

*CHEN20012 Fun Chem Eng*

# ***CHEN20012: FUNDAMENTALS OF CHEMICAL ENGINEERING***

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## Outline

Fundamentals of Chemical Engineering (or Fun Chem Eng as we like to call it) is an introductory subject to Chemical Engineering. It introduces a lot of basic theory and tools for chemical engineering, as well as helping to set the context for the industry (where you might work and what you might do).

These notes approximate the course content but will not follow lectures verbatim. So, they are meant as a useful companion to the lectures (another perspective to explain the same ideas).

## Pedagogical Underpinnings

*This chapter isn't examinable, so you can skip reading it if you want. This section outlines 'what's under the hood' or the teaching philosophy underpinning the design of the course. So, it might be of interest to know the strategies we're trying to employ to help your learning.*

### Context of subject

The *Fundamentals of Chemical Engineering* will primarily be taken in 2<sup>nd</sup> year of the Chemical Engineering Systems major in the Bachelor of Science. With the subject *Material and Energy Balances* it will form the first contact point with a chemical engineering subject for undergraduate pathway students. Prior to this, students will have only completed generalist maths and chemistry core subjects.

### Implicit broader goals of the subject

Outside of the specific subject curriculum, what broad values/paradigms/motives would we ideally instil in students taking the subject?

These aren't specific topics covered in a module or lecture but are general themes that influence the subject's content as continual touchstones. Ideally, these form a continuous background tone that is 'baked into' the subject.

- Establishing student's identity as chemical/biochemical engineers: Having completed the subject, do students think of themselves as 'chemical engineering students' rather than just as generalist 'students'? Do students feel excited to tell their friends what they're studying in chemical engineering?
- Setting motivations for studying chemical engineering: Do students leave the subject with a clearer idea of why they want to study chemical engineering? Can students articulate a general destination they might like to achieve after completing the degree (even if these change over time, for example as general concepts like mining, water, sustainability, food, renewables)?
- Understanding of the field of possibilities for chemical engineering: Having completed the subject, do students have a clearer understanding of the types of problems chemical engineers work on currently, where the field is going and how they fit into that field?
- Sustainable development: Developing an appreciation of the UN Sustainable Development Goals and the importance of chemical engineers in achieving this. This does not mean memorizing the specific goals but developing an implicit paradigm for operating sustainably.
- Fun: Perhaps the subject has less focus on technical content (compared to later core subjects) and more focus on inspiration: the subject design itself has a focus on being enjoyable, social and engaging and helps set the motivations and destination for later more technically-heavy subjects.

### Threshold Concepts

A *threshold concept* (Meyer, Land et al. 2010, Baillie, Bowden et al. 2013) has a transformative character on students' thinking: it is a key principle that once understood changes that students' perspective and the concept cannot be "unlearned" over time. It is often initially difficult or counter-intuitive, but once understood it creates an epistemic shift; it opens previously inaccessible ways of thinking. Threshold concepts are often associated with discipline specific knowledge, for example "thinking like an engineer" and accumulating threshold concepts is often part of a 'rite of passage' in an area of study. For example, in *CHEN20010 Mass and Energy Balances*, a key threshold concept could be mass balances; the specific set up may change, but the concept of balancing mass and the mathematical tools invoked become permanently internalized. The concept can be applied to supply chain management, so exists beyond chemical

engineering alone. In *CHEN30016 Momentum, Mass and Heat Transport*, a key threshold concept might be the application of vector calculus to 3 seemingly disparate and unrelated physical phenomena, to unite them conceptually (momentum transfer, heat transfer and mass transfer).

As threshold concepts are so fundamental and transformative, they are often assessed in multiple forms: it's important that competency is deliberately developed in assessment, so students can form and then demonstrate understanding, rather than mimicking comprehension (for example, through rote learning or memorizing solution templates without deeper understanding).

Not all subjects will contain threshold concepts (many subjects focus on specific technical competencies). A typical subject might have 0-3 threshold concepts. The key threshold concepts in Fun CE might be:

- Graphical lexicon: Using established schematic methods (BFDs, PFDs and P&IDs) to graphically visualize sequencing of units. Engineering and science can be described in spoken languages (e.g., English) in mathematics, but in this subject, we seek to offer a new graphical language to communicate specialized knowledge. Language can also shape the way we conceive of the problem and identify solution, so the visual representation also helps develop systems thinking.
- Applying mathematical tools. Use of previously abstracted mathematical tools (e.g., calculus) to real-world problems. In Fun CE, these tools are not learned in isolation, so students can begin to appreciate when and how to apply them in real-life, as a descriptor or a real system.

### Capability Theory

*Capability theory* (Bowden and Marton 2003, Baillie, Bowden et al. 2013) centres on the idea that the specific knowledge required by a profession changes over time, so the pedagogical focus is on developing students' capabilities; fostering problem-solving that can be applied to currently unknown situations. In essence, students are trained to act independently, be self-motivated, cope with flexibility and new situations (rather than focusing on specific technical knowledge). They learn to apply taught concepts to new applications. They're then measured against the capabilities they acquire (rather than specific knowledge they might rote learn).

The key capability we would like to build in Fun CE undergraduate students is the confidence and independence to want to try to build a solution and then resilience to persevere to completion (so not become frustrated and give up if it doesn't immediately work).

Some key capabilities in this area would be:

- Spatial reasoning: Developing students' practical skills to build equipment (e.g., through use of hand tools or 3D printers or CAD software) to develop an understanding of what can and cannot be built. Developing students' confidence to try to build things themselves: the use of hand-tools isn't a key capability in itself (we're not training students to be metal workers) but the connection between theory and application, and spatial awareness of how to build equipment, is a capability we could develop.
- Applying mathematics: Recognizing when mathematical tools can be applied to new contexts (particularly to problems students may not have seen before). Developing a willingness to try to apply mathematical models to solve a problem. For example, recognizing that the calculus or a linear fit regression that has been learnt previously, can be applied to provide insight on a new problem (where the new problem might be phenomenologically different to previously taught examples)

### Problem-based learning

In *problem-based learning* (PBL) a scenario or case-study is used as a trigger to drive learning objectives (Perrenet, Bouhuys et al. 2000, Wood 2003). Students' learning would be more self-directed than in a traditional lecture-based courses, before they return to a group context to refine learning (Masek and Yamin 2012). So PBL is not about problem-solving per se, but about using appropriate problems to stimulate curiosity in developing deeper understanding and knowledge about the problem. PBL also tends to develop social skills, such as cooperative work, independent responsibility for learning, communication skills and respect for others.

Rather than teaching a series of discrete theoretical tools, PBL places the challenge at the centre that then prompts the desire to develop these theoretical tools to solve the over-arching problem.

Fun CE sits halfway between the two: We have a strong desire to move away from traditional 'chalk and talk' subject design and place more emphasis on PBL teaching structures. For example, the subject uses an open-ended lab design (building a heat exchanger and developing a testing methodology) to stimulate interest about specific topics. The need to meet pre-requisite knowledge and accreditation requirements and the difficulty of creating a PBL task that aligns to all those requirements, makes it difficult to fully abandon a traditional modular teaching structure.

### Gamified Learning

University teaching is often expositional: lectures are designed to instruct, and students receive information passively. An alternative pedagogical model is *kinaesthetic learning* where students learn through play.

The closure of University campuses in 2020 due to COVID meant learning was migrated to online platforms (e.g., Zoom or Canvas). But another platform for online learning and student socializing are video games. Games designed specifically for learning are sometimes called *serious games*, to distinguish them from games designed primarily for entertainment, but there is no reason that serious games can't also be highly entertaining and engaging.

The subject tries to use gamified learning tools (for example in a TSC Simulation Software of a real 3-Phase separator and in a mod to Factorio currently being developed). Learning can come both from explicit learning activities (the goal you must complete, valve you must turn, the P&ID you must read) and implicit learning immersion (the staging of the world, the details built into the passive architecture of the game such as what real tanks or valves look like). The ultimate goal for the teacher is a learning experience that is so engaging and so much fun that people simply want to play it and learn, without the need for an assessment requirement at the end to motivate students.

### Sustainable Development Goals

As discussed above, understanding and appreciation of sustainable development is one of the broad goals of Fundamentals of Chemical Engineering. Sustainable development is part of modern chemical engineering, and chemical engineers are crucial to sustainable development. This subject will introduce you to the basic concepts and definitions of sustainable development, including the United Nations Sustainable Development Goals (SDGs). The SDGs are a common language used by nations, industries and institutes worldwide working towards global development.

We will not be discussing the SDGs in significant detail: that is outside the scope of FCE. Rather, the SDGs provide context for the principles and concepts that form the foundation for your chemical engineering education.

While the information provided about sustainable development and the SDGs in this course is general, there is a wealth of information available online if you wish to research them further. A great place to start is the [UN's page](#) on the goals.

## Content Outline

(This is still subject to change)

MODULE 1: Introduction to chemical engineering. Big problems facing the world and why we need chemical engineers to solve them. We may tailor this section to the interests of students within the class, but may include discussion of: vaccine production, water, food production (examples like chocolate/milk/wine/cheese), soil remediation, waste to energy, minerals & materials (examples like uranium/iron ore/green steel), plastics for sustainability (bioplastics)/black carbon, sustainable production and environmental remediation.

- The module introduced chemical engineering design concepts and principles, as well as basic sustainable development concepts.
- We will continue to use these principles throughout the course to discuss chemical engineering processes, and these concepts will be built on throughout your chemical engineering education

Complimentary Learning Activities

- In-class activities to discuss these concepts

MODULE 2: Graphical process diagrams. This module introduces visual representation of process sequencing. It is meant to flow on from the discussion in Module 1 as we now develop graphical representations of the case studies discussed in the first module.

- The module introduces Block Flow Diagrams (BFDs), Process Flow Diagrams (PFDs) and Piping and Instrumentation Diagrams (P&IDs)
- We will continue to use these schematics through the rest of the course, to communicate and discuss specific equipment and processes (this module is not self-contained or separate from the course). The schematics represent a new kind of 'visual language' that we will use throughout the course (in the same way that we use English and mathematics to describe processes).

Complimentary Learning Activities:

- The software packages Visio and AutoCAD as tools for drawing schematics.
- The software HYSYS will first be introduced in this module (the 'simulation environment' in HYSYS is a PFD)

MODULE 3: Small kit. Piping and Instrumentation diagrams naturally leads to a conversation about how piping and instrumentation work in a real plant, and how they can be automated (or how the process is controlled). How do different types of valves and instruments actually work? How can we scale up production through large scale automation?

- This module will give a brief overview of different types of sensors (for measuring temperature, level, flowrate etc)
- The module will outline different types of valves (gate valve, ball valve, butterfly valve).

Complimentary Learning Activities:

- We will use the Telstra Creator Space on campus and students have the option to build a valve, a thermocouple and 3D print a fitting for a heat exchanger.

MODULE 4: Medium kit. From small-scale equipment (valves, pressure sensors, thermocouples in Module 3) the course advances to a few examples of larger ancillary equipment and unit operations (mid-scale equipment items, meaning both in terms of physical size and conceptual difficulty to understand). This topic discusses the physics involved in the equipment items and how they work as well as their industry-specific context, as well as how the unit might be controlled (building on Module 2 and Module 3). Specific topics covered will include:

- Tanks and filling/emptying (calculating static head and suction within the tank).
- 3-Phase separator
- Heat exchanger and basic heat transfer theory
- Boilers

Complimentary learning activities:

- The heat exchanger practical will directly pair with this module (the design, build and testing of a heat exchanger).
- Operator Training Software (controlling a 3-phase separator) will directly pair into this module for a gamified learning activity that is (hopefully) a lot of fun.

MODULE 5: Large kit: Reactors. This module will introduce simple reaction kinetics and the design of reactors. Specific topics will include:

- Solving the rate equation for zero, first and second order equations
- Establishing how we could solve other orders or more complicated reaction kinetics
- Basic design of plug flow reactors, batch reactors and continuous stirred tank reactors

Complimentary learning activities:

- HYSYS assignment (all the reaction kinetics we solve by hand can also be solved in software packages, as well as the kinetics that are too complicated to solve by hand)

MODULE 6: Large kit: Basic thermodynamic cycles. This module provides an outline of heat engines and heat pumps as well has how to solve basic thermodynamic cycles.

- The basics definition of heat engines/pumps and how to define cycle efficiency
- Processes: Isochoric, Isothermal, Isobaric, Adiabatic
- Carnot cycle
- Defining work from a variety of other cycles (as examples)

Complimentary learning activities:

- As this is the last module in the course, it can't really be assessed in assignments, so is instead assessed in the exam, with the content from all previous modules.

Software competencies from subject:

1. HYSYS
2. AutoCAD or Visio
3. Excel

## Module 1: An introduction to Chemical Engineering

*This module introduces you to key chemical engineering concepts that will form the foundation for your chemical engineering education over the next several years. Learning these concepts, and how they relate to each other and chemical engineering in general will help you understand the field more fully and deeply.*

*Module 1 introduces different types of design seen in chemical engineering, key chemical engineering principles, and how chemical engineering relates to other fields. The module also introduces sustainable development and its relationship to chemical engineering.*

### Outline

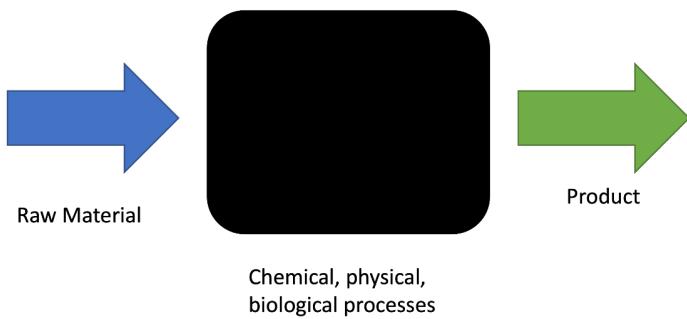
Primary learning outcomes for the module:

1. Develop an understanding of the different types of chemical engineering design and chemical engineering principles
2. Develop an understanding of sustainable development and how it relates to chemical engineering
3. Analyse real-world chemical engineering processes and identify types of design and chemical engineering principles
4. Analyse real-world sustainable development issues and identify how chemical engineering can contribute to solving them

### 1.1 Introduction to Chemical Engineering

#### 1.1.1 What is chemical engineering?

At its core, chemical engineering is about taking a raw material, transforming it through chemical, physical, and biological processes, and producing a product.



This basic chemical engineering recipe can take many forms; it includes a wide range of raw materials, lots of different processes (with new ones being invented all the time) and many different products, including waste streams. It can get complex quickly, with lots of moving parts. But we'll break all these parts down and look at them individually over the course of this module.

Here are some examples of chemical engineering in action:

- Vaccine and pharmaceutical production
- Bioplastics in packaging

- Natural gas in your stove
- Biolipids produced by algae
- Water and wastewater treatment
- Mining and processing the metals in your smartphone
- Producing solar panels
- Remediating soil on a construction site
- Food production (from chocolate to meat-alternative burgers)

Chemical engineering is sort of like a “jack of all trades”; we use chemistry, physics, biology, mathematics, technology, and design to track and transform material and energy through complex systems with lots of moving parts.

There are also several sub-disciplines of chemical engineering. Process engineering is the application of chemical engineering principles on an industrial scale, and many chemical engineers become process engineers. Biochemical engineering is an emerging sub-discipline, focusing on the biological side of chemical engineering and is common in industries such as pharmaceuticals and food processing. Chemical engineers can move into other sub-disciplines, depending on their area of specialisation.

### 1.1.2 What does a chemical engineer do?

There are lots of different ways to be a chemical engineer, and not all people with a chemical engineering degree become chemical engineers (or chemical engineering lecturers). Because of the different skills picked up in chemical engineering degrees, they can do well in lots of different types of roles. In fact, CEOs of several big companies such as 3M, General Electric, and Dow Chemical are chemical engineers.

But here in this module, we'll focus specifically on chemical engineers.

Chemical engineering work generally falls into two camps: working with new technology and working with existing technology. Engineers working with new technology can be designing a new process, creating a new product, processing a new raw material, processing a new kind of waste/ finding a use for a product previously considered “waste”. Engineers working with existing technology often focus on optimising existing process, products etc. based on new knowledge, new technology, or new regulations.

One of the big jobs of chemical engineers (and all engineers, to a degree) is design, and there are several “flavours” of design found in chemical engineering: process design, mechanical design, and control design.

- **Process design:** designing physical and chemical processes to turn raw material into products.
  - Based on chemical engineering concepts and principles (discussed below)
  - Includes factors such as calculating/ selecting the correct size, conditions (temperature, pressure, flow rate etc.) solvents, conversion etc.
- **Control design:** designing how chemical and physical processes will run efficiently and safely.
  - Based on process design.
  - Considers changes over time and plant operation.
  - Generally based on maintaining operating conditions for safe and efficient production.

- **Mechanical design:** designing physical unit operation/ piece of equipment that will perform chemical/ physical process.
  - Based on process design.
  - Considers material science and basic mechanical engineering principles.
  - Includes design factors such as equipment dimensions (height, length, width, diameter), any inlet and outlet pipes (including instrumentations requirements), and required safety features (wall thickness for pressure rating, pressure relief valves etc.)

#### Worked Example 1.1 Chemical Engineering Design

Ethanol is an important feedstock chemical in many industries, from fuel production (e.g., E-10 petrol) to medicine (e.g., sanitizing work surfaces). One example everyday example of ethanol is hand sanitizer: ethanol at 65% or above will disrupt cell membranes and denature proteins of bacteria and viruses (although not all micro-organisms).

Ethanol can be produced from several sources but is mostly produced by yeast via fermentation. The yeast can only produce ethanol to approximately 12% (above this concentration, it acts as a toxin and harms/kills the yeasts). Because of this, the ethanol needs to be purified before it can be used in hand sanitiser: we need to separate the ethanol from the water in the solution in a process called "distillation". (Distillation is a very important unit operation in chemical engineering, and you will learn more about it in later subjects).

Distillation is based on volatility (how much the component wants to turn into a vapour) of the different components (ethanol and water) at different temperatures. Ethanol is more volatile than water, so it will turn into a vapour at a lower temperature. A distillation tower is built, then heated and pressurised to a certain temperature and pressure that allows the ethanol to boil off (turn into a vapour and exit the tower at the top) but keeps the water liquid (so it runs down to the bottom of the tower). (The real process is much more complicated, but this is a simplified version for the worked example).

Based on the above information, briefly describe the process design, control design, and mechanical design decisions made to distil an ethanol-water mixture into ethanol that can be used in hand sanitiser.

Process Design:

Control Design:

Mechanical Design:

Engineering as a field cannot function with teamwork. Chemical engineers work with each other to design a whole process, from material to product. They also work with other engineering disciplines as chemical engineers cannot know everything. Chemical engineers bring their knowledge to the table and work with other specialists' knowledge to come up with the best solution to that particular problem. Chemical engineers will also work with lots of other people like managers, executives, scientists, regulators, operators, consumers and almost every kind of stakeholder imaginable. While some chemical engineers may work alone much of the time, no job in chemical engineering takes place in a vacuum (although maybe in a vacuum pump...), they are always working with other people.

Some chemical engineers will be inside all day working on simulations and excel spreadsheets. Some will be in a lab creating and playing with new technologies. Some will be out on site/ on a plant seeing how big pieces of technology operate. Some will be doing a combination of all sorts of jobs.

There are lots of different ways of working in chemical engineering and using your chemical engineering knowledge: there is no "one perfect way" to be a chemical engineer.

#### **1.1.3 What principles and concepts does chemical engineering use?**

We use a wide variety of principles and concepts in chemical engineering, because we work in many different industries and across many different scientific disciplines. We won't discuss these in much detail, but we will discuss how they relate to chemical engineering problems.

**Material and Energy Balances:** one of the key parts of chemical engineering. Chemical engineers track material and energy, and how they transform, through complex systems. Material and energy cannot be created or destroyed, so we account for everything that comes into and out of our systems. It's like complex accounting, but things can explode if we count wrong, so it's a bit more exciting than normal accounting.

- You'll learn this in Material and Energy Balances and will use it throughout your chemical engineering education.

**Systems Thinking:** all engineers use system thinking, but it is especially important in chemical engineering. Chemical engineers think in terms of whole systems and how they operate, not only focusing on specific parts of a system.

- You'll learn this throughout your chemical engineering education.

**Unit Operations:** all systems are made up of individual pieces, and chemical engineering processes are made up of unit operations.

- You'll learn basic unit operations in Fundamentals of Chemical Engineering and Material and Energy Balances, and learn more advanced unit operations as you move through the degree.

**Thermodynamics:** the study of energy use and transformation, thermodynamics looks at how we can harness and manipulate energy

- You'll learn basic thermodynamics in Module 4 and more advanced thermodynamics in Chemical Engineering Thermodynamics.

Reaction Kinetics: this puts the “chemical” in “chemical engineering”. Reaction kinetics looks at controlling chemical reactions to efficiently produce the products we need.

- You’ll learn basic reaction kinetics in Module 5, and advanced reaction kinetics in Reactors and Catalysis and Chemical Engineering Thermodynamics.

Transport Phenomena: the control momentum, heat, and mass as they move through a piece of equipment and through a system.

- You’ll learn about heat transport in Module 4 and learn more advanced content on transport phenomena in Momentum, Mass, and Heat Transfer, and Thermal and Separation Design.

Separation Processes: chemical engineers never deal with pure substances – everything is a mixture. These mixtures need to be separated so raw materials, products, and other streams contain the right components.

- You’ll learn separation processes throughout your chemical engineering education.

Fluid Mechanics: chemical engineers work with water, air, and many other kinds of fluids. Understanding how fluids behave allows engineers to control them and their processes effectively and safely.

- You’ll learn about fluid mechanics in Fluid Mechanics, Momentum, Mass and Heat Transfer and Thermal and Separation Design.

Safety: chemical engineers need to make sure all our processes operate safely, protecting people and the environment

- You’ll learn about safety throughout your chemical engineering education

Control: chemical engineers need to control processes to make sure they’re safe, efficient, and producing the required products.

- You’ll learn the basic of control in Module 3 and advance this knowledge throughout your chemical engineering education.

Worked Example 1.2

Let's look at a simplified version of a real chemical engineering situation in the pharmaceutical industry. Some pharmacological compounds are built through organic chemistry, and some needed to be extracted from natural sources, often plants. A common example of this is extracting opiate compounds from poppies. In this (simplified) example, chemical engineers take the raw material of poppies, crush them, add a solvent, and heat the solution. The solvent and heat dissolve the opiate compounds in the poppies, and a few other unwanted compounds. The fluid, made up of solvent and dissolved compounds, is sent to a crystalliser. The fluid is then cooled to a specific temperature, which lets the opiate compounds crystallise out of solution while the unwanted compounds and solvent remain in the liquid phase. The crystals (solids) are sent to further refining. The solvent with unwanted compounds and the exhausted poppies are sent to waste treatment. These processes take place at ambient temperature and pressure (no significant increases or decreases compared to 25°C and 101 kPa) and only physical transformation (phase change) occurs.

From this example, identify and explain the chemical engineering principles used. From this list, identify the decisions made in the process design, control design, and mechanical design stages.

Principles:

Process Design:

Control Design:

Mechanical Design:

#### 1.1.4 How is chemical engineering different from chemistry and other engineering disciplines?

There is a lot of crossover between chemical engineering and chemistry as well as chemical engineering and other engineering disciplines. This doesn't mean that chemical engineering isn't unique; instead, it means that chemical engineers can talk to and understand other kinds of science and engineering specialists.

Chemists generally look at chemistry on a small scale. For example, a chemist might work out how to extract a pharmaceutical from a plant source like poppies. But a chemical engineer looks at how to get that pharmaceutical from poppies on a large scale, including factors like product purity, waste processing, energy efficiency etc., much more than the chemical steps from the plant chemical to the extracted chemical.

Chemical engineers think in a similar way to many other engineers, but we see everything through a chemical engineering lens. For example: water. Chemical engineers see water as a solvent, solution, mixture, and a fluid with physical and chemical properties. Civil engineers see water as a fluid to be controlled over large distances. A similar analogy can be applied to mechanical design for mechanical engineers, model development to software engineers, and material properties to material engineers.

This means that chemical engineers can understand what happens in lots of engineering contexts, and can even translate between scientific and engineering disciplines, which is pretty powerful!

#### 1.1.5 Why is chemical engineering important?

Society doesn't run without engineers, and that includes chemical engineers. The roles that chemical engineering fills can be split into three broad categories: past, present, and future.

Previous generations of chemical engineers have left a legacy: unfortunately, it is a legacy to fix. It is the current and future generation of chemical engineers' responsibility to deal with pollution in various environments and the effects of this pollution (e.g., climate change, habitat degradation)

Our present-day society needs goods and services that engineering, specifically chemical engineering, provides such as clean water, food, energy, Doritos, fancy face washes, vaccines etc.

Chemical engineers are contributing to and will continue to contribute to the future as well: designing new technologies, solving new problems we haven't seen yet, working with digital technology, creating a more equitable world and more.

The list of chemical engineering contributions to the world, and thus the reasons why chemical engineering is important, is wide reaching and ever-growing.

And we need chemical engineers now, in Australia, more than ever. There is a significant engineering shortage in Australia: many of the country's engineers are imported. This shortage has been increased by international border closures as well. Graduate employment for chemical engineers remains high. Studying chemical engineering will set you up well for your future and the world's future.

## 1.2 Sustainable Development

We know that there are a lot of problems in the world at the moment, on a global and local scale. This section will look at how chemical engineering can contribute to solving these problems.

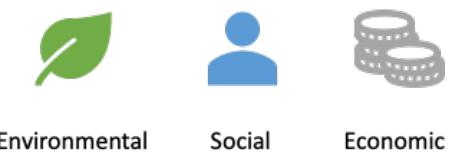
We'll look at one such problem in detail as a case study on chemical engineering and sustainable development: pollution.

The first step of this case study is acknowledging that pollution is a complicated topic that affects billions of people around the world. There is no one perfect solution to this problem. But instead of feeling disheartened by this, we can choose to look at pollution through the lens of sustainable development and come up with a plan to contribute to fixing it. Chemical engineering cannot solve this problem on its own, but that's okay. Sustainable development is about working together and contributing to a solution with other parties.

#### 1.2.1 What is Sustainable Development?

Sustainable Development (SD) can be defined in several ways. One of the most common definitions is "development that meets the needs of the current generation without compromising the ability of future generations to meet their own needs". This definition entered Western discussion in the late 1980s (but has been around for much longer than that in many societies around the world).

We can also look at the different dimensions, or pillars, of SD: environmental, economic, and social. (There are other pillars that get used, but we will focus on these three). Let's look at our case study of pollution through the lenses of the different pillars.



- **Environmental:** different types of pollutants impact different natural habitats such as acid rain in the atmosphere (and land/ water when it rains), hydrocarbons in soil and groundwater, textile pollution in freshwater, and sewage pollution in fresh water and the ocean. These pollutants often impact animal and plant life in the area as well, stressing and damaging the ecosystem.
- **Economic:** depending on regulation, it is often cheaper to dump pollutants than treating them to a safe standard. This gives pollution an economic advantage compared to waste treatment. However, valuable chemicals are wasted if process streams are left un-treated: those valuable chemicals cannot be recovered if there is no waste treatment. The true economic cost of pollution, such as the loss of productive soil and impact on healthcare costs, are often omitted from cost estimate and thus do not show the true economic impact of not treating pollution.
- **Social:** pollution can lead to a range of poorer outcomes for the impacted community. Minority populations are more likely to be impacted due to existing economic and social factors. Pollution often leads to worse health outcomes for those living in the area (e.g., respiratory conditions from particulate pollution), including both acute and chronic conditions. This often reduces educational and economic opportunities for the community, further lowering quality of life.

All three pillars are important: there's no one dominant pillar. Their importance can shift depending on the situation and context, but they are always linked together.

### 1.2.2 Sustainability vs. Sustainable Development

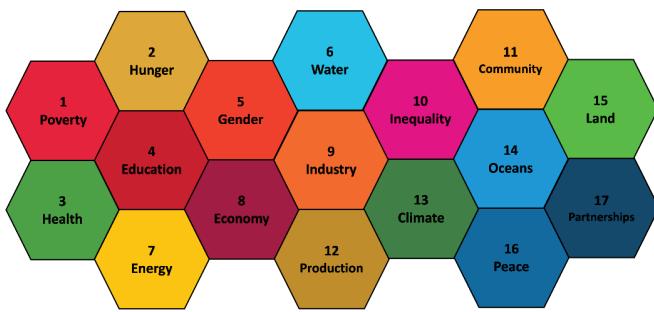
Even if you haven't heard about sustainable development before now, you've very likely heard the term "sustainability", but what's the difference between the two? Is there a difference?

Well, it depends on the definition that people are using. Some people use the two terms interchangeably, but they're not the same thing. A definition I like is that sustainable development is the road towards sustainability: sustainable development is a tool and sustainability is the end goal.

Many people also use sustainability only when referring to the environment i.e., environmental sustainability. But the other pillars are important as well, so using "sustainable development" clarifies that we are referring to all the pillars.

### 1.2.3 Sustainable Development Goals

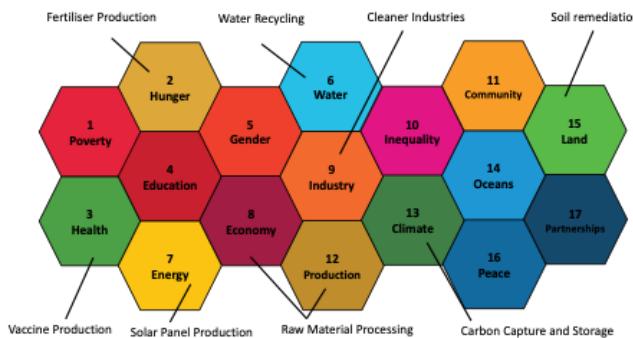
The United Nations developed the Sustainable Development Goals (SDGs) in 2015: a set of 17 goals to guide global development to 2030. They replaced the Millennium Development Goals produced in 2000. The SDGs are not a complete set of goals but represent a compromise on the important issues to all the signatory countries. The SDGs are a useful tool when considering the impacts of different projects and different actions. The topics of the 17 goals can be seen in the diagram below and lay across all 3 pillars.



It's important to keep in mind while we're learning all this that sustainable development is more than the sum of its parts. Sustainable Development is a holistic paradigm, looking at transforming the world as a whole, not focusing on discrete areas.

### 1.2.4 How can chemical engineering contribute to sustainable development?

There are lots of different ways chemical engineering can contribute to sustainable development. If we look at the SDGs, for example, we can see that chemical engineering can easily contribute to a number of the goals. The diagram below shows some examples, such as soil remediation helping Goal 15 (Life on Land) and fertiliser production helping Goal 2 (End World Hunger).



But we can look at these issue more deeply through our pollution case study. How can chemical engineering contribute to solving pollution?

There are many different sources of pollution, and we'll need a different strategy for each source. We'll begin with sulfur from natural gas causing acid rain:

To look at this issue systematically (using our “systems thinking” principle), we can look at removing the source of pollution, changing how the waste/ pollution is processed, how to mitigate the existing effects of the pollution.

- Removing the source: using renewable energy such as solar, wind, hydro instead of natural gas (coal and other fossil fuels often also have sulfur in them when extracted from the ground) would mean sulfur wouldn't need to be removed.
- Changing how the waste is processed: Separate out the sulfur from the natural gas and treat it so it doesn't escape into the atmosphere (in this example, it would likely be a “wet scrubber” which basically dissolves the sulfur in water droplets in a shower, so only air escapes).
- Mitigating the effects: produce acid-resistant coatings for exposed infrastructure, remediating the soil to balance the pH

**Worked Example 1.3**

Explain how chemical engineering can contribute to solving the issue of textile processing wastes in local water sources, including removing the source of pollution, changing how the waste is processed, and mitigating the effects. Textile waste is a mixture of dyes, fasteners and a range of other chemicals, often with pH values far away from neutral (either acid or basic). These mixtures can also have high salt and particulate loads, and may also contain heavy metals.

- Removing the source:
- Removing the source:
- Changing how the waste is processed:
- Mitigating the effects:
- Mitigating the effects:
- Mitigating the effects:

There are many other ways to solve this problem, but we are looking specifically at what chemical engineering can do.

## Module 1 Summary

### Key Points:

- What chemical engineering is
- What chemical engineers do
- Chemical engineering principles and concepts
- Difference between chemical engineering, chemistry, and other engineering disciplines
- Why chemical engineering is important
- What is sustainable development
- How chemical engineering contributes to sustainable development

### Key Skills:

- Identifying chemical engineering principles and concepts
- Identifying process, control, and mechanical design decisions
- Identifying how chemical engineering contributes to sustainable development

## Module 2 – Schematics

This module introduces you to a new ‘graphical language’, which you can use to describe very complicated processes. You will learn to read the schematics and be introduced to computer-aided design (Visio, HYSYS) as tools to help draw schematics.

The module introduces 3 basic types of schematic representations for a chemical plant: the block flow diagram (BFD) and Process Flow Diagram (PFD) and Piping and Instrumentation Diagram (P&ID). The P&ID can be used to show how a plant is controlled, and so we will discuss this, then we will then apply your new symbolic lexicon to understand specific case studies in later modules.

### Outline

Primary learning outcomes for the module:

1. Develop an understanding of the 3 types of chemical engineering diagrams: Block Flow Diagrams (BFDs), Process Flow Diagrams (PFDs) and Piping and Instrumentation Diagrams (P&IDs)
2. Develop an understanding of control logic including: control loop variables, direct and indirect control, cascade control, and equipment control schemes (for flow, level, temperature, and pressure).
3. Design, analyse and describe control logic based on Piping and Instrumentation Diagrams

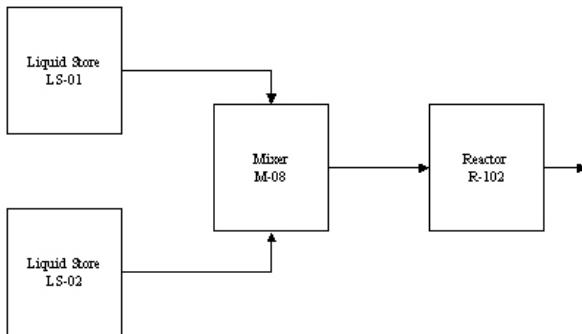
### 2.1 Diagrams Overview

#### 2.1.1 Block Flow Diagram

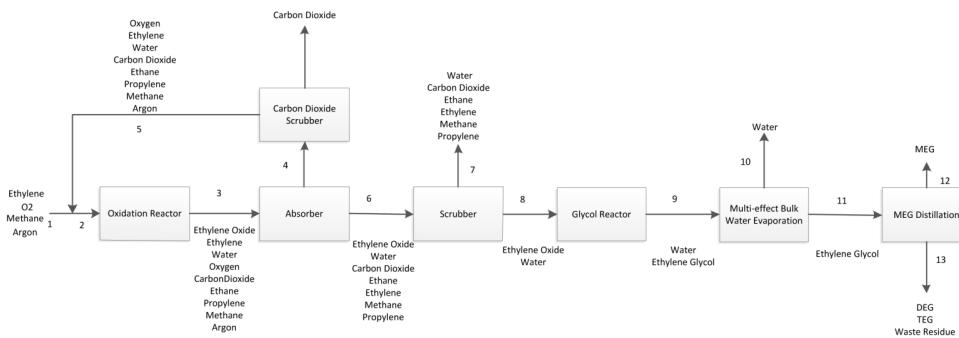
The Block Flow Diagram (BFD) is the simplest schematic, and it would usually be associated with the earliest stages in a design process, such as the feasibility study stage. It shows major processing steps as square blocks, and it is what you draw in M&EB to help visualize a mass and energy balance. So, it would include reactors, separators, treatment but not individual pumps.

Block flow diagrams conventionally depict:

- Only show major equipment items (mixers, separators, reactors, heat exchangers)
- Shows as blocks (not symbols)
- Can group many units together
- Flow direction shown by arrows
- All straight lines (horizontal and vertical)
- Flow from left to right (where possible)



Below is shown a BFD for a mono-ethylene glycol synthesis process.

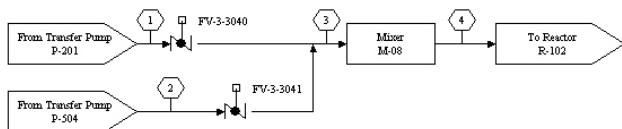


### 2.1.2 Process Flow Diagram

The Process Flow Diagram (PFD) is a diagram of the relationship between major equipment items and system components (but not more minor components like pipe schedule, control valves, measurement devices etc.). It is what you draw when you do a layout in HYSYS and it would usually be associated with the second major step in a design process, which is the Process Development Report (PDR).

Process Flow Diagrams conventionally depict:

- Process piping connections (but not diameter, thickness etc.)
- Major equipment symbols, names, and ID numbers
- Equipment items are shown as symbols, not blocks
- Valves that affect system operations
- Interconnection to other systems
- Major bypass and recirculation
- Operating values, maximum and minimum, temperature, pressure, and flowrate
- A PFD is accompanied with a table containing approximate stream compositions, temperature, and pressure
- Stream direction shown with arrows



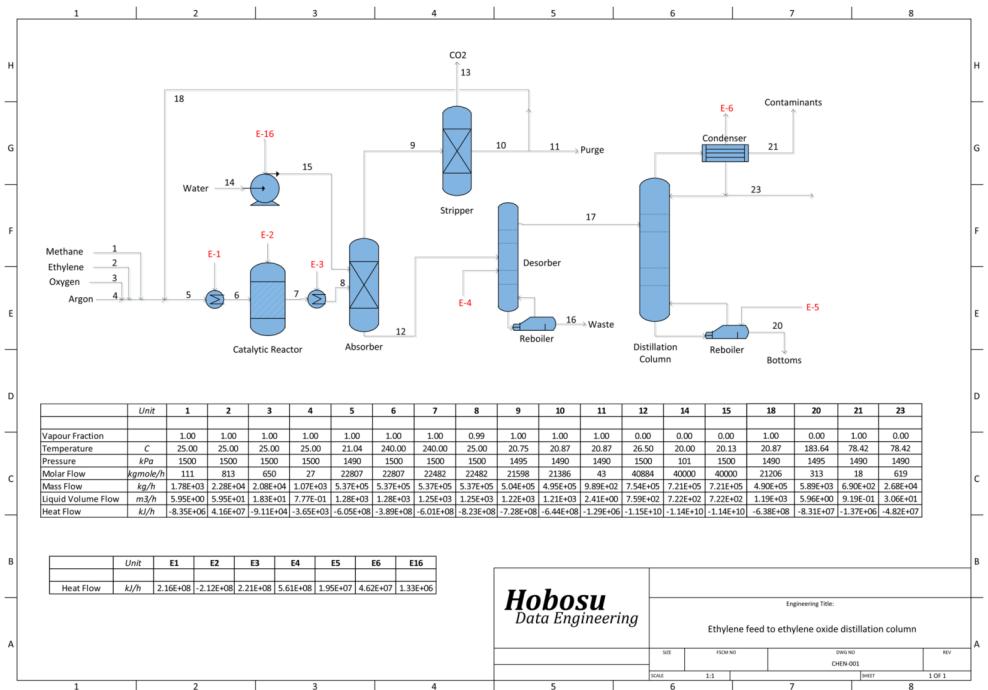
Mode	Parameter	Points			
		1	2	3	4
Normal	Pressure MPa				
	Temp °C				
	Flow m³/hr				
Maximum	Pressure MPa				
	Temp °C				
	Flow m³/hr				
Minimum	Pressure MPa				
	Temp °C				
	Flow m³/hr				

PDF template:

Identifiers/Description					
Flowsheet					
<b>M &amp; E Table</b>			Title Block		
Revisions					

A PFD showing a process that converts ethylene to ethylene oxide is shown below

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#### 2.1.3 Piping and Instrumentation Diagram

The Piping and Instrumentation Diagram (P&ID) is the complete schematic of the plant. It is associated with the final stage of design, the Detailed Design Report (DDR) and gives the outline of all equipment, instrumentation, piping, and valves. If something is not shown on the P&ID, it will not be bought and included in the facility. So, it's important everything is included. The P&ID will be designed over many, many iterations. Thousands of work hours may go into designing and refining it, and so the document itself can be worth hundreds of thousands of dollars. When designing the P&ID, you will need to think about more than just the everyday operation of the facility, but also start-up, shutdown (for routine maintenance every few years) and emergency operations. Given the size and complexity of the P&ID, it may be drawn across many schematic sheets.

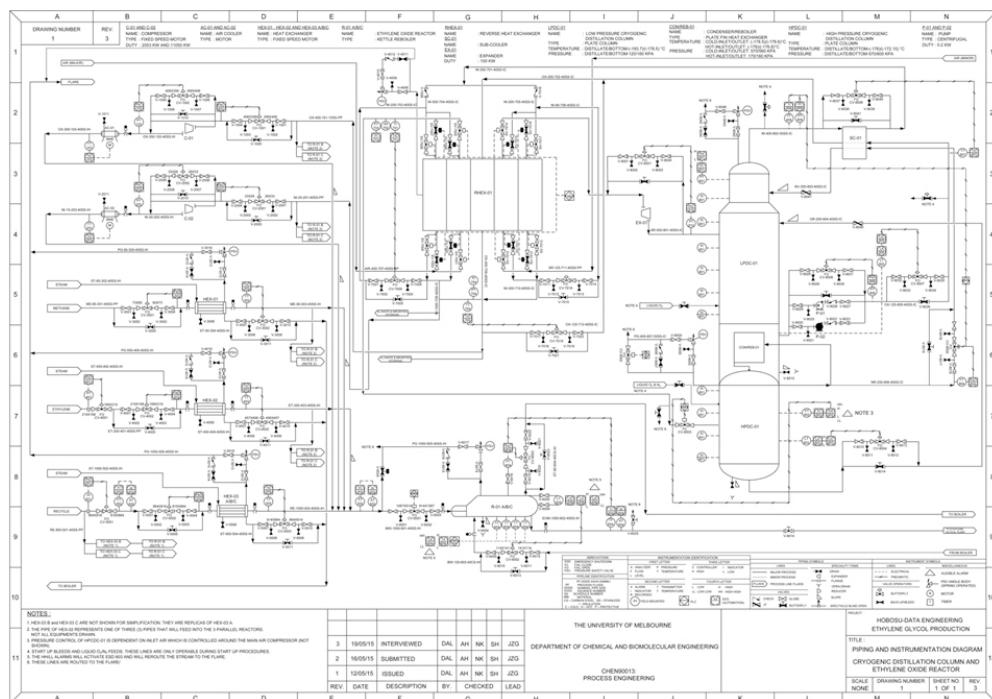
The P&ID typically includes:

- All mechanical equipment with an equipment number
- All pipes with a line number, size, and identification
- Permanent start-up and flush lines
- Flow directions
- Pumps with code number (if applicable)
- Valves (control and block) with an identification number

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- Ancillary fittings (such as steam traps, mixers, strainers) with identification numbers
- Control loops and instruments

A P&ID is shown below for a cryogenic distillation column. This is just an example to show the complexity and level of detail.



Feasibility Study	Process Development Report	Detailed Design Report
Block Flow Diagrams	Process Flow Diagrams (PFDs)	Process and Instrumentation Diagrams (P&IDs)

We outline the basic elements of a P&ID here but will apply them in later modules to discuss specific units.

**Worked Example 2.1**

LPG (Liquefied Petroleum Gas) may be extracted from crude oil by refining the light fractions. Typically, the process train would include the following basic units:

- Pump (crude oil)
- Atmospheric distillation column
  - Separate gas, light naphtha, heavy naphtha, kerosene, diesel oil, bottoms.
  - Condenser at top of column
  - Reboiler at bottom of column.
- Gas processing unit
  - Separates Fuel gas from Butane
- Butane undergoes Merox treatment
  - Mercaptan oxidation: Thiol (sulphydryl) extracted using NaOH or NH<sub>3</sub>
- Compressor
- Heat Exchanger/Cooler to liquefy to LPG

Draw a Block Flow Diagram (BFD) which includes all the relevant equipment items for a BFD from the dot points above.

## 2.2 Drawing Block Flow Diagrams

Drawing BFDs is focused on in Material and Energy Balances (CNEH20010), and so it will not be reintroduced in detail here. The key conventions to remember when drawing a BFD are:

- Units are collected into major processing steps and included in a single box
- All lines should be straight
- It should be drawn and read right-to-left
- It's meant to convey information clearly and succinctly

For Fun Chem Eng, you will need to be able to read and draw a BFD, but usually as part of a larger, separate question. So, we use the diagram format as a tool (or a language) for discussing more specific problems within the subject.

## 2.3 Drawing Process Flow Diagrams

We will now go into detail into how to draw a PFD (with a primary focus on drawing in AutoCAD and Visio). It is the layout you see in the HYSYS simulation environment.

General advice for drawing PFDs (and P&IDs):

- Do rough sketch first
- Select appropriate icons for units
- Layout to reduce cross-over lines
- Do draft drawing
- Get someone else to check and sign off

All equipment items are designated with a code. For example, T-101 would refer to tank 101. These equipment codes are usually set by a company standard (there is no industry wide standard) but in general they're designed to be simple; the first letter relates to the equipment item name and a number differentiates the equipment item from similar units on site.

T = tank R = reactor C = column

P = pump, M = mixer F = filter,

D = dryer HEX = heat exchanger

Q = furnace V = vaporizer G = gas movers

General rules for spatial layout of schematics:

- The schematic should be drawn to flow from left to right
- All major equipment items should be well-spaced to allow for easier reading
- The top section of the schematic is usually reserved for identifiers and descriptions
- The bottom section of the schematic usually has other information; engineering sign-offs and mass and energy table (in a PFD)
- Schematics have a border, title block, revision notes and space for all contributing engineers to sign-off
- Usually, utility lines are shown along the bottom of the drawing (for PFDs and P&IDs)
- Usually, vapor lines/vents are shown along the top of the drawing

There are a range of tools to draw schematics. The two most common you are likely to encounter in industry are Visio and AutoCAD (The CAD stands for Computer Aided Design). Within AutoCAD is an add on called Plant3D which is great for drawing P&IDs.

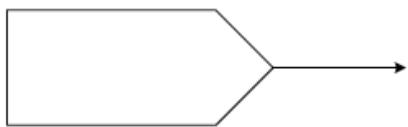
When drawing in Visio, you can select a template specifically for drawing PFD processes: File>New>Process Engineering> Process Flow Diagram (metric). You can also use the snap and glue function.

A PFD would usually be drawn on larger sized paper (A3 or above) and follow these general conventions in Visio:

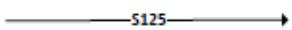
- 1.2 mm (thick) for main flow streams
- mm (medium) for recycle streams
- 0.7 mm (medium) for secondary lines
- 0.4 mm (thin) for tertiary lines
- 0.5 mm (thin) for services

Make sure all fonts are readable (it's common to accidentally produce them too small in the final drawing). A PFD has a table at the bottom that give basic material properties of all major flow and utility streams.

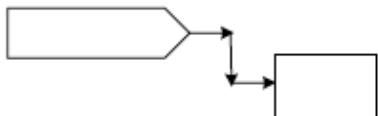
You will use identifier icons to connect streams between adjacent pages. You usually make sure these stream lines align between pages. When a stream connects between pages, we use an identifier icon (a hollow arrow) with a description of the stream to show it's connecting to another page:



We also label all streams with number for identification (you can do this automatically in Visio).



On a PFD, an arrow is usually shown on the stream line when it changes direction (i.e., makes a 90° turn).



Control loops are not normally shown on a PFD, but pumps and other ancillary equipment are shown.

## 2.4 Drawing Piping and Instrumentation Diagrams

We will now move on to discuss the most detailed plant design schematic, the P&ID, which shows a detailed plant equipment layout as well as the control scheme (the automated processes included for safety and plant operation). We will begin by discussing the P&ID schematic and layout, then discuss common control arrangements.

Based on the P&ID:

- Mechanical and civil engineers will design and install pieces of equipment
- Instrument engineers will specify, install, and check control systems
- Piping engineers will develop plant layout and elevation drawings
- Project engineers will develop plant and construction schedules
- Hazard and Operability (HAZOP) studies will be conducted
- Operators will be trained
- Start-up/shutdown procedures will be developed
- Troubleshooting/debottlenecking and plant upgrades will be conducted.

So, the P&ID is an essential document. When the plant is being built, if a valve or other piece of kit is left off the P&ID, it will not be purchased and installed. Changes after the plant has been built come at an extremely high cost. Each PFD will require many P&IDs.

The P&ID is drawn to a set of international standards. Many large companies may have their own internal standards, for example after the [Deepwater Horizon spill](#), BP updated and reviewed many of its internal design standards and is often considered best practice in the oil and gas industry.

International standards you may be required to design to (depending on location in the world, company you work for):

- PIP: Process Industry Practices
- ISA: Instrumentation Systems and Automation Society
- ISO 10628: Diagrams for the Chemical and Petrochemical Industry (International Standard)
- TEMA: Tubular Exchanger Manufacturers Association
- OSHA: Occupational Safety & Health Administration

As the P&ID is so essential to the final design of the plant and its safe operation, the design of the P&ID is done by a team of engineers and goes through a range of review procedures to verify it is correct and facilitates safe operation.

- Revision A: General layout, based on PFD. Equipment details, piping, control & block valves, PSVs (pressure safety valves)
- Revision B: Line sizes, design conditions, miscellaneous equipment. Material selection, spec breaks.
- Revision C: Issue for Review. Update controls & instruments, preliminary elevations.
- Revision D: Issue for Preliminary Hazard Analysis
- Revision E: Issue for Design
- Rev F: Issue for HAZOP. HAZOP is a systematic process designed to review safe operation of the plant and review current safeguards around the plant. Update equipment, piping, instrument data during the HAZOP.
- Rev G: Incorporate HAZOP comments

- Rev 0 Issue for Construction. Collect final vendor bids & piping data.
- Rev 1 onwards: As Built. Field verification

## 2.5 Layout of your P&ID

General conventions and considerations for laying out a P&ID:

- Amount of detail. You need to balance information & clarity. You may need to split your P&ID across more sheets or condense sheets to ensure there is sufficient information and clarity on each page.
- Avoid clutter. Typically, a P&ID would have a maximum of 3-4 equipment items per sheet
- Allow for additions. This can mean leaving space in the design for more detail in later revisions. But in the design of the plant, we also want to consider future expansion of the facility and so it can also mean designing with sufficient room to allow later additions to the plant.
- Typical details on separate sheets: Compressor Seal systems, Vendor P&IDs

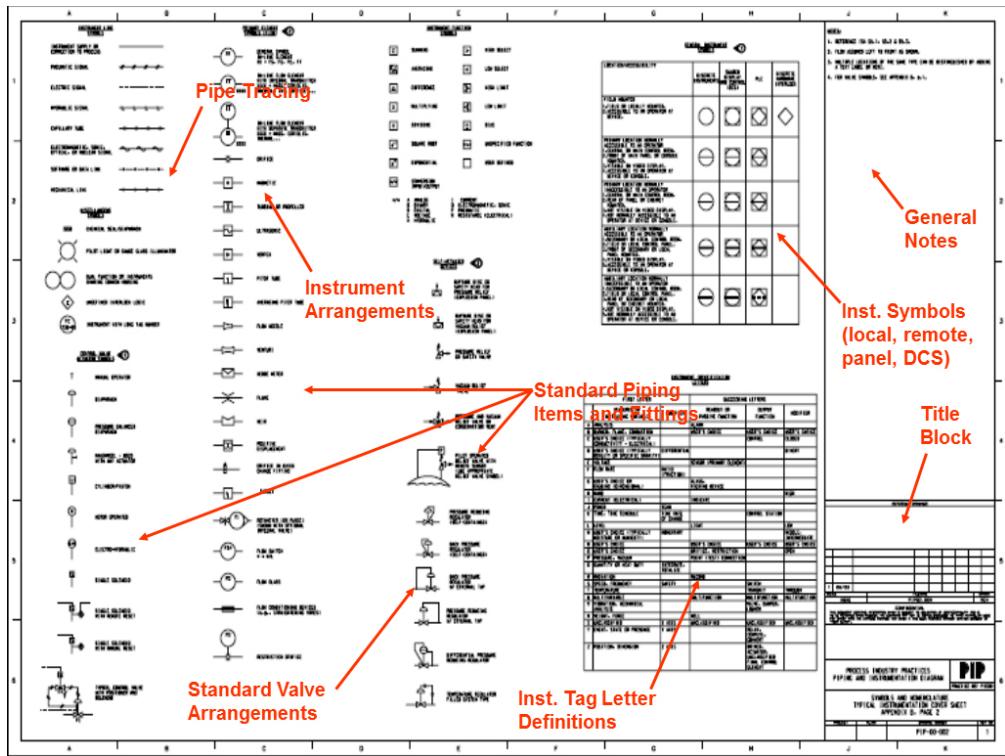
The P&ID should be designed to follow the PFD sequence (in equipment ordering etc.). It shows the actual configurations of all units, which means the vessel orientation, a rough drawing of the internals of each of the units, where pipes connect to equipment items, flow paths within a heat exchanger, relative elevations (for example a pump near the bottom of a unit, not near the top which would imply it was housed on a scaffold or platform).

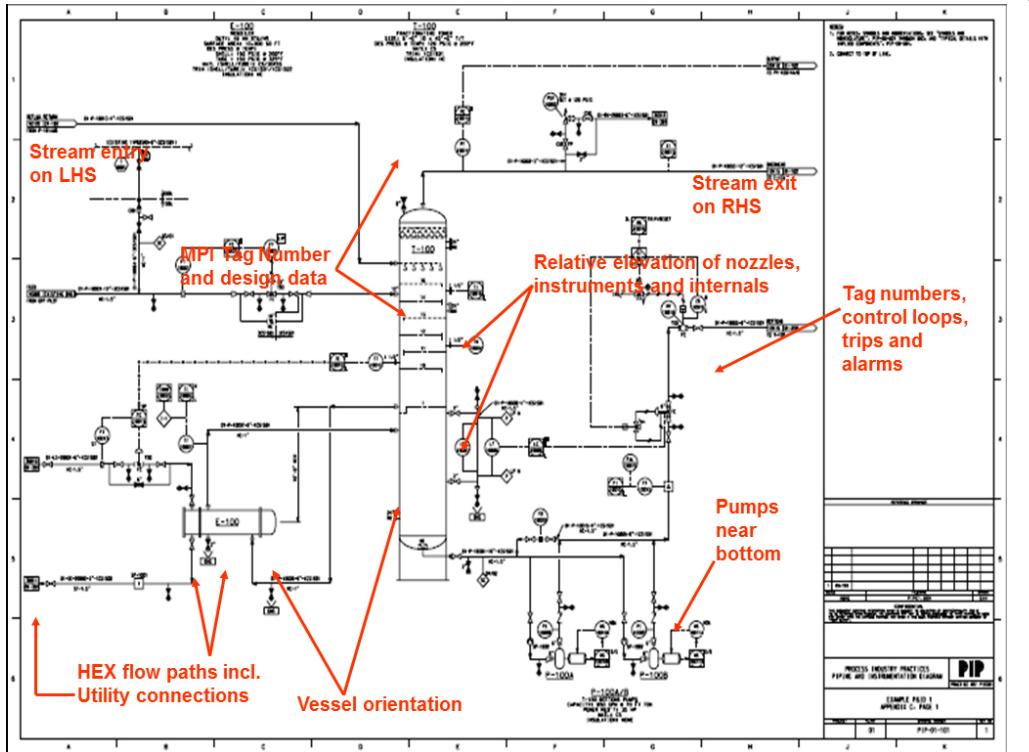
Each project will have a specific legend sheet and title block that will be common across all P&ID drawings for the project (each sheet in the final design and in each version across all revisions).

The P&ID will be accompanied with a legend sheet that describes all the symbols used within the schematic. The legend should show:

- Symbols for equipment, instrumentation, controls, piping items
- Line numbering convention, insulation, or tracing symbology
- Equipment and Instrument tagging conventions
- Accepted abbreviations and other notes

Note: a symbol library for drawing P&IDs is available in Visio under Create -> Piping and Instrumentation Diagram (the same library is available if "Process Flow Diagram" is selected). The symbols available in Visio are not entirely standardised, as there is no complete standardisation across the industry. However, a common-sense approach should be used to identify and select the most appropriate symbol for any diagram.





When drawing your P&ID, you need to consider more than just the normal steady state operation of the plant. The P&ID should also show vents and drains, lines for drawing samples as well as lines for purging, commissioning, start-up, shutdown, and off-spec product.

Process lines are normally drawn with a heavier weight, while utility lines usually have a lighter weight.

On the drawing, the line code should show the line size (pipe diameter), class, metallurgy (material of construction) and insulation on the pipe (if any). So, it might have a code like: Unit-Service-Number-Size-Class-Insulation (16-P-101-150-CS300-H) or Size-Service-Unit-Number-Class-Ins (150-P-16-101-CS300-H).

- 150: 150mm diameter pipe
- P: Signifies fluid service
- 16: Signifies the unit number
- 101: Would be the series number for the unit
- CS300: Carbon steel and the grade
- H: Insulation class (here H could mean hot in the legend)

When designing the piping, we need to consider slopes in the pipes to prevent liquid build up. A small wedge can be used to indicate a slope in the pipeline (it denotes the direction of the gradient).

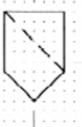
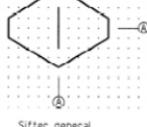
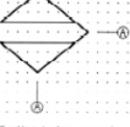
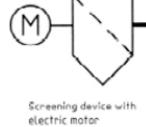
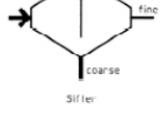
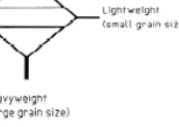


We want to avoid pockets in lines that can facilitate vapour or liquid build-up. We also need to consider whether material will be withdrawn from a vessel at the top or bottom. Liquid is usually drawn from the bottom of a vessel, and this may mean the base of the vessel needs to be sloped, with the draw point at the bottom of the slope, to prevent liquid accumulating around the edges.

When designing equipment and lines, we usually consider the maximum and minimum design pressure and temperature the system might experience, and design to these limits (considering contingencies and unusual operations). This then allows us to set the material of construction (different metals have different tensile strengths), establish breaks for connecting systems and identify isolation requirements (valves, check valves and isolation such as spectacle blinds).

Developing the P&ID will require you to identify all nozzles, internals of equipment items (trays, baffles, vortex breakers), denote relative elevations, show approximate liquid levels within units in normal operation, show all safeguards and show spare units and parallel units (for example as pumps are usually relatively inexpensive, pumps are usually placed so that there are 2 in parallel; if one breaks down the second can automatically come into service while the first is repaired).

Sample graphical symbols for sifters, screen machines and sorting devices:

Basic series Subject group 6	Graphical symbols Detailed series		Examples
	Sifters (F) Screening devices (F) Screening machines (F)	Sorting devices (F) Sorting machines (F)	
  	 		<p>Screening device with electric motor</p>
		 	<p>sifter</p> <p>Lightweight (small grain size) Heavyweight (large grain size)</p>

As you're developing your P&ID, remember that the plant needs to operate in a whole range of modes beyond the normal steady-state operation you might have designed in your HYSYS simulation. You need to consider scenarios like:

- Testing and troubleshooting. For example, testing pressure, temperature and flow measurements as well as leaving sample points

- Start up, shutdown, upset conditions: Vents and drains
- Bypasses
- Equipment isolation and inspection: Purge gases and ‘double block and bleed’ lines around equipment and valves you want to isolate.
- Maintenance

The P&ID will show instrumentation for making stream measurements as well as the type of valves used for control. You need to decide if a piece of instrumentation will be used as an:

- Indicator. i.e., just to display the conditions.
- Recorder. Log all values either local or within a distributed control system (DCS)
- Controller. The output is used to modify something within the plant, such as a valve position
- Connected to an alarm, trip, or emergency shutdown (ESD)

The P&ID should also show valve types and whether the valves are fail open, fail closed or fail last position.

The P&ID would exclude information about the stream flowrates and operating conditions (for example temperature and pressure of lines). It is designed to be the document from which the plant can be built and so these types of considerations that are relevant in the design of the facility are much less relevant in the construction stage.

The P&ID also does not show equipment locations or pipe length. These are often fitted on site. The P&ID also doesn't show supports, structures, or foundations, which may be designed by mechanical and civil engineers in separate drawings.

Things that would usually be considered when checking the P&ID:

- Consistency between P&IDs: Drawing connector blocks between sheets, making sure there is no duplication of equipment between sheets
- Consistency with engineering documents: i.e., making sure the P&ID still matches the PFD, equipment datasheets (for the individual equipment items), safeguard documentation.
- Speculation (spec) breaks: Double checking the design pressure and temperature are appropriate for the metallurgy and there is sufficient over-pressure protection (pressure safety valves (PSVs) etc.).
- Commissioning, start-up, shutdown requirements

## 2.6 Control Logics and Process Measurement

A piping and instrumentation diagram not only shows equipment, but also the control scheme for the equipment. By ‘control’ we mean the automated and manual equipment used to manage the plant for safe, quality, and economic operations. A valve may need to be opened to change a cooling water flowrate, to bring a reactor back to a design temperature. This means there needs to be a temperature sensor, to know the reactor temperature and a valve to change the water flowrate. Will these adjustments be made manually (by a person monitoring the temperature) or automatically (by a computer)? This information would be conveyed within the P&ID.

There's usually no single ‘correct’ control scheme. There are usually a variety of different options that can achieve the goal but have competing advantages/disadvantages. So, it often helps to have a broad conversation about the overarching objectives and priorities for control, then look at specific options.

In general, the function of process measurement and control is:

1. Safe operation: to protect personnel and equipment by keeping process variables in a safe range and by responding to dangerous situations
2. Production rate: To keep product being produced at the desired quantity and rate
3. Product quality: Maintain product quality within required standards.
4. Economic operation: Minimize waste, limit utility demand where possible.

If the plant is a water treatment facility, personnel safety controls may be less of a concern than a petrochemical plant, that handles large volumes of flammable material. If the facility is making food products for human consumption, then product quality may be more important than mineral tailings from an iron ore site (a waste stream primarily made up of unwanted dirt). So, the relative priority of these 4 criteria tends to shift depending on the specific context.

### 2.6.1 Basic Terminology

#### *Direct vs Indirect Control*

Direct measurement is when a parameter being measured is the parameter we want to know (e.g., reading the system temperature with a thermocouple).

Indirect measurement is when another variable is measured to infer a parameter we want to know. An example would be measuring temperature in a distillation column to infer composition. For example, a mixture of ethanol and water boils at different temperatures depending on the ratio of ethanol to water; measuring the boiling point can tell us the composition if we know only ethanol and water are present in the mixture. Measuring composition can be quite slow and the instrumentation is expensive, so we measure temperature instead, knowing that the boiling point of a mixture is a function of the composition.

**Controlled Variable:** The process variable to be controlled. This would be measured directly if possible.

**Dependent Variable:** A variable whose value depends on the controlled variable value. This would be measured if the controlled variable could not be measured directly (indirect control).

**Set Point:** The control scheme will try to maintain the controlled variable at its set-point; it is the value of the controlled variable that adjustments are made to try to keep constant.

**Manipulated Variable:** The property adjusted to keep the controlled variable at its set point.

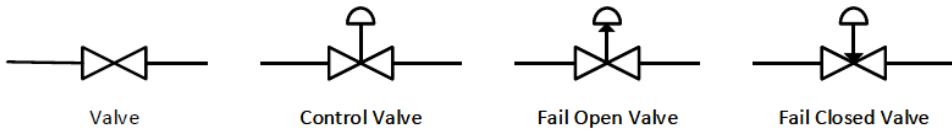
#### Worked Example 2.2

A control scheme is designed to keep a reactor at a constant temperature of 50°C. The reactor contains an exothermic reaction, so the reactor temperature is modified by changing the flowrate of cooling water.

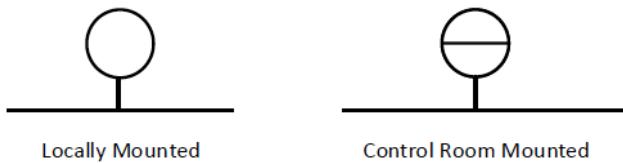
List the controlled variable, manipulated variable and set point of the control system.

## 2.6.2 Diagrammatic representation of process equipment in P&ID

Valves and control valves:



Location of the valve (is it operated at the site in the plant or remotely in a control room):



When displaying a control scheme, we would sequence letters to describe how the control works. The first letter usually indicates the parameter being measured. The second letter indicates the instrument function.

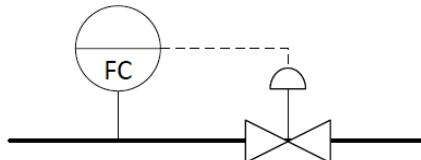
### 1<sup>st</sup> Letter Property

- F: Flowrate
- P: Pressure
- L: Level
- T: Temperature

### 2<sup>nd</sup> Letter Property

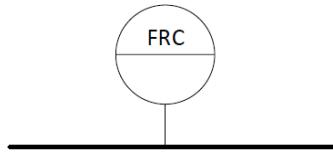
- I: Indicator
- C: Controller
- R: Recorder
- A: Alarm

For example, a flowrate controller:



Flowrate is being measured and controlled (by the manipulated variable, a valve on the line).

Another example of a control scheme:



Flowrate recorded and controlled in a control room mounted panel.

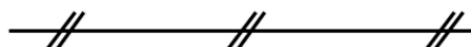
We can also designate the type of signal being used for control. An electrical signal sends an electric current to drive an actuator (or motor) to turn a valve open or closed. If the valve is large or the fluid generates significant resistance, the actuator can be quite large and expensive. An alternative type of control signal is a pneumatic drive; here compressed air can be transferred through a line which connects to a diaphragm or piston at the point of the valve. Rather than having a large electric motor to drive the valve open or closed, changes in the line pressure can cause a pneumatic force to drive the valve open/closed (hence they can be cheaper and lighter in the event the valve is elevated).

A P&ID will show the type of control signal (electric vs pneumatic).

Electric signal (dashed line):



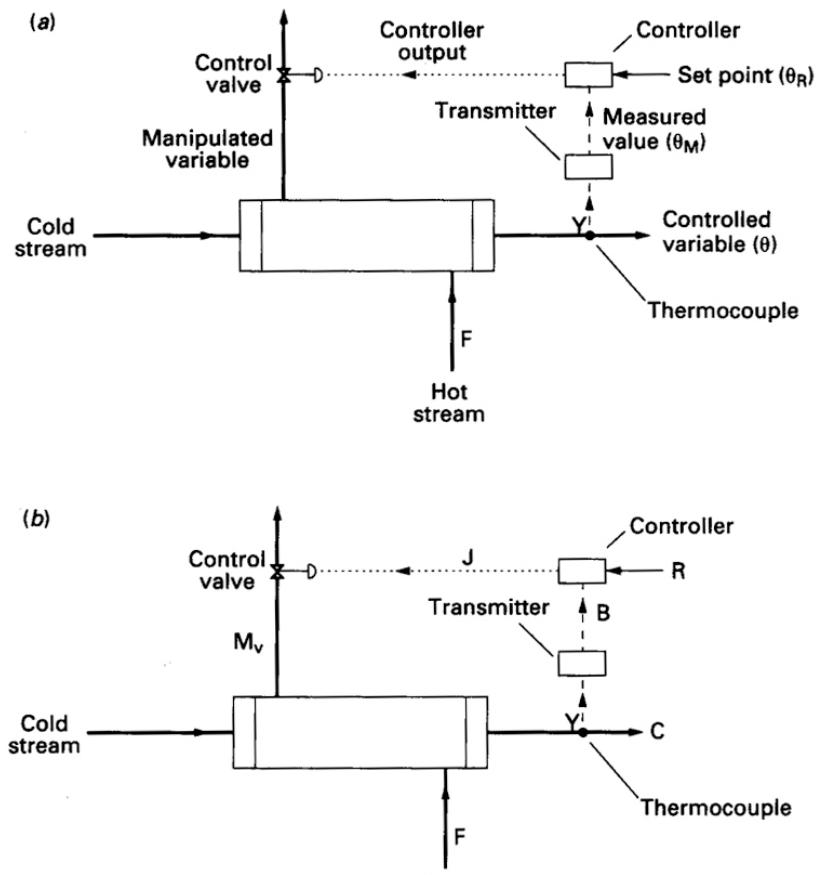
Pneumatic signal (hashed line). Pneumatic signals are very rare in new plants today because of the reduction in cost of electronic equipment (they are almost always lower cost now). But in case you see pneumatic signals in older P&IDs:



A table of common control signification is shown below.

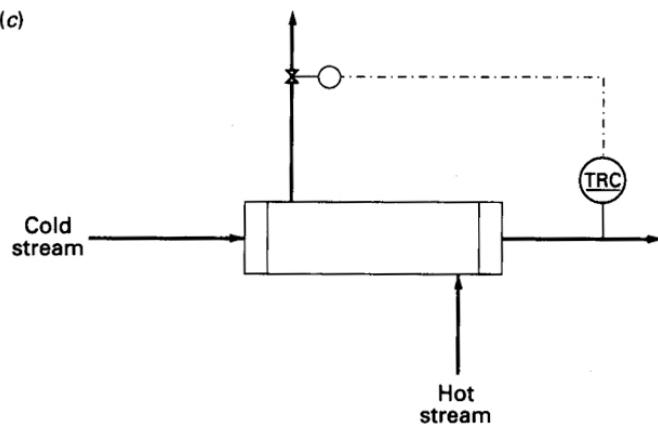
<b>Location of Instrumentation</b>	
<input type="radio"/>	Instrument located in plant
<input checked="" type="radio"/>	Instrument located on front of panel in control room
<input type="radio"/>	Instrument located on back of panel in control room
<b>Meanings of Identification Letters (XYY)</b>	
<i>First Letter (X)</i>	<i>Second or Third Letter (Y)</i>
A Analysis	Alarm
B Burner flame	
C Conductivity	Control
D Density or specific gravity	
E Voltage	Element
F Flowrate	
H Hand (manually initiated)	High
I Current	Indicate
J Power	
K Time or time schedule	Control station
L Level	Light or low
M Moisture or humidity	Middle or intermediate
O	Orifice
P Pressure or vacuum	Point
Q Quantity or event	
R Radioactivity or ratio	Record or print
S Speed or frequency	Switch
T Temperature	Transmit
V Viscosity	Valve, damper, or louver
W Weight	Well
Y	Relay or compute
Z Position	Drive
<b>Identification of Instrument Connections</b>	
	Capillary
	Pneumatic
	Electrical

A variety of intermittent equipment items are required to complete a control operation. Say we want to control the outlet temperature of a stream from a heat exchanger by varying the flowrate of hot oil. A thermocouple is first used to measure the outlet stream temperature, this is then sent to a transmitter which converts the thermocouple signal into a measured value and transmits the information to the controller. The controller calculates the discrepancy between the measured temperature (from the transmitter) and the set point. If there is no discrepancy, it makes no adjustment. If the temperature is too low/high, the controller sends a signal to the valve actuator on the hot oil line to further open/close the hot oil valve.



We will typically condense all these steps to just show the basic control logic (as shown below):

(c)



### 2.6.3 Multivariable control

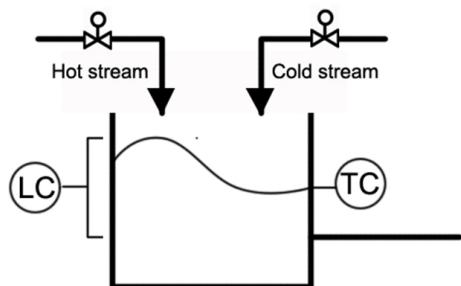
Each controlled variable must be paired to a different manipulated variable. Two controlled variables cannot be paired to a single manipulated variable. One controlled variable is not usually paired to two manipulated variables over the same range of operations.

So, this raises a question about the possible control options.

#### Worked Example 2.3

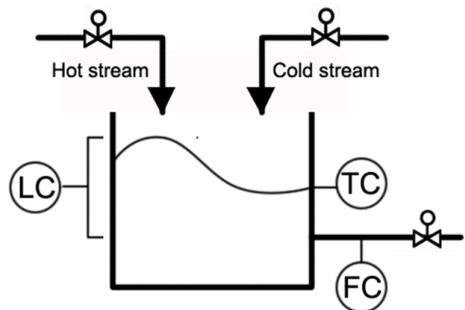
Two water streams at different temperatures are being mixed. We would like to control the level of water in the tank and the final temperature of the tank. Like filling a bath to get it to the right level, we can change the flow rate of water to change the height and the ratio of cold:hot to change the final temperature.

How many ways of arranging the control pairings are available given we have 2 sets of controlled-manipulated variable pairs?



#### Worked Example 2.4

Like Worked Example 2.3, we now also want to control the flowrate of water out of the mixing unit. Although not all options may equally practical, how many different ways of arranging control scheme are available, when we have 3 pairs of controlled-manipulated variable pairs?



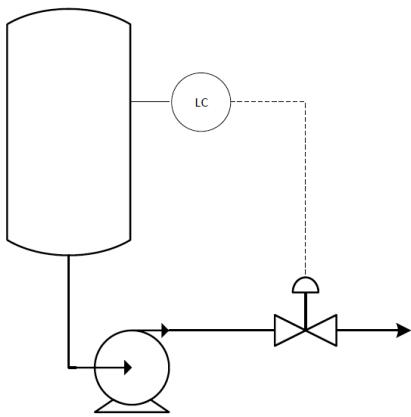
The key message from these two worked examples is that if there are  $N$  controlled-manipulated variable pairings, then there are  $N!$  control options. So, in reactors and distillation columns where there can be a high degree of interconnection and control pairings, the control schemes can get really complicated quickly; there can be a huge number of alternative control options to consider.

### 2.6.4 Typical Control Systems

Given the wide range of potential control pairings available, it makes sense that we discuss common sense control design; we usually want to pair a manipulated variable that will have a direct effect on the controlled variable.

#### *Level Control*

It makes sense to pair level in a tank to inlet or outlet flowrate from the tank. Clearly this would have a more direct effect on level than say the storage tank temperature.



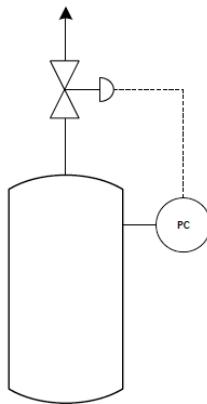
#### *Pressure Control*

Pressure control usually discussed in the context of gases; over most practical ranges liquids are usually considered incompressible. Using the ideal gas law equation of state, we can think about ways to control the pressure in a vessel.

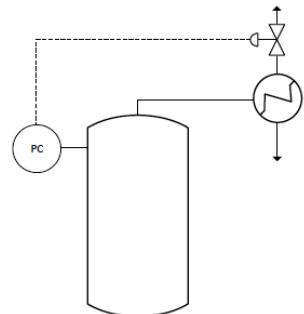
$$PV = nRT$$

Controlling pressure usually means changing the number of moles in a vessel (by opening a valve to move material in or out or by controlling the reaction rate), by changing the temperature (cooling drops the system pressure for a given number of moles) or by changing the volume of the vessel itself (for example changing the liquid level in a 2-phase vessel or for a floating roof tank).

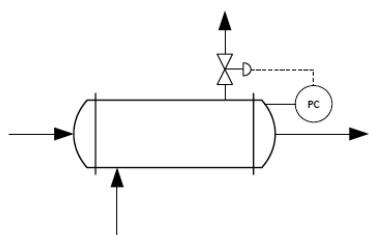
How might we draw pressure control systems in a P&ID:



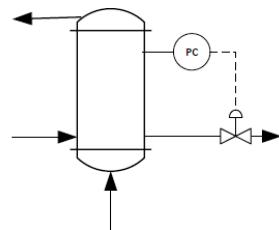
Direct venting of material from a vessel



Venting after a condenser (for example  
in distillation column)



Controlling pressure by changing coolant  
flowrate (changing duty)

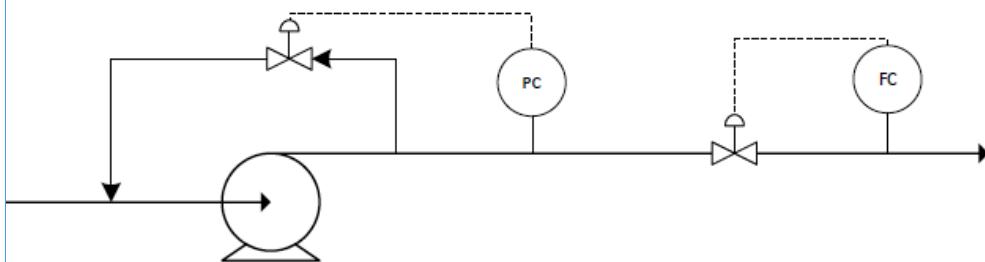


Controlling pressure by changing heat  
transfer area (by changing liquid level to  
control duty)

### Flow / Pump Control

A common problem for pumps is called 'surge'. Surge occurs when the flow in a line becomes unstable and begins to fluctuate; it creates an oscillating output pressure at the pump that can exceed the maximum pressure delivered by the pump and hence creates a reverse flow across the direction of the pump. Apart from damaging downstream equipment, flow reversal can shred the impellers of the pump itself (it's considered really bad for the operation of a pump). Surge tends to onset at high output pressure but low flow conditions in a pump. There are a variety of ways to suppress the effects of surge (for example, bursting disks that will rupture if the line exceeds a pre-set value, spring-loaded safety valves that mitigate the effects) but one of the simplest control mechanisms that causes no venting of product is a recycle line around the pump: the output side of the pump shown will be higher than the inlet side. Opening a recycle line from the pump outlet to inlet, allows backflow around the pump, back to the inlet and shifts the pump's location on a pump-curve (volumetric flowrate vs output pressure). As long as the pressure control loop can respond faster than the frequency of the oscillating surge pressure (typically on the order of 1 Hz) the control scheme can protect the pump.

Commented [CH1]: Redraw properly.



Once the pump delivers a stable output pressure, the flowrate can be controlled by shifting the position of a valve.

### Cascade Control

In cascade control, the output of one controller is used to adjust the set point of another control loop. It is used to give smoother control in a situation where direct control would lead to unstable operation. Usually the outer loop (that adjusts the set point of the inner loop) is called the primary control loop (also called the "master" loop). The inner loop (that responds to the adjustments of the primary control loop) is called the secondary control loop (also called the "slave" control loop). For the cascade control to work effectively, the primary control loop should respond more slowly than the secondary loop; in this way, the secondary loop can implement changes dictated by the primary control loop before a new change is made.

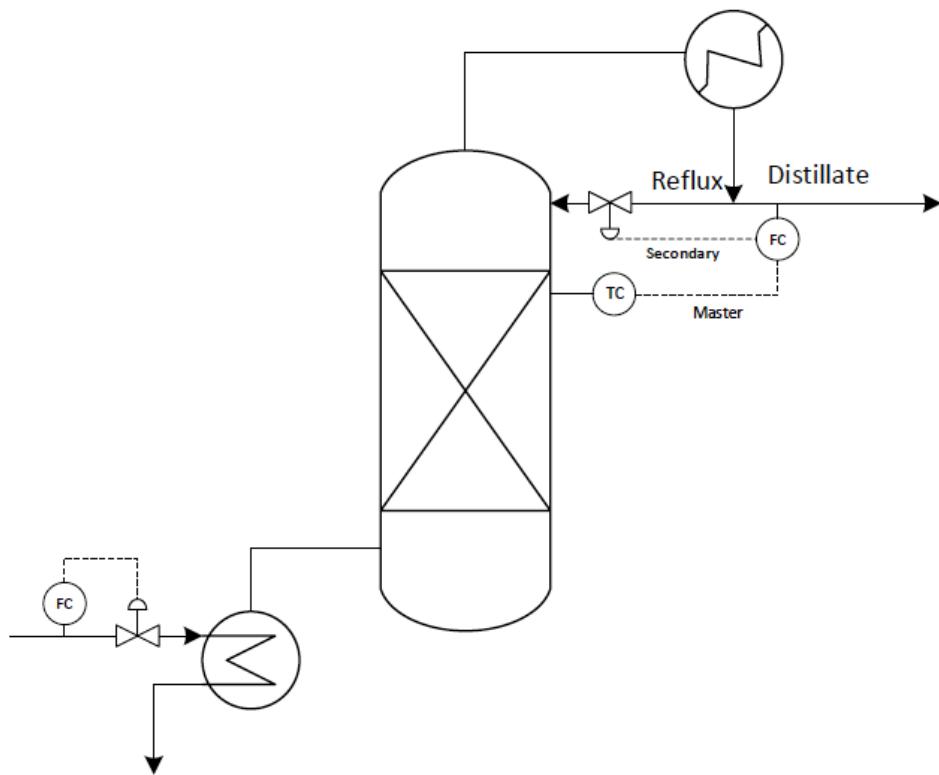
For example, in the control loop below, the temperature of the distillation column sets the set point of the flowrate of the distillate stream (primary control loop). The flowrate of the distillate stream then adjusts a valve position on the reflux line based on its new set point (secondary control loop). Adjustments by the secondary control loop would happen over a very short time scale (on the order of 1 second). If the flowrate on the distillate stream is measured to be too high, the reflux control valve opens and so the flowrate of the distillate line quickly drops down. As the reflux flow rate increases it tends to drop the temperature of the column. But this change in column temperature might take 30 minutes to fully propagate through the column. After 30 minutes, when the column has reached a new condition, it might set a new set point for the secondary loop. So, this control loop tends to smooth out any perturbations in the system; the flowrate control on the distillate line can smooth out any short-term perturbations in product flowrate and over longer time scales the temperature (as an indirect measure of composition) can smooth out any perturbations in inlet conditions (that might affect the fractional purity of the 2 product lines).

Now imagine the timescales were reversed. If the secondary controller took 30 mins for a change to propagate and the primary control loop only took 1 second. The primary loop would issue new set points every 1 second, but the secondary

Commented [NB2]: would be keen to change this to primary and secondary loops, rather than master and slave. That way it matches the PDC notation and doesn't use out-of-date language

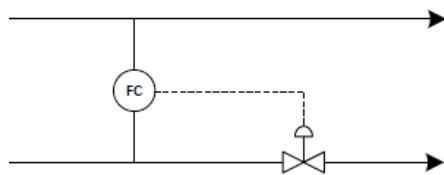
Commented [CH3R2]: Yes ok good point. I'll just use both so there's no confusion.

loop would never be able to accommodate these changes (because it takes 30 mins for the change to propagate through the system). This control arrangement would tend to create artificial instability in the output; the primary control loop would keep issuing orders the secondary control loop could never fulfil, and so the secondary control loop would keep making radical adjustments to the valve position without ever coming to steady state operation.



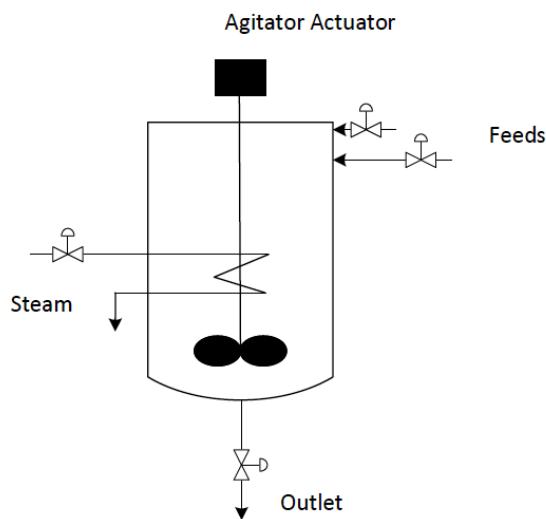
Ratio Control

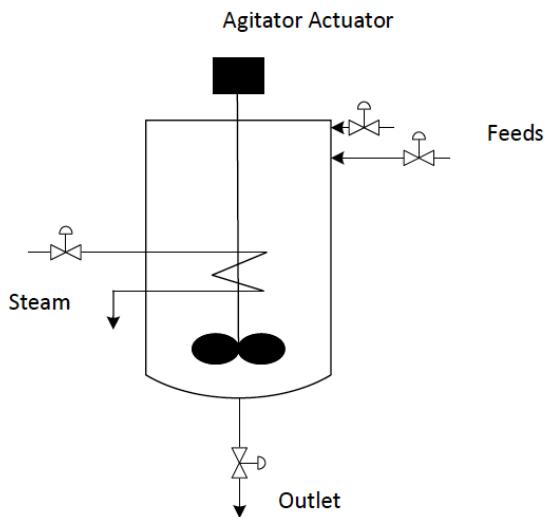
Ratio control is designed to maintain two flows at a constant ratio (for example reactants in a specific stoichiometric ratio into a reactor). It would be an example of MISO control (multiple input, single output). MIMO, SIMO and MISO control arrangements are all possible, but they are rarely used. Control schemes are usually designed to be as simple as possible, which means the overwhelming majority of control pairings are SISO arrangements (Single Input, Single Output) as we've discussed so far.

Worked Example 2.5

We want to design a control scheme for a continuous flow stirred tank reactor (as shown below). Reactants are charged into the reaction vessel continuously and mixed (by an agitator) and heated (from steam passing through heating coils). Product material is withdrawn constantly from the reactor.

Design a control scheme for the unit. (I have given the diagram twice so you can attempt it yourself in class and copy a solution we will go through together).





#### Safety Systems

The control shown on the P&ID needs to function to protect personnel on site and the equipment itself. So, process measurement will often be used to trigger safety systems built into the design, which can include:

- Alarms (visible and audio). An alarm must be associated with an operator action; they should not be included just for 'information' (which would be the function of an indicator). When drawing P&IDs, it's easy to get carried away and just alarms on everything, but you need to consider what action the alarm will require (for example evacuation, emergency operation procedures or something else). Redundant alarms should always be removed from a control scheme; they can foster an onsite culture that alarms can be ignored. You also need to leave time for operator response: 10-30 minutes minimum on an alarm.
- Safety trips. Safety trips are an automated control action that does not require operator input. They would be included when a delayed decision could be dangerous. So, examples would usually be associated with an emergency operation (for example emergency venting to prevent rupture). Safety trips would often cause shutdown operations: e.g., pumps trips that shut them down, closing feed valves, opening purge valves etc.
- Interlocks. Interlocks usually prevent an operation from proceeding if another operation has not completed. For example, most elevators are fitted with a mechanical interlock: the elevator cannot move if the door has not closed. Another example would be a microwave oven: the microwave cannot turn on if the door registers as open because of a mechanical interlock designed into the oven.

- Pressure control. Control should be implemented around vessel to prevent pressure build up, but in the event of unusual operation, most vessels will be fitted with pressure safety valves (PSVs) or rupture disks (sometimes called bursting disks). In the event that the pressure builds up to unsafe levels, the PSVs or rupture disks are designed to trip first (before the pressure reaches the design pressure of the vessel) so the pressure can be relieved in vent lines. This protects the equipment itself (from mechanical rupture) but also ensures material is vented safely (away from personnel on site and to a flare in the case of flammable or toxic material).

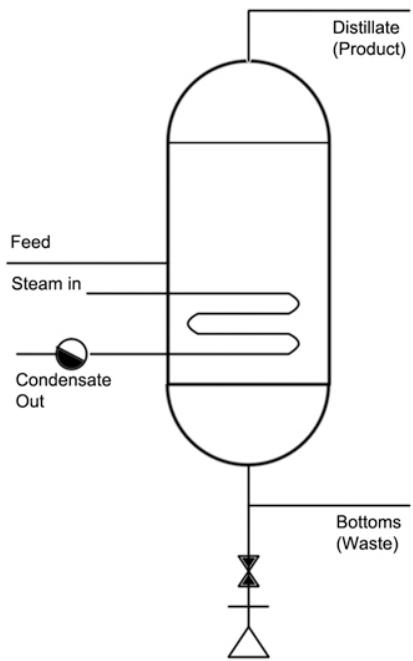
#### *Simple control is usually good control*

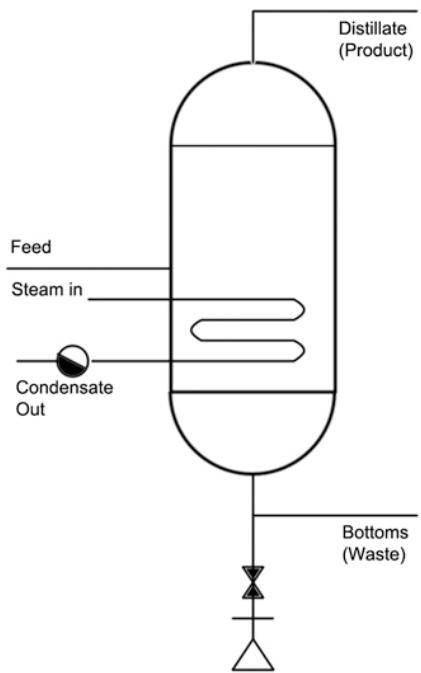
If you're drawing a control scheme on a P&ID, a common student mistake is to overdesign the control. A general rule in control is to use the simplest control scheme that will accomplish the job; it makes the plant operation easier to understand, particularly when something goes wrong. In the event of unusual or emergency operation there are usually many possible causes that may be affecting normal operation; simpler control can often help diagnose the possible problem.

#### Worked Example 2.6

Draw a sample control scheme for a still (shown below). By fermenting sugars in water, we can produce alcohol. The still is designed to concentrate the alcohol from the water-alcohol mix after fermentation. We want to produce an alcohol rich steam with a fractional purity >70%.

You may assume an online analyser takes 15 minutes to measure composition. Thermocouples, level indicators, flowrate and pressure can all effectively be measured instantaneously.





## Module 2 Summary:

### Key Points:

- Block Flow Diagrams (BFDs) are the simplest diagrams
- Process Flow Diagrams (PFDs) show large and intermediate pieces of equipment, as well as stream tables
- Piping and Instrumentation Diagrams (P&IDs) show every piece of equipment, as well as control loops
- Control logic:
  - Controlled Variable
  - Dependent Variable
  - Set Point
  - Manipulated Variable
  - Direct Vs. Indirect Control
  - Cascade Control
  - Equipment Control Schemes
- Safety Systems

### Key Skills:

- Drawing BFDs
- Identifying controlled, dependent and manipulated variable in a control scheme
- Understanding and designing control schemes for basic equipment items

## Module 3 – Small Kit: Sensors and Valves

In Module 2 we introduced the Piping and Instrumentation Diagram (P&ID) which shows the interconnection of sensors and control valves. Now we focus our attention on how these sensors physically work (temperature, flowrate, pressure, and level sensors) and the different types of valves we may use within the control.

### Outline

Primary learning outcomes for the module:

1. Develop an understanding of how instruments for measuring temperature, pressure, flow, and level operate
2. Develop an understanding of the different types of valves and their uses
3. Select and describe the appropriate valve or measurement for a specific context

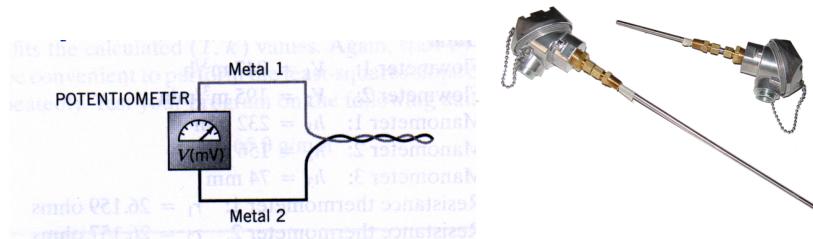
### 3.1 Temperature Measurement

#### 3.1.1 Thermocouple

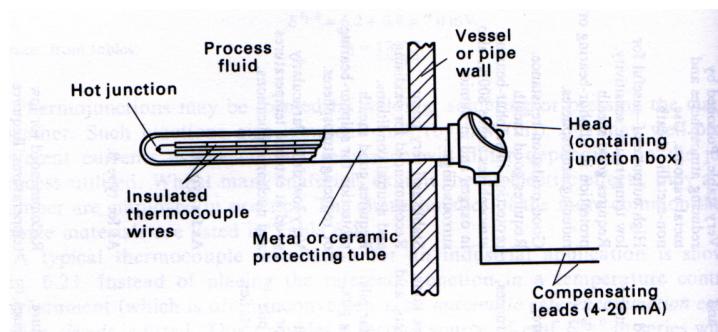
A device for measuring temperature. The thermocouple takes advantage of the thermoelectric effect; when a temperature gradient is applied to a thermoelectric material, it generates a voltage difference.

The thermocouple usually obeys an approximately linear relationship between potential and temperature, so that  $V = aT + b$ . By measuring the voltage generated across the material (typically in the microvolt range) we can determine the system temperature, after calibration of the linear constants.

The thermocouple is made up of 2 dissimilar wires joined at one end and coiled together (usually inside a metal tube). An example would be a junction of platinum and a platinum-rhodium alloy.

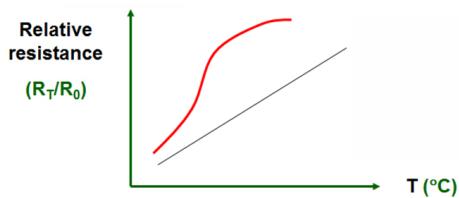


The thermocouple sits in a thermocouple well to penetrate the bulk of the fluid.



### 3.1.2 Resistance Thermometer

A resistance thermometer exploits the fact that conductivity tends to drop as temperature rises. As the thermal energy of the atoms rises, the chance of the electrons being driven by a potential difference tends to drop (there is a greater chance they scatter in alternate directions to the potential gradient). For this reason, most computers are cooled with a fan. But the phenomenon can also be used to measure temperature; the resistance of a material will vary monotonically as a function of temperature.



$$R_T = R_0 \exp \left[ \beta_\theta \left( \frac{1}{\theta} - \frac{1}{\theta_0} \right) \right]$$

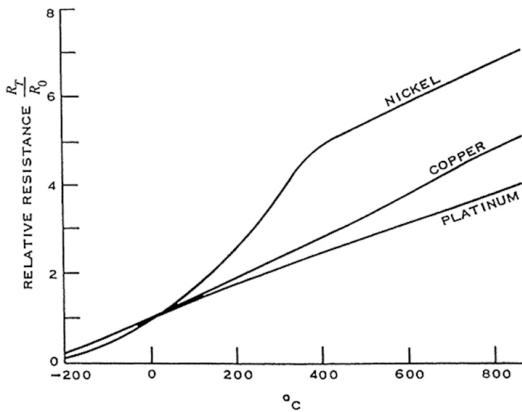
$R_T$  – resistance at  $\theta$  K

$R_0$  – resistance at  $\theta_0$  K

$\beta_\theta$  – constant for specific metal

$\theta_0$  K – normally 298K

Sample resistances as a function of temperature are shown below for various metals.



### 3.1.3 Bimetallic thermometer

Two metal strips (with different thermal expansion coefficients) are fused together to make a bimetallic strip. As the bimetallic strip is heated, one side tends to expand more than the other side, causing the strip to bend. The amount of bending can be used to gauge temperature (for example by connecting the bimetallic strip to a dial) or the bending

bimetallic strip can be used to open/close a circuit (this is a cheap way to create an 'off' switch in inexpensive kettles, like you might use to make tea at home).

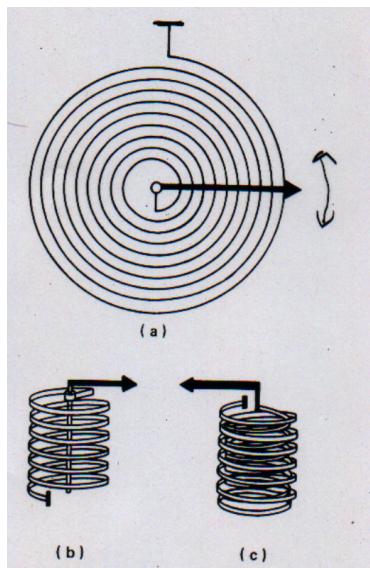


Figure (a) shows a flat bimetallic strip connected to a temperature dial. Figure (b) shows a single helix and figure (c) shows a multi helix. The dial may be connected to a calibrated temperature gauge as shown below.



### 3.2 Pressure Measurement

Before we talk about how we measure pressure, it's important to remember there are several difference scales for measuring pressure (i.e., that have different datum points, or reference zeros).

Pressure can be measured as either:

Absolute Pressure: From a perfect vacuum as reference zero and it would not be possible to measure a negative pressure on an absolute scale.

Gauge Pressure: From ambient pressure as reference zero, so this would give the pressure above or below atmospheric pressure. It would be possible to have up to 1atm negative pressure when measuring gauge pressure.

$$P_{\text{Absolute}} = P_{\text{Gauge}} + P_{\text{Atm}}$$

Differential Pressure: The pressure difference between 2 points. Here the datum does not matter. In essence gauge pressure is a differential pressure between a line and the atmosphere.

#### 3.2.1 Mercury Barometer

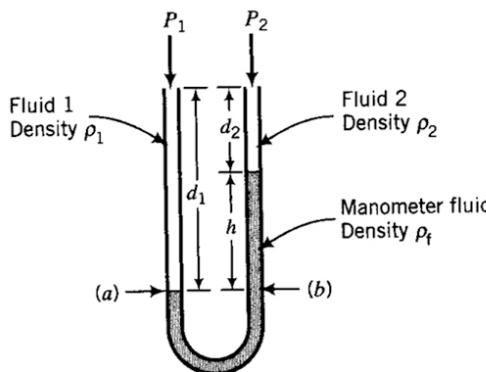
Indicates the absolute pressure of the atmosphere by the height a column of mercury can be pushed up a glass tube. Mercury barometers are the origin of the unit of pressure mmHg (760 mmHg is equivalent to 1 atm).

##### Worked Example 3.1

Draw a schematic of a mercury barometer.

#### 3.2.2 Manometer

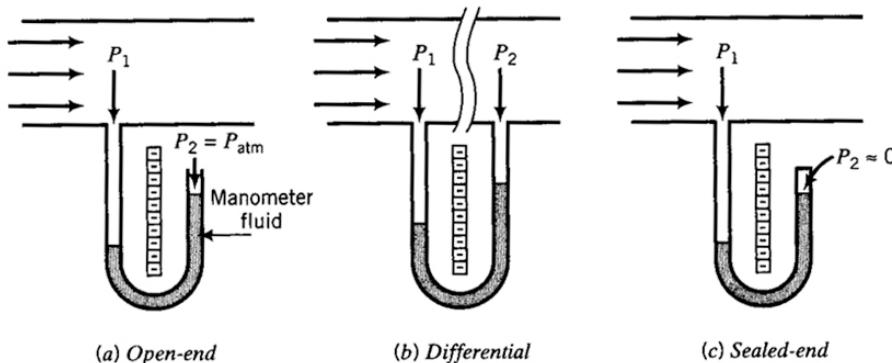
A manometer measures differential pressure. It is a glass u-shaped tube with each end open to a different pressure. A high-density fluid in the u-tube is free to move in response to a differential pressure between the 2 openings. The fluid in the u-bend comes to rest when the weight of the fluid balance the differential pressure at each end of the tube.



By completing a force balance between point (a) and (b) we can see that:

$$P_a = P_1 + \rho_1 g d_1 = P_2 + \rho_2 g d_2 + \rho_f g h = P_b$$

The manometer can operate in several ways, where  $P_1$  is connected to an equipment item or pipeline and  $P_2$  is open to atmosphere (to measure gauge pressure of the line), closed against a vacuum (to measure absolute pressure of the line) or open to a second position in the line (to measure differential pressure).



(a) Open-end

(b) Differential

(c) Sealed-end

If one fluid is gas

$$P_1 + \rho_1 g d_1 = P_2 + \rho_f g h$$

$$\rho_1 = \rho_2 = \rho$$

$$P_1 - P_2 = (\rho_f - \rho) g h$$

If both fluids are gases

$$P_1 - P_2 = \rho_f g h$$

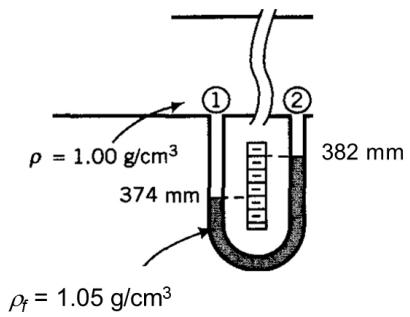
$$P_1 + \rho_1 g d_1 = \rho_f g h$$

If  $P_1$  fluid is gas

$$P_1 = \rho_f g h$$

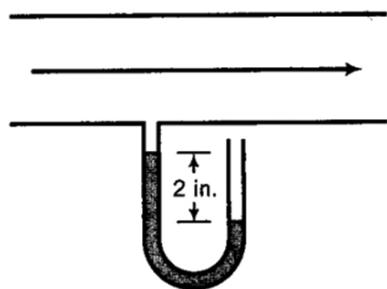
### Worked Example 3.2

A differential manometer is used to measure the drop in pressure between two points in a process line containing water. The specific gravity of the manometer fluid is 1.05. The measured levels in each arm are shown below. Calculate the pressure drop between points 1 and 2 in Pa.



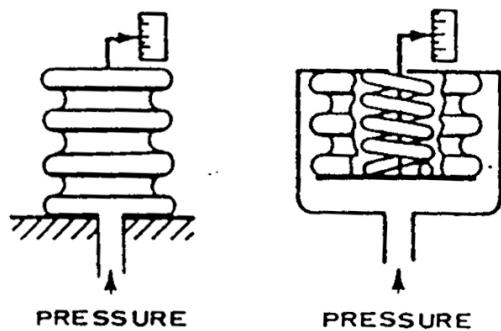
**Worked Example 3.3**

The pressure of gas being pulled though a line by a vacuum pump is measured with an open-end mercury manometer. A reading of -2 in. is obtained. What is the gas gauge pressure in inches of mercury? What is the absolute pressure if  $P_{atm} = 30$  in. Hg?



### 3.2.3 Bellows

Bellows expand in the presence of a pressure force acting against them. The bellows are typically spring loaded (to give a restoring pressure for the system to act against) or they may be unopposed, to simply measure whether the system pressure is above or below ambient pressure.



### 3.3 Flow Measurement

Flow meters often measure flow indirectly by measuring a pressure drop across a system of known geometry. From Bernoulli's principle (which you should have covered in Engineering Systems and Design) you should be aware that for a horizontal tube, pressure drop across a flow restriction scales with the fluid velocity squared. If there is no flow, there is no pressure drop. As a pressure drop is applied across the flow restriction, the velocity scales as the square root of the pressure drop. A simplified expression of Bernoulli's principle:

$$\frac{\Delta P}{\rho} \propto v^2$$

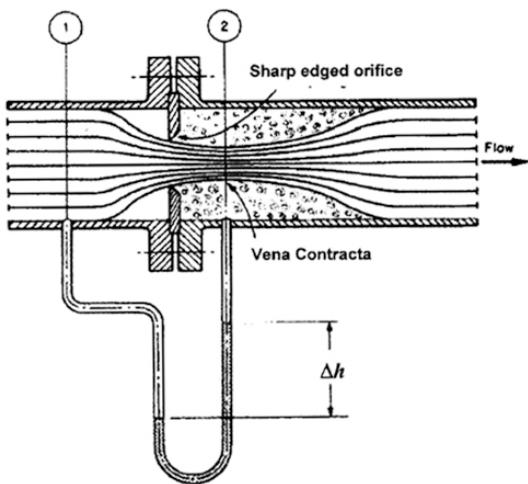
Where  $\Delta P$  is the pressure drop

$\rho$  is the density

$v$  is the fluid velocity

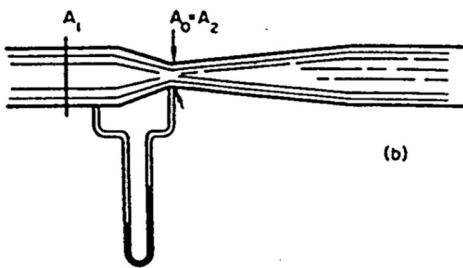
### 3.3.1 Orifice Plate

A plate with a hole (orifice) of known dimension is placed in the pipe and the pressure drop across the plate is measured. From Bernoulli's principle, the volumetric flowrate of the fluid may be determined.



### 3.3.2 Venturi Meter

Operates on the same principle as the orifice plate but the geometry of the flow obstruction is different and reduces the chance of the onset of turbulence.



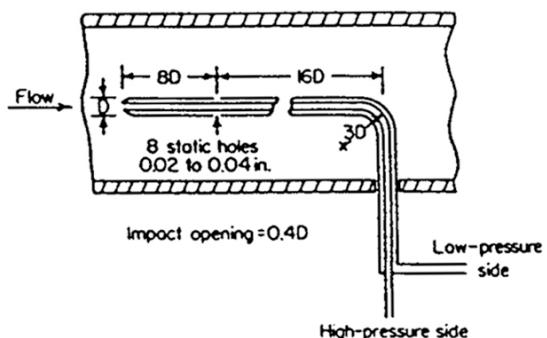
### 3.3.3 Pitot Static Tube

All 3 devices discussed so far can only measure an average or overall flowrate; they cannot determine the velocity profile across a pipe or find the velocity of a fluid streamline at a given point. The Pitot Static tube is designed to measure the velocity at a given point in the pipe and can measure the full velocity profile across the pipe.

A simple Pitot tube is just a pipe that points towards the direction of fluid flow. The tube has an inlet (pointing towards the direction of flow), but the other end is sealed, so there is a static fluid contained within the tube. The pressure of the fluid at the base of the tube can then be measured as a function of radial (cross-sectional) position in the pipe. The pressure measured in the pipe is not directly proportional to the fluid flow however (because there can still be a static pressure in the line). From Bernoulli:

$$P_{Tube} = P_{Static} + \left( \frac{r v^2}{2} \right)$$

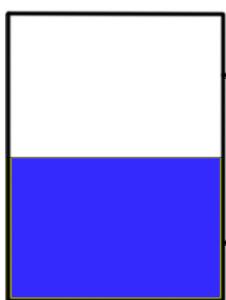
To determine the fluid velocity, it is necessary to measure the static pressure. This can be done through a static port or in the case of the Pitot-static tube (an alternative configuration to the simple Pitot tube) it is measured on the side of the Pitot tube. In the diagram below, the pressure is being measured at 2 points: a high-pressure side (the opening faces the direction of flow) and the low-pressure side (the opening faces the wall of the pipe, ie perpendicular to the direction of flow). The low-pressure side thus measures the static pressure, the high pressure side measures  $P_{Tube}$ , the static pressure and the additional pressure from the fluid velocity.



### 3.4 Level Measurement

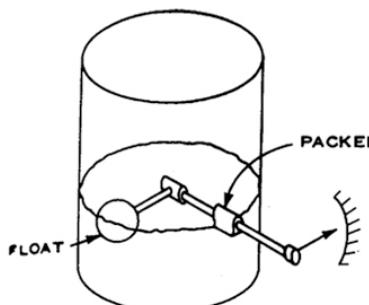
#### 3.4.1 Gauge Glass

A small pipe connects a glass display above and below the liquid level. The gauge is very simple, but it's essential that there is a connection both above and below the liquid level; if the gauge was only connected below the liquid level, a back pressure would mean the display level never changed.

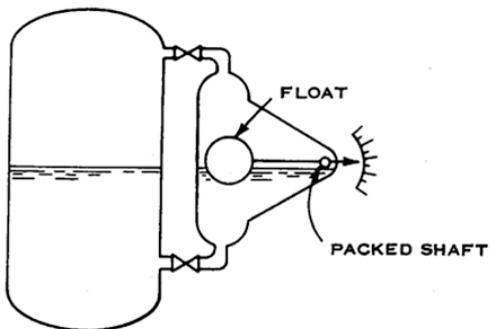


### 3.4.2 Float System

Float system contain a buoy that sits at the liquid-vapour interface in the tank and move up/down with the liquid to display level.



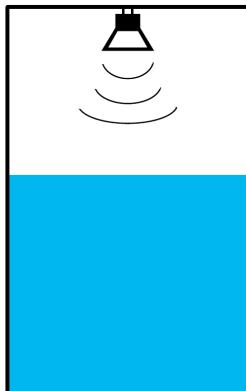
Internal Float Gauge



External Float Gauge

### 3.4.3 Sonar (Ultrasonic) Devices

Ultrasonic devices input a soundwave at the top of the tank and measure the time for the sound to reflect. By knowing the material properties of the vapour phase, it's possible to determine the distance between the sound source and the interface (gas-liquid, liquid-liquid, gas-solid or liquid-solid interface).

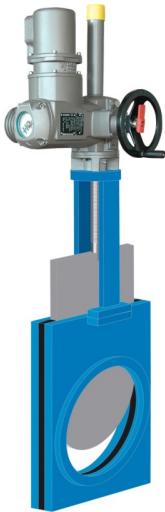


### 3.5 Types of Valves

So far, we have spoken about devices that can be used to measure system parameters (temperature, pressure, flow, level). But once our operator or automated control scheme has collected this data, we often want to implement some change in the facility to maintain control over the properties. For example, if the temperature of a reactor catalysing an exothermic reaction starts to rise, we may need to provide additional cooling to prevent a runaway reaction; this may mean increasing the flow rate of cooling water by opening a valve.

#### 3.5.1 Gate Valve

A piece of metal (the gate) can be wound down to close off the fluid flow. Gate valves are usually used for on/off operation although they can be designed to regulate flow. They cause minimal pressure drop across the gate and as the gate and sealing seat are all in plane, they may be appropriate when a minimum restriction is required. The bottom of the gate can be designed to be quite sharp, when regulating the flow of high viscosity liquids (for example in the petroleum industry) and are sometimes referred to as knife gate valves in this case.



#### 3.5.2 Butterfly Valve

The valve regulates flow by turning a disk so that the plane of the disk is either perpendicular or parallel to the flow direction or any position in between. The valve can go from fully open to fully closed with a quarter turn. Unlike gate valves or ball valves, the flow regulating disk is always in the flow field, so it will always induce some pressure drop. Butterfly valves can be used for regulating flow and are generally favoured because they are inexpensive and as they don't have a seat, they are often lighter than other types of valves and hence require less mechanical support.



### 3.5.3 Ball Valve

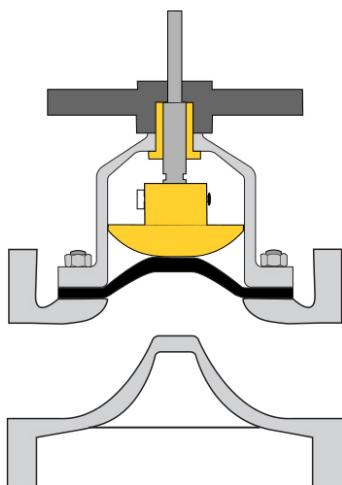
A ball valve is effectively a ball with a hole drilled through the centre, sitting in a seat. The ball can turn so that when the hole aligns to the flow direction, the valve is open, but when the ball is rotated 90° the flow is fully obstructed, and the valve is closed. Like the butterfly valve, the ball valve can go from fully open to fully closed in a quarter turn. The key advantage it offers over a gate valve and butterfly valve, is that when the valve is closed, the pressure in the line tends to push the valve more firmly into the seat and hence provides a better seal; higher line pressure tends to improve the seal, but a butterfly valve or gate valve would tend to leak more at higher line pressure. Ball valves are reliable and durable, they perform well after many uses and continue to close reliably after long periods of inactivity. So, they are very popular in the chemical industry. The key limitation of the valve is that although they are excellent for on/off operations (reliable, good seal, quarter turn to open/close so they respond fast) they are not appropriate for regulating flow.

One common mechanical problem with ball valves regulating water flow around the freezing point is that when they are in the closed position, sometimes water can seep into the seat. If this fluid freezes in the seat, its expansion can create mechanical stresses in the seat; the repetition of this process can create cyclic fatigue that gradually reduces the mechanical integrity of the valve.



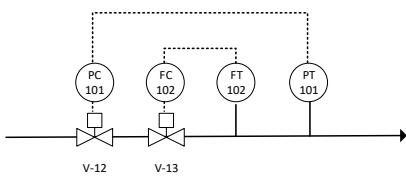
### 3.5.4 Diaphragm Valve

A flexible membrane is inserted between the pipe internals and the mechanism of the valve to separate the valve components from the line fluid. This would be used in biological or food processing industries that are particularly susceptible to bacteria and hence need to remove any space for bacterial growth (around the mechanism of the valve for example). They're also common for handling corrosive materials; coating a valve in plastic or stainless steel can wear through with successive opening/closing operations. So, a diaphragm valve can reduce cost of the valve by preventing the entire valve from being made from a non-corrosive material.



Worked Example 3.4

A control schematic is drawn to control both the flowrate and pressure on a single line using 2 valves in series. Will this control scheme work? To help answer this, you can think about how valves work to regulate flowrate or pressure (for example can they increase the pressure above the upstream pressure). You can also think about a degree of freedom analysis (for example if you get a 'consistency error' in HYSYS).



**Commented [CH4]:** For solutions: No it will not work. The line is over-specified. A valve is really just an obstruction to the flow that reduces the flowrate or pressure. 2 valves in series is still really just 1 obstruction. So it can't define 2 separate variables. Think if the flowrate 102 sensor was reading too high and the pressure sensor 101 was reading too low. FC-102 would tend to want to close but PC-101 would want to open- the 2 effects would cancel each other out and they would fight each other, until they ended with V-12 fully open and V-13 fully closed.

## Module 3 Summary

### Key Points:

- Measurement
  - Temperature
  - Pressure
  - Flow
  - Level
- Valves
  - Gate
  - Butterfly
  - Ball
  - Diaphragm

### Key Skills:

- Understand and explain how different measurement instruments work
- Understand and explain how different valves work
- Select the appropriate valve or measurement instrument depending on situation

## Module 4 – Medium Kit: Tanks, Separators, Heat Exchangers and Boilers

We will now discuss how specific units work and their function in a facility, and then directly apply all the content we have learnt previously to specific problems. So, we will be able to look at the control of these units in P&ID schematics we learnt in Module 2.

### Outline

Primary learning outcomes for the module:

1. Understand processes and design of: tanks and pressure vessels, separators, heat exchangers, and boilers
2. Apply basic enthalpy and heat transfer equations to a range of heat exchanger configurations
3. Analyse, describe and design control schemes for heat exchangers and boilers

### 4.1 Tanks and Pressure Vessels

A *storage tank* is a term used for a container that holds liquids and compressed gases but at close to atmospheric pressure (it is not designed for significantly elevated pressures or vacuum conditions). This is distinct from a *pressure vessel* which is designed for holding liquids or gases at pressures significantly away from atmospheric conditions, so it will have a larger wall thickness and pressure rating.

If a tank is holding a flammable liquid, it is desirable not to have any oxygen in the cavity space at the top of the tank (if the tank is only partially full). This means storage tanks sometimes have a *floating roof* (the roof of the tank moves up and down with the liquid level so there is no vapour space at the top) or for *fixed roof* tanks, the space at the top is often nitrogen blanketed (nitrogen is used to fill the vapour void space at the top of the tank).

A pressure vessel can be designed for any storage pressure, but in a normal storage tank the main source of pressure in the vessel can be the hydrostatically induced pressure from the contained liquid (hydrostatic head meaning the pressure from the weight of the liquid).

Just like for a manometer calculation in Module 3, the hydrostatically induced pressure from a liquid can be calculated from the weight force of the liquid:

$$\Delta P = \rho_f g h$$

Where  $\Delta P$  is the hydrostatically induced pressure (difference in pressure between the top and bottom of the liquid level)

$\rho_f$  is the density of the liquid

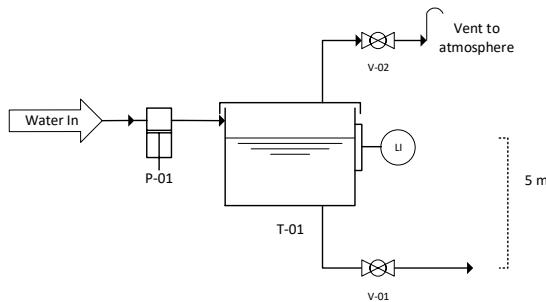
$h$  is the height of the liquid

$g$  is the acceleration due to gravity (9.8 m/s<sup>2</sup> at the surface of the earth).

An example of this hydrostatically induced pressure is if you dive to the bottom of a pool and feel a force in your ears (the weight force of the liquid water above you). As a guide, diving 10m below the surface is equivalent to 1 additional atmosphere of pressure.

When draining a tank, it is important that no vacuum is created at the top of the tank. This can either stop the flow (if the design pressure of the tank is larger than the hydrostatically induced pressure difference) or can cause the tank to implode (if the design pressure of the tank is less than the hydrostatic head).

As a simple everyday example: Imagine putting a straw into your glass of soft drink. If you put your thumb over the mouth end, and raise the straw up, you can lift soda out of the cup within the straw. If you remove your thumb, the drink immediately drains out. Putting your thumb over the end of the straw means that when the liquid goes to flow out, it creates a small vacuum at the top of the straw, that acts against the hydrostatic weight force of the liquid in the straw (thus preventing it from flowing out). Only by releasing this vacuum at the top of the straw is the liquid able to freely drain out of the straw.

Worked Example 4.1

A closed roof tank is used for storing water. The tank can freely vent to atmosphere, so when the tank is filling, air at the top can be pushed out. If the positive displacement piston pump (P-01) is off, water can still freely drain out by opening V-01 (note that a positive displacement piston pump cannot have liquid 'sucked through' it, the way a rotary pump could if there was a downstream low pressure; it's not open on both sides). So if the system is open to atmosphere, the pressure at the surface of the liquid water is always at atmospheric pressure.

In error, one day V-02 is closed. P-01 is off (liquid cannot be pulled through the pump so this is essentially a closed valve). The tank has a liquid height of 5m. If the tank has been rated to a differential pressure of +2atm (it will not rupture unless the internal pressure is 2atm larger than the external pressure) and -0.4 atm (it will not implode unless the internal pressure is 0.6 atm less than the external pressure) will the tank implode?

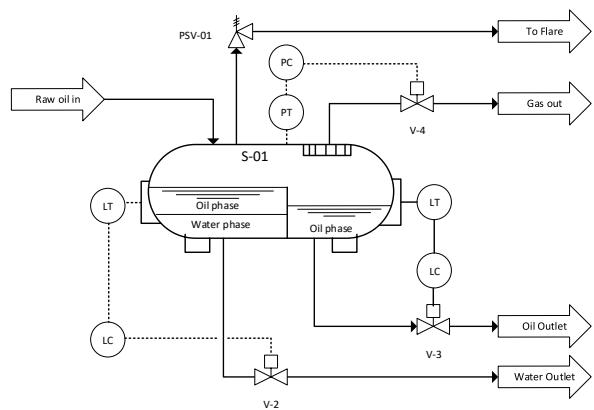
What changes could be made to the design to better protect the tank?

## 4.2 Separator

A separator is a pressure vessel used for separating a multiphase flow into different streams (usually gas and 1 or more liquid phases). It can be used when transporting steam as a trap to collect condensate (separating steam and liquid water that may have condensed in the line). In the oil and gas industry, 3-phase separators are used for separating raw oil from a well head into natural gas, crude oil, and a water-rich stream (the oil and water will phase separate out, making 2 liquid phases).

Separators work on the principle that different phases have different densities, which allows them to stratify due to 'gravity' settling (gas on the top and most dense phase on the bottom). A 3-phase separator will usually contain a weir, that allows the lighter liquid phase (usually oil) to spill over, while the heavier liquid phase (usually water) to remain behind. A gas stream can be collected in the overhead space (usually after passing through a demister to collect any entrained liquid mist).

3 Phase separators are usually fitted with a pressure safety valve (PSV) if the system pressure builds up. The PSV is a spring-loaded valve, that pushes down to keep the valve closed with a pre-defined force. If the system pressure exceeds this set tension (a mechanical set-point) the valve is forced open, and the gas is allowed to vent. The PSV will usually be set to a pressure 10-20% below the pressure rating of the vessel (providing a last line of defence to prevent catastrophic failure). One possible sample control scheme for a 3-phase separator is shown below.



## 4.3 Heat Exchanger

Heat exchangers are used to move thermal energy between liquid streams, but usually without the streams coming into physical contact (usually the 2 liquids are separated by a physical wall). They can be used for both heating and cooling operations on a process stream. Heat exchangers are used throughout your day in a range of devices (few simple examples below):

1. Refrigerator: a fridge has an air-cooled condenser at the back of the unit (the back of your refrigerator often feels hot) which exchanges heat between the working fluid in the fridge and the surrounding air.
2. Gas heaters. When using a gas heater, you do not burn natural gas and let the hot fumes fill your house (that creates a risk of carbon monoxide poisoning). Instead, you burn the methane, which then heats a 'hot box', so

that air can be blown through, which is heated and goes into your home. The exhaust gases from the combustion are sent via a chimney flue to the outside. So, the air and flue gases are physically separated from mixing by the walls of the hotbox.

3. Hot water systems. If you have a gas hot water system, the gas is burnt to heat up a vessel of water. Like the gas heater, the methane combustion flue gases and the water do not come into physical contact. So, they exchange heat.
4. Cars. The radiator in your car (if it is a combustion engine, as opposed to an EV) is used to cool the engine while it runs (the coolant in a car is usually water, which may also contain ethylene glycol to lower its freezing point).

The enthalpy change experienced in one of the streams (assuming no phase change) can be given by:

$$\Delta H = m C_p \Delta T_{fluid} \quad \text{or} \quad \Delta H = m C_p \Delta T_{fluid}$$

$m$  is the mass of the liquid (kg). Or it can be expressed as  $m$ , as a mass flow rate (kg/s)

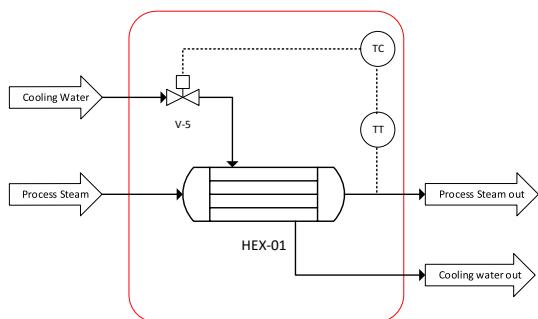
$C_p$  is the specific heat capacity (J/kg K)

$\Delta T_{fluid}$  is the change in temperature (K or °C, as it's a difference in temperature these will be the same). This temperature change refers to the change in temperature of the liquid (as it is heated or cooled).

This means  $\Delta H$  is the change in enthalpy (J). Or it can be expressed as a flow of energy  $\Delta H$  (J/s) meaning the change in enthalpy of the stream per second.

What is the physical origin of this? In a single phase (e.g., a liquid) we can think about the amount of energy that is has as relative to the system temperature- the temperature gives a measure of the kinetic energy motion of each atom, so multiplying the temperature by the amount of matter (the mass) and a constant that relates energy and temperature (heat capacity) gives a way to determine the total energy of the system. Adding or removing energy from the system (by heating or cooling it) will change this total energy.

Imagine a process stream is leaving a reactor at a high temperature and we want to cool it to constant lower temperature. The process stream is sent to a heat exchanger and the flowrate of cooling water can be tuned to keep the process stream temperature at a defined set point. A sample control scheme is shown below:



Thinking about an energy balance around the heat exchanger. If no energy is lost to the surroundings across the system boundaries, then any energy lost by the process stream must be gained by the cooling water. Or to express it another way:

$$|\Delta H_{\text{Process stream}}| = |\Delta H_{\text{Cooling water}}|$$

The conventions for energy changes can be a little confusing. In this case the process stream is losing energy (it's getting cooler) while the cooling water stream is gaining energy (it's getting warmer). So, when talking about the streams, we would say the process stream has a negative enthalpy change and the cooling water undergoes a positive enthalpy change. But if we were talking about the system boundaries in the example above, the process stream tends to add energy to the system (it comes in hot and leaves cold, so dumps some energy into the system) but the cooling water comes in cold and leaves hot (it takes energy from the system).

If energy is also lost across the system boundaries, then the process stream might be cooled by a little bit extra (due to heat leakage). So, we could write:

$$\Delta H_{\text{Process stream}} + \Delta H_{\text{Cooling water}} + \Delta H_{\text{Environment}} = 0$$

So, we can complete the energy balance between the 2 streams (and use a term to account for any environmental losses). But if we're given the specific dimensions of the heat exchanger, can we calculate how much energy is transferred between the streams? (If the heat exchanger is larger, we might intuitively expect more heat transfer). How can we size our heat exchanger or if we are given all the physical dimensions and properties of an existing heat exchanger, can we calculate the heating duty we might expect? Yes, we can solve this, and we'll discuss it next.

To reason through an answer from a physical perspective, we'll begin with a simple thought experiment: Imagine a metal rod is heated on a stove until it becomes red hot. Dropping the rod into a pot of water causes the water to boil vigorously and bubble up everywhere: we can conclude there has been a large and fast transfer of thermal energy into the water (causing a phase transition or bubbles of steam that cause the violent bubbling). We remove the rod from the water and heat it again over the flame, but only until it is lukewarm. Dropping it into a fresh pot of water, we observe the water gradually heat up, but there is no vigorous boiling as in the first case. We can conclude that less energy has been transferred to the water (the rod contained less thermal energy when dropped in), but also that the rate of energy transfer has occurred much more slowly.

The conclusion we might draw from this is that the rate of heat transfer (the speed at which thermal energy is transferred from the rod into the water) is proportional to the temperature difference between the 2 materials (we can think of the temperature as an amount of thermal energy per atom). The large temperature difference in the first case causes a high rate of energy transfer. The smaller temperature difference in the second case means the rate of energy transfer is much smaller. To express the result another way: the temperature difference provides the driving force to energy transfer. In later subjects, you will also learn analogous principles that a concentration difference can provide a driving force to mass transfer (diffusion) and a velocity gradient can create a shear stress (momentum transfer).

To express our finding on thermal energy transfer mathematically, we could say the heat flow ( $Q$ , also called the duty, J/s) is a function of the temperature difference ( $\Delta T$ ):

$$Q = f(\Delta T_{\text{between fluids}})$$

Now imagine the rod was much larger in size, or more specifically if it had a larger surface area for the same mass. When dropping it into the water, we might expect the thermal energy could discharge much faster. There is more contact area between the hot surface and the bulk liquid, so more places for the energy to transfer through. So, our second finding could be that:

$$Q = f(\Delta T_{\text{between fluids}}, A)$$

Heat flow (duty) is dependent on the area (through which the heat transfer takes place,  $A$ ). This area is not the cross-section of the rod, but the external area of the rod that contacts the liquid phase.

Finally, we can see the rod rapidly discharges its thermal energy when dropped into water, but it does not rapidly lose this energy in the air (it will cool gradually in the air but at a much slower rate than in the water). If it were in the air, we could blow on it to cool it faster (like blowing on hot soup). So perhaps we can conclude there is some material effect, where a physical property of the phase that surrounds the rod, and its motion, changes the rate of thermal energy transfer. We refer to this as the heat transfer coefficient ( $U$ ) and it is a material property of the 2 phases (the metal and the water/air) as well as their interfacial effects as well as bulk conditions (like the movement of the surrounding liquid phase). We often imagine the interface as having an immobile layer of fluid at the surface (often called a laminar boundary layer). This layer of fluid tends to impede the heat transfer, as the heat needs to conduct through it. But if we mix the fluid over this boundary layer, convection helps carry the energy away from the surface through the bulk flow of the liquid phase. This can help explain why blowing on the surface can help cool it (we're constantly exchanging the warm air around the surface with low temperature air). Heat exchangers are sometimes designed with baffles, to help fluid flow patterns to aid this mixing.

Bringing all terms together, to express it mathematically now, we can say the heat flow is then a function of these 3 properties of the system:

$$Q = f(\Delta T_{\text{between fluids}}, A, U)$$

From experiment, we find that the heat flow is linearly proportional to each one of these parameters: doubling the temperature difference, doubles the heat flow if everything else is equal; doubling the heat transfer area doubles the heat flow if everything else is equal.

So, the relationship can be expressed as:

$$Q = U A \Delta T_{\text{between fluids}}$$

Where:

$Q$  = heat duty (flow of energy, J/s)

$U$  = heat transfer coefficient (J/s m<sup>2</sup> K)

$A$  = area for heat transfer (m<sup>2</sup>)

$\Delta T_{\text{between fluids}}$  = temperature difference (between the 2 streams, not the change in temperature in one stream, °C or K- as this is a difference, these units give the same result)

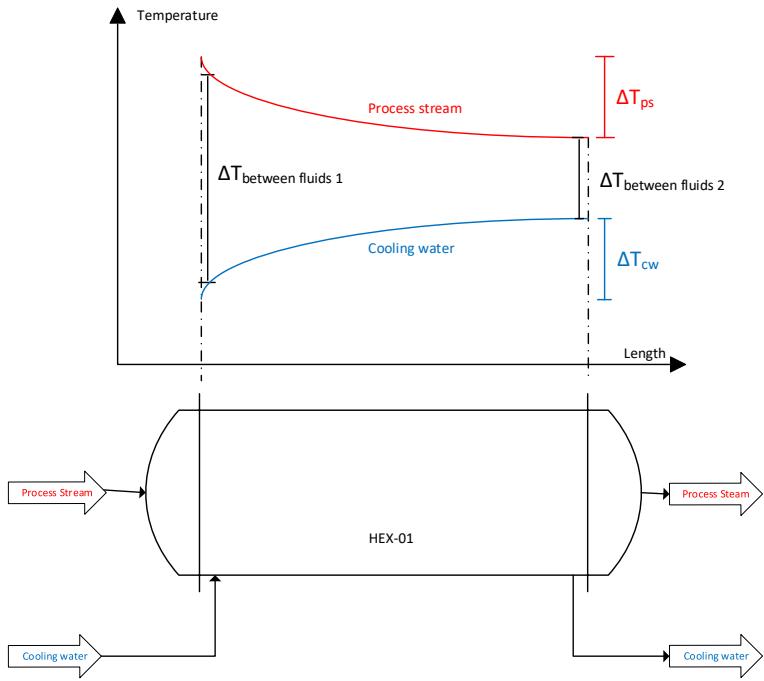
Imagine a scenario where a hot process stream is being cooled by cooling water. The process stream enters a heat exchanger at high temperature, then as it passes through it and loses thermal energy by contacting the colder cooling water stream. So, the process stream is cooled as it passes through the exchanger, while the cooling water is heated as it moves through (this is sometimes called a co-current heat exchanger arrangement).

If the system is well insulated and there are no energy losses to the environment, then we can say:

$$Q = m_{\text{process stream}} C_p_{\text{process stream}} \Delta T_{\text{Process stream}} = m_{\text{cooling water}} C_p_{\text{Cooling Water}} \Delta T_{\text{Cooling water}} = U A \Delta T_{\text{between streams}}$$

From an overall energy balance, the energy lost by the process stream must match the energy gained by the cooling water stream. And, also, for the specific design of the heat exchanger, this duty moved between streams must also equal the energy moved through the walls of the heat exchanger.

The situation is represented in the diagram below:



One problem now arises: The difference in temperature between the two process streams is not constant. It varies as a function of length through the heat exchanger. This heat exchanger has been designed in a co-current flow configuration (both streams flow in the same direction). So, the temperature difference between the 2 flow streams is greatest at the inlet, then they tend towards a common point (they asymptote towards a weighted halfway point).

A more accurate way to write the heat transfer between the 2 streams is then to write it in the differential form:

$$dQ = UA dT$$

The duty between the 2 streams ( $Q$ ) is then the integral for all possible temperatures along the length of the heat exchanger. One way to approximate this solution, for constant  $U$  along the length of the heat exchanger (no temperature dependence in  $U$ ) is to take an average temperature. But we use the log-mean temperature difference between the 2 streams (not the average temperature difference).

$$\Delta T_{LM} = \frac{\Delta T_{between\ fluids\ 1} - \Delta T_{between\ fluids\ 2}}{\ln\left(\frac{\Delta T_{between\ fluids\ 1}}{\Delta T_{between\ fluids\ 2}}\right)}$$

$$So Q = UA \Delta T_{LM} = m_{process\ stream} C_{process\ stream} \Delta T_{process\ stream} = m_{cooling\ water} C_{cooling\ water} \Delta T_{cooling\ water}$$

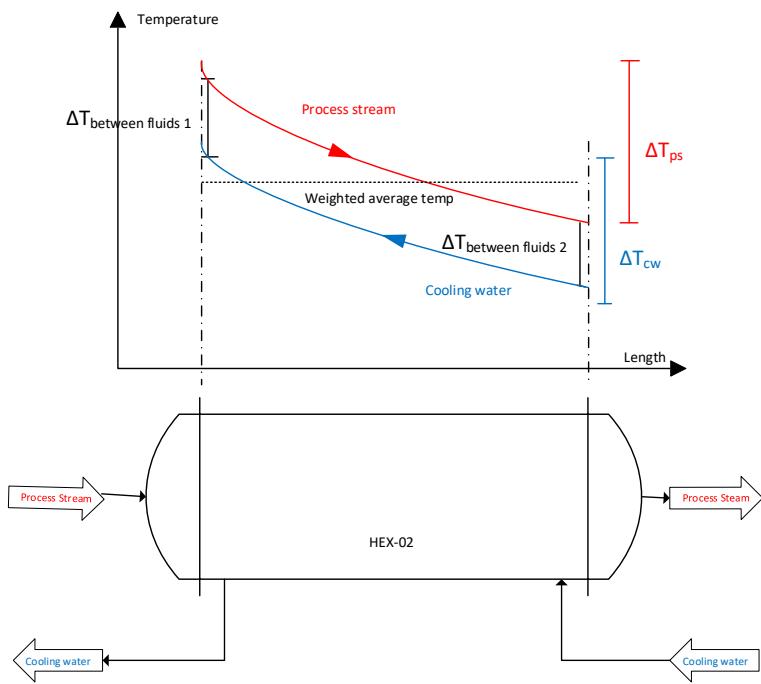
#### 4.3.1 Co-current vs Counter Current

In the example above, the flow configuration is drawn as a co-current arrangement. The 2 streams flow in the same direction through the heat exchanger. The hottest part of the hot stream (the process stream) and the coldest part of the cold stream (the cooling water) contact at the same point and trend towards a common mid-point (a weighted average temperature). If the heat exchanger is made larger (larger A) the system tends closer towards this mid-point, but can never reach it (it as an asymptote). As the 2 streams approach thermal equilibrium, the driving force to heat transfer keeps getting smaller and smaller.

An alternative arrangement is a counter-current heat exchanger flow configuration. In this arrangement, the flows of the streams are in opposite directions in the heat exchanger. The hottest part of the hot stream contacts the hottest part of the cold stream. The coldest part of the cold stream contacts the coldest part of the hot stream. So, in this arrangement, there is always a larger temperature difference maintained between the 2 streams, which maintains a larger driving force for the heat transfer.

In a counter-current heat exchanger, the outlet temperatures of the hot and cold stream can pass the weighted average temperature, so for a given sized area heat exchanger (fixed area) it can produce a larger temperature change in both fluid streams.

This is an important point to understand, because all the internal configuration stays the same. Just by changing a little bit of piping and switching the inlet/outlet of a single stream, you can often produce a 10-25% improvement in the heat exchanger performance; it just comes from understanding how the system works. Most importantly, you don't need to take my word for this. In the Fun CE practical, you will design and build a heat exchanger, then test it in the wetlabs. So, you will have the opportunity to test this statement for yourself (if you would like to).

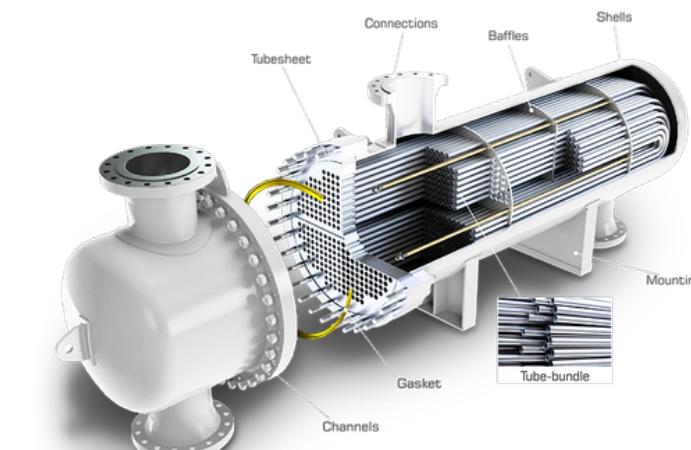
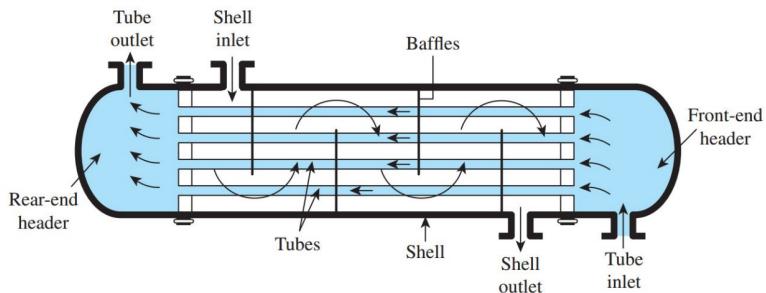
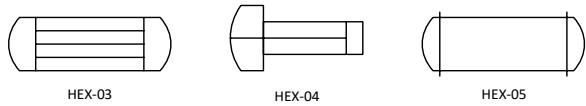


Minimizing the capital costs of a heat exchanger usually means minimising the required area (which reduces the size and amount of material required) for a given heat transfer duty. Minimizing the area therefore comes by maximising the temperature difference (for example by changing the flow configuration) or by increasing the heat transfer coefficient (this can be by using material with a high thermal conductivity or arranging a flow configuration to improve heat transfer, such as using baffles).

#### 4.3.2 Type of Heat Exchangers

There are many different physical designs for heat exchangers. All the theory we have discussed in this sub-section remains the same, but how the flow is laid out (and how the heat transfer area is arranged) may change for specific industrial needs and for ease of fabrication (as tubes and pipes come pre-manufactured, it is easier to build equipment from this rather than an irregular custom design).

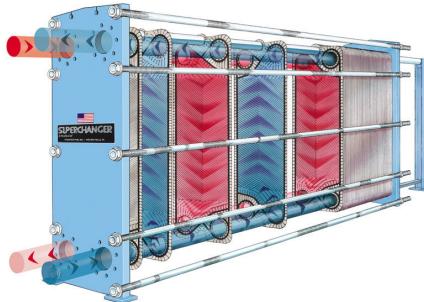
1. Shell and tube heat exchanger. A series of tubes inside of a larger shell, where one fluid can flow through the tubes, while the other fluid flows around the tubes through the shell. Perhaps the most common type of heat exchanger and widely used in the oil and gas industry.



- Plate heat exchanger. These are widely used in food handling because they can be easily opened and cleaned and have few dead spaces for bacteria to grow. So, for example plate heat exchangers are commonly used to pasteurize milk.



HEX-06



3. Co-axial heat exchanger. This is a very rare type of heat exchanger because it is difficult to service. AutoCAD Plant 3D and Visio don't have a pre-defined P&ID symbol for this unit. But it is arranged as a pipe within a pipe, so a jacket always surrounds the tube. (I've really just included it here because it is easy to understand and build, so might be of help when thinking about your practical).

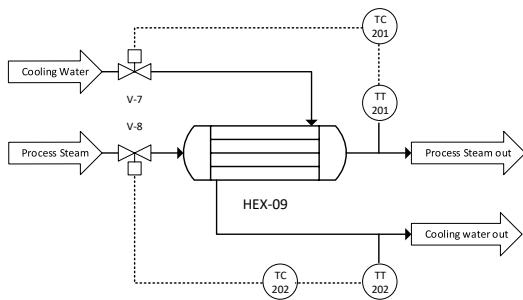


A common problem with all types of heat exchangers is *fouling*. If material attaches to the heat transfer surface, it can act like insulation to increase the resistance to heat transfer (lowering  $U$  and reducing the heat exchanger performance). This is particularly common when processing heat sensitive fluids. For example, in the pasteurization process, milk is heated for a short period of time to kill bacteria. But overheating the milk or leaving it at elevated temperature for too long can 'cook' the milk (denature the proteins) which can cause it to stick to the surface. Removing the fouling layer usually means shutting down the process, opening the heat exchanger and manually cleaning off any solids attached to the heat transfer surface.

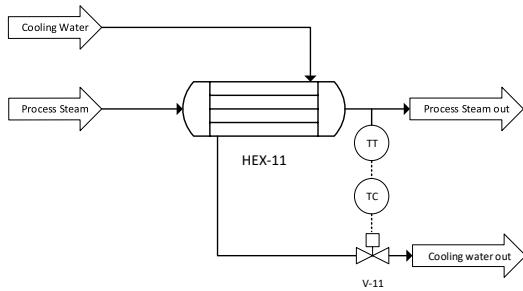
#### Worked Example 4.2

Consider the control arrangement of the heat exchanger below. The shell side and tube side are both full of liquid (there is no room for a liquid hold up). Will the control arrangement work? Explain your reasoning. You can think about a degree of freedom analysis or the mathematical operations from [above](#).

**Commented [CH5]:** For the worked example solutions. No it will not work. You can't specify the flowrate on both streams (one has to be floating to meet the energy balance requirement). You can also think about what would happen if TC-201 was too high and TC-202 was too low. TC-201 would tend to open V-7 to get more flow, but this would tend to push T-202 lower. It would open V-8 more further exacerbating the problem at TT-201. So the 2 loops would fight against each other.

Worked Example 4.3

Consider the control arrangement of the heat exchanger below. The shell side and tube side are both full of liquid (there is no room for a liquid hold up). Will the control arrangement work? Explain your reasoning. You can think about a degree of freedom analysis or the mathematical operations from above.



**Commented [CH6]:** Yes it will work. Although the valve is on the outlet of the CW, a pressure wave will propagate up the water stream at the speed of sound. As the line and heat exchanger is full of water, it will almost instantaneously adjust the flow through the line. Thinking about a mass balance around the CW side: at steady state (no accumulation within the system) the flowrate in must equal the flowrate out.

#### 4.4 Boilers and Power Generation

Boilers are used to produce steam. The latent heat of steam is very high (relative to other fluids) so steam can be used to move energy throughout a plant (i.e., heating steam). Steam can also be superheated beyond its boiling point and used to drive a turbine to generate electricity (i.e., high pressure superheated steam). In both cases, the steam is generated within a boiler.

Boilers function like a heat exchanger, in that they supply energy to a fluid stream (typically water). But boilers are designed to generate a phase change to create steam. So, although the core principles and heat transfer theory are the same, the physical design, layout and control can differ from a heat exchanger design.



**B&W's water-tube package boiler offers more water-cooled surface, which in turn helps to meet today's stringent emissions regulations.**

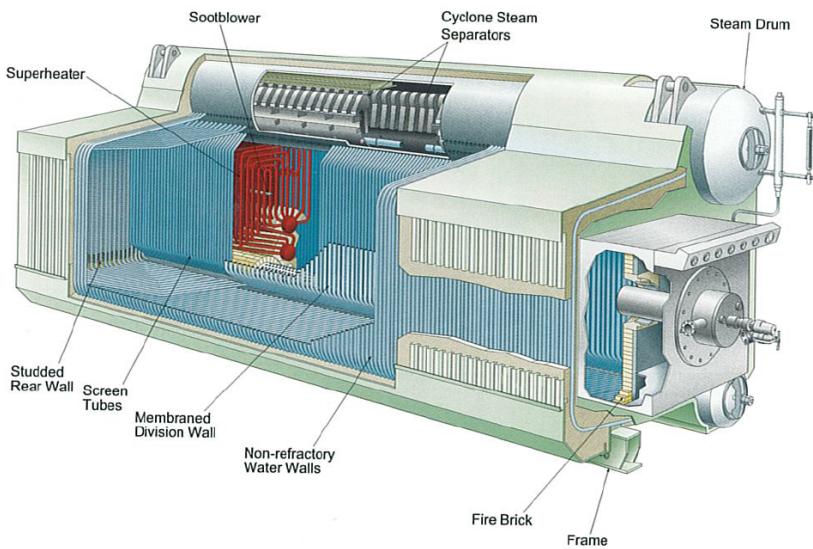
A steam generator usually consists of 2 drums: an upper drum (commonly called the steam drum) and a lower drum (commonly called the mud drum). Tubes called the down-comer connect the steam drum and mud drum. The down-comer tubes do not go through the furnace so the water passing through here has comparatively higher density and will

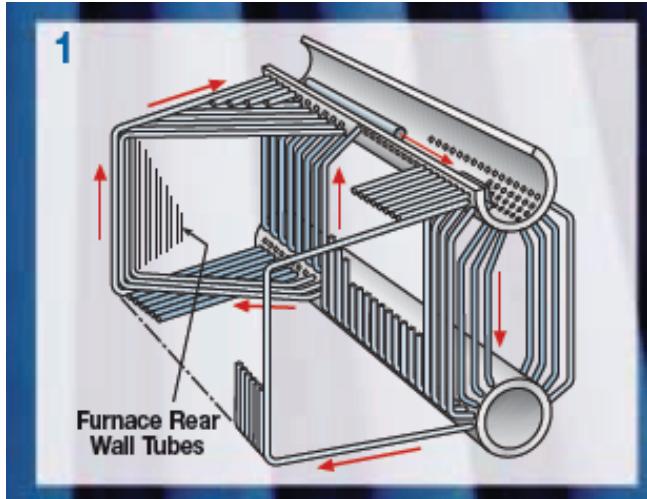
tend to sink (thus the name 'down-comer'). A second set of tubes connects the mud drum back to the steam drum, but these pass through a furnace; water in these lines boils and rises, driving the steam and any unboiled water back to the steam drum and forcing recirculation of the water between the drums.

In the steam drum, the saturated steam is separated from the boiling water for use within the plant (e.g., generating power, or as a heating utility). Impurities entering in the boiler will tend to accumulate in the lower drum, as the water is boiled off (hence the name mud drum). So, at periodic intervals a valve on the bottom of the mud drum is opened to push out the accumulated sediment (a process known as blowdown).

Most boilers are designed to keep water at a minimum level in the steam drum, so water remains in the down comer. Without water recycling in the system, many furnaces will over-heat.

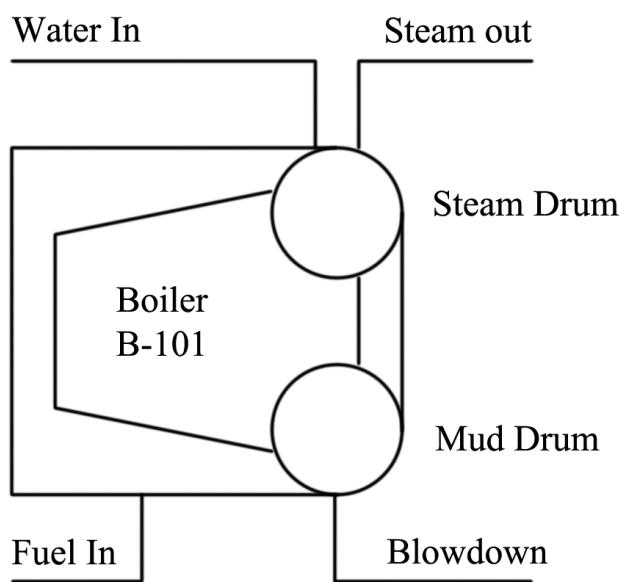
As the water in the steam drum is at its boiling point, the only way to change the temperature of the steam generated by the boiler is to change the temperature of the steam drum. Increasing the fuel flowrate in the furnace will only increase the rate at which the water boils; it cannot change the outlet temperature of the saturated steam (for example turning up the gas on a pot of boiling water does not change the temperature the steam boils at, it only changes the rate at which steam comes off the pot). After the steam has left the boiler, we can drop the pressure of the line to produce superheated steam (steam heated beyond its boiling point). Usually, superheated steam would be used to drive a turbine to generate power (because the turbine is only designed to handle vapour and any condensation on the turbine blade can damage them). If the steam is being used to move energy it would be kept closer to saturation, because steam has a low specific heat capacity but a high latent heat; the energy in the steam comes from condensing it to a liquid, not heating it beyond condensation to superheated conditions. Super-heating the steam a little bit beyond saturation (from a small pressure drop) can reduce condensation in the pipelines as it cools (due to incomplete insulation on the line).

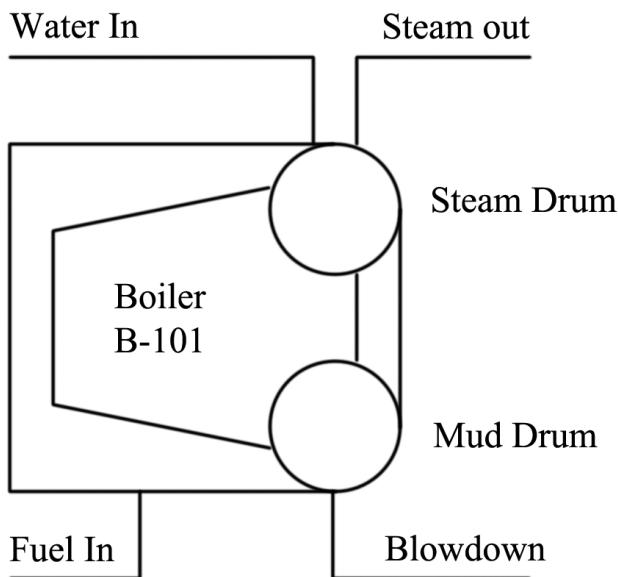




Worked Example 4.4

Based on your understanding of the operation of a boiler, sketch a control scheme for the simplified steam boiler schematic below.





#### 4.4.1 Steam

Boilers will produce steam at the highest pressure required in the system (it's easy to drop the pressure of the steam after the boiler but relatively expensive to try to increase the line pressure with compressors). Pressure energy from the steam line can be converted to electricity (with a turbine) which generates lower pressure steam. For grades of steam (and normal operating ranges of a boiler):

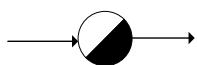
Low pressure steam	5 bar gauge	160°C
Medium pressure steam	10 bar gauge	184°C
High pressure steam	40-50 bar gauge	up to 250°C

If you want to heat process streams above 250°C it would usually be done with hot oil or direct heating, rather than with a steam line.

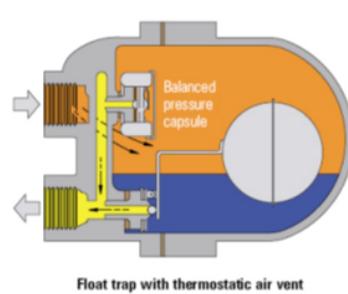
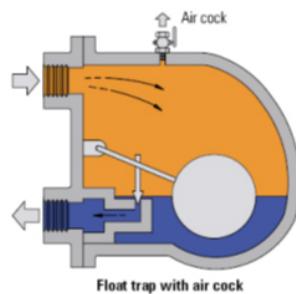
Once the steam has been generated, it needs to be distributed throughout a plant. Steam distribution can sometimes cause losses as high as 60% (pressure drop losses, inadequate insulation etc). Steam condensate is usually collected and returned to the boiler for reuse; it saves the energy required to heat the water from ambient conditions up to the boiling point. But collecting this hot water requires a condensate trap in a steam line and a condensate pipeline to return the water.

**Steam Trap**

A steam trap is a device designed to pass liquid water but hold up steam. It is used in the condensate trap above to prevent steam from leaving in the condensate line. It could also be used on a heat exchanger, to ensure any water entering as steam condenses in the exchanger before leaving.



Steam traps can be designed on a range of different principles, but a common one is a mechanical trap that passes liquid water (but holds up steam) based on the density of the fluid (i.e., a float trap).

**Module 4 Summary****Key points:**

- Tanks and pressure vessels
- Separators
- Heat Exchangers:
  - Heat transfer (enthalpy)
  - Configuration (co-current vs. counter-current)
  - Types (shell and tube, plate, co-axial)
- Boilers

**Key Skills:**

- Understand design, operation, and safety features of the above equipment
- Analyse, describe, and design heat exchanger control

## Module 5 – Large Kit: Reactors and Reaction Kinetics

Chemical reactors are one of the core major units everyone thinks of when thinking about chemical engineering. But a chemical reactor can encompass a very wide range of industries: a digester for processing waste water (water industry), a blast furnace for making steel (mining), a fermenter for making beer (food industry), a bioreactor for making vaccines or pharmaceuticals (medtech), a biomass boiler (renewable energy). And many, many other examples.

In this section we will first introduce the theory for understanding reaction kinetics. Then we will introduce a few idealized concepts for reactors and build on these core assumptions to solve useful problems with reactors (for example sizing the unit from our first principles).

### Outline

Primary learning outcomes for the module:

1. Develop an understanding of basic definitions in reaction kinetics: elementary vs non-elementary reactions; reaction order; Arrhenius law; reactor types
2. Derive solutions to a range of irreversible reaction kinetics at constant volume and temperature: zeroth order, first order and second order
3. Develop an appreciation of more complicated reaction kinetics, with an understanding of how they would be solved: reversible reactions; changing order reactions; autocatalytic reactions and variable volume reactions.
4. Apply simple rate equations to a range of reactors to size the units: Batch reactor, Plug flow reactor and mixed flow reactors

**Commented [CH7]:** We should have this for every module so students know what they're suppose to know at the start.

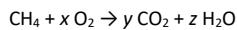
**Commented [NB8R7]:** Good idea, I'll make them for the other modules too

A useful resource is Levenspiel's *Chemical Reactor Engineering*.

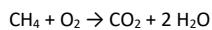
### 5.1 Recap of your pre-existing knowledge

In Chemistry pre-requisites for Fun CE, you will have already come across the concept of reaction stoichiometry. It's founded on the law of conservation of mass: material can be transformed from one molecular to another, but the atoms themselves are not created or destroyed (this rule is not true if there are nuclear reactions).

It allows us to balance the number of molecules that will be created or consumed during a reaction, by tracking the atoms during the reaction. For example, the combustion of methane:



$x$ ,  $y$  and  $z$  are unknown stoichiometric numbers for the combustion of 1 molecule of methane ( $\text{CH}_4$ ). Following the carbon atom first, we have 1 carbon atom on the left (in the methane). So, we must have 1 carbon atom on the right. There is currently 1 carbon atom in the  $\text{CO}_2$  so if  $y=1$ , the atoms will balance. Next looking at the water ( $\text{H}_2\text{O}$ ) and following the hydrogen atoms, we have 4 hydrogens on the left-hand side and 2 hydrogen atoms in the water. So, if  $z = 2$ , the hydrogen atoms will balance. Finally following the oxygen atoms (O), there are now 2 oxygen atoms on the right-hand side (one oxygen in the water, but  $z=2$ , the stoichiometric number of the water). There are 2 oxygen atoms in the  $\text{O}_2$  on the left and so if  $x=1$ , the equation now fully balances.



In Material and Energy Balances you will be exposed to defined metrics which quantify overall reaction conditions. For example, for a chemical species A in a reactor, you could define the:

$$\text{Conversion} = \frac{\text{Amount of Reactant A Consumed (in all reactions)}}{\text{Total amount of Reactant A}}$$

$$\text{Yield} = \frac{\text{Amount of desired product produced}}{\text{Maximum theoretical amount of product (all limiting reactant in desired rxn)}}$$

$$\text{Selectivity Ratio} = \frac{\text{Amount of A consumed in Rxn 1}}{\text{Amount of A consumed in Rxn 2}}$$

These types of values (conversion, yield, selectivity ratio or selectivity as a percentage) are all based on the overall performance of the reactor and the reaction pathway. You can calculate the conversion of component A, if you know the amount of A in and the amount of A out. But you can't *predict* the conversion of A, if you knew the reactor volume, reaction pathway and other parameters like the reactor temperature.

This module is interested in predictive calculations. We will model the **reaction rate** so for example, we can predict how the conversion of species A changes as a function of time (or as a function of distance through the reactor). So, we are building on the knowledge from Material and Energy Balances to get a more advanced understanding of chemical reactions.

We can already intuitively understand reaction rate, for example consider these 2 oxidation reactions: 1) burning natural gas (in a cigarette lighter) and 2) the rusting of iron. Although both involve the oxidation of a reactant (methane or iron) the reactions proceed at very different rates (or time scales). The higher reaction rate in burning the methane can create high localised temperatures (for lighting a cigarette) for a short time.

Reactions can take place in homogeneous media (single phase, consistent material, and thermodynamic properties) or heterogeneous media (multiple phases, inconsistent material, or thermodynamic properties). But in this subject, we will primarily be studying homogeneous single-phase reactions.

## 5.2 Manual Calculations vs Software Packages

This module is designed to teach you the basic theory of reaction kinetics and will focus on *manual* solutions of the rate equation. However, often the reaction kinetics may be too complicated to solve by hand (sometimes an analytical solution may not even be possible). While doing this module, you should also concurrently be learning about reaction models in HYSYS (in the tutorial classes). This module is designed in conjunction with the HYSYS module: the manual analytical solution and the iterative computational solution.

## 5.3 Defining Reaction Rate

Reaction rate is designed as a measure of the speed at which reactants are converted into products. So, stated in words (rather than as an equation) what do you think would be an appropriate definition of reaction rate? What units might reaction rate have?

A common initial guess is that reaction rate would be the change in number of moles of reactant per unit time (units of say moles/sec). At first, this might seem like a good definition that fits our criteria, except that number of moles is an extensive property (it depends on the total amount of reactant). So, defining reaction rate in terms of an intensive

property is more convenient for us (so it is independent of total amount). Therefore, a reaction rate is usually defined as the moles of reactant consumed, per unit time and per unit volume.

$$-r_A = -\frac{1}{V} \left( \frac{dN_A}{dt} \right)$$

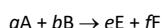
Where:

- $r_A$ : Reaction rate (rate of consumption of molecule A)
- V: System volume
- $N_A$ : Total moles of A
- t: time

So the units of rate are (moles of A disappearing)/(volume time) or in SI g-mole/(m<sup>3</sup>sec). Taking the volume inside the integral, you could think of the rate as the change in *concentration* of A as a function of time (rather than total moles). This definition only applies for a closed system so for example adding water to cordial to dilute it might reduce the concentration of the cordial, but not because it has reacted (the system is open so there is a mass transfer across the system boundary).

The negative sign is included to emphasise that the moles of A are being consumed (A is the reactant and so its concentration is dropping with respect to time).

For a given reaction stoichiometry, we can relate the reaction rate by the ratio of stoichiometric numbers. So for example, if we have a reaction stoichiometry given by:



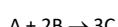
We can say that:

$$r = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{e} \frac{d[E]}{dt} = \frac{1}{f} \frac{d[F]}{dt}$$

Where [X] denotes the concentration of the species. Remember that stoichiometric numbers are negative for reactants and positive for products.

#### Worked Example 5.1

Say we have a stoichiometric equation given by:

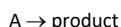


- a) If we know the initial rate of change of A to be -2 moles/m<sup>3</sup>sec, what is the initial rate of production of component C?
- b) What is the initial rate of change of component B?

What parameters might affect the reaction rate? Things like: concentration of reactants (or pressure for gas phase reactions); system temperature; activation energy; and the presence of a catalyst. Perhaps we already intuitively understand from our experiences with the real world that reaction rates are likely to be a function of temperature and concentration.

$$\text{Rate} = f(T, C)$$

Stated more explicitly, a stoichiometry like:



Will usually have a rate equation form like:

$$-r_A = k(T) \times [A]^n$$

Where:

*k*: A temperature dependent rate constant

[A]: Concentration of A

*n*: A power the concentration is raised to (or the *order* of the rate equation)

#### 5.4 Elementary and non-Elementary Reactions

An elementary reaction is one in which the chemical species react directly to form the products in a single reaction step (and with a single transition state). i.e., no reaction intermediates are detected and there is no need to postulate intermediate states to describe the reaction on a molecular scale.

A non-elementary reaction has a series of intermediate reaction steps between the reactant and product, which are required to describe the reaction pathway.

In general, it is impossible to know whether a reaction is elementary or non-elementary based on the reaction stoichiometry. But if we know the reaction is elementary, we can use the stoichiometry to determine the rate equation. You can reason this through from collision theory; if 2 species need to react (A and B) then a drop in the concentration of either has a corresponding drop in the reaction rate.

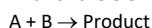
So, for the elementary reaction:



The rate equation is:

$$-r_A = k(T) [A] \quad (\text{Eqn 3.1})$$

And for the elementary reaction:

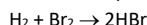


The rate equation is:

$$-r_A = -k(T) [A][B] \quad (\text{Eqn 3.2})$$

For non-elemental reactions, there is no correlation between the stoichiometry and the rate equation. The reaction rate cannot be known without a reaction model or experimental data.

So, for example for the reaction:



The rate equation is:

$$-r_{\text{HBr}} = \frac{k_1(T)[\text{H}_2][\text{Br}_2]^{\frac{1}{2}}}{k_2(T) + [\text{HBr}]} \quad (\text{Eqn 3.3})$$

So, it does not correlate to the reaction stoichiometry. You can reason this though because the reaction pathway from reactants to products is a stepwise reaction with several reaction intermediates. One of these steps may be the rate limiting step in the reaction pathway and so the overall reaction rate may be harder to predict.

## 5.5 Order of a reaction

Reaction rates often have a form like:

$$-r_A = k[A]^m[B]^n$$

The exponents in the reaction rate equation ( $m$  and  $n$ ) are called the reaction orders. We can refer to the order of the reaction (meaning the overall order =  $m + n$ ) or we can refer to the order of a species within the reaction (for example the order of reactant A is  $m$ ). In elementary reactions, the reaction order of each chemical species equals the stoichiometric number. So, in equation 3.1, 3.2 and 3.3 above, the reaction orders would be: first order; second order and 1.5 order respectively.

## 5.6 Temperature dependence: Arrhenius Law

So far, we have written the rate constant,  $k(T)$ , only as a function of temperature in each rate equation. The temperature dependence of the rate constant is modelled by the Arrhenius Law:

$$k(T) = k_0 e^{\left(\frac{-E_a}{RT}\right)}$$

Where:

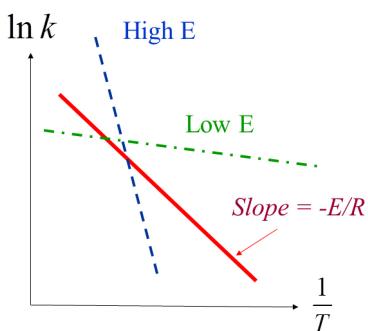
- $k(T)$ : Rate constant
- $k_0$ : frequency factor (sometimes called the pre-factor constant and sometimes written as  $A$ )
- $E_a$ : Activation Energy
- R: Universal Gas Constant (8.314 J/K mol)
- T: Temperature

The logic of the Arrhenius law is that the molecular bonds are held within activation energy wells ( $E_a$ ). If the thermal energy ( $kT$ ) is sufficient to overcome this activation energy, the reaction can proceed to a new lower energy state. As the bonds vibrate with some fixed thermal energy (at all temperatures above 0K) there is always a finite possibility of the reaction proceeding, but as macroscopic scale we perceive this as happening at a lower rate.

Taking the natural log of both sides of the rate constant we can show that:

$$\ln(k) = \ln(k_0) - \frac{E_a}{RT}$$

$k_0$ ,  $E_a$  and R are all constants. So another way of presenting the relationship is to plot  $\ln(k)$  against  $1/T$ :



Looking at this graph emphasises a number of important conclusions:

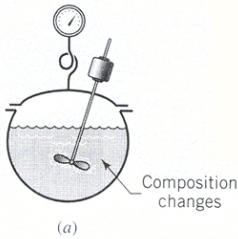
1. For higher activation energies, the rate constant is more sensitive to T
2. A given reaction is more sensitive to T at low temperatures
3. The pre-factor constant ( $k_0$ ) does not affect the reaction rate's sensitivity to T
4. For a given reaction, changes in the activation energy indicate a change in the reaction mechanism

### 5.7 Reactor Design

Once we know the reaction kinetics (the form of the rate equation) we can begin to design a reactor. What parameters might affect the design of the reactor? Temperature certainly (as we know it affects the rate). But this is something we will probably try to control after the reactor is built (for example by changing a flowrate of cooling water). What parameters might affect the physical design: things like the reactor volume (which changes the residence time for a given flowrate); the type of reactor; the method of operation of the reactor.

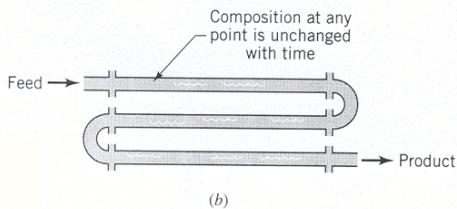
Types of reactors can include:

1. **Batch Reactor:** Material is feed into the reactor; the reaction begins and after a predetermined time period the reaction ends and products are removed. A simple example would be baking a cake; all the ingredients are put into a pan, then the pan is loaded into the oven until the reaction is complete and the cake is removed.  
Advantages of batch reactors are that they're typically simple and so don't need a lot of supporting equipment. In industry, they're commonly used when small amounts of material are to be treated.

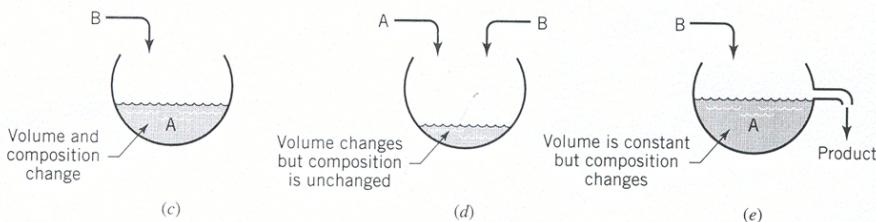


2. **Steady State Flow:** Material passes through the reactor continuously, so product is continually produced (rather than being produced in batches). Unlike the batch reactor, these reactors operate at steady state. An example would be the catalytic converter in cars: the exhaust gases from the engine often have large concentrations of

nitrous oxides ( $\text{NO}_x$ ) which can contribute to smog in a city and environmental pollution. The catalytic converter uses carbon monoxide to reduce the nitrous oxides to  $\text{N}_2$  and  $\text{CO}_2$  which are less environmentally harmful. Once the engine is running, it releases exhaust gases continuously (it is not practical to release the gases in batches) and so the catalytic converter operates continuously, to remove the more harmful gases from the exhaust.



### **3. *Semi-batch / Unsteady State Flow:***

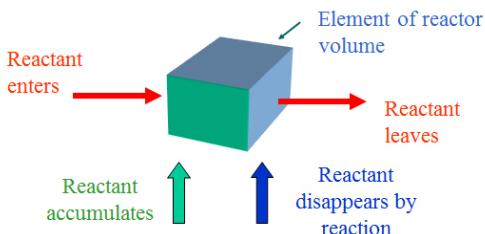


Like a batch process, except that it allows for the addition of reactant over time. Batch and semi-batch reactors tend to have smaller upfront capital costs to build and install but larger operating costs than a steady state flow reactor. This makes them economically preferable for small scale processes. But their cost effectiveness drops off as the production capacity scales up: there are non-productive periods during change over or when switching blades; the material handling costs (filling, emptying, cleaning) scale up at a higher rate for batch and semi-batch processes.

## 5.8 Solving Reaction Rates

In this section we will look at a range of different rate equations and derive solutions to track how the concentration (or conversion) of a reactant species will change as a function of time.

From Material and Energy Balances, you should be familiar with the mass balance equation with a reaction taking place. For a given volume unit in a reactor, operating at steady state, we can write a mass balance as:



$$\text{Rate of reactant flow in} = \text{Rate of reactant flow out} + \text{Rate of reactant loss} + \text{Rate of reactant accumulation}$$

??

We want to solve the rate of reactant loss (i.e., the rate of reactant consumption). In M&EB you have only looked at this as an overall figure (total conversion or selectivity) but here we will determine the rate and can hence calculate the conversion as a function of time.

In a constant volume system, the reaction rate is related to the change in number of moles of reactant:

$$r_i = \frac{dC_i}{dt} = \frac{1}{V} \left[ \frac{dn_i}{dt} \right]$$

Where  $r_i$  is the rate of reaction of component  $i$ .

- $C_i$  is the concentration of  $i$  at a given time
- $t$  is time
- $V$  is volume of the system
- $n_i$  is the number of moles of  $i$  in the system

This relationship can be quite powerful. For example, if we substitute in the ideal gas law equation of state, we can say:

$$PV = nRT$$

$$\begin{aligned} r_i &= \frac{dC_i}{dt} = \frac{1}{V} \left[ \frac{dn_i}{dt} \right] \\ &= \frac{1}{RT} \left[ \frac{dP_i}{dt} \right] \end{aligned}$$

In a gas system, pressure exerted by one component (the partial pressure) is usually used in place of concentration, which would be used to describe a liquid.

Rather than writing the rate in terms of concentration or partial pressure, we can also write it in terms of the conversion of A ( $X_A$ ).

The conversion of A is given by:

$$\begin{aligned} X_A &= \frac{N_{A0} - N_A}{N_{A0}} = 1 - \frac{N_A}{N_{A0}} = 1 - \frac{C_A}{C_{A0}} \\ C_A &= C_{A0}(1 - X_A) \\ dC_A &= -C_{A0}dX_A \end{aligned}$$

For a reactant A, we can write the rate equation in a generalised way:

$$r_A = k(T)f(C)$$

Where  $k(T)$  follows the Arrhenius Law and  $f(C)$  depends on the order of the reaction for an elementary reaction.

To begin we will look at the simplest solution case and so we will assume the reactor is operating at steady state, so there is no accumulation term. Secondly, we will consider an isothermal reactor; although the reaction may be exothermic or endothermic, we will assume there is sufficiently good temperature control (a cooling or heating jacket

around the reactor) that it maintains the temperature constant. This is important because the rate constant is a function of temperature (following the Arrhenius law) and would complicate our solution if temperature was also a function of time.

For an isothermal system ( $k$  is a constant) we can now write:

$$r_A = \frac{dC_A}{dt} = k f(C)$$

$$\frac{dC_A}{f(C)} = k dt$$

$$\int_{C_{A0}}^{C_A} \frac{dC_A}{f(C)} = kt$$

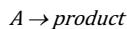
Where  $C_{A0}$  is the concentration at time  $t = 0$ .

### 5.8.1 Irreversible Reactions

#### *Irreversible Unimolecular First Order Reactions*

To solve we would need to know the functional form of  $f(C)$ . For elementary reactions, this functional form is often quite simple, but it can be extremely complex for non-elementary reactions. Consider an irreversible, unimolecular 1<sup>st</sup> order reaction (elementary).

For a unimolecular reaction (only one reactant reacting with itself), the reaction stoichiometry is:



For a first order reaction, the rate is linearly proportional to the concentration of reactant, so the rate equation can be expressed as:

$$f(C) = C_A^1$$

So, the rate equation for an isothermal ( $k$  is constant) 1<sup>st</sup> order unimolecular reaction is:

$$-r_A = -\frac{dC_A}{dt} = k C_A$$

$$\begin{aligned} -\ln\left(\frac{C_A}{C_{A0}}\right) &= kt \\ -\ln(1 - X_A) &= kt \end{aligned}$$

#### Worked Example 5.2

A liquid decomposes by first order reaction kinetics. 50% of A is converted to product in 15 mins. How long would it take to reach 75% conversion?

*Zeroth Order Irreversible Reactions*

A zero-order reaction implies the rate equation is independent of concentration of any reaction species.

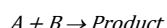
$$-r_A = -\frac{dC_A}{dt} = k$$

Integrating and observing that  $C_A$  can never be negative gives:

$$C_{A0} - C_A = C_{A0} X_A = k t \quad \text{for } t < C_{A0} / k$$

*Irreversible Bimolecular Elementary Second Order Reactions*

For a bimolecular (two reactant molecules) that's second order and elementary (the order of each reacting species is the stoichiometric number in the reaction) we might expect a reaction like:



It's an elementary reaction and hence we know the rate equation:

$$-r_A = k C_A C_B$$

Although the initial amount of A and B may not be the same ( $C_{A0}$  is not necessarily equal to  $C_{B0}$ ) we do know that based on the reaction stoichiometry, the rate at which A is consumed must be the same as the rate at which B is consumed. So, we can also write:

$$-r_A = k C_A C_B = -r_B$$

As with the first order reaction before, we can write this in terms of the conversion of A and B (X):

$$-r_A = k C_{A0} (1 - X_A) C_{B0} (1 - X_B)$$

As the amount of A consumed is the same as the amount of B consumed, we can also write and then substitute in:

$$\begin{aligned} C_{A0} X_A &= C_{B0} X_B \\ X_B &= \frac{C_{A0}}{C_{B0}} X_A \end{aligned}$$

So

$$-r_A = k C_{A0} (1 - X_A) C_{B0} \left(1 - \frac{C_{A0}}{C_{B0}} X_A\right)$$

We will let the ratio of ( $C_{B0} / C_{A0}$ ) be a constant  $M$ , So  $C_{B0} = M C_{A0}$ . So

$$\begin{aligned} -r_A &= k C_{A0} (1 - X_A) (C_{B0} - C_{A0} X_A) \\ &= k C_{A0} (1 - X_A) (M C_{A0} - C_{A0} X_A) \\ &= k C_{A0}^2 (1 - X_A) (M - X_A) \end{aligned}$$

$$-r_A = C_{A0} \frac{dX_A}{dt} = k C_{A0}^2 (1 - X_A) (M - X_A)$$

$$\int_{X_A}^{t} \frac{dX_A}{(1 - X_A)(M - X_A)} = k C_{A0} \int dt$$

Now how do we solve the left-hand side of this integral? We can use a partial fraction method to rearrange this into a form that can be integrated.

$$\frac{1}{(1 - X_A)(M - X_A)} = \frac{A}{(1 - X_A)} + \frac{B}{(M - X_A)}$$

Where:

$$A(M - X_A) + B(1 - X_A) = 1$$

To solve for A and B, we can take the 2 limits. When  $X_A = 1$ :

$$A(M - X_A) = 1$$

$$A = \frac{1}{(M - 1)}$$

When  $X_A = M$ :

$$B(1 - X_A) = 1$$

$$B = \frac{1}{(1 - M)} = \frac{-1}{(M - 1)}$$

Substituting back into the integral, we can now solve:

$$\int_{X_A}^{t} \frac{dX_A}{(1 - X_A)(M - X_A)} = k C_{A0} \int dt$$

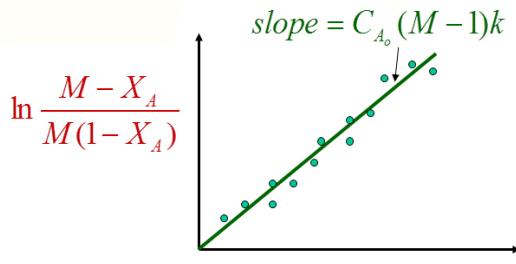
$$\frac{1}{M - 1} \int_{X_A}^{t} \frac{1}{1 - X_A} dX_A + \frac{-1}{M - 1} \int_{X_A}^{t} \frac{1}{(M - X_A)} dX_A = k C_{A0} \int dt$$

$$\frac{1}{M - 1} [-\ln(1 - X_A) + \ln(M - X_A) - \ln(M)] \Big|_{X_A}^{t} = k C_{A0} t$$

$$\frac{1}{M - 1} \ln \left( \frac{M - X_A}{M(1 - X_A)} \right) = k C_{A0} t$$

This holds providing that  $M \neq 1$  (which would require a different integral solution). Rearranging into a final more convenient form, we could check this relationship against real experimental data.

$$k C_{A0} (M - 1) t = \ln \left( \frac{M - X_A}{M (1 - X_A)} \right)$$



#### Worked Example 5.3

In the above solution, we have assumed  $M \neq 1$ . When  $C_{A0} = C_{B0}$  and so  $M = 1$ , show that the conversion as a function of time can be represented as:

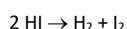
$$\frac{X_A}{1 - X_A} = k C_{A0} t$$

You will need to go back to the initial assumptions of the previous derivation and follow this logic through again for the new condition.

*CHEN20012 Fun Chem Eng*

Worked Example 5.4

Hydrogen iodide breaks down very slowly to hydrogen and iodine.



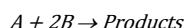
The rate equation for the decomposition is second order, so given as:

$$-\dot{r}_{\text{HI}} = k [\text{HI}]^2$$

At 25 °C the rate constant is  $2.4 \times 10^{-11} \text{ L/mol s}$ . If 1 mol of gaseous HI is placed in a 1 L container, determine the time until 20% of it has decomposed.

*Irreversible Bimolecular Non-Elementary Second Order Reactions*

One important thing to be aware of is that the stoichiometry does not always match the rate equation (as in non-elementary reactions). For example, a reaction with the stoichiometry



Can still be second order and hence have the rate equation:

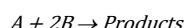
$$-r_A = -\frac{dC_A}{dt} = k C_A C_B = k C_{A0}^2 (1 - X_A)(M - 2X_A)$$

The solution to this rate equation will not be the same as the elementary second order reaction (in the previous section).

In fact, completing the integral we can show that

$$\ln\left(\frac{M - 2X_A}{M(1 - X_A)}\right) = C_{A0}(M - 2) k t \quad M \neq 2$$

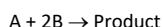
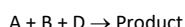
If M does equal 2 (ie the reactants A and B are initially mixed in their stoichiometric ratio) then we can derive a new solution to the rate equation (you should try this for yourself):



$$\begin{aligned} -r_A &= -\frac{dC_A}{dt} = k C_A 2C_A = 2k C_A^2 \\ \frac{dC_A}{C_A^2} &= 2k dt \\ \frac{1}{C_A} - \frac{1}{C_{A0}} &= \frac{1}{C_{A0}} \frac{X_A}{1 - X_A} = 2k t \end{aligned}$$

*Other forms of the rate equation for irreversible trimolecular reactions*

As we go to higher overall reaction order, there are an increasing number of potential solutions to the reaction rate. For example, for an elementary trimolecular reaction, the original stoichiometry could be:



For  $A + 2B \rightarrow \text{Product}$

$$\begin{aligned} -r_A &= k C_A C_B^2 \\ \frac{(C_{A0} - C_{B0})(C_{B0} - C_B)}{C_{B0} C_B} + \ln \frac{C_{A0} C_B}{C_A C_{B0}} &= (C_{A0} - C_{B0})^2 k t \end{aligned}$$

For 3A → Product

$$-r_A = k C_A^3$$

$$\frac{1}{C_A^2} - \frac{1}{C_{A0}^2} = k t$$

If you want practice solving these types of problems, you can complete all these derivations, but they're stretch exercises beyond the scope of the course.

I would strongly recommend you try to understand the steps required to solve the rate equations, rather than trying to memorize the solutions. Because of all the solutions we've just derived, there are also reactions that can be 3<sup>rd</sup> order and non-elementary. Given that this stoichiometry can become increasingly variant for higher order reactions, it becomes necessary to be able to derive solutions (rather than trying to memorize all potential solutions) if we intend to solve the rate equation by hand calculation.

#### *Empirically Determined Rate Equations of n<sup>th</sup> Order*

Often the rate equation may not be known a priori. In this case we would need to determine the rate equation empirically.

For a rate equation:

$$-r_A = -\frac{dC_A}{dt} = k C_A^n$$

$$C_{A0}^{1-n} - C_A^{1-n} = (n-1) k t \quad n \neq 1$$

To determine n (the reaction order) this relationship may then be checked against real data by trial and error, by curve fitting or graphically:

$$\ln(-r_A) = \ln(k) + n \ln(C_A)$$

#### *A List of Solutions for Irreversible Reactions*

We've included a list of solutions to kinetic equations below. But a word of caution: Know how to do these derivations, but it is not worth trying to memorize these (We would not usually ask memory questions in an exam: We are trying to test your understanding not your memory).

Order	Stoichiometry	Rate Equation	Solution To Rate Equation
Zero	Any	$-r_A = k$	$C_{A0} - C_A = C_{A0} X_A = k t$
1 <sup>st</sup>	$A \rightarrow \text{Prod}$	$-r_A = k C_A$	$-\ln(1 - X_A) = k t$
2 <sup>nd</sup>	$A + B \rightarrow \text{Prod}$	$-r_A = k C_A C_B$	$\frac{X_A}{1 - X_A} = k C_{A0} t \quad M = 1$ $k C_{A0} (M-1)t = \ln\left(\frac{M-X_A}{M(1-X_A)}\right) \quad M \neq 1$
2 <sup>nd</sup>	$2A \rightarrow \text{Prod}$	$-r_A = k C_A^2$	$C_A^{-1} - C_{A0}^{-1} = k t$

2 <sup>nd</sup>	$A + 2B \rightarrow \text{Prod}$	$-r_A = k C_A C_B$	$\frac{1}{C_A} - \frac{1}{C_{A0}} = \frac{1}{C_{A0}} \frac{X_A}{1 - X_A} = 2 k t \quad M = 2$ $\ln\left(\frac{M - 2X_A}{M(1 - X_A)}\right) = C_{A0}(M - 2) k t \quad M \neq 2$
3 <sup>rd</sup>	$A + B + D \rightarrow \text{Prod}$	$-r_A = k C_A C_B C_D$	$\frac{1}{(C_{A0} - C_{B0})(C_{A0} - C_{D0})} \ln\left(\frac{C_{A0}}{C_A}\right) + \frac{1}{(C_{B0} - C_{D0})(C_{B0} - C_{A0})} \ln\left(\frac{C_{B0}}{C_B}\right)$ $+ \frac{1}{(C_{D0} - C_{A0})(C_{D0} - C_{B0})} \ln\left(\frac{C_{D0}}{C_D}\right) = k t$
3 <sup>rd</sup>	$A + 2B \rightarrow \text{Prod}$	$-r_A = k C_A C_B^2$	$\frac{(2C_{A0} - C_{B0})(C_{B0} - C_B)}{C_{B0} C_B} + \ln\left(\frac{C_{A0} C_B}{C_A C_{B0}}\right) = (2C_{A0} - C_{B0})^2 k t$
3 <sup>rd</sup>	$3A \rightarrow \text{Prod}$	$-r_A = k C_A^3$	$\frac{1}{C_A^2} - \frac{1}{C_{A0}^2} = 2k t$

### 5.8.2 Reversible Reactions

So far, we have only investigated irreversible reactions (the reaction only proceeds in a single direction). But for many reactions, it is more appropriate to conceive of an equilibrium reached between the reactants and products; the reactants can react to form products, but also the products can react to produce reactants. We can frame this mathematically, like the irreversible reactions we have just looked at, with a forward rate constant and a reverse rate constant.



It's important to note that a reversible reaction is a distinct concept from a reversible thermodynamic process (discussed in a future module).

The ratio of forward and reverse rate constants is usually defined as the equilibrium constant ( $K_C$ ) so that:

$$K_C = \frac{k_1}{k_2}$$

For the stoichiometry above, we can make several statements about the relationship between the rate of consumption of A and the rate of production of R.

$$\frac{dC_R}{dt} = - \frac{dC_A}{dt} = C_{A0} \frac{dX_A}{dt}$$

If the forward and reverse reactions are both first order with respect to the species A and R respectively, then the rate equation can further be written as:

$$\frac{dC_R}{dt} = - \frac{dC_A}{dt} = C_{A0} \frac{dX_A}{dt} = k_1 C_A - k_2 C_R$$

You would then be able to solve this as you have for irreversible reactions. We have included a sample solution below, but this is at the limit of your expected knowledge for the course.

**Solving Reversible Reaction Example**

If we define M as  $C_{R0}/C_{A0}$  and recognising that the amount of A consumed ( $C_{A0}X_A$ ) equals the amount of R produced, we can further write the rate equation as:

$$\begin{aligned}\frac{dC_R}{dt} &= C_{A0} \frac{dX_A}{dt} = k_1(C_{A0} - C_{A0}X_A) - k_2(C_{A0}M + C_{A0}X_A) \\ \frac{dX_A}{dt} &= k_1(1 - X_A) - k_2(M + X_A)\end{aligned}$$

At equilibrium, the rate of change of reactants or products has come to zero. So:

$$\begin{aligned}\frac{dX_A}{dt} &= 0 = k_1(1 - X_{Ae}) - k_2(M + X_{Ae}) \\ \frac{k_1}{k_2} &= K_C = \frac{M + X_{Ae}}{1 - X_{Ae}}\end{aligned}$$

Or we can write the relationship between  $k_1$  and  $k_2$  as:

$$k_2 = \frac{1 - X_{Ae}}{M + X_{Ae}} k_1$$

Substituting this back into the rate equation, we can write:

$$\frac{dX_A}{dt} = k_1(1 - X_A) - \frac{1 - X_{Ae}}{M + X_{Ae}} k_1(M + X_A)$$

With a few lines of algebra, this reduces to:

$$\frac{dX_A}{dt} = \frac{k_1(M + 1)}{M + X_{Ae}} [X_{Ae} - X_A]$$

So we can solve the integral in a fairly straight forward way.

$$\begin{aligned}\int_0^{X_A} \frac{1}{X_{Ae} - X_A} dX_A &= \int_0^t \frac{k_1(M + 1)}{M + X_{Ae}} dt \\ -\ln(X_{Ae} - X_A) + \ln(X_{Ae}) &= \frac{k_1(M + 1)}{M + X_{Ae}} t \\ -\ln\left(\frac{X_{Ae} - X_A}{X_{Ae}}\right) &= \frac{k_1(M + 1)}{M + X_{Ae}} t \\ -\ln\left(1 - \frac{X_A}{X_{Ae}}\right) &= \frac{k_1(M + 1)}{M + X_{Ae}} t\end{aligned}$$

**Worked Example 5.5**

A first order reversible reaction takes place in a batch reactor.



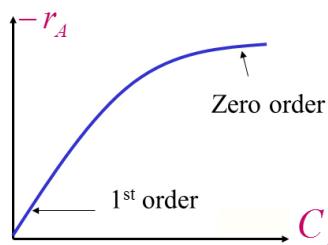
Initially there is 0.5 mol/L of A and no R. After 8 minutes, the conversion of A is 33.3% while the equilibrium conversion is 66.7%. Find the rate constants and then the rate equation for this reaction.

### 5.8.3 Reactions of Changing Order

Sometimes the reaction rate behaves differently at different concentration limits. So, modelling these real reaction kinetics means allowing for the reaction order to change as a function of concentration. For example, consider the irreversible reaction:



Imagine the reaction behaves as first order at low concentrations of A but becomes zeroth order at high concentrations of A; if the concentration of A is sufficiently high, the reaction rate becomes limited by another factor, such as the number of unoccupied reacting sites on the surface of a catalyst.



How might we model a reaction rate like this?

1. We can use a functional form of the rate equation like:

$$-r_A = -\frac{dC_A}{dt} = \frac{k_1 C_A}{1 + k_2 C_A}$$

$k_1$  and  $k_2$  don't refer forward and reverse rate constants here, instead they represent 2 separate constants in the forward rate equation. As we have done in all other example, we can solve this form of the rate equation to give the concentration profile (or conversion) as a function of time.

$$\begin{aligned} \int_{C_{A0}}^{C_A} \frac{1 + k_2 C_A}{k_1 C_A} dC_A &= -t \\ \ln\left(\frac{C_{A0}}{C_A}\right) + k_2(C_{A0} - C_A) &= k_1 t \end{aligned}$$

2. We could consider 2 different parallel pathways of different order, occurring simultaneously but where one dominates in a certain limit.

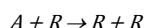
Path 1: $-(r_A)_1 = k_1$	Zero Order
Path 2: $-(r_A)_2 = k_2 C_A$	First Order

Overall:  $(-r_A)_{overall} = k_1 + k_2 C_A$

Note that this solution will be a kind of inverse of point 1 above (which was first order for low concentrations of A and zero order for high concentrations of A). Solution 2 is first order for high concentrations of A and zero order for lower concentration. So, it doesn't apply to the previous graph.

### 5.8.4 Autocatalytic Reactions

Autocatalytic means one of the products functions as a catalyst for the forward reaction. So as more product is produced, the reaction can proceed faster.

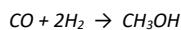


How might we express the rate equation and then a solution to the rate equation?

$$-r_A = -\frac{dC_A}{dt} = k C_A C_R$$

### 5.8.5 HYSYS Simulation of Reaction Kinetics

Until now, we've only considered isothermal processes in the solutions we've derived here (so  $k$  was a constant). We've also only considered solutions for a batch reactor, not a mixed reactor. We've also only considered relatively simple rate equations. For example, the stoichiometry to produce methanol from carbon monoxide and hydrogen via a solid catalyst has the stoichiometry:



But its rate equation is given by in [Kiler *et al.* (1981)]:

$$r_{MeOH} = \frac{K_f \left( p_{CO_2}^3 p_{H_2}^2 \right) - K_r \left( \frac{p_{CO_2}^3 p_{MeOH}}{p_{CO}^3} \right)}{\left[ 1 + K_{CO} p_{CO} + K_{CO_2} p_{CO_2} + K_{H_2} p_{H_2} + K' \left( \frac{p_{CO_2}}{p_{CO}} \right) + K_{CO} K' p_{CO_2} + K_{CO_2} K' \left( \frac{p_{CO_2}^2}{p_{CO}} \right) + K_{H_2} K' \left( \frac{p_{CO_2} p_{H_2}}{p_{CO}} \right) \right]^3}$$

The reaction is a heterogeneous catalytic reaction, meaning that a catalyst is used to accelerate the reaction, but active sites on the surface of the catalyst can be blocked by the adsorption of reactant or product molecules, slowing the reaction rate. For this reason, there is a denominator term in the rate equation (that represents a slowing of the reaction rate). In the numerator, we can see there are forward and reverse rate constants.

This reaction rate would be tremendously difficult to solve by hand to generate a concentration profile (as we have previously done in this module). For this reason, we simultaneously teach you how to create simulations in HYSYS. Simple rate equations can be solved by hand (and you get a better understanding for what they mean) but more complicated rate equations (as above) are typically solved numerically using software packages.

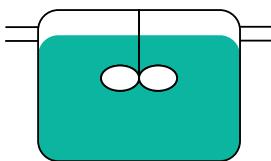
There are a range of software packages available to investigate reaction rates (for example Aspen HYSYS, Comsol, Matlab) but as Aspen HYSYS is commonly used in industry and is quite user friendly, it's what we focus on in CPA. But hopefully you can see how the workshop modules on HYSYS are complimentary to what we're covering in lectures.

## 5.9 Design of Single Ideal Reactors

### 5.9.1 Batch Reactor

The simplest kind of reactor is a Batch Reactor:

- Feed enters the reactor (i.e., the reactor is charged), it mixes and reacts to form product over a certain period, and a mixture of feed and product exists the reactor (i.e., the reactor is discharged).
- The composition changes over time, therefore this system is unsteady state
- But we can still assume that the composition is spatially uniform

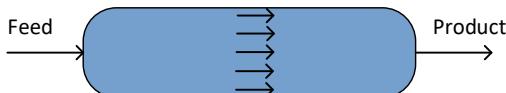


An example of a batch reactor is simply baking a cake, where all the ingredients fed into the reactor and mixed, then the reactor (the cake tin) is heated to the correct temperature (the oven providing the heat), and then the product is removed and consumed.

### 5.9.2 Plug Flow Reactor

The next type of ideal reactor we'll look at is a Plug Flow Reactor:

- Also called slug flow, piston flow, ideal tubular, or unmixed flow reactor
- In this course, we'll call them Plug Flow Reactors (PFR), due to the fluid flow pattern inside the reactor: plug flow, which means no back-mixing. An element of fluid flows straight through the reactor.
- This system is steady-state which means it does not vary over time, but the composition does change along the length of the reactor.
- For the assumption of plug flow to be valid, the residence time for all fluid elements must be constant i.e., all fluid spends the same amount of time inside the reactor

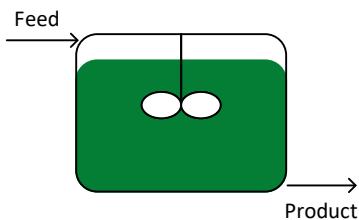


An interesting example of a Plug Flow Reactor is the growth of algae for biofuel and biodiesel production. The algae is grown in long clear tubes called Photobioreactors, allowing light into the reactor for the algae: [Algae Photobioreactor](#).

### 5.9.3 Mixed Flow Reactor

The last ideal reactor we will examine is a Mixed Flow Reactor:

- Also known as mixed reactor, back mix reactor, ideal stirred tank reactor, C-Star, Continuously Stirred Tank Reactor or Constant Flow Stirred Tank Reactor
- In this reactor, all elements of fluid are well-mixed and are uniform in space, and the composition of the exiting fluid is the same composition as the fluid in the reactor
- Because the system is steady-state, the system does not change over time
- In comparison to a PFR, the flow pattern of the MFR is mixed



Mixed Flow Reactors are often used in the traditional chemical industry to react two liquids in homogenous liquid-phase flow, but they can also be used in the biochemical industry as bioreactors, where oxygen and temperature can be easily manipulated to keep microorganisms alive.

Most real reactors are a combination of ideal reactors/ on a spectrum of ideal reactors. In this module, we'll look at designing ideal reactors, and then we'll move onto real reactors in later modules and subjects.

### 5.9.4 Sizing a Batch Reactor

To analyse the performance of a reactor, we use performance or design equations; performance equations are a way of comparing reactors and working out if our designs are reasonable). To derive these equations, we can take a mass balance over the reactor. We can use the whole reactor because composition is assumed to be constant throughout the whole volume.

Starting with our basic mass balance over the reactor:

Input= output + disappearance by reaction + accumulation

However, we know nothing enters or leaves the system boundary during operating in a batch reactor; we only have loss and accumulation due to chemical reactions

$$\text{Rate of loss of } A \text{ through reaction} = -(\text{rate of accumulation of } A \text{ within reactor})$$

$$\text{Disappearance} = \text{rate} \times \text{volume} = \frac{\text{moles}}{\text{time} \times \text{volume}} \times \text{volume} = (-r_A) \cdot V$$

$$\text{accumulation} = \frac{dN_A}{dt}$$

$$N_A = N_{A0}(1 - X_A) \therefore \frac{dN_A}{dt} = \frac{d[N_{A0}(1 - X_A)]}{dt} = -N_{A0} \frac{dX_A}{dt}$$

Where  $N_{A0}$  is a constant, as the initial number of moles of A in the system

*Disappearance of A= - Accumulation of A, so*

$$(-r_A) \cdot V = -\left(-N_{A0} \frac{dX_A}{dt}\right)$$

After separation of variables and integration:

$$\begin{aligned} dt \cdot (-r_A) V &= N_{A0} dX_A \\ \int_0^t dt &= N_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A) \cdot V} \\ t &= N_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A) \cdot V} \end{aligned}$$

This is the time it takes to achieve the desired conversion given a specific rate and volume. This is the design equation for a batch reactor.

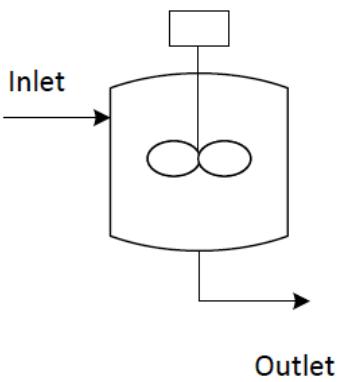
[Here](#) is a YouTube Video explaining the derivation.

The volume of this batch reactor, as discussed in the previous module, can be constant or variable. If the density of the fluid remains constant, then so will the volume, which means we can use the constant volume version (i.e., assuming there is no expansion  $\varepsilon_A=0 \therefore \Delta p=0$ )

### 5.9.5 Sizing a Steady State Mixed Flow Reactors

To find the design equation of the mixed flow reactor, we'll start with a mass balance over the system:

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Input = output + disappearance by reaction + accumulation

Here we have written the rate as disappearance of A. The rate ( $r_A$ ) refers to the rate of change of A; a positive rate would mean A is being produced and a negative rate would mean A is being consumed. So rate of disappearance by reaction =  $-r_A$ . So note that you could also write input = output - production of A + accumulation and you would end up for the same final formula.

Rate of disappearance =  $-r_A$  (negative rate of production)

If the system is operating at steady state there is no accumulation.

Assuming a simple reaction of  $A \rightarrow B$ : A is being consumed but not produced.

$$\text{Input} = F_{A0}(1 - X_{A0}) = F_{A0} \quad X_{A0} = 0$$

$$\text{Output} = F_A = F_{A0}(1 - X_A)$$

$$\text{Disappearance} = (-r_A) \cdot V = \frac{-\text{moles of } A \text{ being produced}}{\text{time} \times \text{volume}} \times \text{volume}$$

Substitute these terms into the mass balance:

$$F_{A0} = F_{A0}(1 - X_A) + (-r_A) \cdot V$$

$$F_{A0} = F_{A0} - F_{A0}X_A + (-r_A) \cdot V$$

$$F_{A0}X_A = (-r_A) \cdot V$$

$$\frac{V}{F_{A0}} = \frac{X_A}{(-r_A)}$$

Re-arrange this expression to find space time:

$$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \frac{X_A}{(-r_A)}$$

$$\tau = \frac{1}{S} = \frac{V}{v_0} = \frac{VC_{A0}}{F_{A0}} = \frac{C_{A0}X_A}{(-r_A)}$$

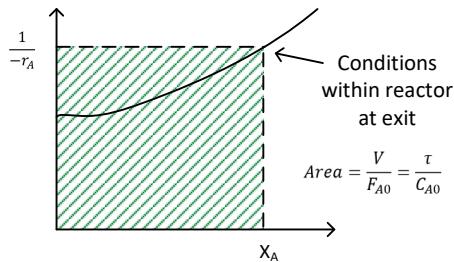
Note that we have used  $\tau$  for the time not  $t$  (as we did for the batch reactor). This is to emphasise that they're not really the same: in a batch reactor all atoms are 'cooked' for the exact same period. In continuous flow reactors (MFR and CSTR) this time represents a mean residence time in the reactor, but each atom can be present for different total lengths. The term  $\tau$  is also sometimes referred to as a space time.

Here are 2 YouTube videos explaining the derivation: [1](#) and [2](#) above.

Note: In these equations, we're assuming all the feed is fresh, not partially converted feed. The inclusion of partially converted feed will be discussed in a later module on Recycle Reactors.

In these design equations, we have 4 variables of interest:  $X_A$ ,  $-r_A$ ,  $V$ ,  $F_{A0}$  ∴ we can find 1 from the other 3. We often try to find  $V$ , to have the smallest reactor possible, or find  $F_{A0}$  to see how much feed our system can handle.

If we plot this relationship, we can find the size of the reactor using the conversion directly, rather than calculating it. Using the following graph (Mixed flow reactor rate conversion curve):



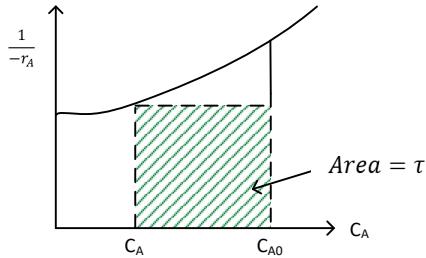
The area of the reciprocal rate curve will give you  $V/F_{A0}$ , allowing you to easily find the volume.

If constant density is assumed, the following expression is true:

$$X_A = 1 - \frac{C_A}{C_{A0}}$$

This expression allows us to write out the design equations in terms of concentration rather than conversion:

$$\tau = \frac{V}{F} = \frac{C_{A0}X_A}{(-r_A)} = \frac{C_{A0} - C_A}{(-r_A)} = \left(\frac{1}{-r_A}\right)(C_{A0} - C_A)$$



We can also find the volume from the concentration version of the Levenspiel graph, taking the rectangular area beneath the curve between the inlet and outlet conditions.

Notice that these expressions have rate in them: we can find the design equation based on the kind of reaction present in the system.

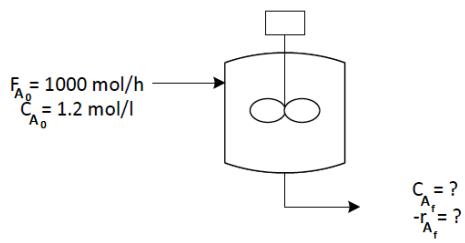
#### Worked Example 5.6

Liquid phase reaction,  $A \rightarrow R$ , the rate of reaction is as follows:

$C_A$ (mol/L)	0.1	0.2	0.3	0.4	0.5	0.6
$-r_A$ (mol/L·min)	0.1	0.3	0.5	0.6	0.5	0.25

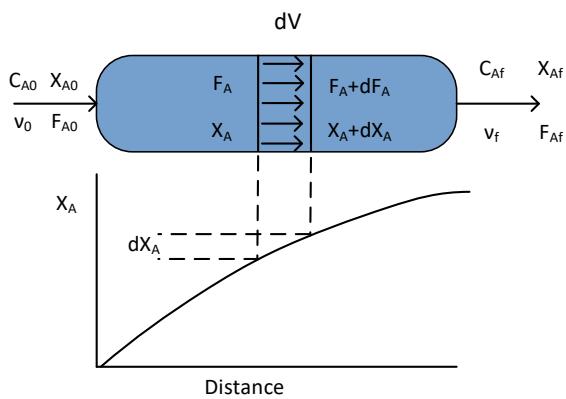
What size Mixed Flow Reactor is needed with  $X_A=0.75$ ,  $F_{A0}=1000$  mol/hr, at  $C_{A0}=1.2$  mol/L.

Commented [NB10]: redraw this diagram



## 5.9.6 Sizing a Steady State Plug Flow Reactor

As before, we'll start with a mass balance over the system. Unlike with mixed flow, the composition does change along the reactor length: therefore, we need a differential across an element of volume:  $dV$



$$\text{Input} = \text{output} + \text{disappearance} + \text{accumulation}$$

As before, there is no accumulation, as A the system is steady state.

$$\text{Input} = F_A$$

$$\text{Output} = F_A + dF_A$$

$$dF_A = d(F_{A0}(1 - X_A)) = d(F_{A0} - F_{A0}X_A) = -F_{A0}dX_A$$

$$\text{Disappearance} = (-r_A) \cdot dV = \frac{\text{moles of A reacting}}{\text{time} \times \text{volume}} \times \text{volume}$$

$$F_A = F_A - F_{A0}dX_A + (-r_A) \cdot dV$$

$$F_{A0}dX_A = (-r_A) \cdot dV$$

The differential means this only represents a slice of the reactor volume. To calculate conversion across the whole reactor, we need to complete the integral across the whole length.

$$\int_0^V \frac{dV}{F_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A}$$

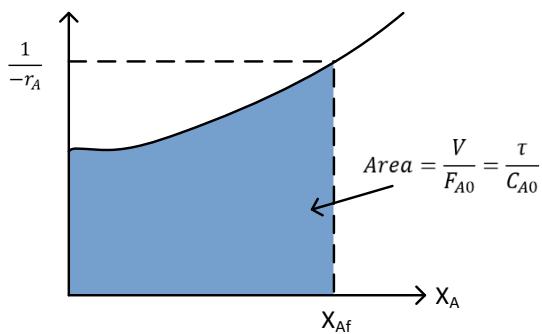
$$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A}$$

Can re-arrange:

$$\tau = \frac{V}{v_0} = \frac{VC_{A0}}{F_{A0}} = C_{A0} \int_0^{X_{Af}} \frac{dX_A}{-r_A}$$

[Here](#) is a YouTube video explaining the derivation:

We can use this design equation to find our reactor volume given how much feed it is given, and the conversion required.



Again, we assume fresh feed  $\therefore X_{Ai}=0$ . If feed is partially converted,  $X_{Ai}$  can be substituted for the lower integral limit. This will be discussed further in later modules.

If the system has constant density:

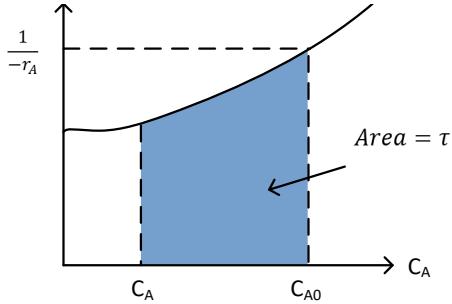
$$X_A = 1 - \frac{C_A}{C_{A0}}$$

$$dX_A = -\frac{dC_A}{C_{A0}}$$

We can use this expression to convert the design equation once again to be in terms of concentration rather than conversion.

$$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A} = \frac{-1}{C_{A0}} \int_{C_{A0}}^{C_{Af}} \frac{dC_A}{-r_A} = \frac{1}{C_{A0}} \int_{C_{Af}}^{C_{A0}} \frac{dC_A}{-r_A}$$

$$\tau = \frac{V}{v_0} = C_{A0} \int_0^{X_{Af}} \frac{dX_A}{-r_A} = - \int_{C_{A0}}^{C_{Af}} \frac{dC_A}{-r_A} = \int_{C_{Af}}^{C_{A0}} \frac{dC_A}{-r_A}$$



We can solve these equations in plug flow for all sorts of kinetics. Some are very complicated and require numerical integration- we use computers, especially programs like HYSYS for that. For some simple kinetics, we can easily derive the equations.

	Conversion	Concentration
<b>Batch</b>	$t = N_{A0} \int_0^{X_A} \frac{dX_A}{V(-r_A)}$ $\epsilon_A \neq 0$	$t = C_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A)}$ $\epsilon_A = 0$
<b>Mixed Flow</b>	$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \frac{X_A}{(-r_A)}$	$\tau = \frac{C_{A0} - C_A}{(-r_A)}$
<b>Plug Flow</b>	$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A}$	$\tau = \int_{C_A}^{C_{A0}} \frac{dC_A}{-r_A}$

### Worked Example 5.7

Molecule A reacts to form R irreversibly:



The reaction is elementary. Will a CSTR or PFR have a smaller volume for the same inlet conditions and conversion?

$$\text{CSTR: } \tau = \frac{V C_{A0}}{F_{A0}} = \frac{V}{v_0} = \frac{C_{A0} - C_A}{(-r_A)}$$

$$\text{PFR: } \tau = \frac{V}{v_0} = C_{A0} \int_0^{X_{Af}} \frac{dX_A}{-r_A} = - \int_{C_{A0}}^{C_{Af}} \frac{dC_A}{-r_A} = \int_{C_{Af}}^{C_{A0}} \frac{dC_A}{-r_A}$$

1. Write the reaction kinetics
2. Plot reaction rate (y-axis) vs concentration (x-axis)
3. Plot  $-1/r_A$  (y-axis) vs  $C_A$  (x-axis)
4. Draw areas on the  $-1/r_A$  vs  $C_A$  plot to represent PFR and CSTR space time
5. From the areas in Qu 4 which reactor configuration will be larger?
6. Provide a brief physical explanation for which reactor you would expect to have a larger final volume.

*CHEN20012 Fun Chem Eng*

*Zero Order Plug Flow* $A \rightarrow R$ 

$$-r_A = k$$

$$\frac{\tau}{C_{A0}} = \frac{V}{F_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A} = \int_0^{X_{Af}} \frac{dX_A}{k} = \frac{X_A}{k}$$

$$k\tau = k \frac{C_{A0}V}{F_{A0}} = C_{A0}X_A$$

*First Order Irreversible Plug Flow* $A \rightarrow R$ 

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1 - X_A)}{V_0(1 + \varepsilon_A X_A)} = C_{A0} \frac{1 - X_A}{1 + \varepsilon_A X_A}$$

$$-r_A = k \cdot C_A = k \cdot C_{A0} \frac{1 - X_A}{1 + \varepsilon_A X_A}$$

$$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \int_0^{X_A} \frac{dX_A}{-r_A} = \int_0^{X_A} \frac{dX_A}{k \cdot C_{A0} \frac{1 - X_A}{1 + \varepsilon_A X_A}}$$

$$\frac{\tau \cdot k \cdot C_{A0}}{C_{A0}} = \int_0^{X_A} \frac{dX_A}{\frac{1 - X_A}{1 + \varepsilon_A X_A}}$$

$$k \cdot \tau = \int_0^{X_A} \left[ \frac{1 + \varepsilon_A X_A}{1 - X_A} \right] dX_A$$

$$k \cdot \tau = \int_0^{X_A} \left[ \frac{1}{1 - X_A} + \frac{\varepsilon_A(X_A - 1)}{1 - X_A} + \frac{\varepsilon_A}{1 - X_A} \right] dX_A$$

Then integrate:

$$k\tau = -\ln(1 - X_A) - \varepsilon_A X_A - \varepsilon_A \ln(1 - X_A)$$

$$k\tau = -(1 + \varepsilon_A) \ln(1 - X_A) - \varepsilon_A X_A$$

**5.10 Design for Single Reactors**

Processing fluids is very important in chemical engineering; so engineers have come up with lots of ways to process fluids, there are different:

- Kinds of reactors: batch or flow
- Configurations: series or recycle
- Augmentations: inter-stage heating/ cooling and feed ratios etc.

This means that designing a scheme to process fluids is a bit of a puzzle- there are no exact formulae to follow, but there's lots of factors to consider and you have to use your pre-existing knowledge.

Some of the important factors to consider:

- Reaction type
- Scale
- Cost
- Occupational Health and Safety

Whichever system is selected, design will influence the economics of the project:

- Size of the units: this is the most important economical impact
- Ratio of products: we won't look at this because we are only looking at single-reaction systems. This will be discussed further in later subjects

### 5.10.1 Comparison of Single Reactors

#### *Batch Reactor vs Plug Flow Reactor*

Batch reactors have both advantages and disadvantages to be aware of:

Advantages	Disadvantages
Small capital cost	High operating cost
Flexibility of operation	Time for cleaning and shutdown
Sterility	Poorer quality of product

This is why small batches of lots of products are recommended for batch reactors, rather than large batches. This is also why batch reactors are used in the food and pharmaceutical industries, where flexibility and sterility are very important.

We can compare the Design Equations of Batch Reactors and Plug Flow Reactors:

If  $\epsilon_A=0$ :

$$\text{Batch: } t = C_{A0} \int_0^{X_A} \frac{dx_A}{(-r_A)} \quad \text{Plug: } t = C_{A0} \int_0^{X_A} \frac{dx_A}{(-r_A)}$$

They're the same design equation i.e. an element of fluid stays inside for the same amount of time. But this conclusion does not hold if density changes in the system.

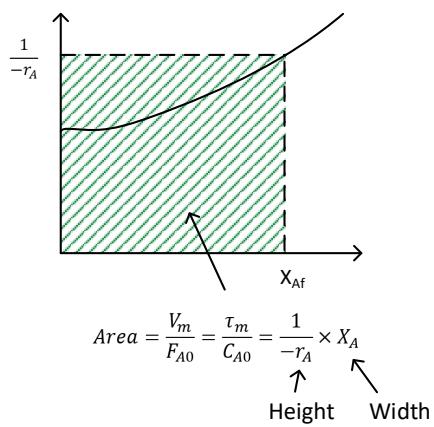
#### *Mixed Flow Reactors vs Plug Flow Reactors: A Graphical Comparisons*

We can graphically compare the volume required of a reactor on a graph called a Levenspiel plot. This is also called a rate-concentration, rate-conversion curve or reciprocal rate curve. These are very useful graphs and we'll use them throughout the next few modules.

[Here](#) is a YouTube video to explain the concept.

These graphs are based on our design equations:

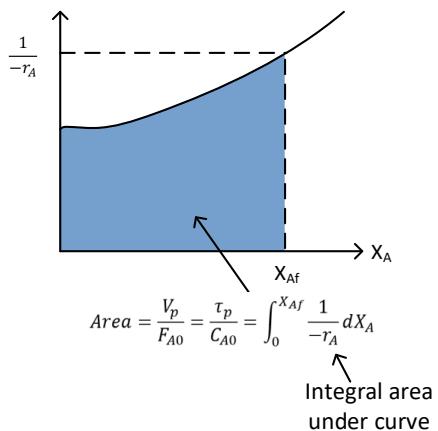
MFR:



This shows that we can find the volume or space time by finding the rectangular area of the graph, using the inlet and outlet conditions.

[Here](#) are YouTube video explaining the concept with an [example](#).

PFR:



This shows that we can find the volume or space time by finding the integral area under the curve, using the inlet and outlet conditions.

This is why the PFR volume is always less (for  $n^{\text{th}}$  order reaction): there is no wasted volume.

Here are YouTube videos explaining the concept with an example: [1](#), [2](#), [3](#) and [4](#).

Fixed values on dimensionless reaction rate groups can be plotted as lines on a graph, which makes it easy to compare systems and impacts of kinetics on our system:

Order	Dimensionless Group
1 <sup>st</sup>	$k\tau$
2 <sup>nd</sup>	$k\tau C_{A0}$

Overall, we know that conversion is affected by many factors, including; order, system, expansion, kinetics, volume ratios ::

$$X_A = f \left( n, \varepsilon_A, k\tau, \frac{V_m}{V_p} \right)$$

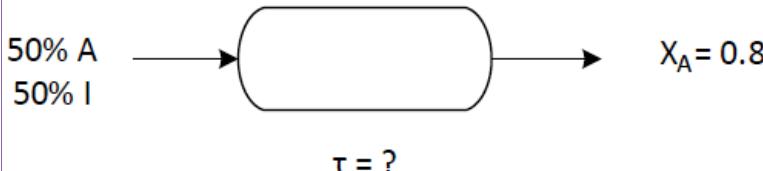
#### Worked Example 5.8

A homogenous gas reaction  $A \rightarrow 3R$  has a reported rate (at 215°C) of:

$$-r_A = 10^{-2} C_A^{\frac{1}{2}} \left[ \frac{\text{mol}}{\text{L} \cdot \text{s}} \right]$$

Find the space time needed for 80% conversion of a 50% A and 50% inert feed to a plug flow reactor, operating at 215°C and 5 atm. Note:  $C_{A0}=0.0625 \text{ mol/L}$ .

Commented [NB11]: redraw this diagram



**Table 5.1** Performance Equations for  $n$ th-order Kinetics and  $e_A = 0$ 

	Plug Flow or Batch	Mixed Flow
$n = 0$ $-r_A = k$	$\frac{k\tau}{C_{A0}} = \frac{C_{A0} - C_A}{C_{A0}} = X_A \quad (20)$	$\frac{k\tau}{C_{A0}} = \frac{C_{A0} - C_A}{C_{A0}} = X_A \quad (14a)$
$n = 1$ $-r_A = kC_A$	$k\tau = \ln \frac{C_{A0}}{C_A} = \ln \frac{1}{1 - X_A} \quad (3.12)$	$k\tau = \frac{C_{A0} - C_A}{C_A} = \frac{X_A}{1 - X_A} \quad (14a)$
$n = 2$ $-r_A = kC_A^2$	$k\tau C_{A0} = \frac{C_{A0} - C_A}{C_A} = \frac{X_A}{1 - X_A} \quad (3.16)$	$k\tau = \frac{(C_{A0} - C_A)}{C_A^2} = \frac{X_A}{C_{A0}(1 - X_A)^2} \quad (15)$
any $n$ $-r_A = kC_A^n$	$(n-1)C_{A0}^{n-1}k\tau = \left(\frac{C_A}{C_{A0}}\right)^{1-n} - 1 = (1 - X_A)^{1-n} - 1 \quad (3.29)$	$k\tau = \frac{C_{A0} - C_A}{C_A^n} = \frac{X_A}{C_{A0}^n(1 - X_A)^n}$
$n = 1$ $A \xrightarrow{\frac{1}{2}} R$ $C_{B0} = 0$	$k_1\tau = \left(1 - \frac{C_{Ae}}{C_{A0}}\right) \ln \left(\frac{C_{A0} - C_{Ae}}{C_A - C_{Ae}}\right) = X_{Ae} \ln \left(\frac{X_{Ae}}{X_{Ae} - X_A}\right)$	$k_1\tau = \frac{(C_{A0} - C_A)(C_{A0} - C_{Ae})}{C_{A0}(C_A - C_{Ae})} = \frac{X_A X_{Ae}}{X_{Ae} - X_A}$
General rate	$\tau = \int_{C_A - r_A}^{C_{A0}} \frac{dC_A}{-r_A} = C_{A0} \int_0^{X_{Ae}} \frac{dX_A}{-r_A} \quad (19)$	$\tau = \frac{C_{A0} - C_A}{-r_A} = \frac{C_{A0} X_A}{-r_A} \quad (13)$

**Table 5.2** Performance Equations for  $n$ th-order Kinetics and  $e_A \neq 0$ 

	Plug Flow	Mixed Flow
$n = 0$ $-r_A = k$	$\frac{k\tau}{C_{A0}} = X_A \quad (20)$	$\frac{k\tau}{C_{A0}} = X_A \quad (14b)$
$n = 1$ $-r_A = kC_A$	$k\tau = (1 + e_A) \ln \frac{1}{1 - X_A} - e_A X_A \quad (21)$	$k\tau = \frac{X_A(1 + e_A X_A)}{1 - X_A} \quad (14b)$
$n = 2$ $-r_A = kC_A^2$	$k\tau C_{A0} = 2e_A(1 + e_A) \ln(1 - X_A) + e_A^2 X_A + (e_A + 1)^2 \cdot \frac{X_A}{1 - X_A} \quad (23)$	$k\tau C_{A0} = \frac{X_A(1 + e_A X_A)^2}{(1 - X_A)^2} \quad (15)$
any $n$ $-r_A = kC_A^n$		$k\tau C_{A0}^{n-1} = \frac{X_A(1 + e_A X_A)^n}{(1 - X_A)^n}$
$n = 1$ $A \xrightarrow{\frac{1}{2}} rR$ $C_{B0} = 0$	$\frac{k\tau}{X_{Ae}} = (1 + e_A X_{Ae}) \ln \frac{X_{Ae}}{X_{Ae} - X_A} - e_A X_A \quad (22)$	$\frac{k\tau}{X_{Ae}} = \frac{X_A(1 + e_A X_A)}{X_{Ae} - X_A} \quad (11)$
General expression	$\tau = C_{A0} \int_0^{X_A} \frac{dX_A}{-r_A} \quad (17)$	$\tau = \frac{C_{A0} X_A}{-r_A} \quad (11)$

## Module 5 Summary

### Key Points:

- Reaction Kinetics
  - Reaction rates
  - Elementary vs. Non-elementary
  - Order
  - Temperature dependence (Arrhenius)
- Reactor Design
  - Flow: Steady State, Batch, Semi-Steady State
  - Irreversible and Reversible reactions
  - Ideal reactors (Batch, Plug Flow Reactor, Mixed Flow Reactor)
  - Sizing
  - Comparison

### Key Skills:

- Solve irreversible and reversible reaction kinetic problems ( $0^{\text{th}}$ ,  $1^{\text{st}}$ ,  $2^{\text{nd}}$  order kinetics)
- Size and compare Batch Reactors, Plug Flow Reactors, and Mixed Flow Reactors with above kinetic expressions

## Module 6 – Large Kit: Thermodynamic Cycles

*Thermodynamic cycles are used to model engines and heat pumps that we all use every day. A combustion engine (in a car) can be described accurately using this theory, as well as refrigerators, reverse-cycle heaters, jet engines and power generators. So thermodynamic cycles are essential to many aspects of our society and economy.*

### Outline

Primary learning outcomes for the module:

1. Understand a range of thermodynamic cycles; heat engines, refrigeration cycles and a series of idealized thermodynamic cycles (e.g., Carnot cycle, Otto cycle, Diesel, and others)
2. Be able to solve basic problems around thermodynamic cycles (e.g., efficiency, coefficient of performance, work, heat, change in internal energy, enthalpy, and entropy)

In completing a cycle, the change in all state functions becomes zero (but path functions can retain a finite value). So for example in a thermodynamic cycle, the change in internal energy ( $\Delta E$ ) becomes zero but work and heat are finite and further  $W_{Net} = -Q_{Net}$ ; heat added to the system can be converted into useful work (in the case of an engine).

Ultimately, we want to answer questions like, for a given amount of available heat, what is the maximum amount of useful work an engine can produce? If I fill up a car tank with fuel, what is the maximum distance it can drive?

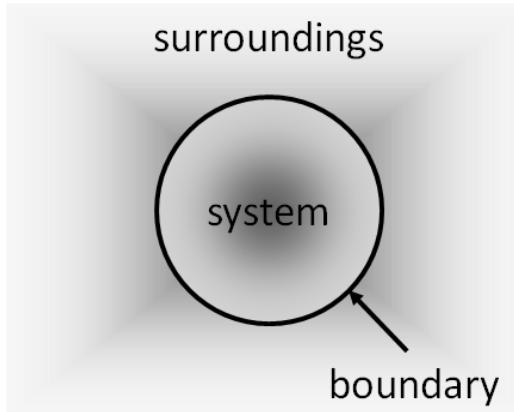
### 6.1 Recap of your pre-existing knowledge (you may choose to skip to 6.2)

Student can come into Fun CE from a range of different backgrounds and so here we will just do a quick recap of the thermodynamics you probably already know.

If you already feel comfortable with this content, please skip ahead to 6.2. This sub-section (6.1) is not directly examinable, it's just assumed background knowledge, so it will not be covered in detail in the course.

Before we can begin, we need to define a series of terms that will be used throughout the course (and throughout your degree) that are essential to describing thermodynamics:

1. System vs surroundings
2. The system is the object we want to study
3. The surroundings are the rest of the universe (everything that is not the system)
4. The boundary represents the interface between the system and surroundings
5. If we were studying a train's efficiency to convert coal into kilometres travelled, the train would be the system (coal as fuel is put in and work is taken out)
6. By convention, a positive energy flow is always into the system (from the surroundings into the system). A negative energy flow implies the system is losing energy.



- Open system: Mass transfer may occur across the system boundary
- Closed system: Mass transfer may not occur across the system boundary
- Isolated system: No mass or heat transfer across the system boundary
- State: the conditions of the system (for example temperature, phase, enthalpy etc)
- Phase: How the system exists (solid, liquid or gas).
- Substance: Pure substance is made up of a uniform composition
- Homogeneous System: The properties are consistent throughout (e.g., density, phase, temperature)
- Heterogeneous System: Properties of the system vary throughout (e.g., if the system is a 2-phase mixture)
- Equilibrium: This has a range of meanings in thermodynamics but here we will use the definition that the system properties do not change with time (ie it is in a fixed, stable state).
- State Variable vs Path Variable
  - For a state variable, their value only depends on the final state of the system.
  - For a path variable, their value depends on how the system has moved from the initial state to the final state.

For example, a variable like work is a path variable: if I want to push a large block across a room, I could expend a small amount of energy by pushing it in a straight line from start to finish. Alternatively, I could push the block through a large detour, out of the room, down to the shops, then back again before I arrive at the final position and hence would expend much more energy to move the block from the initial to final position. As the amount of energy expended to move the block (the work) depends on the path to get the block from the initial to final position, we would say it is a path variable.

Alternatively, variables like temperature or density are not a function of how I move between states. A glass of water would be heated directly from 25°C to 100°C or it could be heated and cooled many times, before finally being heated to 100°C. The final temperature is always still 100°C (hence temperature is a state variable) however the amount of energy supplied to the system (the heat) would not be the same in both scenarios and hence heat is a path variable.

- Intensive property: The value of the property is independent of the amount of material present. Examples would be density or temperature. Whether we have 1kg or 2kg, the density of the material is the same.

- Extensive property: The property does depend on how much material is present. Examples would be volume or mass; 1kg and 2kg of a material will not have the same volume or the same mass.
- Process: When a system moves from one state to another.
- Cyclical process: In the next module we will look at a series of *cyclical processes* (where the system returns to its initial conditions), for example a heat engine which converts heat into work.
- Reversible process: The system can always be returned to its initial condition and there is no entropy change in the process.
- Adiabatic: No heat flow into the system during the process
- Isothermal: Constant temperature (isothermal process implies the temperature does not change)
- Isochoric (isometric): Constant volume (a process occurs but the total volume of the system does not change during the process)
- Isobaric: Constant pressure
- Isenthalpic: Constant enthalpy
- Isentropic: Constant entropy
- Heat: Transfer of energy related to a temperature difference
- Work: Transfer of energy involving mechanical motion across a system boundary

### 6.1.1 Temperature

We're familiar with the concept of temperature (we can look up the daily temperature on our phone), but how would you describe what temperature is physically?

Descriptions of temperature tend to rely on implicit thermodynamics understanding:

A classical thermodynamic description: temperature is related to the thermal energy of the system and indicates the direction of heat flow; energy always flows from high to low (never spontaneously from low to high) to maximise an overall entropic condition. When 2 objects are at the same temperature, they are said to be at thermal equilibrium and there is no heat flow (this is a restatement of the zeroth law of thermodynamics).

A statistical thermodynamic description: temperature is related to the vibrational motion of atoms within matter. When atoms have no vibrational motion, this constitutes a fundamental lower limit on temperature (defined as absolute zero). Heat tends to flow from high concentration (high temperature) to low concentration (low temperature) because of the transfer of vibrational motion between adjacent atoms; atoms knock adjacent atoms. Given all atoms are equivalent, distributing the vibrational energy evenly between all atoms in the system represents the most probable final state for the system (thus why the thermal energy tends to distribute evenly throughout the system).

### 6.1.2 Zeroth Law of Thermodynamics

If object A is in thermal equilibrium with object B and object B is in thermal equilibrium with object C, then objects A and C must also be in thermal equilibrium.

This is a basic formal definition and doesn't really allow us to show anything particularly interesting or solve useful problems.

### 6.1.3 Internal Energy

The internal energy represents the energy contained within the system. It does not include the kinetic energy of the system as a whole (if the whole system were moving) or the potential energy of the whole system (in an external field)

because this would require a reference frame outside of the system. Internal energy is the energy contained within the system relative to the reference frame of the system (i.e., the system boundary).

Thinking about the statistical thermodynamic model, internal energy would represent things like the translational kinetic energy of individual molecules, vibrational and rotational states as well as the potential energy of intermolecular forces.

#### 6.1.4 First Law of Thermodynamics

Sometimes called conservation of energy, it says the total energy of an isolated system must be constant. It is the law that prohibits perpetual motion machines. It is usually formulated to say that the change in internal energy of a closed system must equal the work supplied plus the heat supplied.

$$\Delta U = Q + W$$

Where  $\Delta U$ : Change in internal energy of the system

$Q$ : Heat flow into the system (flow of energy from a temperature gradient)

$W$ : Work put into the system (flow of energy from motion)

Note that we refer to the *change* in internal energy and there is no absolute measure for internal energy itself (only relative to a datum).

#### Calculating work

Hopefully from previous physical based subjects, you know that work is the integral of force ( $F$ ) with respect to distance ( $x$ ).

$$W = - \int F dx$$

Given that pressure ( $P$ ) is force per unit area, and volume ( $V$ ) is length  $\times$  area, this can be rearranged to give:

$$W = - \int P dV$$

NB Note the minus sign to indicate work being done on the system. If the final volume is smaller than the initial volume the integral would be negative, but the system has gained energy (work has been done on it). The minus sign is required to set the sign of work to be consistent with our definition that positive energy implies the system has gained energy.

#### 6.1.5 Enthalpy

So far in the notes we have invoked the concept of internal energy (in the first law of thermodynamics). The internal energy is the energy contained within the system boundary (how much energy the system has) but it doesn't consider anything beyond the system boundary.

Now we introduce the concept of enthalpy, which is the internal energy of the system, plus some extra energy beyond the system boundary. This extra energy we include is the work required to create room for the system in the universe. Unless the system is created in a vacuum, there will be some energy required to displace the surrounding atmosphere, for the system to exist within (which would not be considered in the internal energy term). For this reason, enthalpy is sometimes called the thermodynamic potential of a system.

$$H = U + PV$$

Where,

- H: Enthalpy
- U: Internal Energy
- P: Pressure
- V: Volume

In Mass and Energy Balances, you used the concept of specific enthalpy widely ( $h$ , enthalpy per unit mass). As a reminder, you would have determined enthalpy 3 different ways: 1) By integrating specific heat values over a temperature range ( $dh = C_p dT$ ) 2) By using averaged specific heat values and 3) By looking up enthalpy values in the steam tables (for water and steam).

We will use all this assumed knowledge in Fun CE.

#### 6.1.6 Simple Mass and Energy Balances

The subject Mass and Energy Balances (CHEN20010) covers how to do mass and energy balances (unsurprisingly). You don't need to know all the content from M&EB to do Fun CE, but it's helpful to understand the very basics:

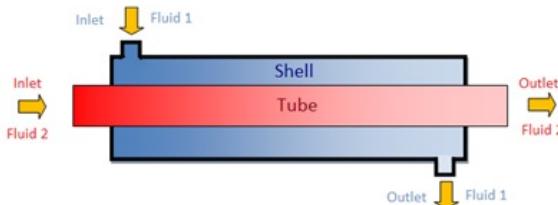
In chemical engineering problems, we usually assume mass is conserved, meaning that although matter can be transformed from one type of molecule into another (by chemical reaction) the mass can't disappear or be destroyed. One kilogram of matter can change into other chemicals, but it's still 1 kilogram. In 1905, Einstein showed this was not true (with the famous formula  $E = mc^2$ ) meaning mass can be transformed into energy, but we'll just put this on hold for the moment. Ignoring nuclear reactions, we assume mass is conserved and it's (almost) always true.

An energy balance is based on the first law of thermodynamics. Energy can be transformed into other forms, but the total amount of energy is always the same.

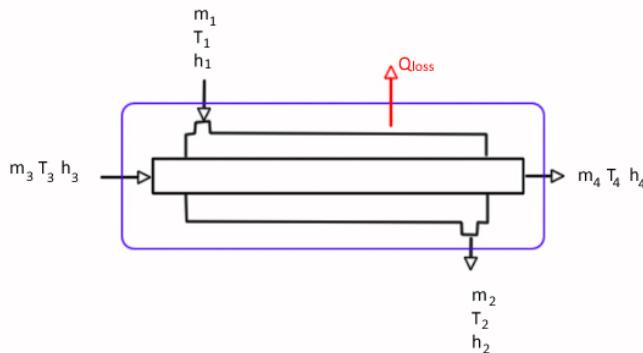
Using these 2 concepts, we can do a balance, to calculate the amount of mass coming out of a system (mass balance) or the temperature (or enthalpy) of mass when it leaves a system (from the energy balance).

#### *Mass and Energy Balance Case Study: Heat Exchanger*

In Fun CE we look at building and testing a heat exchanger in the practical. The purpose of a heat exchange is to move energy from one stream to another, but without mixing the streams. In the figure below, a hot stream (fluid 2) flows through a tube. Around the tube is a second larger tube (called the shell) that contains a cold fluid. If the tube is made of a highly conducting material (a metal like copper) then energy can flow from the hot steam (fluid 2) into the cooler stream (fluid 1). In this context, the energy moving from fluid 2 to fluid 1 is called *heat*. Fluid 1 will be warmer when it leaves the system and fluid 2 will be cooled.



A basic mass and energy balance problem can be set up as below:



As the 2 fluids do not physically mix and only transfer heat, if we assume steady state (nothing is changing with time and so there is no accumulation of mass within the system) we can write:

$$m_1 = m_2$$

$$m_3 = m_4$$

The mass flow in through each tube must equal the mass flowrate out. We can also complete an energy balance by saying the energy lost by the hot stream must equal the energy gained by the cold stream, plus the energy lost to the environment (through the walls of the shell). In this case, the energy balance becomes:

$$\text{Energy In} - \text{Energy Out} + \text{Accumulation} = 0$$

Again, assuming steady state, accumulation = 0

$$m_1 h_1 + m_3 h_3 - m_2 h_2 - m_4 h_4 - Q_{\text{loss}} = 0$$

Just a reminder about the temperature profiles,  $T_3 > T_4$  (the hot stream is being cooled);  $T_2 > T_1$  (the cold stream is being heated). Substituting in the mass balance relationships and collecting common terms on a single side, we can write:

$$m_3(h_3 - h_4) = m_1(h_2 - h_1) + Q_{\text{loss}}$$

The energy lost by the hot stream must be greater than the energy gained by the cold stream. In the diagram we have defined  $Q_{\text{loss}}$  as being out of the system, so if  $Q_{\text{loss}}$  is positive, it means the system is losing energy. If we drew the arrow the other day (going into the system) a  $Q$  would need to be negative for the system to lose energy. Direction is important in thermodynamic problems. In this module, we will use the convention that positive  $Q$  is always into the system (a positive heat flow implies the system is gaining energy).

We can now define an efficiency of the exchanger. 100% would imply all energy is transferred usefully from the hot stream to the cold. Less than 100% efficiency would imply some loss to the environment (the exchanger is not doing what it is designed to do).

$$h_{\text{HEX}} = \frac{m_1(h_2 - h_1)}{m_3(h_3 - h_4)} \times 100$$

$$h_{\text{HEX}} = 1 - \frac{Q_{\text{loss}}}{m_3(h_3 - h_4)}$$

We also know that:

$$Q = UA \Delta T_{LM}$$

**Q:** Heat flow between the hot and cold streams (usually expressed as joules/sec aka watts). This is not the same as  $Q_{loss}$ , it is the heat flow through the inner tube (between the tube and shell from hot to cold).

**U:** Heat transfer coefficient (a material property of the wall material, here the inner tube, as well as the fluid properties- you will learn to calculate this in Heat and Mass Transport Processes CHEN30005)

**$\Delta T_{LM}$ :** The log-mean temperature difference between the hot and cold stream sides. As the hot steam is getting colder and the cold stream is getting hotter, we need to take an average temperature difference between the 2 sides. You will learn about the origin of the log-mean temperature difference in Transport Processes.

So, the heat transferred between streams (Q) can be increased by:

1. Increasing the temperature difference between hot and cold streams ( $\Delta T_{LM}$ ). A large temperature difference leads to a larger driving force for heat transfer. Touching something hot leads to a lot of energy being transferred into your hand (which scolds your fingers).
2. Increasing the heat transfer area (A). If there is more area of contact between the hot and cold streams, the total amount of energy transferred will be greater. If the length of pipe of the HEX is very short, the stream temperatures will only change a little bit. If the length of pipe is very long, they will have more time to come to thermal equilibrium.
3. Lowering the resistance to heat transfer (U). Typically, this means making the tube out of a highly conducting material. You can also lower U by agitating the fluid flow so no stagnant boundary layer of fluid forms near the wall to provide more heat transfer resistance.

#### 6.1.7 Second Law of Thermodynamics

The second law of thermodynamics establishes the concept of entropy and then requires that for any isolated system the entropy always tends to a maximum. This has a number of important consequences: 1) the condition that heat flows from hot to cold (it never flows spontaneously from cold to hot) and 2) heat (a low-grade energy) cannot be completely converted into work (a high grade energy).

Entropy was developed as a concept first in the classical thermodynamic description when describing the isothermal step in a Carnot cycle (discussed in next module).

$$dS = \frac{dQ}{T}$$

Around a closed loop:

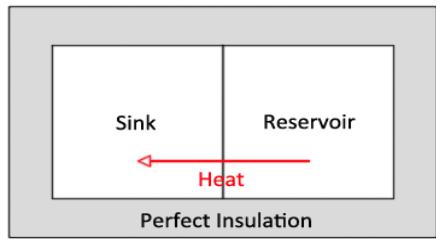
$$\oint \frac{dQ}{T} = 0$$

So, entropy (S) is path independent and can be defined as a state function.

To illustrate how entropy tends to a maximum with a simple example:

Imagine a heat sink in contact with a hot reservoir and isolated from the universe. Initially an insulated divider separates the sink and reservoir to prevent heat flow. The divider insulation is then removed allowing heat to flow between the 2

systems. For energy to flow into the sink, the temperature of the sink must be less than the reservoir. So, imagine that  $T_{SINK} < T_{RES}$ .



From the first law of thermodynamics, the energy lost by the reservoir must equal the energy gained by the sink.  $\delta Q_{SINK} = -\delta Q_{RES}$

Considering the sink and reservoir as a single isolated system (within the surrounding insulation):

The total change of heat of the system becomes:

$$\delta Q_{SYS} = \delta Q_{SINK} + \delta Q_{RES} = 0$$

Now consider the entropy change:

$$S_{SYS} = S_{SINK} + S_{RES}$$

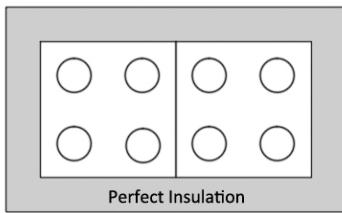
$$= \delta Q_{SINK}/T_{SINK} + \delta Q_{RES}/T_{RES}$$

As  $\delta Q_{SINK} = -\delta Q_{RES}$  and  $T_{SINK} < T_{RES}$ ,  $S_{SYS}$  must be  $> 0$ .

i.e., the entropy of the system as a whole must increase. This is the classical thermodynamic description of entropy; it is a parameter that is useful for describing heat flow, because it can be differentiated from energy (it came about from a description of the Carnot thermodynamic cycle, discussed in the next module). Although enthalpy change within the isolated system has remained zero, the entropy change has increased during the process of removing the thermal divider.

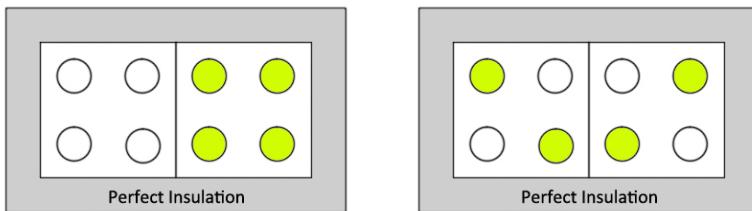
Entropy can also be described from a statistical thermodynamic perspective.

Imagine a box containing 8 atoms: 4 fixed on the left-hand side of the box and 4 fixed on the right-hand side.



Imagine 4 quanta of energy are dropped into the box. One quanta of energy can associate with any one atom. The probability of all 4 units of energy going into the right-hand side of the box is very low (1/70). But the probability that 2 units of energy land on the right-hand side and 2 units land on the left-hand side is comparatively high (there are 36 configurations out of 70 total that give this outcome).

In essence there are many more ways for the energy to organize so that 2 atoms on the left and 2 on the right have energy (rather than all the energy on one side). If each configuration is equally probable and random, then the chance is it divided into 2 units of energy on the LHS and RHS is much more likely than it is dividing so that all energy is on a the RHS (36/70 vs 1/70).



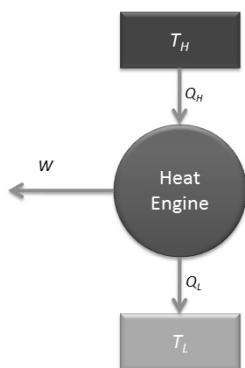
Imagine a thermal barrier is placed in the centre of the box. Energy is transferred from an external source into the right-hand side of the box. The thermal divider is then removed. If the energy is free to move between atoms, then over time it will organize itself to divide approximately evenly between the 2 halves. Why, because if the energy is free to move between atoms, then the probability of this outcome is much higher than all energy staying on one side of the box; there are more ways for the energy to configure itself. As the number of atoms increases and the amount of energy increases, the probability of dividing only increases.

This is why entropy is sometimes called a measure of the disorder of the system; the energy isolated in one half of the box represents an ordered state. This stored, concentrated energy can be used to extract useful work when it flows. Once the entropy of the system has been maximised (the energy quantas have been evenly distributed, the system has come to equilibrium,  $\delta Q/T$  inside the box is maximised) it can no longer extract work; our key resource is not energy, but an energy gradient. Energy evenly distributed throughout the universe has no use to us (this is sometimes called the entropic heat death of the universe and represents a theoretical point where the universe has reached its maximum entropic state and cannot sustain life and where no further work can be extracted).

## 6.2 Thermal Efficiency

Consider a steam engine. A furnace burns coal to release energy: some of this energy boils water to produce steam, which drives a piston/turbine to extract some useful work (e.g., for power generation in a coal-fired power plant, moving a locomotive in a steam train etc). However, some of the energy from the combustion of the coal cannot be recovered; it leaves in the flue gases as an exhaust. As this exhaust gas is not at absolute zero, we must consider this as lost energy that returns to the atmosphere and is not recovered for useful work.

A simplified way of thinking about the engine is shown below. The furnace represents a high temperature thermal source. Heat flows from this thermal source into the engine ( $Q_H$ ) which extracts some useful work ( $W$ ) but not all the energy from the heat source can be recovered and some of the heat is lost to a low temperature thermal sink ( $Q_L$ ).



We will define the efficiency of the engine ( $\eta$ ) as the amount of useful energy recovered (work,  $W$ ) over the amount of heat supplied ( $Q_H$ ) so that:

$$\eta = \frac{W}{Q_H} = \frac{Q_H - |Q_L|}{Q_H} = 1 - \frac{|Q_L|}{Q_H}$$

We could only obtain an efficiency of 100% if  $Q_L = 0$  (i.e., the exhaust gas left the system at absolute zero, 0 K). We put the modulus around  $Q_L$  to emphasise that it has a positive value in the context of the calculation here (i.e., we do not expect an efficiency above 100% because heat is leaving the system).

## 6.3 Thermodynamic Processes

Simulating a real engine can often be so complex that it becomes impossible. To make problems solvable, we make a few simplifying assumptions. These assumptions are usually about the process taking place in each step in the cycle (usually that one parameter is constant), which comes to represent an optimal limit of the engine but are practically unattainable. This doesn't make the thermodynamic simulation unrealistic or useless; it sets an upper limit on efficiency, for the best possible case and functions as a guide to how the performance of the engine will be affected when certain conditions are tuned.

We now want to derive the work, heat, change in internal energy and change in enthalpy for a range of processes:

- Isochoric
- Isobaric
- Isothermal
- Adiabatic
- Isenthalpic

- Isentropic

For an ideal gas, the internal energy and enthalpy can be expressed as:

$$dU = m C_V dT$$

$$dH = m C_P dT$$

Where  $C_V$  is the specific heat capacity at constant volume and  $C_P$  is the specific heat capacity at constant pressure. The derivation for the internal energy relationship is provided in Appendix A.

For an ideal monatomic gas,  $C_V$  and  $C_P$  are related to the degrees of freedom of the atoms and so  $C_V = 3/2R$  and  $C_P = 5/2R$ . The ratio of  $C_P / C_V$  is sometimes called the polytropic index and can be used to calculate the energy change in adiabatic systems.

Using these simplifications, we can complete the following derivations for ideal gases in the following processes:

*Isochoric: Constant Volume*

$$W = - \int P dV$$

=0

$$\Delta U = Q + W, \text{ so } \Delta U = Q = m C_V \Delta T$$

*Isobaric: Constant Pressure*

$$W = - \int P dV$$

$$= -P \Delta V$$

$$\Delta H = \Delta U + \Delta(PV) = Q + W + V\Delta P + P\Delta V$$

Substituting in our solution for work.

$$\Delta H = Q - P\Delta V + V\Delta P + P\Delta V$$

And as P is constant

$$\Delta H = Q = m C_P \Delta T$$

*Isothermal: Constant Temperature*

$$W = - \int P dV$$

Using the ideal gas law

$$PV = nRT$$

$$P = nRT/V$$

Substitute into the work

$$W = - \int \frac{nRT}{V} dV$$

$$W = -nRT \ln(V_2/V_1)$$

Constant temperature, so  $\Delta U = \Delta H = 0$

$$\text{So } Q = nRT \ln(V_2/V_1)$$

***Adiabatic: No heat flow (perfect insulation)***

For adiabatic processes, we can make use of the polytropic relationship.

$$PV^\gamma = \text{constant}$$

Where  $\gamma$  is the polytropic index. The polytropic index is the ratio of the specific heat capacity at constant pressure over the specific heat capacity at constant volume, so for monatomic ideal gases, this is usually assumed to be 5/3. But the specific value of  $\gamma$  makes no difference to the derivation here.

$$W = - \int P dV$$

$PV^\gamma = \text{constant}$  (only for adiabatic processes)

$$\text{So, } C = PV^\gamma = P_1 V_1^\gamma = P_2 V_2^\gamma$$

$$\begin{aligned} W &= - \int_{V_1}^{V_2} \frac{C}{V^\gamma} dV \\ &= -C \left( \frac{V_2^{1-\gamma} - V_1^{1-\gamma}}{1-\gamma} \right) \end{aligned}$$

C can be  $P_1 V_1^\gamma$  or  $P_2 V_2^\gamma$  depending on which is more convenient because these are equal.

So the work simplifies to:

$$W = (P_2 V_2 - P_1 V_1) / (\gamma - 1)$$

Adiabatic, so  $Q = 0$

$$\text{So } W = \Delta U = m C_V \Delta T$$

***Isoenthalpic: Constant Enthalpy***

As the enthalpy is constant, for an ideal gas this implies a constant temperature.

$$\Delta U = \Delta H = 0$$

$$Q = -W = nRT \ln(V_2/V_1)$$

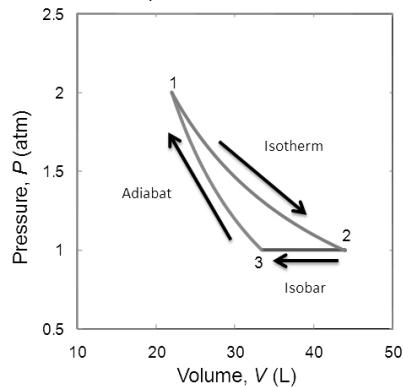
A summary of all solutions to all the processes is shown below. You need to know how to derive all of these relationships (do not try to just memorize them).

Process	Isobaric ( $\Delta P = 0$ )	Isochoric ( $\Delta V = 0$ )	Isothermal ( $\Delta T = 0$ )	Adiabatic ( $Q = 0$ )
<b>Energy Conservation</b>	$\Delta U = Q + W$	$\Delta U = Q$ $W = 0$	$\Delta U = 0^*$ $Q = -W$	$\Delta U = W$ $Q = 0$
<b>Work <math>W = -\int P dV</math></b>	$-P(V_2 - V_1)$	0	$P_1 V_1 \ln(V_1/V_2)$	$(P_2 V_2 - P_1 V_1) / (\gamma - 1)$
<b>Heat, <math>Q</math></b>	$m c_p (T_2 - T_1)$	$m c_v (T_2 - T_1)$	$P_1 V_1 \ln(V_2/V_1)$	0
<b><math>\Delta U</math></b>	$m c_v (T_2 - T_1)$	$m c_v (T_2 - T_1)$	$0^*$	$m c_v (T_2 - T_1)$
<b>Ideal Gas</b>	$V_1/T_1 = V_2/T_2$	$P_1/T_1 = P_2/T_2$	$P_1 V_1 = P_2 V_2$	$P_1 V_1^\gamma = P_2 V_2^\gamma$

**Worked Example 6.1:**

One mol of an ideal monatomic gas undergoes the following reversible cycle in a frictionless cylinder:

1. An Isothermal expansion
2. An Isobaric compression
3. An adiabatic compression



The conditions are:

Point 1:  $P_1 = 2 \text{ atm}$ ,  $V_1 = 22 \text{ L}$

Point 2 and Point 3:  $P_2 = P_3 = 1 \text{ atm}$

1. Calculate the pressure, volume and temperature at each point in the cycle
2. Calculate the change in enthalpy, internal energy, heat and work in each step
3. Calculate the thermal efficiency of the engine

As the gas is ideal, we may assume that  $C_p$  of the gas =  $5/2R$  and  $C_v = 3/2R$

*CHEN20012 Fun Chem Eng*

## 6.4 Types of Cycles

### 6.4.1 Heat Engine

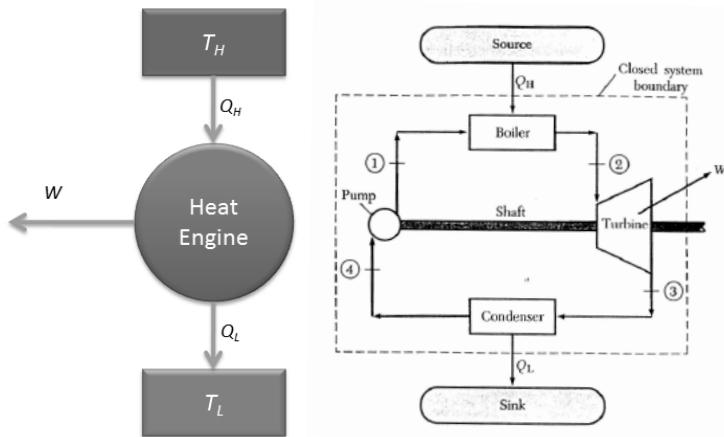
A heat engine converts heat into mechanical work so on a P-V diagram a thermodynamic cycle for a heat engine would be sequenced in a clockwise direction; it has a positive net heat into the system and negative net work (the system does work on the environment).

Heat engines are essential to everyday life: internal combustion engines (petrol and diesel engines for cars) and external combustion engines (gas turbines and steam turbines to generate power).

We can conceptualize heat engines with the diagram below. Heat flowing from a hot source to a cold sink can be exploited to generate useful work. The heat engine diagram is set out next to a schematic for a steam turbine, to illustrate how the engine works.

A furnace (coal fired, gas fired, nuclear powered) generates heat which is used to boil steam ( $Q_H$ ). As this steam builds up pressure and can be used to drive a turbine (to generate useful shaft work,  $W_s$ ). The low-pressure steam leaves the turbine and must be recompressed so it can be sent back to the boiler. To do this, the steam is condensed, but in doing so it loses some energy to the environment ( $Q_L$ ). The now liquid water is pumped back up to the design pressure of the boiler (using some of the shaft work from the turbine) and recycled to be boiled again.

Thinking about an energy balance around the steam engine, shows that the only energy crossing the system boundary is  $Q_H$ ,  $Q_L$  and  $W_s$  such that  $Q_H = Q_L + W_s$ .

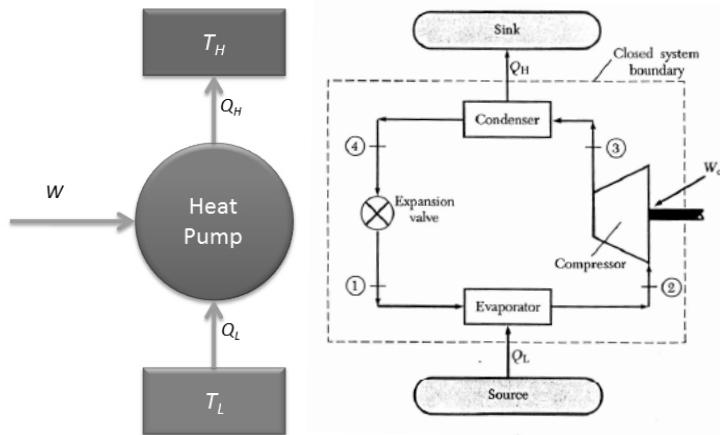


#### 6.4.2 Heat Pump

In essence, a heat pump works in the opposite way to a heat engine. It converts shaft work into heat flow, or more specifically, by taking in shaft work we can pump energy from cold to hot (where it would usually flow spontaneously from hot to cold). On a P-V diagram, this manifests as a thermodynamic cycle in a counter-clockwise direction; the net work is positive and net heat flow is negative into the system. The standard example of a heat pump is your refrigerator.

To help illustrate, a diagram of a heat pump is laid out next to a schematic for a refrigerator below. Beginning at point 1 in the refrigerator schematic, a low boiling point liquid held at low pressure is passed through an evaporator. The liquid evaporates, pulling heat from the cooling the heat source ( $Q_L$ ) and dropping its temperature (this would be the inside of your refrigerator).

A compressor is then used to increase the pressure of the low temperature – low pressure saturated vapour from the evaporator. This compressor needs shaft work to do the compression ( $W_c$ ), typically provided by an electric motor. As the pressure increases, the gas heats, and the boiling point rises, which results in a super-heated state for the vapour after the compressor. So, when it passes to the condenser, its temperature is now well above the ambient air temperature. Energy can be pulled from the high temperature super-heated vapour ( $Q_H$ ) first cooling it to its boiling point and then condensing it. The condensed vapour is then passed through an expansion valve, where its pressure drops (which also drops its boiling point). The vapour will partially flash and cool and so it can be returned to the evaporator at low temperature again.



Initially a heat pump may appear to violate the second law of thermodynamics; energy is being pumped from cold to hot, essentially creating more order. But it's important to remember that the shaft work used to drive the heat flow must come from somewhere; this shaft work creates a greater entropy somewhere else in the universe. So, the net entropy of the universe still increases and the second law of thermodynamics has not been violated.

## 6.5 Model Cycles

There are a range of theoretical models that can be used to describe heat engines and heat pumps. These consist of at least 3 (usually 4) thermodynamic processes. There are not real engine cycles, but rather theoretical cycles to describe idealized (maximally efficient) operations.

### 6.5.1 Carnot Cycle

In a Carnot cycle, there are 2 temperature reservoirs (at temperatures  $T_H$  and  $T_C$  respectively). They are considered to be sufficiently large that the temperature of the reservoirs is not affected by the process of each cycle.

The cycle itself consists of 4 processes:

1. Isothermal expansion: Heat added to system, Work extracted from system

Heat is added to the system, so it expands, but the heat is added sufficiently slowly and incrementally so that there is no localized heating. The system remains at constant temperature and in thermal equilibrium with the surroundings as the system expands.

2. Adiabatic expansion: Work extracted from system

The system is insulated from the surroundings and continues to expand, but now its temperature drops (as no heat flows into the system during expansion).

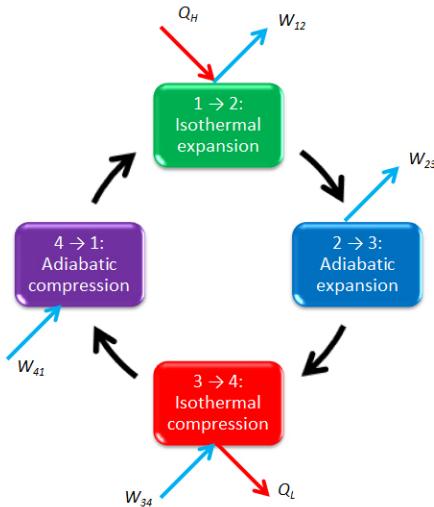
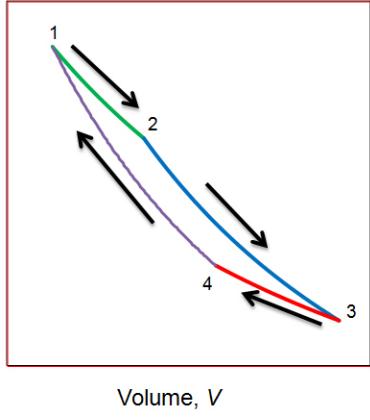
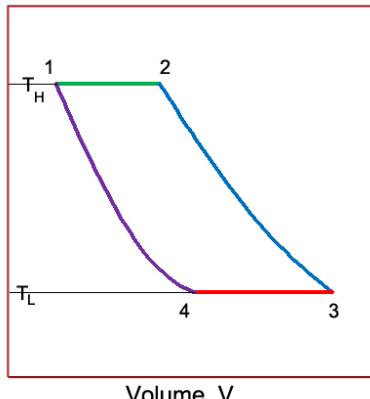
3. Isothermal compression: Heat extracted from system; Work added to the system

The system is placed in surroundings at the same temperature as this new low temperature. The insulation is removed, and the system is slowly compressed. The compression is sufficiently slow and incremental so that any localised heating keeps the system in thermal equilibrium with the surroundings.

4. Adiabatic compression: Work added to the system

The system is again thermally insulated and compressed (adiabatically). As the system is compressed, its temperature increases from the low temperature (thermal sink) back to the higher temperature (thermal reservoir).

As the 4 steps all represent idealized processes, the Carnot cycle is used to represent the highest possible thermal efficiency for an engine (a theoretical upper limit on engine performance).

Pressure,  $P$ Temperature,  $T$ 

- 1 → 2: Isothermal Expansion**
  - $\Delta U_{12} = 0, Q_{12} = -W_{12}, nRT_H \ln(V_2/V_1)$
- 2 → 3: Adiabatic Expansion**
  - $Q_{23} = 0, \Delta U_{23} = W_{23}, (C_V/R) \ln(T_H/T_L) = \ln(V_3/V_2)$
- 3 → 4: Isothermal Compression**
  - $\Delta U_{34} = 0, Q_{34} = -W_{34}, -nRT_L \ln(V_3/V_4)$
- 4 → 1: Adiabatic Compression**
  - $Q_{41} = 0, \Delta U_{41} = W_{41}, (C_V/R) \ln(T_L/T_H) = \ln(V_4/V_1)$

The cycle is reversible (no entropy change, maximum efficiency) and so the entropy lost by hot reservoir balances the entropy gained by the cold reservoir. The amount of heat extracted from the hot reservoir ( $Q_H$ ) and deposited in the cold reservoir ( $Q_L$ ) can therefore be written as:

$$Q_H = T_H \Delta S$$

$$Q_L = T_L \Delta S$$

And the difference between  $Q_H$  and  $Q_L$  is written as the work ( $W_S$ )

$$W_S = (T_H - T_L) \Delta S$$

*Carnot Cycle Efficiency*

The Carnot cycle represents the maximum possible efficiency for an engine given a particular temperature limit between the heat source and heat sink (think of the temperature of a boiler vs the exhaust temperature).

$$\eta = 1 - \frac{|Q_L|}{Q_H}$$

From the figure above, heat is only added or removed in 2 steps in the Carnot cycle (in the isothermal expansion and isothermal compression; by definition no heat is added/removed in the adiabatic steps).

We previously derived the heat flow during an isothermal process to be:

$$Q = nRT \ln(V_2/V_1)$$

So  $Q_H = nRT_H \ln(V_2/V_1)$  ( $V_2 > V_1$  so  $Q_H$  is positive as expected)

and  $Q_L = nRT_L \ln(V_4/V_3)$  ( $V_4 < V_3$  so  $Q_L$  is negative as expected)

$$|Q_L| = nRT_L \ln(V_3/V_4)$$
 (so it has a positive sign)

For the adiabatic step 4→1, we have previously shown that:

$$P_1V_1^\gamma = P_4V_4^\gamma$$

Using the ideal gas law,  $PV=nRT$

$$V_1^{\gamma-1} \cancel{nRT_H} = V_4^{\gamma-1} \cancel{nRT_L}$$

$$T_L/T_H = V_1^{\gamma-1}/V_4^{\gamma-1}$$

Similarly for the adiabatic step 2→3:

$$P_2V_2^\gamma = P_3V_3^\gamma$$

Substituting in the ideal gas law

$$T_L/T_H = (V_2/V_3)^{\gamma-1}$$

$$\text{So } T_L/T_H = (V_1/V_4)^{\gamma-1} = (V_2/V_3)^{\gamma-1}$$

$$\text{So } V_3/V_4 = V_2/V_3$$

$$\text{Rearrange: } V_2/V_1 = V_3/V_4$$

Substituting into the efficiency calculation:

$$\eta = 1 - \frac{nRT_L \ln(V_3/V_4)}{nRT_H \ln(V_2/V_1)}$$

$$\ln(V_3/V_4) = \ln(V_2/V_1)$$

$$\eta = 1 - \frac{T_L}{T_H}$$

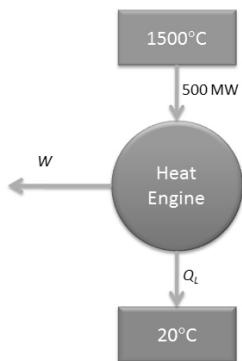
For a Carnot cycle, the ratio of temperatures (between heat source and heat sink) is related to the ratio of heat flows and the efficiency of the cycle.

To maximise the efficiency of the Carnot cycle, we want to minimise the ratio of  $T_L/T_H$ ; this means lowering the temperature of the sink (reducing heat losses) or raising the temperature of the heat source (to minimise the percentage of heat lost to the thermal sink).

The Carnot cycle (the theoretical maximum efficiency engine) can only have 100% efficiency when the temperature of the heat sink is 0 K (i.e., absolute zero).

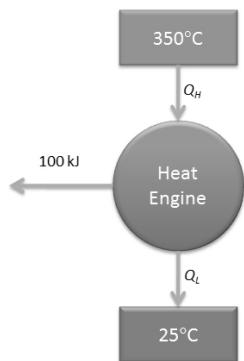
**Worked Example 6.2**

Determine the maximum amount of work that may be extracted from a heat engine with a heat source at a temperature of  $1500^{\circ}\text{C}$  which provides 500 MW of power, given the heat sink is at a temperature of  $20^{\circ}\text{C}$ .



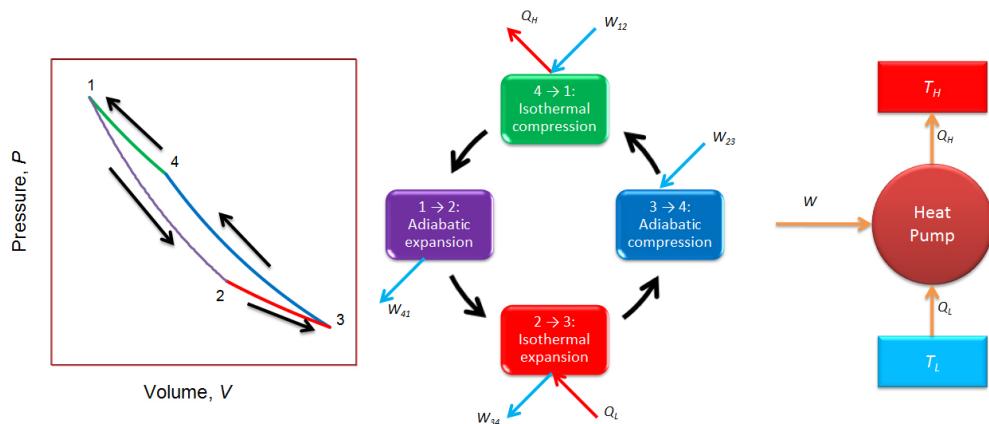
**Worked Example 6.3**

Determine the heat input into a Carnot engine that operates between temperature limits of 350°C and 25°C and produces 100 kJ of work output.



### 6.5.2 Reverse Carnot Cycle

So far, we have spoken about the Carnot cycle as a model for a heat engine. If we reverse the direction of thermodynamic processes in the cycle (on a P-V diagram this now moves in a counter-clockwise direction) we can consider the Carnot cycle as a model for a heat pump: Net work is added to the system and net heat is taken out of the system; the heat source is the low temperature, and the heat sink is now at the high temperature.



Rather than thinking about the efficiency of a reverse Carnot cycle, we introduce the concept of coefficient of performance (COP). Like the efficiency, the COP is still defined as ‘what we get out’ vs ‘what we pay for it’ but here the benefit is the cooling duty at the low temperature source and the cost is the work supplied to drive the heat transfer from cold to hot.

$$COP = \frac{Q_L}{W}$$

$W = |Q_H| - Q_L$  (we add the modulus to  $Q_H$  to denote it as positive here)

$COP = Q_L / (|Q_H| - Q_L)$

As before,  $Q_L / |Q_H| = T_L / T_H$

$$COP = \frac{T_L}{T_H - T_L}$$

Note that because of the definition of coefficient of performance, it can be above 100% (unlike the efficiency calculation)

### 6.5.3 Otto Cycle

The Otto cycle is a thermodynamic cycle typically used to model a spark ignition engine (for example a 4-stroke petrol engine in a car).

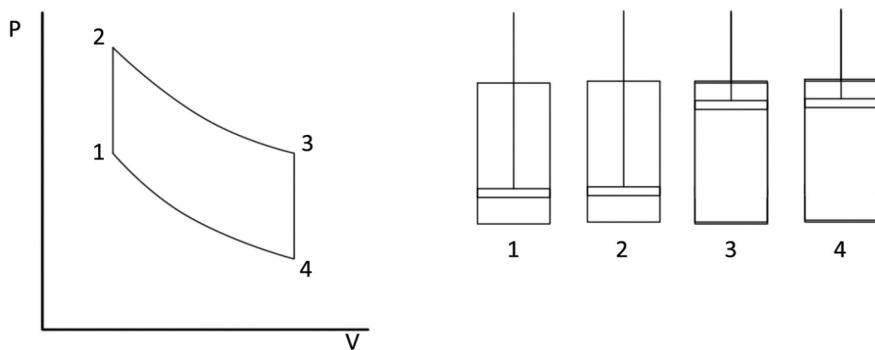
The Otto cycle consists of the following steps:

1→2 Isochoric heat addition: This is intended to represent the ignition of the fuel-air mixture in the engine cylinder. The cylinder is at its most compressed position and a spark plug ignites the fuel-air mix. Before the piston has time to physically move, the pressure dramatically increases due to rapid combustion. This step takes place almost instantaneously (a very short time scale).

2→3 Adiabatic expansion: This is often called the power stroke. It is intended to represent the expansion of the cylinder as it now has time to move from the higher pressure generated after ignition of the fuel. It takes place over a longer time scale than step 1→2.

3→4 Isochoric heat removal: Heat is rejected from the exhaust gases while the piston is at its highest position (commonly called bottom dead centre, because of the distance from the crank shaft)

4→1 Adiabatic compression: New fuel is injected into the cylinder and it is compressed from bottom dead centre to top dead centre position, ready for ignition again, so the cycle is completed.



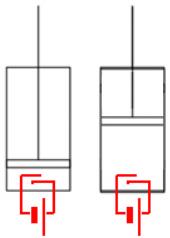
From the known thermodynamic relationships derived earlier, we can determine the efficiency of the Otto cycle (as we did for the Carnot cycle) for an ideal gas. This derivation is left as an exercise in one of the tutes but should yield the result:

$$\eta_{Otto} = 1 - \frac{1}{r^{\gamma-1}}$$

Where  $\gamma$  is the polytropic index as used before ( $C_p/C_v$ ) and  $r$  is the compression ratio, which represents the highest piston volume (bottom dead centre) over the lowest piston volume (top dead centre).

$$r = \frac{V_4}{V_1}$$

To conceive of this another way, imagine a piston with a spark plug at the bottom. The spark plug can be turned on manually at any time to ignite the fuel. Imagine the piston is charged with fuel. The plunger is manually pushed down towards the bottom of the cylinder, and then the fuel is ignited with the spark plug. The piston will push against atmospheric resistance for a long stroke and hence will do a lot of work. Imagine the experiment is repeated but that the plunger is only pushed halfway down the cylinder. When the fuel is ignited, the system will do less work because the length of the stroke will be shorter (for the same input of fuel). So, the compression ratio (how far down the plunger can be pushed before ignition) is essential to the overall efficiency of the engine.



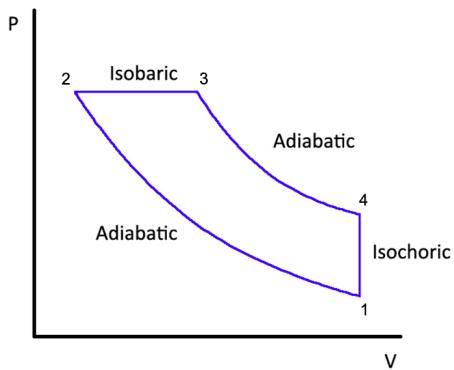
Worked Example 6.4

A petrol engine can be modelled as an Otto cycle. The maximum pressure in the cycle is 30 atm and the minimum pressure in the cycle is 1 atm. The cylinder has a maximum volume of 1L and a compression ratio of 10. Assuming a polytropic index of 1.2, calculate the net work in the cycle and heat into the system ( $Q_H$ )

### 6.5.4 Diesel Cycle

The Diesel cycle is an idealized thermodynamic cycle used to model a diesel engine. The diesel engine is named after Rudolph Diesel who developed the theory and patent for the engine in the early 1890s. The first Diesel engine was not built until 1897. In the history of science, this is an example where theory preceded invention; Diesel understood that the fuel efficiency in a petrol engine was limited by its compression ratio and built an engine to pass this limit.

Unlike a conventional petrol engine, a diesel engine has no spark plug (a spark plug is connected to the car battery and provides a spark ignition for the fuel). Instead, the fuel-air mixture is compressed to a point where the temperature increases to the auto-ignition temperature of the fuel. This means the fuel-air mixture needs to be compressed to a smaller volume (greater compression ratio) which results in higher overall efficiency.



The cycle is similar to an Otto cycle, but steps 2→3 are an isobaric expansion (not isochoric).

1→2 Adiabatic (isentropic) compression of the fuel; work is done by the piston compressing the fuel-air mixture. The system is compressed further than in an Otto cycle, to the auto-ignition temperature of the fuel.

2→3 Constant pressure heating from the combustion of the fuel

3→4 Adiabatic expansion of the working fluid to push the piston out and produce usable work

4→1 Isochoric cooling by venting the exhaust gases from the piston

The efficiency of the Diesel engine may be derived to give:

$$\eta_{Diesel} = 1 - \frac{1}{r^{\gamma-1}} \left( \frac{\alpha^\gamma - 1}{\gamma(\alpha - 1)} \right)$$

Where r: compression ratio ( $V_1/V_2$ )

$\alpha$ : Cutoff Ratio ( $V_3/V_2$ )

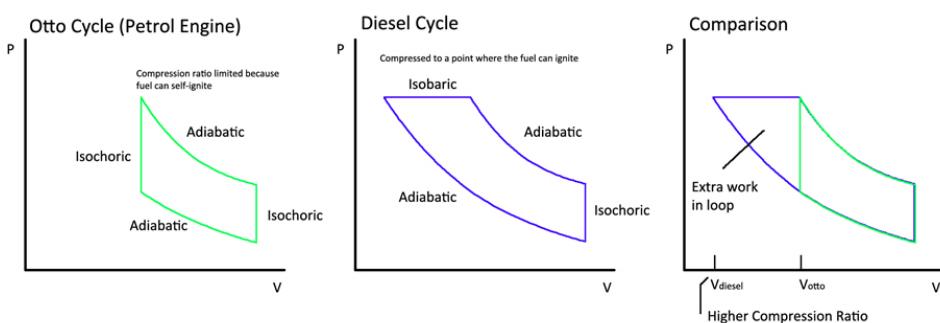
$\gamma$ : Polytropic index

### 6.5.5 Comparing Otto Cycle and Diesel Cycle

The Otto and Diesel cycles are very similar; they would be identical except for the isobaric step after fuel ignition in the diesel cycle. The diesel cycle usually produces more fuel-efficient engines; the reasoning can be seen when overlaying the thermodynamic cycles below.

Imagine 2 cylinders are made with equal maximum volume; one for an Otto cycle and one for a Diesel cycle. The same amount of fuel-air mix is put into both cylinders. As the Diesel cycle compresses the cylinder to a smaller final volume (to reach the auto-ignition temperature of the fuel) it extracts more work in each cycle.

This can be reasoned graphically as well. The area enclosed by the cycle on the P-V diagram represent the work done per cycle. When overlaying the 2 cycles, for the same total cylinder volume and the same maximum pressure in the cycle, the Diesel cycle encloses a larger area than the Otto cycle, because it can compress the plunger to a smaller volume.



## 6.6 Other Thermodynamic Cycles

A summary of other cycles you may encounter.

Cycle	Compression	Heat Addition	Expansion	Heat Rejection
External combustion or heat pump cycles				
Carnot	adiabatic	isothermal	adiabatic	isothermal
Brayton	adiabatic	isobaric	adiabatic	isobaric
Stoddard	adiabatic	isometric	adiabatic	isometric
Stirling	isothermal	isometric	isothermal	isometric
Ericsson, 2 <sup>nd</sup>	isothermal	isobaric	isothermal	isobaric
Internal combustion				
Otto (petrol)	adiabatic	isometric	adiabatic	isometric
Diesel	adiabatic	isobaric	adiabatic	isometric
Brayton (jet)	adiabatic	isobaric	adiabatic	isobaric
Lenoir (pulse jet)	isobaric	isometric	adiabatic	isobaric

**Module 6 Summary****Key Concepts:**

- Basic thermodynamics
  - Laws of thermodynamics
  - Thermal efficiency
  - Thermodynamic cycle stages (isochoric, isobaric, isothermal, adiabatic)
- Thermodynamic cycles
  - Heat engine/ pump
  - Carnot/ Reverse Carnot
  - Otto
  - Diesel
  - Other cycles

**Key Skills:**

- Calculate thermodynamic efficiency, work, and power for a cycle
- Derive expression for efficiency, work and power based on cycle stages (isochoric, isobaric, isothermal, adiabatic)

**Appendix A: Derivation of Internal Energy for an Ideal Gas**

$$dU = dQ + dW \text{ (first law of thermodynamics)}$$

$$dS = dQ/T \text{ (defined by the second law of thermodynamics)}$$

$$dW = -PdV \text{ (definition of work)}$$

So we can rewrite the internal energy as

$$dU = TdS - PdV$$

$$\begin{aligned} dS &= (\partial S / \partial T)_V dT + (\partial S / \partial V)_T dV \\ \text{so } dU &= T(\partial S / \partial T)_V dT + T(\partial S / \partial V)_T dV - PdV \\ &= T(\partial S / \partial T)_V dT + [T(\partial S / \partial V)_T - P]dV \\ &= (\partial Q / \partial T)_V dT + [T(\partial S / \partial V)_T - P]dV \end{aligned}$$

The Helmholtz free energy (A) can be written as:

$$A = -SdT - PdV$$

So from the symmetry of second derivatives of A with respect to T and V

$$(\partial S / \partial V)_T = (\partial P / \partial T)_V$$

$$dU = (\partial Q / \partial T)_V dT + [T(\partial P / \partial T)_V - P]dV$$

$(\partial Q / \partial T)_V$  is the heat capacity at constant volume by definition (i.e.,  $mC_V$ ).

$dU = mC_VdT + [T(\partial P / \partial T)_V - P]dV$  This is a really useful thermodynamic relationship and come from the first and second law.

Now substituting in the Ideal Gas law equation of state:

$$PV=nRT$$

$$\begin{aligned} dU &= C_VdT + [T(\partial P / \partial T)_V - P]dV \\ &= mC_VdT + [P - P]dV \\ &= mC_VdT \end{aligned}$$