9.

Figure 13.3.9: The separation of two components in fixed-bed chromatography. The dotted lines show how the concentrations of the two components vary across the column. The separation is sufficiently large to enable them to be collected separately as they emerge from the column.

Moving bed chromatography

In order to make chromatographic separation of two substances into a continuous process, a system could, in theory, be set up in which the bed of adsorbent material is made to move at a speed that is in between the rates at which the two components pass through it. If the mixture is fed in perpendicular to the direction of movement of the bed, then the two components will emerge from the column on different sides, as shown in Figure 13.3.10.
However, the practical problems in creating a moving bed mean that in practice a simulated moving bed system is used. Rather than moving the adsorbent bed, the points at which the components are collected at the bottom of the column move in a way that simulates the movement of the bed itself.

**Take it further**
The website [http://www.organo.co.jp/technology/hisepa/en_hisepa/ chromatography/c2.html](http://www.organo.co.jp/technology/hisepa/en_hisepa/ chromatography/c2.html) has more information about industrial chromatography, including some helpful simulations of the different methods mentioned in this section. This is part of the website of the Organo Corporation, a Japanese company which uses chromatography in the water treatment and purification systems that it manufactures.

**Other separation methods**

**Filtration and decanting**
These are familiar laboratory methods. Filtration is used where solid particles are in suspension in a liquid (or gas). The pores of the filter medium are smaller than these solid particles, which therefore accumulate on the filter. In decanting, a sediment is allowed to settle to the bottom of a vessel, and the liquid above it can be poured off. Centrifugation can be used to increase the rate of sedimentation.

**Calcination**
Calcination is the process of driving off volatile components from solids by heating them to a temperature below their melting point. This is commonly done to decompose simple inorganic compounds, such as metal carbonates, by driving off carbon dioxide, although, strictly, this is a chemical process, not a separation technique. However, it is also used to remove water from hydrated salts, and ammonium ions that may be attached to the surface of substances such as zeolites.

**Take it further**
Further details of a range of industrial separation techniques can be found at [http://www.separationprocesses.com/Mainmenu.htm](http://www.separationprocesses.com/Mainmenu.htm).
Portfolio activity (3.2)

For your chosen process, describe the separation and purification techniques that are used during its operation. In your answer you should:

- identify what substances are being removed in each procedure
- name the type of technique being used
- describe the principles on which this technique is based
- describe the details of the technique as it is used in the process.

Scaling up a process

Most new chemical processes will be discovered during small-scale laboratory research, using familiar laboratory glassware and utilising common separation techniques such as distillation or solvent extraction.

Even at this R&D stage, the process will need to be evaluated, using some of the ideas discussed in Topic guide 13.2, and any problems that may emerge at pilot plant level need to be anticipated. If the process appears to be suitable for further investigation, it will be scaled up to pilot plant level.

Pilot plant

A pilot plant is, essentially, a reduced scale version of the chemical system that could eventually be used in industry. It allows investigation of a product and process on an intermediate scale before large amounts of money are committed to full-scale production:

- the optimum conditions can be investigated
- the product quality can be tested
- the hazards of the process can be evaluated
- data can be obtained to allow costings of the process to be carried out.

Pilot plants typically might use reactors with a volume of 100 dm$^3$; for batch processes they may involve the production of 20–100 kg of products.

Scaling up to plant scale

Although the pilot plant is, essentially, a chemical plant in miniature, scaling this up to plant scale is not simply a matter of multiplying all the dimensions by the appropriate factor. Many key features of the process, such as heat transfer, flow rates and reaction kinetics, do not change in a linear manner as the size of the system increases, and all of these changing factors will, in turn, affect one another. Data from the pilot plant can be used to predict the problems that will be encountered in scale-up.

Professional profile

I work for a process engineering company as a consultant. We work with small chemical producers to design, install and commission new production units. When working with a client I will review the laboratory-scale or pilot-scale process that’s been developed. By applying principles of mass and heat transfer I will be able to calculate the technical specifications of the scaled-up operation, and work with the client throughout the design, installation and eventual operation of the process.

Safety and environmental impact are critical factors to take into account, and I will also be responsible for carrying out risk assessments and hazard studies relating to the operation of the final process. After start-up of the operation, I will also be involved in reviewing the ongoing performance and quality control of the process.
3 Transfer of materials

All industrial chemical processes involve a sequence of steps, called unit operations, and material and energy is transferred from one operation to another, sometimes in a linear fashion and sometimes in recycling loops. A simple flow diagram, such as the one in Figure 13.3.11, shows this.

The following materials and resources may be transferred during the process:

- starting materials, which are fed into the reactor
- solvent, which may be reclaimed and recycled during the separation and purification stage
- catalyst, which, if it is not immobilised, may need to be reclaimed and recycled
- products, which are passed through various stages of separation and purification
- energy, in the form of heat, which is supplied and removed from the various unit operations
- water (and steam), which is used in heat exchangers to enable the transfer of heat between unit operations.

Heat exchangers

Heat exchangers allow heat energy from one unit operation to be removed and transferred to another operation, which requires heat energy. In some cases, any excess heat energy is converted to electricity, which can be sold to the National Grid.

The basic design of a heat exchanger is shown in Figure 13.3.12. Water (or another coolant fluid) circulates through a pipe that is in contact with the hot fluids in a reactor. Various designs exist to ensure that heat is exchanged most effectively, but the key principles are to ensure that the surface area in contact with the two fluids is maximised.
Flow diagrams

The flow of materials in a chemical process is often represented by flow diagrams. These can be simple block flow diagrams (see Figure 13.3.11), which usually only show the general principles of material flow between the unit operations, or process flow diagrams, which provide detailed information including direction of flow and presence of equipment, such as heat exchangers, pumps and valves.

Take it further

More information about process flow diagrams can be found at http://www.rff.com/process-flow-diagrams.htm, which also includes downloadable software enabling you to construct simple process flow diagrams.

Activity

Find a flow diagram of your chosen process. Use it to describe some of the transfers of materials or energy that occur during the process.

Portfolio activity (3.3)

For your chosen process, describe the importance of transfer of materials (and energy). In your answer you should explain the following:

• what materials need to be transferred between unit operations
• how these materials are transferred between the unit operations
• unit operations which may produce or require energy
• how energy is transferred between these unit operations.

Further reading

An understanding of how kinetic and equilibrium factors are used to select appropriate reaction conditions is a component of many level 3 courses in chemistry, and textbooks such as Chemistry in Context (Hill and Holman, 2000, Nelson Thornes) have chapters devoted to this (Chapter 21, pages 305–320).

The Essential Chemical Industry (Allan Clements et al., 2010) has an excellent general discussion of the use of catalysts in industrial processes (pages 11–20) and details of the specific catalysts used in a range of processes.

More details about analytical chromatography can be found in the RSC publication, Modern Chemical Techniques (Ben Faust, 1997), Chapter 5.

The principles of phase equilibria and how they apply to separation techniques are covered at an introductory level on The Chemguide website (www.chemguide.co.uk). From the homepage, select the ‘Physical Chemistry’ section and then use the ‘Phase Equilibria’ menu to select the relevant pages for this topic guide. The sections on ‘General principles of equilibria’ are also helpful.

Acknowledgements

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