

FOUNDATIONS OF CHEMICAL AND BIOLOGICAL ENGINEERING I



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CHAPTER OVERVIEW

1: Introduction to Chemical Processes and Process Diagrams

- 1.1: Project Scoping
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1.1: Project Scoping

Learning Objectives

By the end of this section, you should be able to:

- **Define** the components of a design basis memorandum

Phases in the Construction of a Plant

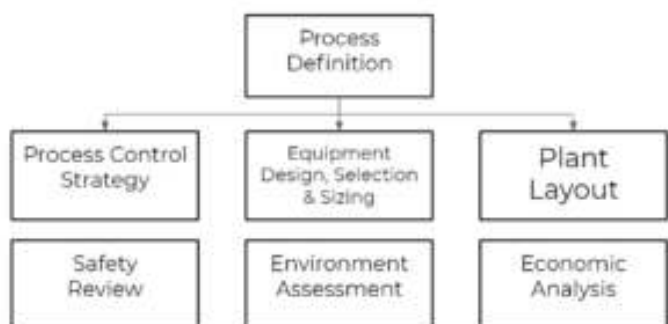
Chemical plant construction can be split into four broad stages which come one after another:

1. **Basic Engineering** – the scale of the plant, the draft of the process flow diagram (PFD, we will introduce this later in the course), cost estimation, preliminary schedule, etc.
2. Detailed Engineering – client approved PFDs, a detailed construction schedule, real data of equipment costs from vendors, etc.
3. Construction
4. Commissioning (start-up)

*In this course, we will only focus on **basic engineering**.*

What do we produce as engineers?

Basic Design Package: This document is provided to clients by engineers and may consist of the following:



A thorough basic engineering design package can be found on the website of [Startail Management and Consulting Services](https://eng.libretexts.org/@go/page/101135).

Design Basis Memorandum (DBM): This document contains key information and data related to the project deliverables.

A design basis memorandum is typically 10-20 pages and mainly consists of the following information:

1. Contractual issues
 - Project scope
 1. High-level description of the product to be made
 2. Feeds used in the process
 3. Technology description
 - Plant capacity and location
 - Product specification
 1. Composition purity
 2. Temperature
 3. Pressure
 - Operating philosophy
 - Deliverables and schedule
 - Gantt chart

2. Plant site-specific issues

- Feed specifications
 1. Temperature
 2. Pressure
 3. Composition
- Utilities
- Emission requirements
 - What the site can emit according to local law
- Site environmental conditions
 1. Atmospheric pressure
 2. Wind
 3. Maximum and minimum temperatures
 4. Rainfall
- Environmental and safety issues
- Control and electrical requirements

3. Design-specific issues

- Equipment, instrument, and line numbering
- Units
- Standards
 - Certain technical equipment have certain standards (pressure vessels, heat exchangers, electrical work)

Process Design Scope

The discussion of what is inside and outside battery limits is usually established early in the design process to give a clear indication of what engineers are responsible for in their design.

- **Inside Battery Limits:** equipment and components that are associated with the main process feed streams ^[1], such as piping on process fluid streams.
- **Outside Battery Limits:** equipment, components, utilities, and other facilities acting on the utilities or waste treatment (not included in inside battery limits) that are associated with the process, but not related to the current design scope. ^[1]

✓ Example: DBM Content – Production of Vinyl Chloride

text

Solution

text.

Say we want to build a plant that produces 360,000 tonnes per year of a vinyl chloride monomer (C_2H_3Cl) to be used in the production of polyvinyl chloride (PVC). One reaction pathway is shown below.



A DBM for this process might consist of the following items:

For contractual issues:

- High level description of vinyl chloride and uses
- Ethane and chlorine feeds to be used
- Reactor type being used
- Plant capacity of 360,000 tonnes/yr of vinyl chloride, located in Houston, Texas
- Operating composition purity, temperature, and pressure
- Operating philosophy

- Gantt chart showing project timeline

For site-specific issues:

- Temperature, pressure, and composition of feed (inside battery limits)
- Cooling water used at 25°C and 2 atm and steam at 20°C and 3 atm (outside battery limits)
- Emission predictions and requirements
- Atmospheric pressure, little wind and rainfall, maximum and minimum temperatures at location
- Environmental and safety issues at locations
- Control and electrical requirements of the plant

For design-specific issues:

- Equipment, instrument, and line numbering
- Units used in calculation (imperial or SI)
- Standards
- Certain technical equipment have certain standards (pressure vessels, heat exchangers, electrical work)

✓ Exercise: Classifying Inside & Outside Battery Limits

Consider a process where benzene is fed into a process for oxidization and purification in a plant. The process also consists of using 2 utility streams (cold water and steam) used in heat exchangers in the plant, as well as an onsite wastewater treatment operation. Your company has been hired to do basic engineering for the oxidation and purification process. Classify the oxidation, purification, wastewater treatment, and utility supply as either inside battery limit or outside battery limit.

Solution

Add example text here.

- Oxidation: inside battery limit – this will be done of the benzene **feed (primary)** stream
- Purification: inside battery limit – this will be done of the benzene **feed (primary)** stream
- Waste Water Treatment: outside battery limit – in this case, wastewater treatment is a **secondary** process and not within the design scope.
- Utility supply: outside battery limit – in this case, utilities are **secondary** process elements

Note that in other cases the outside batter limit elements above could be included inside the battery limits depending on what the client asks the engineering design firm to do. However with our example above we had clearly stated the design firm was only focusing on the oxidation and purification steps.

An interactive or media element has been excluded from this version of the text. You can view it online here:

<https://pressbooks.bccampus.ca/chbe220/?p=1756>

References

[1] CII – CII Glossary. [Online]. Available: <https://www.construction-institute.org/resources/knowledgebase/about-the-knowledge-base/glossary/cii-glossary>. [Accessed: 29-May-2020].

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1.2: Basic Economic Analysis

Learning Objectives

By the end of this section, you should be able to:

- **Apply** basic measures of economic merit to perform initial estimates of project economic feasibility

Basic Process Economics

As with any venture, we want to ensure a chemical plant is profitable to operate. In order to get an initial sense of this in a project, we may perform basic economic analysis. This analysis relies on four basic figures of merit and we will see how these are used to perform basic economic analysis on a process.

The four basic figures of merit are:

1- Gross Economic Potential (GEP): generally in dollars/yr

$$\text{GEP} = \text{Value of Products} - \text{Value of Feeds} \quad (1.2.1)$$

GEP has to be positive, otherwise, our product is worth less than our feed and we will definitely be losing money accounting for the operating costs.

2- Net Economic Potential (NEP): generally in dollars/yr

$$\text{NEP} = \text{GEP} - \text{Production Costs (utilities, labour, maintenance)} \quad (1.2.2)$$

NEP again has to be positive, otherwise, we cannot pay for the process to operate.

3- Capital Costs (CC) : generally in dollars

Cost of design plant and construction

4- Return on Investment (ROI) : generally in %yr

$$\text{ROI} = \frac{\text{NEP}}{\text{CC}} * 100 \quad (1.2.3)$$

ROI also has to be positive, generally most processes require a certain minimum ROI, typically above 10%. ROI represents the percentage of capital costs recovered each year. The higher the ROI is, the more favorable the process is.

One thing that is essential to find our first figure of merit, GEP, is chemical pricing data. We will look at how to find this data now as it is so essential for evaluating processes. For now, we will not focus on how to assess production and capital costs but will revisit these later in the course.

Finding Chemical Pricing Data

Finding this data can be very challenging. Companies typically want to keep pricing information secret (for competition reasons). The best way I have found to search for chemical pricing data is as follows:

1. Go to [Texas A&M Chemical Pricing Database](#)
2. Enter a chemical name (i.e. Ethylene) or CAS number (Chemical Abstracts Services; can be found on Wikipedia), click "EXECUTE QUERY".

Chemical Price: Select Criteria



- Find a citation from “ICIS Chemical Business” and note the edition and page number (i.e. 2018, April 6; 19). Make sure the chemical name matches the one you are searching for.

Chemical Price

ICIS#	Chemical	Region	Date Type	Publication Date	Source Title	Notes	Citation
157-21-1	Methylolurea (MOLU)	US	Range	6/12/2022	ICIS Chemical Business	Price and Market Trends	Anonymous (2022) June 12) Price & Market Trends: Pricing: ICIS Chemical Business, 20(122), 12-13.
1602-81-4	Polystyrene	US	Range	6/12/2022	ICIS Chemical Business	Price and Market Trends	Anonymous (2022) June 12) Price & Market Trends: Pricing: ICIS Chemical Business, 20(122), 12-13.
14-62-5	Ethylene	Global S.E. Asia, Europe	Chart	5/12/2022	ICIS Chemical Business	Price Chart	Anonymous (2022) May 12) Value Chart: Ethylene: ICIS Chemical Business, 20(122), 20-22.
157-08-2	Ethylene Isobutene	Global S.E. Asia, Europe	Chart	5/12/2022	ICIS Chemical Business	Price Chart	Anonymous (2022) May 12) Value Chart: Ethylene: ICIS Chemical Business, 20(122), 20-22.
14-62-5	Ethylene	US	Single Value	4/6/2018	ICIS Chemical Business	Price and Market Trends	Anonymous (2018) April 6) US ethylene rises, April 19th call, 17th Chemical Business, 20(122), 18.

- Go to [UBC Library](#) and type in “ICIS Chemical Business” into the search bar and search
- Click on the source by Factiva, Business Source Ultimate



- Click on “Browse Journal”. Find the issue of the journal from the list on the right.

+ Jun 2018
 + May 2018
 -- Apr 2018
 Issue 5793 - 4/27/2018
 Issue 5792 - 4/20/2018
 Issue 5791 - 4/13/2018
 Issue 5790 - 4/6/2018
 + Mar 2018
 + Feb 2018

- Find the specific article you found from the Texas A&M Database citation using the dates



- Once you find your article, click “UBC eLink”. This should take you to a new page where you can access the full text
- Search through the article for the chemical of interest’s price

This process is tedious and often takes some time, even for people experienced in this process. So don’t get discouraged when looking for this data and feel free to ask questions (through the discussion board, in tutorials or office hours, etc.).

✓ Example: Pricing of Vinyl Chloride

text

Solution

text.

- Go to [Texas A&M Chemical Pricing Database](#)
- In the ‘Chemical’ textbox, type in ‘Vinyl Chloride’ and click on ‘Execute Query’.

- Note the citation “Ho, Z.X. (2019, September 6). PVC. ICIS Chemical Business, 296 (9), 36.” This citation is sourced from ICIS Chemical Business, which we can access from UBC Library
- Go to [UBC Library](#) and type in “ICIS Chemical Business” into the search bar and search
- Click on the source by Factiva, Business Source Ultimate
- Click on ‘Browse Journal’
- On the right side of the page, there will be a list of issues. Click on “Sep 2019” and then on “9/6/2019”
- Scroll down to the 18th article. This article is by “Ho, Zhi Xuan”, which is consistent with the source we found in the [Texas A&M Website](#)
- Click on “Check UBC eLink for Full Text”. You will be directed to a new page. Click on the third “Full Text Online” link from ABI/INFORM Collection.
- You will be directed to a ProQuest page. Scroll down to the 6th link by “HO, Zhi Xuan.”. Click on the “PVC” link.
- Search through the article for PVC pricing

From this article, we find that vinyl chloride was priced at **870-895 USD/tonne** by CFR India, **840-870 USD/tonne** by CFR GCC (Gulf Coast in the southern US) and **860-870 USD/tonne** CFD East Med.[2] This range of values is dependent on multiple factors, and as you see depend on geography. We may choose a value depending on where our plant is located. Since our vinyl chloride plant is in the Gulf Coast, we might choose **855 USD/tonne** as a rough average for that specific range.

✓ Example: Vinyl Chloride Production Economic Analysis

text

Solution

text.

Our client wants to produce 360,000 tonnes/yr (800 million lbs/yr) of vinyl chloride monomer. We decide to use the following reaction pathway, which contains two reaction steps as follows:



We gather the following information on the process:

Name	Formula	Molecular Weight (g/mol)	Price (USD/tonne)
Ethene	C_2H_4	28.05	733
Chlorine	Cl_2	70.91	240
Dichloroethane	$C_2H_4Cl_2$	98.96	300
Hydrogen Chloride	HCl	36.46	140
Vinyl Chloride	C_2H_3Cl	62.50	750

Assume as well that our production costs are $200 \frac{USD}{tonne}$ of VC produced, and assume our VC production plant costs 50,000,000USD to build. Note these values usually depend on the size of the plant, location, and other factors.

Calculate or find all four economic figures of merit.

We know that one of the product streams will be 360,000 tonnes/yr of vinyl chloride. Hydrogen chloride is produced in a 1:1 molar ratio with vinyl chloride:



$$HCl = 5,760 \frac{tonne - mol}{yr} * 36.46 \frac{tonnes}{tonne - mol} = 210,000 \frac{tonnes}{yr} \quad (1.2.6)$$

Similarly for ethane and chlorine, we get:

$$C_2H_4 = 5,760 \frac{\text{tonne} - \text{mol}}{\text{yr}} * 28.05 \frac{\text{tonnes}}{\text{tonne} - \text{mol}} = 162,000 \frac{\text{tonnes}}{\text{yr}} \quad (1.2.7)$$

$$Cl_2 = 5,760 \frac{\text{tonne} - \text{mol}}{\text{yr}} * 70.91 \frac{\text{tonnes}}{\text{tonne} - \text{mol}} = 408,000 \frac{\text{tonnes}}{\text{yr}} \quad (1.2.8)$$

Process Economics

1 – Gross Economic Potential (GEP) in USD/yr

GEP = Value of Products – Value of Feeds

$$GEP = 140 \frac{\text{USD}}{\text{tonne}} * 210,000 \frac{\text{tonnes}}{\text{yr}} + 750 \frac{\text{USD}}{\text{tonne}} * 360,000 \frac{\text{tonnes}}{\text{yr}} - 733 \frac{\text{USD}}{\text{tonne}} * 162,000 \frac{\text{tonnes}}{\text{yr}} - 240 \frac{\text{USD}}{\text{tonne}} * 408,000 \frac{\text{tonnes}}{\text{yr}} \quad (1.2.9)$$

$$GEP = 83,000,000 \frac{\text{USD}}{\text{tonne}} \quad (1.2.10)$$

2 – Net Economic Potential (NEP) in USD/yr

NEP = GEP – production costs

Using our assumed production costs of $200 \frac{\text{USD}}{\text{tonne}}$ of VC produced.

$$NEP = 83,000,000 \frac{\text{USD}}{\text{tonne}} - 200 \frac{\text{USD}}{\text{tonne}} * 360,000 \frac{\text{tonne}}{\text{yr}} \quad (1.2.11)$$

$$NEP = 11,000,000 \frac{\text{USD}}{\text{yr}} \quad (1.2.12)$$

3 – Capital Costs (CC) in USD

Total cost of plant design and construction

This will be our VC production plant capital building cost of 50,000,000USD.

4 – Return on Investment (ROI) in %/yr

ROI = NEP/CC*100%

$$ROI = 11,000,000 \frac{\text{USD}}{\text{yr}} * \frac{1}{50,000,000 \text{USD}} * 100 \quad (1.2.13)$$

$$"class = \quad (1.2.14)$$

ROI is generally written simply in % and this is assumed to be %/yr. The higher the ROI the better.

References

[1] CII - CII Glossary. [Online]. Available: <https://www.construction-institute.org/resources/knowledgebase/about-the-knowledge-base/glossary/cii-glossary>. [Accessed: 29-May-2020].

[2] Ho, Z. X. (2019). PVC. ICIS Chemical Business, 296(9), 36. [Online]. Available: <http://ezproxy.library.ubc.ca/login?url=https://search.proquest.com/docview/2292001228?accountid=14656> [Accessed: 06-June-2020].

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1.3: Introduction to Flowsheeting

Learning Objectives

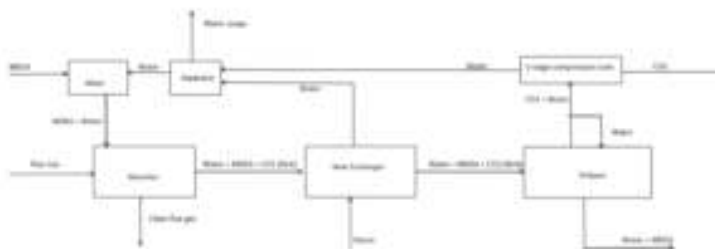
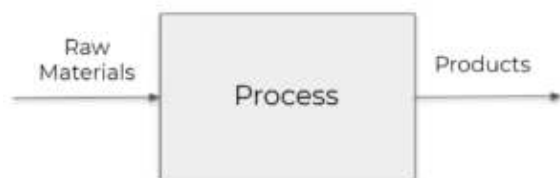
By the end of this section, you should be able to:

- **Recognize** the 4 key types of flow sheets

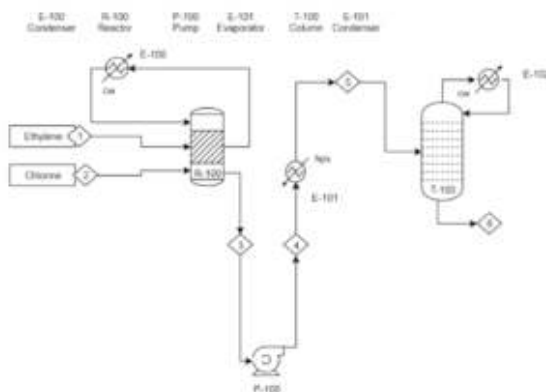
Types of Diagrams

There are 4 key types of flow sheet and they are shown below in increasing complexity:

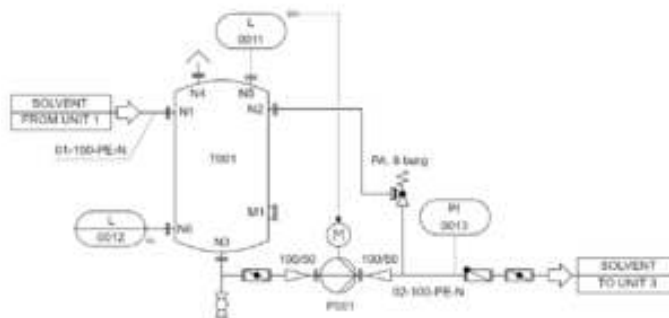
1. Input-Out Diagrams



2. Block Flow Diagrams (BFDs)



3. Process Flow Diagrams (PFDs)



4. Piping and Instrumentation Diagrams (P&IDs)

Image from [Con-struct](#) / CC BY-SA

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1.4: Input-Output Diagrams

Learning Objectives

By the end of this section, you should be able to:

- **Create** input-output diagrams

Input-Output Diagrams

These diagrams are considered to be the simplest of process flow sheets. In input-output diagrams, the entire process is represented by 1 block only. They usually only reference the main process streams in and out of a process.



✓ Example: Ammonia Production Input-output Diagram

text

Solution

text.

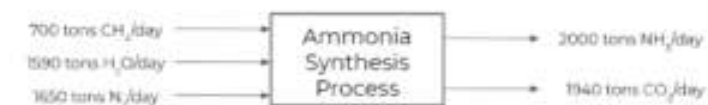
Consider an ammonia production process where 3 main streams of raw materials enter the process:

- 700 tons/day of methane
- 1590 tons/day of water
- 1650 tons/day of nitrogen

The process produces 2 main product streams:

- 2000 tons/day of ammonia
- 1940 tons/day of carbon dioxide

We can put together the following input-output diagram for this process:



✓ Exercise: Benzene Production Input-output Diagram

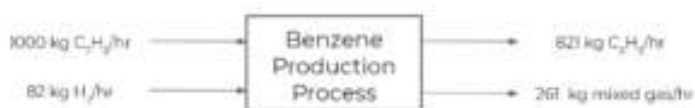
Consider a process where toluene is fed into a process at 1000 kg/hr and hydrogen is fed at 82 kg/hr. The following reaction takes place in the process:



The reaction achieves 75% conversion and the products of the process are separated into 2 streams. The first product stream is benzene, exiting at 821 kg/hr. The second product stream is a mixed gas stream (including the unreacted reactants and by-products) exiting at 261 kg/hr. Draw an input-output diagram for this process.

Solution

Add example text here.



✓ Exercise: Production of Vinyl Chloride

Our client wants to produce 360,000 tonnes/yr (800 million lbs/yr) of vinyl chloride monomer. We decide to use the following reaction pathway, which contains two reaction steps as follows:



We gather the following information on the process:

Name	Formula	Molecular Weight (g/mol)	Price (USD/tonne)
Ethene	C_2H_4	28.05	733
Chlorine	Cl_2	70.91	240
Dichloroethane	$C_2H_4Cl_2$	98.96	300
Hydrogen Chloride	HCl	36.46	140
Vinyl Chloride	C_2H_3Cl	62.50	750

Assume as well that our production costs are $200 \frac{USD}{tonne}$ of VC produced, and assume our VC production plant costs 50,000,000USD to build. Note these values usually depend on the size of the plant, location, and other factors.

Create an input-output diagram of the process.

Solution

Add example text here.

We know that one of the product streams will be 360,000 tonnes/yr of vinyl chloride. Hydrogen chloride is produced in a 1:1 molar ratio with vinyl chloride:



$$HCl = 5,760 \frac{tonne - mol}{yr} * 36.46 \frac{tonnes}{tonne - mol} = 210,000 \frac{tonnes}{yr} \quad (1.4.4)$$

Similarly for ethane and chlorine, we get:

$$C_2H_4 = 5,760 \frac{tonne - mol}{yr} * 28.05 \frac{tonnes}{tonne - mol} = 162,000 \frac{tonnes}{yr} \quad (1.4.5)$$

$$Cl_2 = 5,760 \frac{tonne - mol}{yr} * 70.91 \frac{tonnes}{tonne - mol} = 408,000 \frac{tonnes}{yr} \quad (1.4.6)$$

From this and the information in the table, we get the following input-output diagram:



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1.5: Block Flow Diagrams

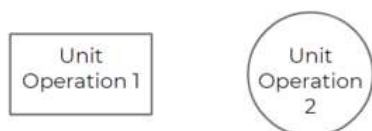
Learning Objectives

By the end of this section, you should be able to:

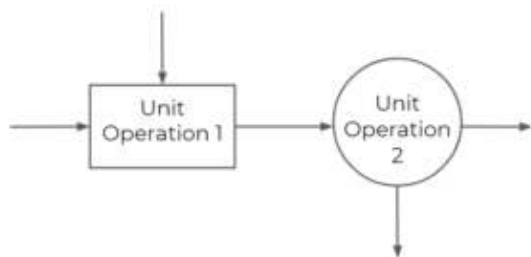
- **Construct** block flow diagrams (BFDs) for chemical processes

Block Flow Diagrams

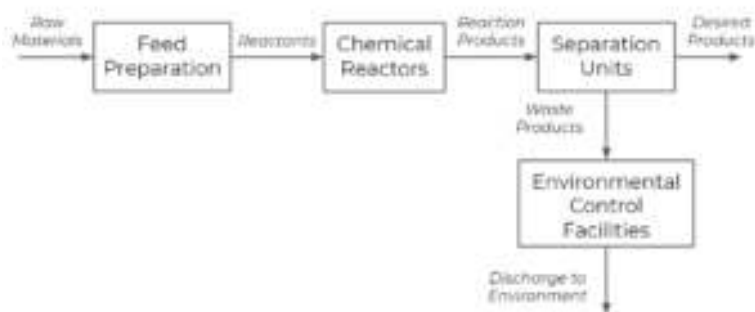
We typically break down chemical and biological processes (or any other process) into units representing equipment. These are called **unit operations** and are drawn as circles or squares:



Lines with arrows represent the flow of materials in streams to and from units. These lines have only 1 arrowhead:

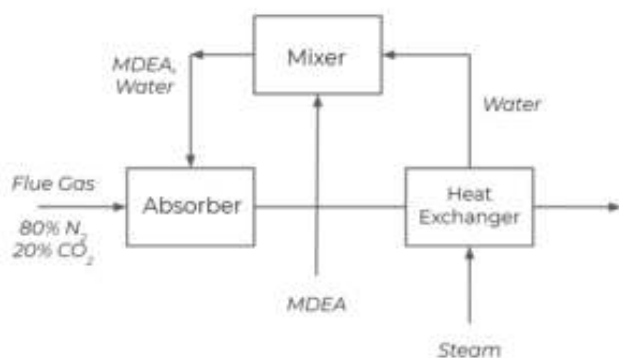


Materials in each stream are labeled above or beside the stream:

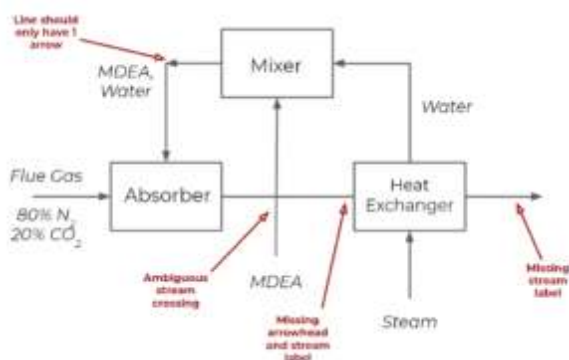


Exercise: BFD Components

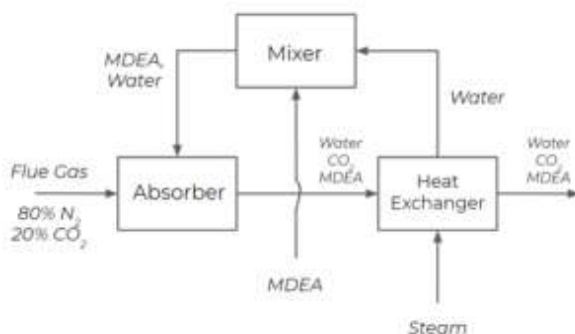
What are some errors in the following flowsheet? How would you change the flowsheet to address these errors?



Solution



We can correct the BFD to following:



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1.6: Unit Operations and Material Balances

Learning Objectives

By the end of this section, you should be able to:

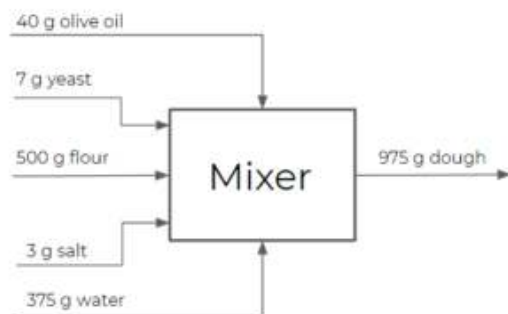
- **Define** common unit operations and use these when constructing process flow sheets

Recognize the need to apply basic material balances

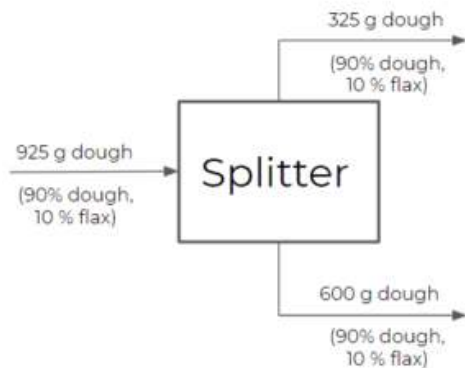
Common Units

We will go over four common unit types below, many other units are variants of these basic types of units.

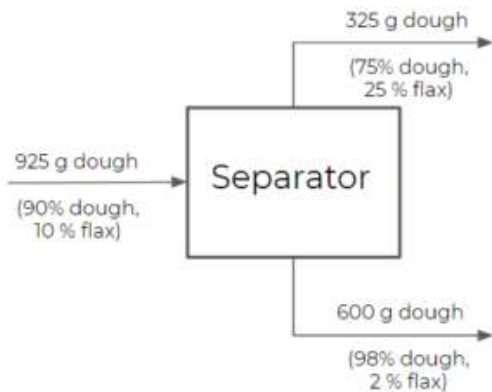
- **Mixer:** has multiple feed streams and mixes these streams into one output stream



- **Splitter:** a splitter will split a feed stream into multiple streams with the same composition. The exiting streams are not necessarily equal in terms of flow rates, but will always have the same composition



- **Separator:** a separator is similar to a splitter, but has the ability to split streams into different exiting compositions



- Reactor: a reactor typically consists of a vessel in which a reaction (or multiple reactions) takes place. There are many different types of reactors, some of which you will learn more about in future courses (e.g. CHBE 376 & CHBE 355)



Processes are often represented as interconnected process units consisting of mixers, reactors, splitters, and separators among other unit operations.

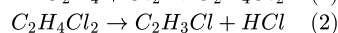
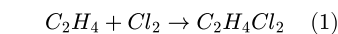
Examples of other common unit operations:

- Distillation (a separation process using the difference in boiling points of components)
- Absorption (removing components from a vapour stream using a liquid) and stripping (removing components from a liquid stream using a vapour)
- Extraction (a process that purifies a dissolved substance using its solubility in two immiscible liquids)
- Heat exchanger
- Filtration

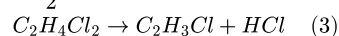
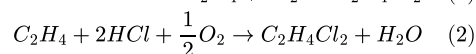
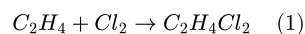
Example

Vinyl Chloride Production Process

Recall the vinyl chloride production process from the last chapter:



We now consider an additional reaction in the vinyl chloride production process. Most vinyl chloride manufacturers use the combination of direct chlorination and oxychlorination, which is called the *balanced process*.



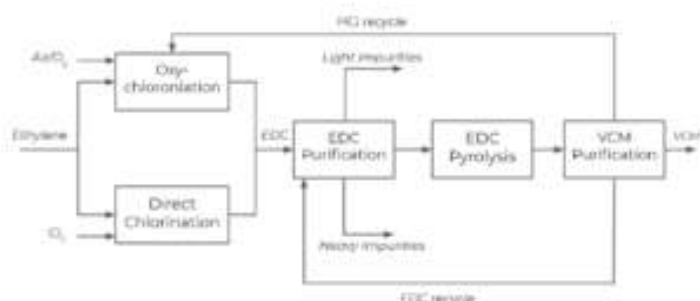
1. Direct Chlorination (last lecture)
2. Oxychlorination
3. Ethylene dichloride pyrolysis (last lecture)

What is the overall reaction and what advantage does this have over what we saw last chapter?

To get the overall reaction, we add all the reactions and cancel any compounds that appear in both the reactants and products of the overall reaction. In the separation process, HCl is recycled back to the oxychlorination reactor if it is not depleted to ensure no HCl is released into the environment. Reaction (1) is balanced with the rest of the process in a way to provide the source of $C_2H_4Cl_2$ for reaction (3). This process gives us only 1 by-product: water. Using the balanced process gives us water as a by-product as opposed to hydrogen chloride.



This process is carried out in multiple unit operations. To achieve the maximum efficiency and avoid releasing hazardous chemicals, hydrogen chloride produced in reaction 3 is recycled back to the oxychlorination reactor and used reaction (2), as well as unreacted EDC(ethylene dichloride, $C_2H_4Cl_2$) in reaction 3 is recycled to react again.



- Ethylene enters the process and is split into 2 streams: 1 stream goes to the oxychlorination reactor and the other stream goes to the direct chlorination reactor
- Air and/or oxygen are fed into the oxychlorination reactor and chlorine is fed into the direct chlorination reactor
- EDC produced by both the oxychlorination and direct chlorination processes, and is fed into a purification unit to separate from the other components in the system
- EDC is then fed into the EDC pyrolysis reactor, followed by the VCM(vinyl chloride monomer, C_2H_3Cl) purification unit, which separates HCl, VCM, and EDC into 3 separate streams

Compound	Boiling Point (°C)
C_2H_4	-103.7
HCl	-85.05
Cl_2	-34.04
C_2H_3Cl	-13.4
$C_2H_4Cl_2$	83.47
$C_2H_3Cl_3$	114

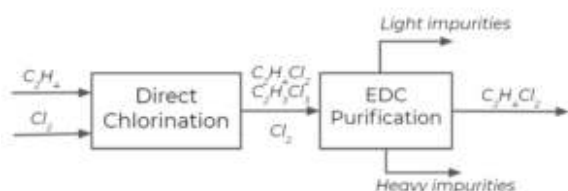
Separation of Components

As depicted above, we have light products (the components that are more volatile than our desired product, EDC), heavy products (the components that are less volatile than our desired product), and a stream of EDC. Let's look at separating the components after direct chlorination:

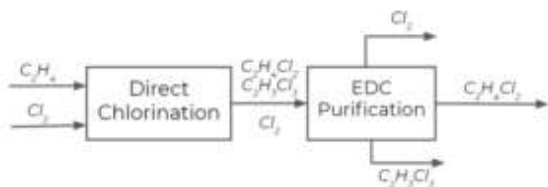


For simplicity, say we only have chlorine (Cl_2), ethylene dichloride (EDC, $C_2H_4Cl_2$), and trichloroethane (TCE, $C_2H_3Cl_3$) produced from a side reaction as products of the direct chlorination step. In reality, there may be other components in the stream, but we will stick to these three as the main components for this analysis. How many streams will come out after the EDC purification processes, and what are the components of each stream? How do we select the temperature for the purification process?

Compound	Boiling Point ($^{\circ}C$)
Cl_2	-34.04
$C_2H_4Cl_2$	83.47
$C_2H_3Cl_3$	114

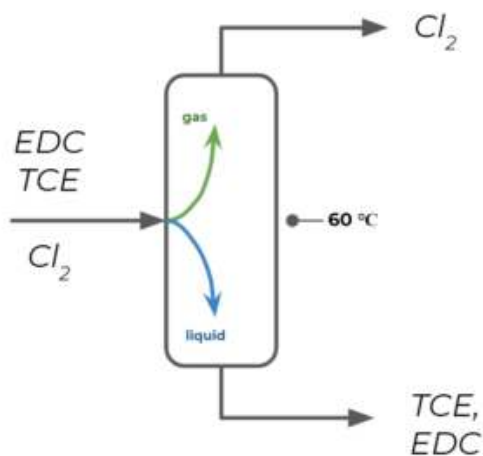


From the boiling point temperatures, we can deduce that the light product will be Cl_2 (boils at a lower temperature) and the heavy product will be $C_2H_3Cl_3$ (TCE) (boils at a higher temperature).

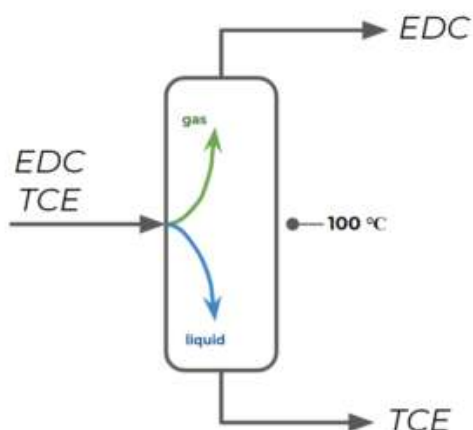


We can consider the separation of EDC from TCE and chlorine using 2 distillation columns. In this course, we'll assume that distillation columns separate a single feed stream into two exit streams. There are more complex column arrangements with a greater number of entering and exit streams, but we won't go over these in this course. Distillation columns usually operate with a range of temperatures inside them, and we'll see why this is later in this course. For now, we'll just assign them an average temperature.

The first column separates EDC and TCE from chlorine by operating at a temperature that is lower than EDC's boiling temperature, but higher than Cl_2 's boiling temperature (let's say on average $60^{\circ}C$):



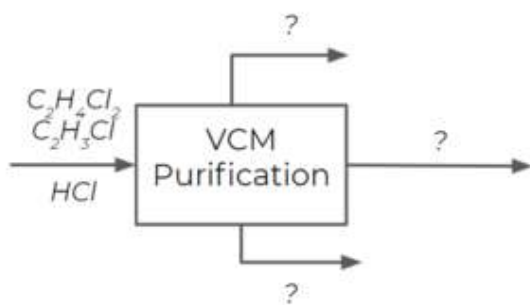
The second column separates EDC from TCE by operating at a temperature that is lower than TCE's boiling temperature, but higher than EDC's boiling temperature (let's say, 100°C):



Exercise

Separation Process

Consider the following vinyl chloride separation process:



The following data is available:

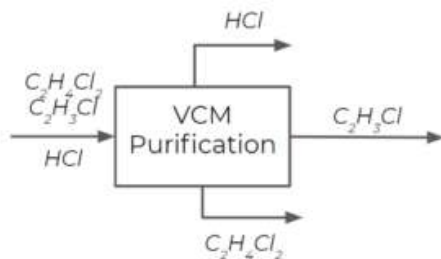
Compound	Boiling Point ($^{\circ}\text{C}$)
HCl	-85.05
$\text{C}_2\text{H}_3\text{Cl}$ (VC)	-13.4
$\text{C}_2\text{H}_4\text{Cl}_2$ (EDC)	83.47

How would you set up distillation columns for the separation of vinyl chloride (VC) from hydrogen chloride and EDC? Provide a temperature estimate could these columns be run at for separation.

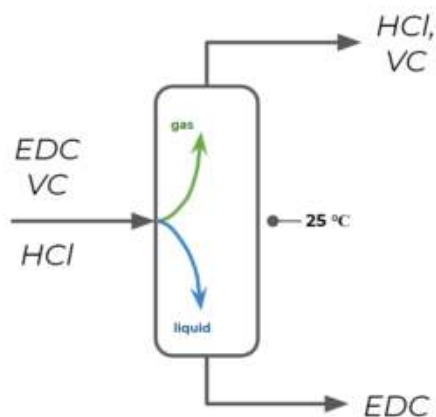
[Click here to see the solution!](#)

Solution

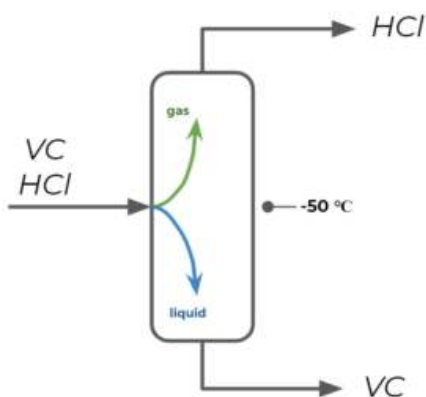
Step 1: Recognize that an easy way to separate 3 compounds is using 2 different distillation columns by separating out EDC in the first column and then separating vinyl chloride from HCl in the second column.



Step 2: For the first column, we separate EDC as a liquid, while HCl and vinyl chloride exit the column as gases. We choose a temperature that is lower than the boiling point temperature of EDC, but higher than the boiling point temperature of vinyl chloride. We have a large temperature range that meets these criteria, but we choose 25° since it is an easy temperature to work with (as it is close to ambient temperatures generally).



Step 3: For the second column, we separate VC as a liquid and HCl as a gas. We choose a temperature that is lower than the boiling point temperature of VC, but higher than the boiling point temperature of HCl . For example, we may choose -50° . *Note: this is a very cold working temperature for a distillation column and we might try to find ways to change this by manipulating pressure, but we will explore this later in this course and you will learn more through other courses.*



Material Balances

General material balance rules:

- What goes in must come out (or react)
- Total mass into and out of a unit should always be equal

- Molecules or moles may not be conserved, but the atoms should be

We won't cover material balances in-depth in this course. Instead, I will rely on you applying the concepts you are learning in your Material and Energy Balances course.

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1.7: Process Flow Diagrams (PFDs)

Learning Objectives

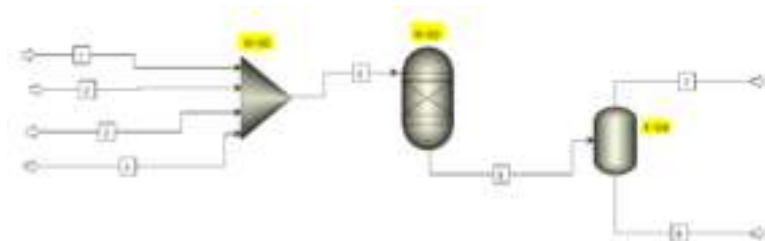
By the end of this section, you should be able to:

- **Build** process flow diagrams (PFDs)

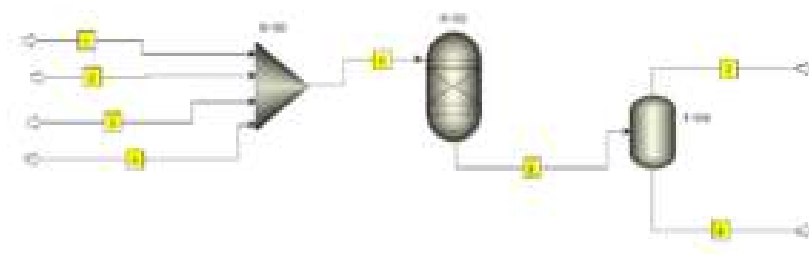
Process Flow Diagrams (PFDs)

Process flow diagrams usually include:

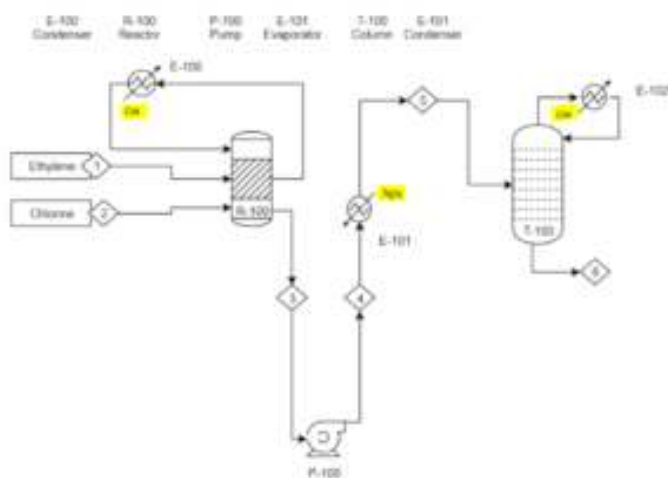
- Major pieces of equipment that are represented by a description and a unique equipment number and name



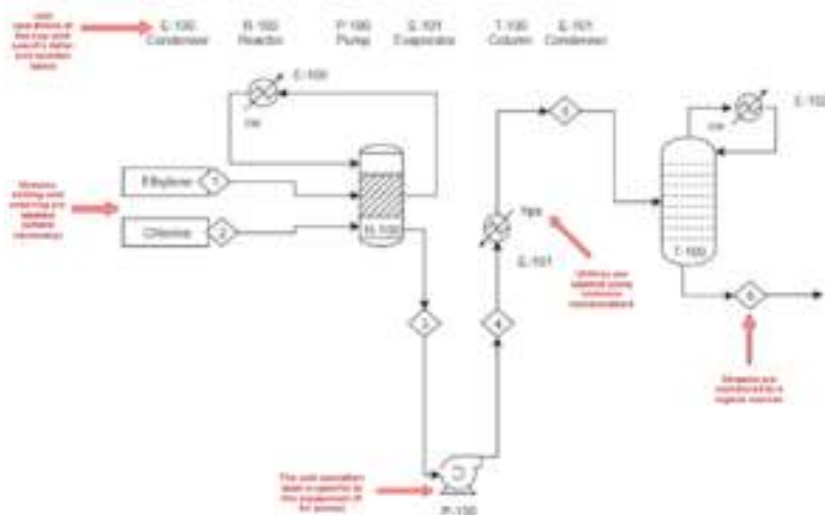
- Process flow streams that are represented by a number and sometimes include process conditions and chemical composition of each stream. This information can be shown on the PFD itself or on an accompanying flow summary table



- Utility streams for major equipment



- Basic control loops that present the overarching control strategy used to operate the processes. These are generally optional, and not shown in the diagrams above.
- An equipment summary table with key details (shown later in this chapter)



PFD Equipment Numbering

This is a typical way to label a piece of equipment using its position in the process. This is not the only way to label equipment, but a very common way. We will stick with this in this class and you will likely see it very commonly.

P-101A

- First letter: equipment (P = pump)
- First number: plant section (1 = section 1 of plant)
- Last numbers: equipment number (01 = pump 1 in this section)
- Last letters: show duplicates/triplicates when two or more of the same equipment is used for the same stage of the process.

Label	Equipment Description
C	Compressor or Turbine
E	Heat Exchanger
P	Pump
R	Reactor
T	Tower
TK	Storage Tank
V	Vessel

PFD Utility Naming

Generally, rather than using numbers, utility streams will be labeled using a certain descriptor. These streams are labeled in this way as the same type of stream will generally have the same conditions, and so this saves repeatedly specifying these streams with numbers.

Label	Utility Description
lps	Low-Pressure Steam (3-5 bar)
mps	Medium-Pressure Steam (10-15 bar)
hps	High-Pressure Steam (40-50 bar)
htm	Heat Transfer Media (organic)
cw	Cooling Water
rw	Refrigerated Water
rb	Refrigerated Brine
cs	Chemical Waste Water
ss	Sanitary Waste Water
el	Electric Heat
ng	Natural Gas
fg	Fuel Gas
fo	Fuel Oil

PFD Legend

The legend should include everything to allow someone to read the PFD with no prior knowledge of the project.



PFD Summary Tables

Stream Summary Table

Certain essential information must be included in stream summary tables, this may vary slightly depending on the industry, what we will stick within this class is the following:

- Stream number
- Temperature
- Pressure
- Vapour fraction
- Total mass flowrate

- Total mole flowrate
- Individual component mole flowrates

Other information may or may not be included as well:

- Stream name
- Component mole fractions
- Component mass fractions
- Individual component mass flowrates
- Volumetric flowrates
- Significant physical properties (density, viscosity, etc.)
- Thermodynamic data (heat capacity, specific enthalpy)

Stream Number	1	2	3	4	5	6
Temperature (°C)	25	25	90	90	95	250
Pressure (atm)	1.5	1.5	1.5	1.5	30	20
Vapor Fraction	1.0	1.0	0.3	0.6	0.5	1.0
Mass Flow (kg/hr)	50,000	105,000	149,000	276,000	276,000	276,000
Molar Flow (kmol/hr)	1,500	1,500	1,500	2,600	1,750	5,000
Component Molar Flow (kmol/hr)						
Ethylene	1,500	0	0	0	0	0
Chlorine	0	1,500	0	0	0	0
1,2-dichloroethane	0	0	1,500	0	0	0
Vinyl Chloride	0	0	0	2,600	0	2,500
Hydrogen Chloride	0	0	0	0	1,750	2,500

Equipment Summary Table

The equipment summary table provides information on equipment specifications. These are essentially a short list of key details used for the designing or costing of equipment. Examples of what might be specified in this table for different types of equipment are shown below. As you can see, these can be quite detailed, and you'll learn more about how to specify these parameters throughout your degree.

Equipment	Required Specification
Vessels	Height; diameter; pressure; temperature; materials of construction
Pumps	Flow; driver type; suction and discharge pressures; temperature; shaft power; materials of construction
Towers	Height; diameter; orientation; pressure; temperature; number and type of trays; height and type of packing; material of construction
Compressors	Inlet flow; driver type; suction and discharge pressures; temperature; shaft power; material of construction
Heat Exchangers	Type; area; duty; number of shell and tube passes; operating temperatures; pressures; pressure drops; material of construction
Fired Heaters	Type; tube pressure; tube temperature; duty; radiant heat transfer area; convective heat transfer area; material of construction

Exercise

PFD Components

Consider the following diagram:

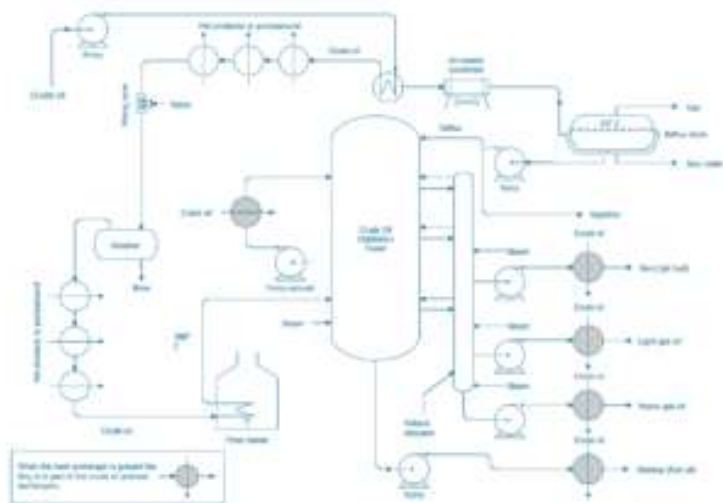


Image from [CS Odessa](#) / CC BY

If we wanted to turn this into a PFD, what would need to be added or modified?

[Click here to see the solution!](#)

Solution

- Add a legend
- Label the streams in a logical manner
- Name the equipment and utilities using the correct naming convention
- Add unit operation labels and description to the top or bottom of the PFD
- Also, consider adding stream and equipment summary tables

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1.8: Piping and Instrumentation Diagrams (P&IDs)

Learning Objectives

By the end of this section, you should be able to:

- **Understand** piping and instrumentation diagrams (P&IDs)

Piping and Instrumentations Diagrams (P&IDs)

P&IDs are based off of PFDs but include more specific information

P&IDs do not include:

- Operating conditions (T,P)
- Stream flows
- Equipment locations
- Supports, structures, and foundations
- Pipe routings (lengths, fittings such as elbows, but connections above a certain size are generally shown)

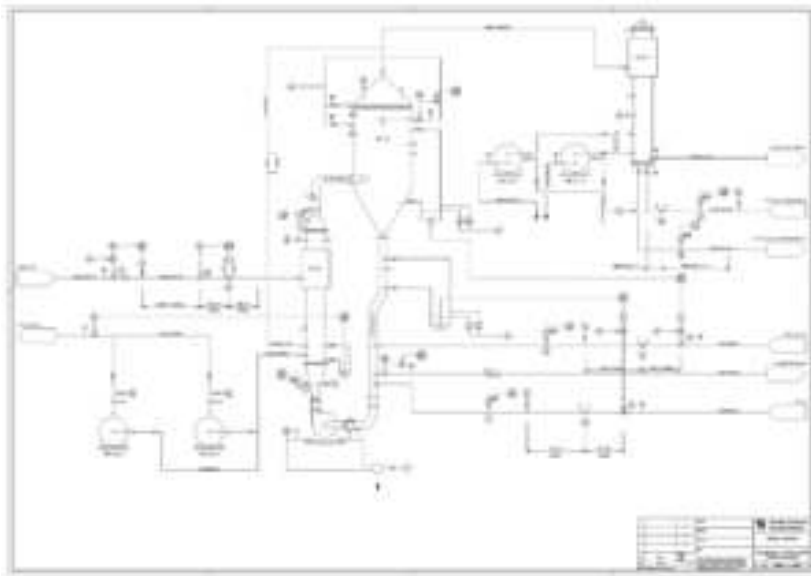


Image from [Ub](#) / [CC BY-SA](#)

A P&ID often depicts one unit operation in thorough detail.

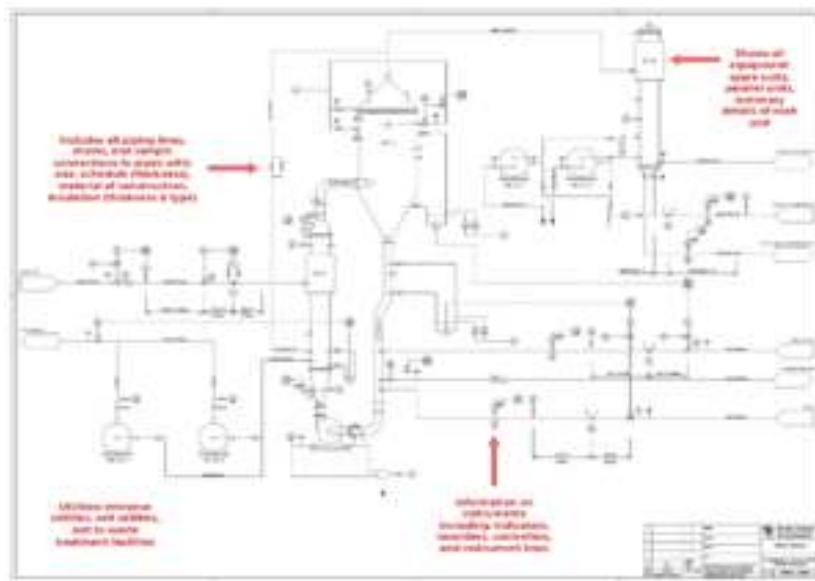


Image from Ub / CC BY-SA

✓ Exercise: P&ID Components

Consider the following diagram:

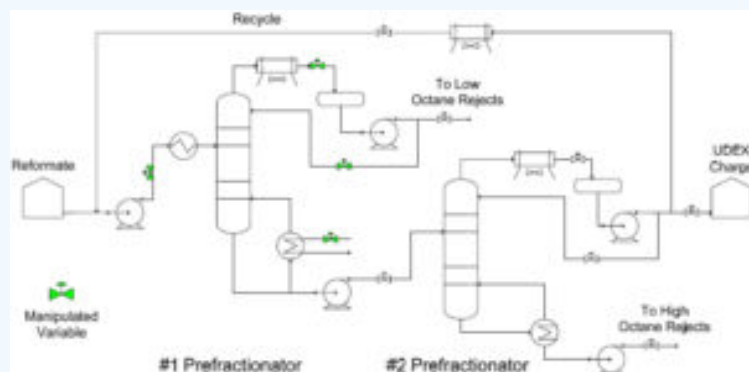


Image from Jim Cahill / CC BY-ND 2.0

What are some components that need to be added or adjusted to turn this into a P&ID?

Solution

Add example text here.

- Equipment details
- Control instrumentation details
- Utility exit and entrance details
- Piping sizing, schedule, material of construction, and insulation

P&ID Control Symbology

You will learn more about control symbols as you go through your degree. However, below we have a brief introduction to some important symbols.

Identification of Instrument Connections

	Capillary
	Pneumatic
	Electrical

Instrument connections

- Capillary: fluid flow control
- Pneumatic: air or gas flow control
- Electrical: electrical currents controls

Location of Instrumentation

	Instrument Located in Plant
	Instrument Located on Front of Panel in Control Room
	Instrument Located on Back of Panel in Control Room

Instrument locations

- Located in plant: generally means the instrument is near what it is measuring (local), it does not go to the control room
- Front panel in control room: Control rooms used to have instrument panels and would have manual controls on the front panel facing the operators, these have been replaced largely with digital (or virtual) screens which the operators can switch between different views. You could think of the main view in these digital screens as the front panel, with the most important controls or indicators shown.
- Back panel in control room: place for instruments that are perhaps less important or do not need to be looked at frequently. In our class we won't distinguish between these, but this is common notation you may see in P&IDs

Control panel rooms have changed quite a bit throughout the years. Below are examples of older and newer control panels.



Image from [XXBuilderXx](#) / CC BY-SA



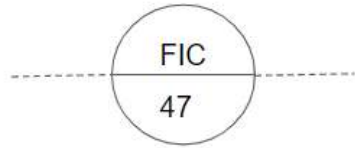
Image from [PEO ACWA](#) / CC BY 2.0

For the control symbology identification with the 'XYY' format:

	First Letter (X)	Second or Third Letter (Y)
A	Analysis (Composition/Concentration)	Alarm
C	–	Control
F	Flowrate	–
H	–	High
I	–	Indicate
L	Level	Light or Low
P	Pressure	–
T	Temperature	Transmit

✓ Exercise: P&ID Control

What information can you derive from the following control symbol?

**Solution**

Add example text here.

This is a flow indicator and controller, with the instrument located on the front panel of the control room with an electrical connection.

Resources for Building PFDs and P&IDs

- Visio: available through the CHBE Parallel's Client portal, as well as the CHBE computer labs
- [Visual Paradigm Online](#): includes specific process engineering equipment
- [Draw.io](#)
- AspenPLUS: you will use this in CHBE 376

Here is a thorough table of control symbology:

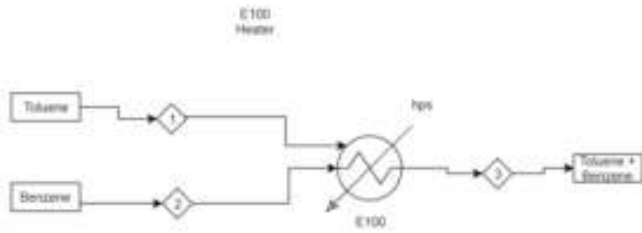
	First Letter (X)	Second or Third Letter (Y)
A	Analysis	Alarm
B	Burner Flame	–
C	Conductivity	Control
D	Density or Specific Gravity	–
E	Voltage	Element
F	Flowrate	–
H	Hand (Manually Initiated)	High
I	Current	Indicate
J	Power	–
K	Time or Time Schedule	Control Station
L	Level	Light or Low
M	Moisture or 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

Exercise

Building a PFD

A simple system consists of two feed streams (stream 1: toluene; stream 2: benzene) that enter a heater separately and combine into 1 stream to exit. The heater uses high-pressure steam as the utility. Build a simple process flow diagram of the process described above.

Solution



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1.9: Introduction to Chemical Processes and Process Diagrams Review

Important Equations

Gross Economic Potential (GEP)	$GEP = \text{Value of Products} - \text{Value of Feeds}$
Net Economic Potential (NEP)	$NEP = GEP - \text{production costs}$
Capital Costs (CC)	$CC = \text{Total cost of plant design and construction}$
Return of Investments (ROI)	$ROI = NEP/CC * 100\%$

Terms to Know

An interactive or media element has been excluded from this version of the text. You can view it online here:

<https://pressbooks.bccampus.ca/chbe220/?p=1801>

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1.10: Practice Exercises

Multiple Choice Questions

✓ Exercise: Design Basis Memorandum

A client for a vinyl chloride production plant is looking to find information in the design basis memorandum you've provided on how long it will take to complete the plant construction. Where can the client look for this information in the DBM?

- a) In the contractual issues section, under project scope
- b) In the plant site-specific issues section, under site environmental conditions
- c) In the design-specific issues section, under standards
- d) In the contractual issues section, under deliverables and schedule

Solution

Add example text here.

d) In the contractual issues section, under deliverables and schedule

The deliverables and schedule section of the DBM will contain a Gantt chart which can give the client information on

✓ Exercise: Process Diagrams

You are upgrading the control system on a reactor and heat exchanger in the plant. You'd like to present these updates to a group of engineers and operators in your company. What would be the best type of diagram to present in this scenario?

- a) P&ID
- b) BFD
- c) PFD
- d) Input-Output

Solution

Add example text here.

c) P&ID

For a technically-literate stakeholder group such as engineers and operators, it would be beneficial to present a process diagram with enough detail about the process and what streams and unit operations are involved. This requirement eliminates choices b and d. Given that this update focuses on the control system of the units, a PFD would not include this information. Therefore, a P&ID would be the best option for this scenario.

✓ Exercise: Equipment Labeling

What information does the label TK-203B give you?

- a) Storage Tank 2 in section 3B of the plant
- b) Storage Tank 3 in section 2B of the plant
- c) Storage Tank 2 in section 3 of the plant with other duplicate storage tanks
- d) Storage Tank 3 in section 2 of the plant with other duplication storage tanks

Solution

Add example text here.

d) Storage Tank 3 in section 2 of the plant with other duplication storage tanks

- First letter: equipment (TK = storage tank)
- First number: plant section (2 = section 2 of plant)
- Last numbers: equipment number (03 = storage tank 3 in this section)
- Last letters: show duplicates/triplicates when two or more of the same equipment is used for the same stage of the process.

Short Answer Questions

✓ Exercise: Unit Operations

What sequence of unit operations can we use to mix the ingredients to make cookie dough, then divide the dough into equal portions, followed by baking to make a batch of cookies?

Solution

Add example text here.

Mixer > Splitter > Reactor.

A mixer combines multiple process streams (separate ingredients) into one stream (one cookie dough). We can use a splitter to separate the dough into equal amounts. A splitter is different than a separator that a splitter divides the stream into streams with the same composition, while a separator separates the stream into streams with different compositions. Finally, a reactor (oven) can be used to bake the cookies.

✓ Exercise: Process Economics

Consider a company that has developed a process that produces cinnamon-scented wax melts used in spas, hotels, and homes for fragrancing. This company prides itself on making everything from the essential oil to the soy wax and beeswax in-house.



What is the gross economic potential of this process?

Solution

Add example text here.

Recall that the gross economic potential (GEP) is:

$$\text{GEP} = \text{Value of Products} - \text{Value of Feeds (\$/yr)}$$

The feed value can be calculated as follows:

- $\text{Cinnamon} = 2 \frac{\$}{\text{kg}} * 20 \frac{\text{kg}}{\text{yr}} = 40 \frac{\$}{\text{yr}}$
- $\text{Rapeseed oil} = 0.6 \frac{\$}{\text{kg}} * 100 \frac{\text{kg}}{\text{yr}} = 60 \frac{\$}{\text{yr}}$
- $\text{Honeycomb} = 10 \frac{\$}{\text{kg}} * 1000 \frac{\text{kg}}{\text{yr}} = 10,000 \frac{\$}{\text{yr}}$
- $\text{Soybean} = 2 \frac{\$}{\text{kg}} * 500 \frac{\text{kg}}{\text{yr}} = 1,000 \frac{\$}{\text{yr}}$

The product value can be calculated as follows:

- $WaxMelts = 500 \frac{\$}{kg} * 250 \frac{kg}{yr} = 125,000 \frac{\$}{yr}$
- $Waste = 0 \frac{\$}{kg} * 1370 \frac{kg}{yr} = 125,000 \frac{\$}{yr}$

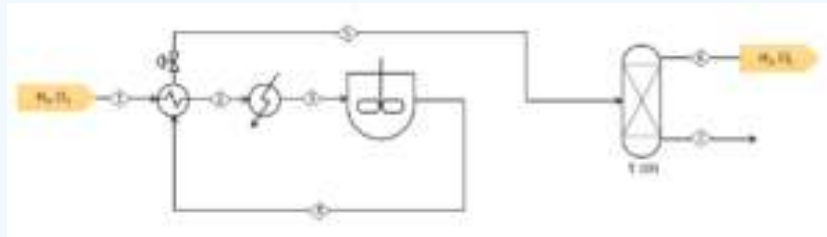
Therefore, the GEP will be:

$$GEP = 125,000 \frac{\$}{yr} - (40 \frac{\$}{yr} + 60 \frac{\$}{yr} + 10,000 \frac{\$}{yr} + 1,000 \frac{\$}{yr}) \quad (1.10.1)$$

$$GEP = 113,900 \frac{\$}{yr} \quad (1.10.2)$$

✓ Exercise: Process Flow Diagrams

What is missing from the following process flow diagram (PFD)?



Solution

Add example text here.

The appropriate **equipment labeling** along with **stream 7 content label** (“HCl” in this case) are missing from this PFD.

Long Answer Questions

✓ Exercises: Block Flow Diagram

Carbon capture is a process that is gaining a lot of attention due to its ability to mitigate the environmental effects in the oil and gas industry (along with other industries). One proposed carbon capture method is through the use of MDEA (N-methyl diethanolamine) absorption. The following steps describe the process:

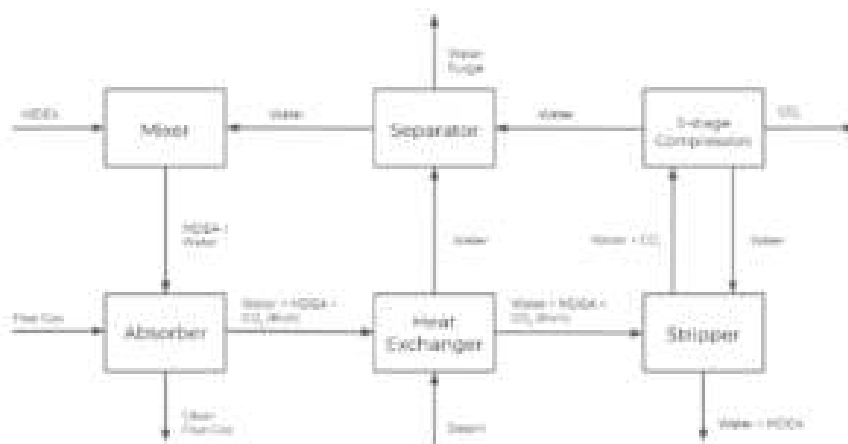
1. A stream of “Flue Gas”* is fed into an absorber
2. An “MDEA + Water” stream is also fed into the absorber
3. “The MDEA + Water” stream comes from a mixer where “MDEA” and a “Water” stream are fed
4. A “Clean Flue Gas” stream and a “Water + MDEA + CO₂ (Rich)” stream exit the absorber
5. The “Water + MDEA + CO₂ (Rich)” stream enters and exits a heat exchanger
6. A “Steam” stream enters and exits the heat exchanger as “Water”
7. The “Water + MDEA + CO₂ (Rich)” stream enters a stripper
8. A “CO₂ + Water” exits the stripper
9. A “Water + MDEA” stream also exits the stripper
10. The “CO₂ + Water” stream enters a 5-stage compression train where three streams (“CO₂” and 2 “Water” streams) exit
11. The first “Water” stream exiting the 5-stage compression and the “Water” stream exiting the heat exchanger are fed into a separator
12. The second “Water” stream exiting the 5-stage compression enters the stripper
13. Two streams (“Water Purge” and “Water”) exit the separator. This “Water” stream is the “Water” stream that is fed to the mixer

Draw a block flow diagram (BFD) for this process

*Flue gas: a gas stream exiting from an upstream process that usually consists of carbon dioxide, nitrogen, and oxygen (only nitrogen and carbon dioxide are considered for this process).

Solution

Add example text here.



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CHAPTER OVERVIEW

2: Reaction Chemistry

[2.1: Definitions of Reaction Rate and Extent of Reactions](#)

[2.2: Reaction Rate Law](#)

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2.1: Definitions of Reaction Rate and Extent of Reactions

Learning Objectives

By the end of this section, you should be able to:

- **Define** Reaction rate and reaction extent

Calculate the reaction rate for the reaction, the rate of formation of compounds and the reaction extent

Reaction Rate

A reaction rate shows the rates of production of a chemical species. It can also show the rate of consumption of a species; for example, a reactant. In general though, we want an overall common reaction rate to describe changes in a chemical system.

Let's look at an example. Say we have reaction represented as: $A + 2B \rightarrow 3C + D$

For this system reaction rate can be expressed as follows:

$$r = \frac{d[D]}{dt} \quad (2.1.1)$$

The reaction rate is represented by the letter “r” or the Greek letter upsilon “ ν ”

NOTE: I will stick with r as upsilon looks like “ ν ” which we will use to represent the stoichiometric coefficient

Above we have written the reaction rate as if a substance with a **coefficient of 1** was reacting (or being produced). This is the typical form of an overall reaction rate describing a reaction.

Rearranging the above equation, we can find the rate of production/consumption for any species based on this overall reaction rate, note that stoichiometric coefficients are positive for products and negative for reactants:

$$r_A = \frac{d[A]}{dt} = -\nu_A \times r = (-1) \times r \quad (2.1.2)$$

$$r_B = \frac{d[B]}{dt} = -\nu_B \times r = (-2) \times r \quad (2.1.3)$$

$$r_C = \frac{d[C]}{dt} = \nu_C \times r = 3 \times r \quad (2.1.4)$$

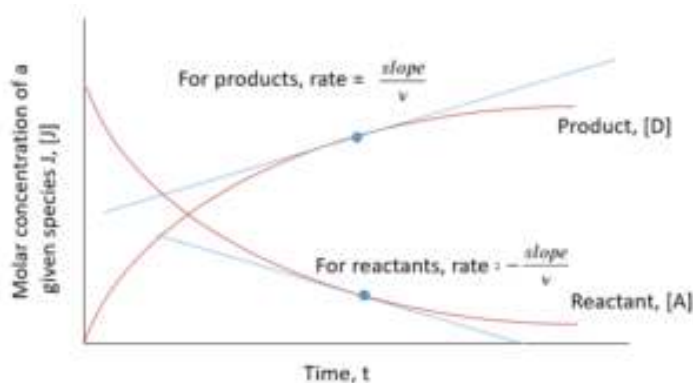
$$r_D = \frac{d[D]}{dt} = \nu_D \times r = 1 \times r \quad (2.1.5)$$

The general equation for calculating the reaction rate:

General notation: J is used to denote any compound involved in the reaction.

$$r = \frac{1}{\nu} \frac{d[J]}{dt}$$

Reaction rate at a given time can also be found from the graph of concentration of components in a system vs. time:



✓ Exercise: Calculating the Reaction Rate

If we have the reaction



and we measure that the rate of formation of NO is $1.6 \text{ mmol}/(\text{L}\cdot\text{s})$, what are the overall reaction rate, and the rate of formation of Br_2 and NOBr ?

Solution

Add example text here.

Step 1: Determine the overall reaction rate from the rate of formation for NO.

$$\begin{aligned} r &= \frac{1}{\nu_j} \frac{d[\text{NO}]}{dt} \\ &= \frac{1}{2} \left(1.6 \frac{\text{mmol}}{\text{L}\cdot\text{s}} \right) \\ &= 0.8 \frac{\text{mmol}}{\text{L}\cdot\text{s}} \end{aligned}$$

Step 2: Use the reaction rate to determine rate of formation for the other compounds

NOTE: rate of formation is positive for products and negative for reactants

$$\begin{aligned} \frac{d[\text{Br}_2]}{dt} &= r \\ &= 0.8 \frac{\text{mmol}}{\text{L}\cdot\text{s}} \\ \frac{d[\text{NOBr}]}{dt} &= -2r \\ &= -1.6 \frac{\text{mmol}}{\text{L}\cdot\text{s}} \end{aligned}$$

Reaction rates can be given in a variety of units over time. In this class we will just explore **molarity** and **partial pressure**, although other forms exist.

Molarity – molar concentration – expressed in units of $\frac{\text{mol}}{\text{volume}\cdot\text{time}}$ (eg. $\frac{\text{mol}}{\text{L}\cdot\text{s}}$)

Partial pressure – the pressure produced by one gaseous component if it occupies the whole system volume at the same temperature, commonly used for gasses – units of $\frac{\text{pressure}}{\text{time}}$ (eg. $\frac{\text{Pa}}{\text{s}}$)

Extent of Reaction

We use the extent of reaction (ξ) to describe the change in an amount of a reacting species J.

$$dn_j = \nu_j d\xi$$

where:

- dn_j = change in the number of moles of a certain substance
- ν_j = the stoichiometric coefficient
- $d\xi$ = the extent of reaction

We can get a relationship between the reaction extent and the rate of reaction when the system volume is constant:

$$r = \frac{1}{V} \frac{dn_j}{dt} = \frac{1}{\nu_j} \frac{1}{V} \frac{dn_j}{dt}$$

where:

$$V \tag{2.1.7}$$

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2.2: Reaction Rate Law

Learning Objectives

By the end of this section, you should be able to:

- **Define** reaction rate law and reaction rate constant (k)

Reaction rate law Definition: The relationship between the rate of reaction and the concentration of reactants.

The rate law is usually proportional to the concentrations of reactants raised to a certain power:

Take the reaction we used as an example before: $A + 2B \rightarrow 3C + D$

The general form for reaction rate law is

$$r = k_r[A]^a[B]^b$$

For gas cases, we can use partial pressure

$$r = k_r p_A^a p_B^b \quad (2.2.1)$$

The rate constant k_r is independent of species concentration but generally dependent on temperature.

For example, let's look at the rate of the gas-phase decomposition of dinitrogen pentoxide,



Say the rate law is found to be directly proportional to the concentration of N_2O_5 , we can express the rate law by^[1]:

$$r = k_r[N_2O_5] \quad (2.2.3)$$

Reaction rate laws can be complicated and may tell us about the mechanism of the reactions. For example, consider the reaction between hydrogen and bromine:

Simple stoichiometry:



Complicated rate law:

$$r = \frac{k_a[H_2][Br_2]^{3/2}}{[Br_2] + k_b[HBr]}$$

Rate Law vs. Equilibrium Constant

Be careful not to confuse equilibrium constant expressions with rate law expressions. The expression for K_{eq} can always be written by inspecting the **balanced** reaction equation, and often contains a term for each species of the reaction (raised to the power of its coefficient) whose concentration changes during the reaction. The equilibrium constant for the reaction $2N_2O_5 \rightleftharpoons 4NO_2 + O_2$ is given below:

$$K_{eq} = \frac{[NO_2]^4[O_2]}{[N_2O_5]^2} \quad (2.2.5)$$

In contrast, the expression for the rate law generally bears no relation to the reaction equation and must be determined experimentally. ^[1]

Reaction Rate Law Units

Reaction rate (r) is generally expressed in units of concentration over time (e.g. $\frac{mol}{L \cdot s}$, $\frac{kPa}{min}$, $\frac{mol}{m^3 \cdot h}$).

This means the rate constant k_r needs to be such that r is expressed in units of concentration over time.

✓ Exercise: Rate Constant Units

For the following example, what are the units for the reaction rate constant (k_r)?

$$r = k_r * p_A * p_B^2 \quad (2.2.6)$$

with p in Pa and time in seconds

Solution

Add example text here.

Since r is expressed in concentration over time, the units of r are $\frac{Pa}{s}$.

$$\begin{aligned} \frac{Pa}{s} &= k_r * Pa * Pa^2 \\ k_r &= \frac{1}{Pa^2 s} \end{aligned}$$

References

[1] Chemistry LibreTexts. 2020. *The Rate Law*. [online] Available at: <[https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_\(Physical_and_Theoretical_Chemistry\)/Kinetics/Rate_Laws/The_Rate_Law](https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Kinetics/Rate_Laws/The_Rate_Law)> [Accessed 23 April 2020].

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2.3: Reaction Order

Learning Objectives

By the end of this section, you should be able to:

- **Define** reaction order and overall order

Determine the reaction order and the rate constant from kinetic data

The dependence of the rate of reaction on the reactant concentrations can often be expressed as a direct proportionality, in which the concentrations may be raised to be the zeroth, first, or second power. The exponent is known as the order of the reaction with respect to that substance.^[1]

The overall order of a reaction is the sum of the orders with respect to the sum of the exponents

For example:

$$r = k_r[A]^3[B]^{1/2}$$

The reaction is:

- Third-order in A
- One-half order in B
- Three and a half order overall

In the more complicated example for the reaction previously given between hydrogen and bromine:



The reaction is:

- First order in H_2
- Indeterminate order in Br_2 (as it's not in a single term)
- Indeterminate order in HBr (as it cannot be isolated to a single term raised to a power)
- Indeterminate order overall (as some orders are indeterminate)

Determining the Rate Law

Isolation Method for Determining the Rate Law

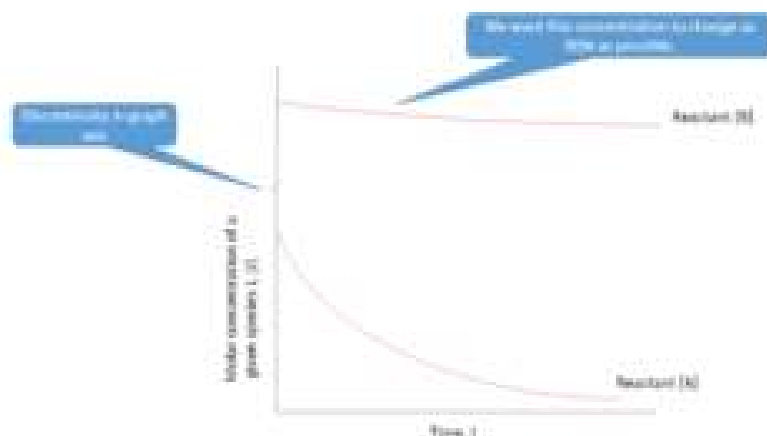
One of the simplest methods for determining the rate law is the isolation method.

Say we have a reaction with two reactants, A and B. We put a **large amount of B** in our reactor compared to A; so much that the **concentration barely changes**.

If the true rate law is: $r = k_r[A][B]^2$

What we would observe is $r = k_{eff}[A]$, where $k_{eff} = k_r[B_0]^2$

- k_{eff} = the effective rate constant
- $[B]_0$ indicating the concentration of B at the start of the reaction (or time zero) or also called B naught (with naught meaning nothing or zero in this case)



With B in great excess: $r = k_{eff}[A]$ where $k_{eff} = k_r[B_0]^2$, reaction appears **first order**.

With A in great excess: $r' = k'_{eff}[B]^2$ where $k'_{eff} = k_r[A_0]$, reaction appears **second order**.

$$k'_{eff} \quad (2.3.1)$$

It is easier to analyse these individual effective rate laws than the more complex combined rate law when both concentrations change significantly.

Method of Initial Rates

The method of initial rates is commonly used in conjunction with the isolation methods to determine reaction order.

✓ Exercise: Method of Initial Rates

Say we have a reaction with two species, A and B. We put in the same amount of B into the reactor each time. The following is our initial rates are observed with different concentrations of A. What is the reaction order in A?

[A] (mol/L)	Initial rate(mol/L·s)
1	1×10^{-2}
2	4×10^{-2}

Solution

Add example text here.

As the concentration of A doubles, the reaction rate quadruples

$$r_0 = k_{eff}[A]^2 \quad (2.3.2)$$

So the reaction is second order in A.

If we take the logarithm of the general equation for reaction rate, we can linearize the equation:

$$\begin{aligned} r_0 &= k_{eff}[A_0]^a \\ \log(r_0) &= \log(k_{eff}) + a * \log([A_0]) \\ y &= \text{intercept} + \text{slope} * x \end{aligned}$$

Plot $\log(r_0)$ vs $\log([A_0])$, where the slope is the reaction order in A; and y-intercept equals to $\log(k_{eff})$

✓ Exercise: Reaction Order and Rate Constant

Sulfuryl chloride (SO_2Cl_2) decomposes to SO_2 and Cl_2 by the following reaction:



Experiment	$[SO_2Cl_2]_0$	Initial rate(M/s)
1	0.0050	1.10×10^{-7}
2	0.0075	1.65×10^{-7}
3	0.0100	2.20×10^{-7}
4	0.0125	2.75×10^{-7}

Solution

Add example text here.

Step 1: determine the reaction order with respect to sulfuryl chloride

$$(2.20 \times 10^{-7}) \div (1.10 \times 10^{-7}) = 2.0 \quad (2.3.5)$$

$$[SO_2Cl_2] \quad (2.3.6)$$

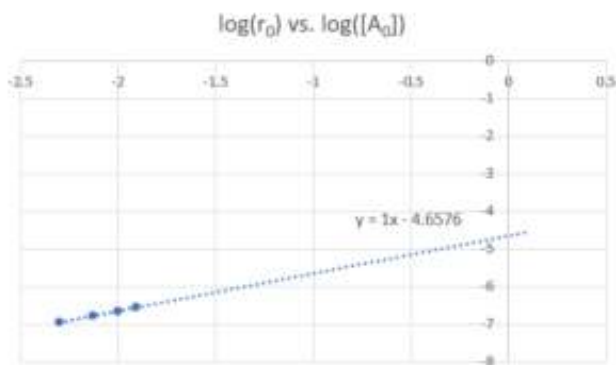
$$k_r \quad (2.3.7)$$

We have $rate = k_r[SO_2Cl_2]$. We can calculate the rate constant (k_r) using data from any experiment in the table.

$$\begin{aligned} rate &= k_r[SO_2Cl_2] \\ 1.10 \times 10^{-7} M/s &= k_r \times 0.0050 M \\ 2.2 \times 10^{-5} s^{-1} &= k_r \end{aligned}$$

Method 2

$$\log(r_0) \quad (2.3.8)$$



$$\log(k_r) = -4.6576 \quad (2.3.9)$$

$$SO_2Cl_2 \quad (2.3.10)$$

References

[1] Chemistry LibreTexts. 2020. *The Rate Law*. [online] Available at: [https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_\(Physical_and_Theoretical_Chemistry\)/Kinetics/Rate_Laws/The_Rate_Law](https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Kinetics/Rate_Laws/The_Rate_Law) [Accessed 23 April 2020].

[2] Chemistry LibreTexts. 2020. *14.4: The Change Of Concentration With Time (Integrated Rate Laws)*. [online] Available at: <[https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_\(Brown_et_al.\)/14%3A_Chemical_Kinetics/14.4%3A_The_Change_of_Concentration_with_Time_\(Integrated_Rate_Laws\)](https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/14%3A_Chemical_Kinetics/14.4%3A_The_Change_of_Concentration_with_Time_(Integrated_Rate_Laws))> [Accessed 23 April 2020].

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2.4: Integrated Rate Laws

Learning Objectives

By the end of this section, you should be able to:

- **Determine** the reaction order and rate constant from kinetic data using the linearized form of integrated rate laws

Integrated Rate Laws

Rate laws are differential equations that can be integrated to find how the concentrations of reactants and products change with time. We can imagine a fairly complex system with multiple reactions described by

$$r_1 = k_{r1} * f(A, B, \dots), r_2 = k_{r2} * f(A, B, \dots), r_3, r_4 \dots \quad (2.4.1)$$

The concentration of all components can be described by equations such as $\frac{d[A]}{dt} = -r_1 - 2r_2 \dots$. We need to integrate these to find concentrations at a given time.

Any of these rate laws can be solved numerically (you'll learn about this in CHBE 230), but some simpler cases can also be solved analytically.

Zeroth Order Reactions

A zeroth-order reaction is one whose rate is independent of concentration^[1]; Say we have a reaction:



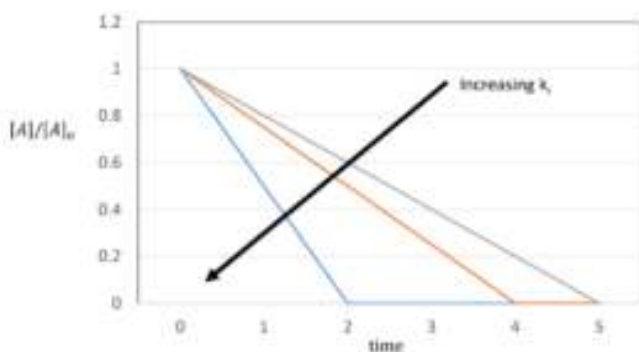
It's differential rate law would be represented as:

$$r = -\frac{d[A]}{dt} = k_r \quad (2.4.3)$$

Integrating from $t=0$, when the system has a concentration of A as $[A]_0$, to some time t , when the system has a concentration represented by $[A]$

$$\int_{[A]_0}^{[A]} d[A] = \int_{t=0}^t -k_r \quad (2.4.4)$$

$$-[A]_0 = -k_r * t \text{ or } [A] = [A]_0 - k_r * t$$



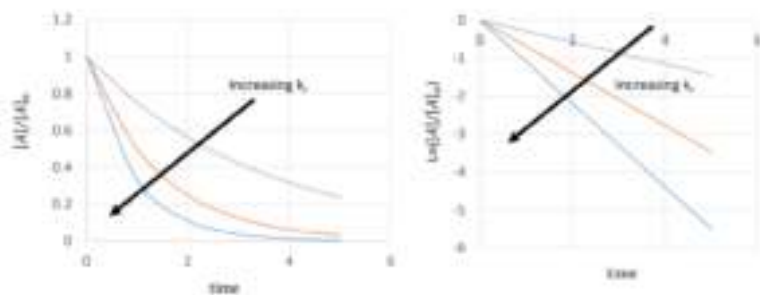
First-Order Reactions

Using a similar approach to the zeroth order reactions:

$$r = -\frac{d[A]}{dt} = k_r[A] \quad (2.4.5)$$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = \int_{t_0=0}^t -k_r \quad (2.4.6)$$

$$\ln[A] - \ln[A]_0 = -k_r * t \text{ or } [A] = [A]_0 e^{-k_r * t}$$



✓ Example: Half-life for First-order Reactions

text

Solution

text.

Based on the equation we derived, what is an expression for the time taken for half of A to be consumed (half-life)?

$$\ln[A] - \ln[A]_0 = -k_r * t \quad (2.4.7)$$

$$\begin{aligned} k_r * t_{1/2} &= -\ln \frac{[A]}{[A]_0} \\ &= -\ln \frac{\frac{1}{2}[A]_0}{[A]_0} \\ &= -\ln\left(\frac{1}{2}\right) \\ &= \ln(2) \end{aligned}$$



Note that this half-life does not depend on [A].

Practice: use $[A] = [A]_0 e^{-k_r * t}$, you should get the same result.

Solution

$$\begin{aligned} [A] &= [A]_0 * e^{-k_r t_{1/2}} \\ \frac{[A]}{[A]_0} &= e^{-k_r t_{1/2}} \\ \frac{1}{2} &= e^{-k_r t_{1/2}} \\ \ln\left(\frac{1}{2}\right) &= -k_r * t_{1/2} \end{aligned}$$



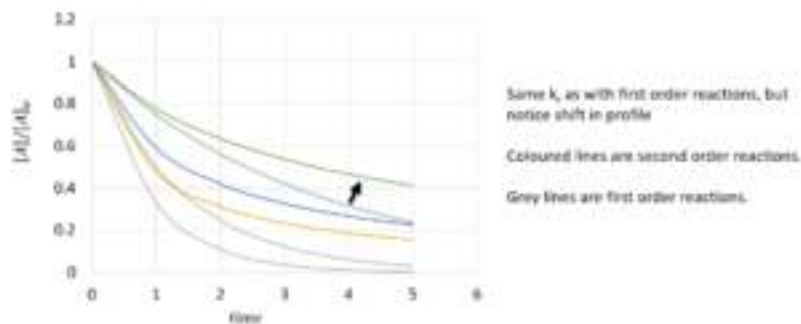
Second-Order Reactions

$$r = -\frac{d[A]}{dt} = k_r[A]^2 \quad (2.4.8)$$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = \int_{t_0=0}^t -k_r \quad (2.4.9)$$

$$\frac{1}{[A]} - \frac{1}{[A]_0} = k_r * t \text{ or } [A] = \frac{[A]_0}{1+k_r*t*[A]_0}$$

Using this to find half life, we find that: 



References

[1] Chemistry LibreTexts. 2020. 12.4 Integrated Rate Laws. [online] Available at: [https://chem.libretexts.org/Bookshelves/General_Chemistry/Book%3A_Chemistry_\(OpenSTAX\)/12%3A_Kinetics/12.4%3A_Integrated_Rate_Laws#:~:text=We%20measure%20values%20for%20the,different%20concentrations%20of%20the%20reactants.&text=Integrated%20rate%20laws%20are%20determined,various%20times%20during%20a%20reaction.>](https://chem.libretexts.org/Bookshelves/General_Chemistry/Book%3A_Chemistry_(OpenSTAX)/12%3A_Kinetics/12.4%3A_Integrated_Rate_Laws#:~:text=We%20measure%20values%20for%20the,different%20concentrations%20of%20the%20reactants.&text=Integrated%20rate%20laws%20are%20determined,various%20times%20during%20a%20reaction.>) [Accessed 24 April 2020].

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2.5: Equilibrium Reactions

Learning Objectives

By the end of this section, you should be able to:

- **Analyze** equilibrium reaction equations

When **the concentrations of reactants and products become constant**, the system is said to have reached a point of equilibrium. The equilibrium state is **dynamic**. At equilibrium, the reactions are **not stopped**, but rather **the rates of opposing reactions have become equal** such that concentrations of chemical species do not change.

Laboratory kinetic studies may be performed on reactions far from equilibrium where products are in low concentration and the reverse reactions are not important (this is what we considered previously).



Closer to equilibrium however we must take these reverse reactions into account.



Equilibrium Constant

Definition of the Equilibrium Constant

$$K \text{ or } K_{eq} = \prod_i a_{i,eq}^{v_i}$$

Unpack the notation:

- K or K_{eq} is the equilibrium constant
- $\prod_i$ is the product notation (similar to $\sum_i$, but terms are multiplied rather than added)
- $a_{i,eq}$ is the activity of compound i at equilibrium, for now we will assume concentration divided by a unit concentration term. This will give us the concentration of the substance in a dimensionless form, eg. $\frac{[A]}{c^\theta}$, where $[A]$ and c^θ are in units of mol/L, and c^θ has magnitude of 1.
- v_i is the stoichiometric coefficient of compound i we saw previously. It is positive for products and negative for reactants.

Consider a system with the following reaction:



Let's say the system is composed of 2 first-order reactions:

Forward reaction: $A \rightarrow B$, where the reaction rate is expressed by: $r = k_r \times [A]$

Reverse reaction: $B \rightarrow A$, where the reaction rate is expressed by: $r' = k'_r \times [B]$

Net rate of change in $[A]$ considering both reactions is:

$$\frac{d[A]}{dt} = r' - r = k'_r \times [B] - k_r \times [A] \quad (2.5.4)$$

If the initial concentration of A is $[A]_0$ and no B is present, then at all times: $[A] + [B] = [A]_0$. Using this in the equation above:

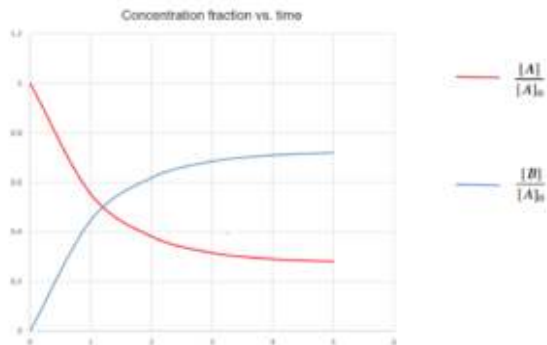
$$\begin{aligned} \frac{d[A]}{dt} &= k'_r[B] - k_r[A] \\ &= k'_r([A]_0 - [A]) - k_r[A] \\ &= k'_r[A]_0 - (k_r + k'_r)[A] \end{aligned}$$

This is what is known as an ordinary differential equation, as $[A]$ is both a differential and a separate term. You may not know how to solve these equations and do not need to know this for this course. However, if we were to solve this ordinary differential

equation, we would get the following:

$$[A] = \frac{k'_r + k_r e^{-(k'_r + k_r)t}}{k'_r + k_r} [A]_0 \quad (2.5.5)$$

Using the expression for $[A]$ above, $[B] = [A]_0 - [A]$, taking arbitrary values of $k_r = 0.693$ and $k'_r = 0.262$, the following graph is produced:



As you can see from the graph, the concentrations change less over time. After a long time, they should reach a state of equilibrium. The length of time to reach equilibrium (or close to it) will depend on the reaction rates.

As $t \rightarrow \infty$, we approach equilibrium and we get the following:

$$[A]_{eq} = \frac{k'_r + k_r e^{-(k'_r + k_r)t}}{k'_r + k_r} [A]_0 = \frac{k'_r}{k'_r + k_r} [A]_0 \quad (2.5.6)$$

$$[B]_{eq} = [A]_0 - [A]_{eq} = \frac{k_r}{k'_r + k_r} [A]_0 \quad (2.5.7)$$

The equilibrium constant in this example is defined as:



At equilibrium, the rates of forward and reverse reactions should be the same (meaning no change in overall concentrations), so it makes sense that when we rearrange this we get:

$$k'_r [B]_{eq} = k_r [A]_{eq}$$

Consider another system with the following reaction:



Forward reaction: $A + B \rightarrow C$, where the forward reaction rate is expressed by: $r = k_r [A][B]$

Reverse reaction: $C \rightarrow A + B$, where the reverse reaction rate is expressed by: $r' = k'_r [C]$

Here, in equilibrium we have:

$$r = r' = k_r [A]_{eq} [B]_{eq} = k'_r [C]_{eq} \quad (2.5.9)$$

The equilibrium constant is defined as dimensionless, so here is where the c^θ terms make a difference. The equilibrium constant can be expressed as:



Recall that k_r and k'_r here will have different units, so the c^θ term ensures that these become dimensionless when one is divided by the other.

✓ Exercise: Equilibrium Constant

1. For the balanced chemical reaction below, write an equation for the equilibrium constant(K).^[1]



2. Consider the following reaction system:



$$k_r = 0.1 \text{ min}^{-1} \quad (2.5.12)$$

What are the values of the equilibrium constant(K) and reverse reaction constant(k'_r)?

$$K \text{ or } K_{eq} = \prod_i a_{i,eq}^{v_i} \quad (2.5.13)$$

Solution

Add example text here.

$$1. K = \frac{[N_2H_4]}{[H_2]^2[N_2]}$$

2. Start with expressing K in forms of concentrations and k_r :

$$\begin{aligned} K &= \frac{[B]_{eq}/c^\theta * [C]_{eq}/c^\theta}{[A]_{eq}/c^\theta} \\ &= \left(\frac{[B][C]}{[A]} \right)_{eq} \frac{1}{c^\theta} \\ &= \frac{k_r}{k'_r * c^\theta} \end{aligned}$$

Calculate K from the expression with concentrations:

$$\begin{aligned} K &= \left(\frac{[B][C]}{[A]} \right)_{eq} \frac{1}{c^\theta} \\ &= \left(\frac{0.1 \frac{\text{mol}}{L} * 0.2 \frac{\text{mol}}{L}}{0.5 \frac{\text{mol}}{L}} \right)_{eq} \frac{1}{c^\theta} \\ &= 0.04 \end{aligned}$$

Substitute the K value into the expression with k_r :

$$\begin{aligned} K &= \frac{k_r}{k'_r * c^\theta} \\ k'_r &= \frac{k_r}{K * c^\theta} \\ &= \frac{0.1 \text{ min}^{-1}}{0.04 * 1 \frac{\text{mol}}{L}} \\ &= 2.5 \frac{L}{\text{mol} * \text{min}} \end{aligned}$$

Back substitute k_r into the rate equations to check this:

$$r = k_r[A]_{eq} = 0.1 \text{ min}^{-1} * 0.5 \frac{\text{mol}}{L} = 0.05 \frac{\text{mol}}{L * \text{min}} \quad (2.5.14)$$

$$r' = k'_r[B]_{eq}[C]_{eq} = 2.5 \frac{L}{\text{mol} * \text{min}} * 0.1 \frac{\text{mol}}{L} * 0.2 \frac{\text{mol}}{L} = 0.05 \frac{\text{mol}}{L * \text{min}} \quad (2.5.15)$$

Forward and reverse reaction rates are the same at $0.05 \frac{\text{mol}}{\text{L}\cdot\text{min}}$, as we would expect at equilibrium.

References

- [1] Chemistry LibreTexts. 2020. *Characteristics of the Equilibrium State*. [online] Available at: <[https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_\(Physical_and_Theoretical_Chemistry\)/Equilibria/Chemical_Equilibria/Principles_of_Chemical_Equilibria/Principles_of_Chemical_Equilibrium/Characteristics_Of_The_Equilibrium_State](https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Equilibria/Chemical_Equilibria/Principles_of_Chemical_Equilibria/Principles_of_Chemical_Equilibrium/Characteristics_Of_The_Equilibrium_State)> [Accessed 24 April, 2020].

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2.6: Arrhenius Equation

Learning Objectives

By the end of this chapter, you should be able to:

Explain the effect of temperature on reaction rates

The Arrhenius Equation describes the relationship between the reaction rate and temperature.

$$\ln(k_r) = \ln(A) - \frac{E_a}{RT}$$

Where

- A in units of $time^{-1}$ (eg. $s^{-1}, min^{-1} \dots$) is called the frequency factor or pre-exponential factor. It describes the frequency that molecules collide with the correct orientation to possibly make a chemical reaction.
- E_a is the activation energy in units of energy per amount of molecules (eg. J/mol, kJ/mol...) This is introduced in more details later in this session.
- R is the ideal gas constant in the appropriate units (eg. $8.314 \frac{J}{mol \cdot K}$)
- T needs to be expressed in absolute units (eg. K)

The Arrhenius Equation is in linear form if we graph $\ln(k_r)$ as y and $\frac{1}{T}$ as x:

$$\ln(k_r) = -\frac{E_a}{R} \times \frac{1}{T} + \ln(A)$$

Where

- The slope of the graph is equal to $-\frac{E_a}{R}$
- The y-intercept is equal to $\ln(A)$

Once E_a is known for a reaction, the rate of reaction can be predicted at a given temperature if it is known at another temperature:

$$\ln(k_{r1}) = \ln(A) - \frac{E_a}{RT_1} \quad (2.6.1)$$

Subtract the first from the second to get:

$$\ln(k_{r2}) - \ln(k_{r1}) = -\frac{E_a}{RT_2} + \frac{E_a}{RT_1} \quad (2.6.2)$$

This simplifies to:

$$\ln\left(\frac{k_{r2}}{k_{r1}}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

✓ Exercise: Reaction Rate Change with Changing Temperature

Say a certain biological reaction has an activation energy of 50 kJ/mol, how much faster will this reaction be at body temperature (37°C) vs room temperature (25°C)?

Note $R = 8.314 \frac{J}{mol \cdot K}$

Solution

Add example text here.

- Be careful with the unit consistency. Use absolute units for temperatures.



$$\frac{k_{r2}}{k_{r1}} = e^{0.781} = 2.18 \quad (2.6.3)$$

So with this 12°C temperature increase, the reaction rate would increase 2.18 times. A rule of thumb is that reaction rates double every 10°C, but we know this depends on the activation energy.

Manipulating the previous Arrhenius equation, we can isolate k_r by taking the exponent of each side to get:

$$k_r = Ae^{(-\frac{E_a}{RT})} \quad (2.6.4)$$

If E_a is 0 (all collisions result in a reaction) then:

$$k_r = Ae^{(-\frac{E_a}{RT})} = Ae^0 = A \quad (2.6.5)$$

Meaning the rate constant when each collision is successful is equal to the frequency factor.

When $E_a > 0$, then only a subset of reactions are successful represented by $e^{(-\frac{E_a}{RT})}$

Catalysts speed up the reactions usually by decreasing the activation energy. Sometimes catalysts can affect frequency factors as well, but the effect of frequency factor is minor in comparison to the decrease of activation energy. This is demonstrated in the example question after the activation energy session.

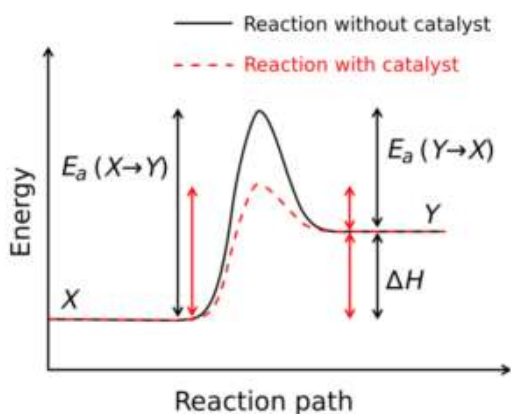


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✓ Exercise: Effect of Temperature on Equilibrium

1. True or False: A reaction is in a state of equilibrium when the equilibrium constant K is equal to 0.^[1]
2. Which of the following does **not** affect the concentration of each component at equilibrium for a reaction system?^[1]
 - a. Adding products
 - b. Increasing temperature
 - c. Using a catalyst
 - d. Decreasing volume

Hint: An understanding of Le Chatelier's principle can be helpful for this question, but you can also analyze this question using the definition of K_{eq}

- **Le Chatelier's principle:** this principle states that temperature, volume, concentration, or pressure changes result in equilibrium shifts that re-establish a new equilibrium state.

Solution

Add example text here.

1. **False**— because for each specific reaction, the equilibrium constant only depends on temperature. The reaction is at equilibrium when the value of $\prod_i a_i^{v_i}$ is equal to K_{eq} (notice a_i instead of $a_{i,eq}$, because we don't know if the system is at equilibrium when we calculate this). Also experimentally, we can say that the system is at equilibrium when the concentrations of each component are not changing.

2. **Answer: c**

Using a catalyst decreases the energy barrier needed for the reaction to proceed (activation energy), but does not affect the equilibrium constant.

Both a and d will cause shifting of equilibrium due to Le Chatelier's principle. For a, the reaction will shift to the reverse, meaning that the reverse reaction will happen more often so more reactants will be formed and more products will be consumed. For d, the system will shift to the side that produces a larger number of gaseous molecules to increase the volume. There may be a case where gas volume stays the same no matter with products or reactants, but this is not known.

If you analyze a and d using K_{eq} , the equilibrium constant will not change, but the concentration of the components will change, and the system will approach the same equilibrium constant after the change.

b – The equilibrium constant will change when temperature changes, shifting reactant and product concentrations.

Activation Energy

The activation energy(E_a) represents the energy needed for the reactants to collide and get to a state such that their bonds can rearrange to form the products.

$$\ln\left(\frac{k_{r2}}{k_{r1}}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (2.6.6)$$

- A high E_a indicates the rate strongly depends on the temperature
- Zero E_a indicates the rate is independent of temperature
- Negative E_a indicates the rate decreases with temperature (this is very rare)

Graph (a) illustrates the general situation in which the products have lower potential energy than the reactants, so the overall reaction releases energy; that is, it is energetically downhill, and $\Delta E < 0$.

In contrast, graph (b) illustrates the case in which the products have higher potential energy than the reactants, so the overall reaction requires an input of energy; that is, it is energetically uphill, and $\Delta E > 0$.

Although the energy changes that result from a reaction can be positive, negative, or even zero, in most cases an energy barrier must be overcome before a reaction can occur. This means that the activation energy is almost always positive.^[2]

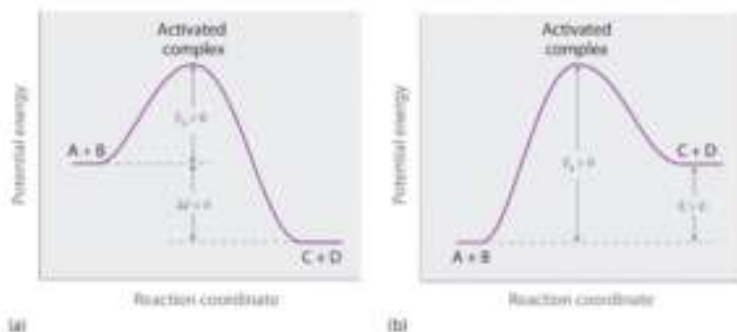


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✓ Example: Catalyst Affecting Activation Energy

text

Solution

text.

Enzymes are biological catalysts. Suppose we have a reaction with an activation energy of 80 kJ and a frequency factor of 1 without catalysts at 298K, calculate the reaction rate constant without catalyst and compare the rate constant (by taking the ratio of k) if the enzyme:

- Decreases the activation energy to 8kJ.
- Increases the frequency factor to 10.

Solution

k without catalyst:

$$\begin{aligned} k(\text{uncatalyzed}) &= Ae^{(-\frac{E_a}{RT})} \\ &= 1 \times e^{(-\frac{80 \times 10^3 \text{ J}}{8.314 \text{ J/(molK)} 298 \text{ K}})} \\ &= 9.48 \times 10^{-15} \end{aligned}$$

a)

$$\begin{aligned} \frac{k'(\text{catalyzed})}{k(\text{uncatalyzed})} &= \frac{Ae^{(-\frac{E'_a}{RT})}}{Ae^{(-\frac{E_a}{RT})}} \\ &= e^{\frac{-E'_a + E_a}{RT}} \\ &= e^{\frac{(-8 + 80) \times 10^3 \text{ J/mol}}{8.314 \text{ J/(molK)} 298 \text{ K}}} \\ &= 4.2 \times 10^{12} \end{aligned}$$

b)

$$\begin{aligned} \frac{k'(\text{catalyzed})}{k(\text{uncatalyzed})} &= \frac{A'e^{(-\frac{E_a}{RT})}}{Ae^{(-\frac{E_a}{RT})}} \\ &= \frac{A'}{A} \\ &= 10 \end{aligned}$$

A decrease in E_a has a drastic effect on reaction rate.

✓ Exercise: Activation Energy Calculation

The equation for the decomposition of NO_2 to NO and O_2 is second order in NO_2 :



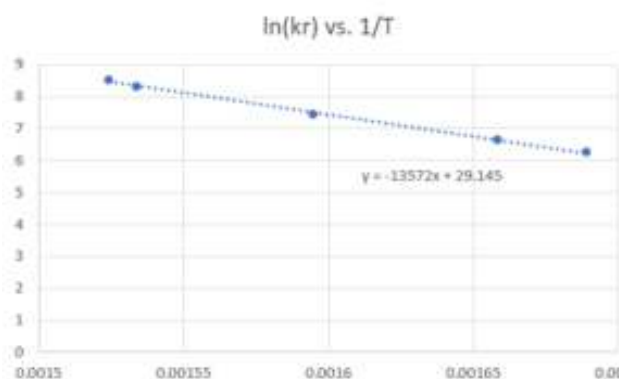
Data for the reaction rate as a function of temperature are listed in the following table. Calculate E_a for the reaction and the rate constant at 700 K.^[2]

T(K)	k ($M^{-1}s^{-1}$)
592	522
603	755
627	1700
652	4020
656	5030

Solution

Add example text here.

Step 1: Plot the Arrhenius Equation in the linear form: $\ln(k_r) = -\frac{E_a}{R} * \frac{1}{T} + \ln(A)$



Step 2: Calculate the activation energy (E_a) and the frequency factor (A) from the slope and intercept

$$\begin{aligned}
 E_a &= -\text{slope} \times R \\
 &= -(-13572K) \times 8.314J/(molK) \\
 &= 112838J/mol \\
 &= 112.8kJ/mol
 \end{aligned}$$

$$\begin{aligned}
 A &= e^{\text{y-intercept}} \\
 &= e^{29.145} \\
 &= 4.545 \times 10^{12} M^{-1}s^{-1}
 \end{aligned}$$

Note that the units of A are the same as k_r , but we tend to then remove the units when we take logarithm as we usually consider products of logarithmic. The important thing to remember is if we use A to solve for k_r (as we do below), we need to include the relevant units.

Step 3: Calculate the rate constant (k_r) using the E_a , A and given temperature

$$\begin{aligned}
 k_r &= Ae^{\left(-\frac{E_a}{RT}\right)} \\
 &= 4.545 \times 10^{12} e^{\left(-\frac{112838J/mol}{8.314J/(molK) \times 700K}\right)} \\
 &= 17265 M^{-1}s^{-1} \\
 &= 1.73 \times 10^4 M^{-1}s^{-1}
 \end{aligned}$$

References

[1] Chemistry LibreTexts. 2020. *Characteristics of the Equilibrium State*. [online] Available at: [https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_\(Physical](https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical)

[_and_Theoretical_Chemistry\)/Equilibria/Chemical_Equilibria/Principles_of_Chemical_Equilibria/Principles_of_Chemical_Equilibrium/Characteristics_Of_The_Equilibrium_State](#)> [Accessed 24 April, 2020].

[2] Chemistry LibreTexts. 2019. 4.6 *Activation Energy and Rate*. [online] Available at: <[https://chem.libretexts.org/Courses/Bellarmino_University/BU%3A_Chem_104_\(Christianson\)/Phase_2%3A_Chemical_Kinetics/4%3A_Kinetics%3A_How_Fast_Reactions_Go/4.6%3A_Activation_Energy_and_Rate](https://chem.libretexts.org/Courses/Bellarmino_University/BU%3A_Chem_104_(Christianson)/Phase_2%3A_Chemical_Kinetics/4%3A_Kinetics%3A_How_Fast_Reactions_Go/4.6%3A_Activation_Energy_and_Rate)> [Accessed 24 April, 2020].

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2.7: Reaction Mechanisms - Elementary Reactions

Learning Objectives

By the end of this section, you should be able to:

- **Analyze** elementary reactions and reaction molecularity

The sequence of events that occur at the molecular level during a reaction is the **mechanism of the reaction**. It describes how individual atoms, ions, or molecules interact to form particular products. The **stepwise changes** are collectively called the reaction mechanism. **Each step of the reaction** is called an **elementary reaction**. The sum of the elementary reactions in the mechanism must give the balanced chemical equation for the overall reaction. ^[1]

The decomposition of ozone, for example, appears to follow a mechanism with two steps:



Elementary reactions add up to the overall reaction:



With the elementary reactions, we do not specify phases, and the formula represents specific processes occurring with individual molecules or atoms.

Notice that the oxygen atom produced in the first step of this mechanism is consumed in the second step and therefore does not appear as a product in the overall reaction. Species that are produced in one step and consumed in a subsequent step are called **intermediates**. ^[2]

Molecularity

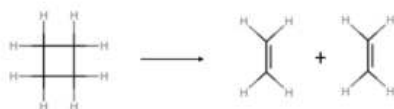
The **molecularity** is the number of molecules or atoms coming together to react in an elementary reaction.

- **Unimolecular reaction** – Only **one** molecule is involved, examples might include an isomerization or decomposition

Example: isomerization of cyclopropane to propene



Example: decomposition of cyclobutane



- **Bimolecular reaction** – **two** molecules collide, interact, and undergo some kind of change. It can be two of the same or different molecules.

Example : Hydrogen attacking a bromine molecule



Reaction Order vs. Molecularity

Reaction order – An empirical quantity obtained from experimentally determined rate law

Molecularity – Number of molecules coming together in an elementary reaction proposed as an individual step in a mechanism

The order of the elementary reaction is the same as its molecularity. In contrast, the rate law cannot be determined from the balanced chemical equation for the overall reaction (unless it is a single step mechanism and is therefore also an elementary step).^[1]

Rate Laws for Elementary Reactions

Unimolecular



$$-\frac{d[A]}{dt} = k_r * [A]$$

Bimolecular



$$-\frac{d[A]}{dt} = k_r * [A] * [B]$$



$$-\frac{d[A]}{dt} = k_r * [A]^2$$

Generally these depend on concentration of reactants. However, these rate laws must be tested against experimental data.

Consecutive Elementary Reactions

Some reactions proceed through the formation of an intermediate (I). One example of this with irreversible reactions is:



The intermediate(I) is present in the reaction steps but does not appear in the overall reaction: $A \rightarrow P$

✓ Example: Express Rate of Formation for Reactive Compounds

text

Solution

text.

Given the consecutive elementary reaction:



The rate of change for [A] is: $\frac{d[A]}{dt} = -k_a * [A]$

What are the equations for the rates of change for the other two species, I and P, in terms of their concentrations and the reaction rate constants?

Solution

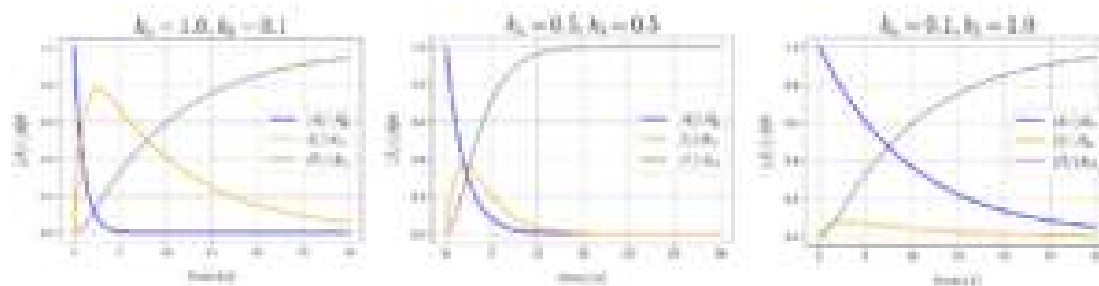
the intermediate I is produced by the reaction that converts A to I and consumed by the reaction that produces P:

$$\frac{d[I]}{dt} = k_a * [A] - k_b * [I] \quad (2.7.9)$$

P is produced by the reaction that converts I to P:

$$\frac{d[P]}{dt} = k_b * [I] \quad (2.7.10)$$

Taking 3 sets of arbitrary values for k_a and k_b , we can plot the following graphs of concentration vs.time:



References

- [1] Chemistry LibreTexts. 2020. 14.6 Reaction Mechanisms. [online] Available at: <[https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_\(Brown_et_al.\)/14%3A_Chemical_Kinetics/14.6%3A_Reaction_Mechanisms#:~:text=A%20balanced%20chemical%20reaction%20does,step%20is%20an%20elementary%20reaction.](https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/14%3A_Chemical_Kinetics/14.6%3A_Reaction_Mechanisms#:~:text=A%20balanced%20chemical%20reaction%20does,step%20is%20an%20elementary%20reaction.)> [Accessed 24 April, 2020].
- [2] OpenStax Chemistry 2016. 12.6 Reaction Mechanisms. [online] Available at: <<https://opentextbc.ca/chemistry/chapter/12-6-reaction-mechanisms>> [Accessed 27 April, 2020].

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2.8: Steady-State Approximation

Learning Objectives

By the end of this section, you should be able to:

- **Select** the rate-determining step given the consecutive reactions and overall rate law of the reaction

Derive the rate law of a reaction given the consecutive reactions

Derive the rate law under pre-equilibria conditions



This approximation assumes intermediate, I, is in a low constant concentration, ie:

$$\frac{d[I]}{dt} = 0 \quad (2.8.2)$$

Generally the approximation is more accurate when $k_b \gg k_a$ (k_b is much greater than k_a). The bigger the difference, the more accurate the assumption.

$$k_b \quad (2.8.3)$$

As we saw before with first order reactions: $\frac{d[A]}{dt} = -k_a[A]$ leads to $[A] = [A]_0 e^{-k_a t}$

Now: $\frac{d[I]}{dt} = k_a[A] - k_b[I] \approx 0$ so $[I] = \frac{k_a}{k_b}[A]$

For product: $\frac{d[P]}{dt} = k_b[I] \approx k_a[A]$ if we solved this, we would find: $[P] = [A]_0(1 - e^{-k_a t})$

Detailed proof: This is not required for the course, but might be useful for understanding.

For reactant:

$$\frac{d[A]}{dt} = -k_a[A] \quad (2.8.4)$$

$$[A] \quad (2.8.5)$$

$$[A] = \text{constant} * e^{-k_a t} \quad (2.8.6)$$

$$[A] = [A]_0 * e^{-k_a t} \quad (2.8.7)$$

For intermediate:

$$\frac{d[I]}{dt} = k_a[A] - k_b[I] \approx 0 \quad (2.8.8)$$

For product:

$$\frac{d[P]}{dt} = k_b[I] \approx k_a[A] \quad (2.8.9)$$

$$\frac{d[P]}{dt} = k_a[A]$$

$$\frac{d[P]}{dt} = k_a * [A]_0 * e^{-k_a t}$$

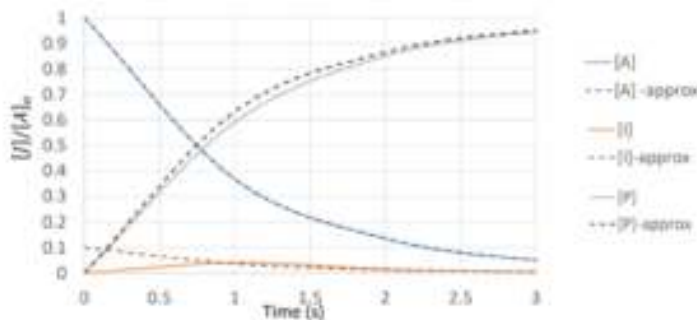
$$[P] = \int k_a * [A]_0 * e^{-k_a t}$$

$$[P] = -[A]_0 * e^{-k_a t} + \text{constant}$$

To find the constant, we know that there is no product in the system, initially. At $t=0$, $[P]=0$. Substitute $t=0$, the exponential term is equal to 1, so we are left with $0 = -[A]_0 + \text{constant}$, so $\text{constant} = [A]_0$, Therefore:

$$[P] = -[A]_0 * e^{-k_a t} + [A]_0 = [A]_0(1 - e^{-k_a t}) \quad (2.8.10)$$

Taking arbitrary values of $k_a = 1$ and $k_b = 10$, we can plot the concentration vs. time for all the components:

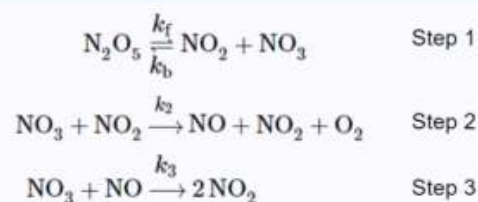


✓ Exercise: Using Steady-state Approximation to Find Rate Law Expressions

To derive the overall rate law for this reaction:



Assume the reaction follows the following three-step mechanism:



The final expression of the rate law should only contain $[\text{N}_2\text{O}_5]$ and the rate constants of the elementary steps.^[1]

Solution

Add example text here.

Step 1: Find the intermediates and express their rate of formation. Equate their rate of formation to 0 due to steady-state approximation.

$$\frac{d[\text{NO}]}{dt} = k_2[\text{NO}_3][\text{NO}_2] - k_3[\text{NO}_3][\text{NO}] = 0 \quad (1) \quad (2.8.12)$$

$$\frac{d[\text{NO}_3]}{dt} = k_f[\text{N}_2\text{O}_5] - k_b[\text{NO}_2][\text{NO}_3] - k_2[\text{NO}_3][\text{NO}_2] - k_3[\text{NO}_3][\text{NO}] = 0 \quad (2) \quad (2.8.13)$$

Step 2: Express the overall rate law. The easiest way is to express $\frac{d[\text{O}_2]}{dt}$ because it is a product that has stoichiometric coefficient of 1.

$$\frac{d[\text{O}_2]}{dt} = k_2[\text{NO}_3][\text{NO}_2] \quad (2.8.14)$$

Step 3: From the expression of $\frac{d[\text{O}_2]}{dt}$, we can see that to find the overall rate law, we need to find $[\text{NO}_3][\text{NO}_2]$ as an expression of the concentrations of reactants or products (no intermediates) by manipulating (1) and (2).

From (1):

$$k_2[\text{NO}_3][\text{NO}_2] = k_3[\text{NO}_3][\text{NO}] \quad (2.8.15)$$

Substitute into (2):

$$\begin{aligned}
 k_f[N_2O_5] - k_b[NO_2][NO_3] - k_2[NO_3][NO_2] - k_2[NO_3][NO_2] &= 0 \\
 k_b[NO_2][NO_3] + 2k_2[NO_3][NO_2] &= k_f[N_2O_5] \\
 [NO_3][NO_2] &= \frac{k_f[N_2O_5]}{k_b + 2k_2}
 \end{aligned}$$

Step 4: We can substitute the expression for $[NO_3][NO_2]$ we just found into the expression for $\frac{d[O_2]}{dt}$, which is the same as the overall rate law.

$$r = \frac{d[O_2]}{dt} = \frac{k_2 k_f [N_2O_5]}{k_b + 2k_2} \quad (2.8.16)$$

Rate-Determining Step

Rate determining step is the step that determines the overall rate of reaction in a series of reactions. The slowest forward reaction step is referred to as the rate-determining step, as it limits the rate of the entire reaction. Note that this must be a forward reaction step, a reverse reaction in an equilibrium reaction cannot be the rate-determining step.

An analogy that illustrates this concept is an hourglass having two different sized openings. The rate of the sand falling to the bottom-most chamber is determined by the smaller of the two openings. Similarly, the rate law of the overall reaction is determined from its rate-determining slowest step.^[2]

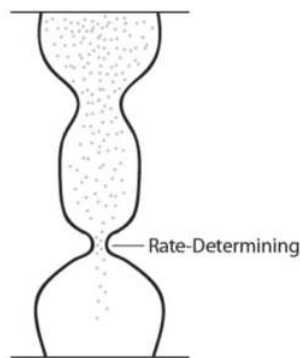
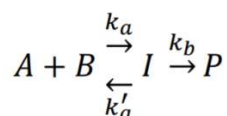


Image from [Introduction to Chemistry, 1st Canadian Edition](#) / CC BY 4.0

Pre-Equilibria

Say we have the following forward and reverse reaction:



Consider a case where an equilibrium is established due to $k'_a \gg k_b$:

The equilibrium constant, expressed using the forward and reverse reaction constants (k_a and k'_a) would remain the same over time

The reaction of $I \rightarrow P$ would decrease $[I]$ over time. Due to Le Chatelier's principle, the equilibrium reaction will shift to produce more I

Because $k'_a \gg k_b$, the reaction will shift concentrations to achieve equilibrium again far faster than the forward reaction (k_b) depletes I

Therefore, we can approximate $[I]$ with only the equilibrium part of the reaction

$$K = \left(\frac{[I]}{[A][B]} \right)_{eq} c^\theta = \frac{k_a}{k'_a} c^\theta$$

Review: From lecture 4: reaction equilibrium:

The forward reaction: $A + B \xrightarrow{k_a} I$, reaction rate $r = k_a[A][B]$

The reverse reaction: $I \xrightarrow{k'_a} A + B$, reaction rate $r' = k'_a[I]$

At equilibrium:

$$\begin{aligned} r &= r' \\ k_a[A][B] &= k'_a[I] \\ \frac{k_a}{k'_a} &= \frac{[I]}{[A][B]} \end{aligned}$$

So

$$[I] = \frac{K}{c^\theta} [A][B] = \frac{k_a}{k'_a} [A][B]$$

Using the equation for $[I]$ based on this equilibrium, we can develop an equation for the rate of formation of P :

$$\frac{d[P]}{dt} = k_b[I] = k_b \frac{k_a}{k'_a} [A][B] = k_r [A][B]$$

Where $k_r = k_b \frac{k_a}{k'_a}$. The final step of $I \rightarrow P$ is rate determining, whereas the steps prior control the amount of intermediate.

Relate k_r to Activation Energy

Recall from Lecture 4:

For each step of the reaction, we can use the Arrhenius equation to substitute $k_r = Ae^{(-\frac{E_a}{RT})}$, where A is the frequency factor and E_a is the activation energy

So we can express the overall rate constant of the reaction above as:

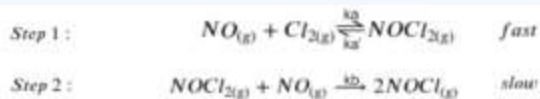
$$k_r = \frac{A_a e^{-\frac{E_{a,a}}{RT}} A_b e^{-\frac{E_{a,b}}{RT}}}{A'_a e^{-\frac{E_{a,a'}}{RT}}} = \frac{A_a A_b}{A'_a} e^{-\frac{(E_{a,a} + E_{a,b} - E_{a,a'})}{RT}} \quad (2.8.17)$$

Although each rate constant may increase with temperature, this may not be true of the overall rate constant k_r .

The effective activation energy is: $E_a = E_a + E_b - E'_a$ and this may be positive or negative depending on E_a of individual steps.

✓ Exercise: Using Pre-Equilibria to Find the Rate Law Expression

The two-step mechanism below has been proposed for a reaction between nitrogen monoxide and molecular chlorine:



Use this mechanism to derive the equation and predicted rate law for the overall reaction.

The rate law should be expressed in terms of $[\text{NO}]$, $[\text{Cl}_2]$, and the rate constants of the elementary reactions shown above.^[3]

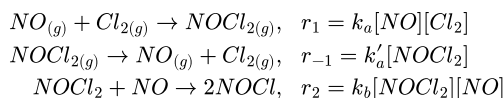
Solution

Add example text here.

Step 1: The overall reaction is the sum of the 2 elementary reactions:



Step 2: Write each reaction separately and express the rate law for each reaction (including the reverse reaction in the equilibrium):



Step 3: Use the equilibrium reaction to express the concentration of the intermediate ($[NOCl_2]$):

$$[NOCl_2] = \frac{k_a}{k'_a}[NO][Cl_2] \quad (2.8.19)$$

Step 4: Express the overall reaction rate using the step 2 elementary reaction, then substitute in $[NOCl_2]$:

$$\begin{aligned} \text{overall rate} &= \frac{1}{2} \frac{d[NOCl]}{dt} \\ &= \frac{2k_b[NO][NOCl_2]}{2} \\ &= k_b[NO][NOCl_2] \\ &= \frac{k_b k_a}{k'_a} [NO]^2 [Cl_2] \end{aligned}$$

References

- [1] Chemistry LibreTexts. 2020. *Steady State Approximation*. [online] Available at: <[https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_\(Physical_and_Theoretical_Chemistry\)/Kinetics/Reaction_Mechanisms/Steady-State_Approximation](https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Kinetics/Reaction_Mechanisms/Steady-State_Approximation)> [Accessed 04 May, 2020].
- [2] Introduction to Chemistry. 1st Canadian Edition. 2014. *Reaction Mechanisms*. [online] Available at: <<https://opentextbc.ca/introductorychemistry/chapter/reaction-mechanisms-2/>> [Accessed 04 May, 2020].
- [3] OpenStax Chemistry 2e. 2019. *12.6 Reaction Mechanisms*. [online] Available at: <<https://openstax.org/books/chemistry-2e/pages/12-6-reaction-mechanisms>> [Accessed 05 May, 2020].

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2.9: Kinetic and Thermodynamic Control

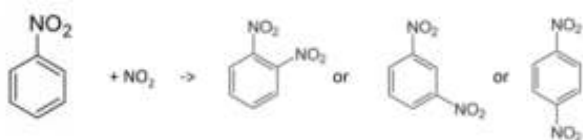
Learning Objectives

By the end of this section, you should be able to:

- **Understand** kinetic and thermodynamic control

Reactants can sometimes give rise to a variety of products.

Consider the nitration of nitrobenzene:



The relative portion of the products before reaching equilibrium is given by the ratio of the rates of production.



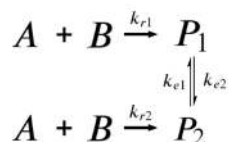
Here, before equilibrium:

$$\frac{[P_2]}{[P_1]} = \frac{k_{r,2}}{k_{r,1}}$$

This is called **kinetic control**, and it is dictated by reaction rates.

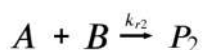
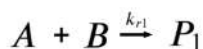
As opposed to **thermodynamic control**, which is dictated by reaction equilibrium (after a long time):

Say we have the system:



If $k_{e1}, k_{e2} \ll k_{r1}, k_{r2}$

Then at any time before the equilibrium reaction start severely affecting product concentration, the reaction simplifies to:



$$\frac{[P_1]}{[P_2]} = \frac{k_{r1}}{k_{r2}}$$

The reaction is **kinetically controlled**: the amount of products depends on the **rates of reaction**.

Proof to show: $\frac{[P_1]}{[P_2]} = \frac{k_{r1}}{k_{r2}}$

$$r_{P1} = k_{r1}[A][B] = \frac{d[P1]}{dt}$$

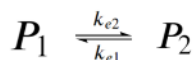
$$r_{P2} = k_{r2}[A][B] = \frac{d[P2]}{dt}$$

Say that both P_1 , P_2 start at a concentration of 0. We can express the change in concentration for P_1 and P_2 at any time before $[A]$ $[B]$ reaches 0. Note that once $[A][B]$ reaches 0, the equilibrium reaction starts to dominate as we no longer have forward reactions that consume A and B to produce P1 and P2.

$$\frac{[P1]}{[P2]} = \frac{\frac{d[P1]}{dt}}{\frac{d[P2]}{dt}} = \frac{k_{r1}[A][B]}{k_{r2}[A][B]} = \frac{k_{r1}}{k_{r2}} \quad (2.9.3)$$

If $k_{e1}, k_{e2} \gg k_{r1}, k_{r2}$

Then at any given time, this reaction simplifies to:



$$\frac{[P_1]}{[P_2]} = \frac{k_{e1}}{k_{e2}}$$

The reaction is **thermodynamically controlled** : the amount of products depends on the **equilibrium state**.

Proof to show: $\frac{[P_1]}{[P_2]} = \frac{k_{e1}}{k_{e2}}$:

At equilibrium:

Forward reaction rate: $\frac{d[P2]}{dt} = k_{e2}[P1]$

Reverse reaction rate: $\frac{d[P1]}{dt} = k_{e1}[P2]$

At equilibrium, the forward and reverse reaction rates are equal:

$$k_{e2}[P1] = k_{e1}[P2]$$

$$\frac{[P1]}{[P2]} = \frac{k_{e1}}{k_{e2}}$$

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2.10: Reaction Chemistry Chapter Review

Important Equations

Reaction rate	$r = \frac{1}{V} \frac{d\xi}{dt} = \frac{1}{\nu_j} \frac{1}{V} \frac{dn_j}{dt}$
Extent of reaction	$dn_j = \nu_j d\xi$
Relating extent of reaction with reaction rate	$r = \frac{1}{V} \frac{d\xi}{dt} = \frac{1}{\nu_j} \frac{1}{V} \frac{dn_j}{dt}$
Rate law (general form)	$r = k_r [A]^a [B]^b \quad (2.10.1)$ $r = k_r p_A^a p_B^b \quad (2.10.2)$
Zeroth-order rate law	$[A] - [A]_0 = -k_r * t$ $[A] = [A]_0 - k_r * t \quad (2.10.3)$
First-order rate law	$\ln[A] - \ln[A]_0 = -k_r * t \quad (2.10.4)$ $[A] = [A]_0 e^{-k_r * t} \quad (2.10.5)$
Second-order rate law	$\frac{1}{[A]} - \frac{1}{[A]_0} = k_r * t \quad (2.10.6)$ $[A] = \frac{[A]_0}{1 + k_r * t * [A]_0} \quad (2.10.7)$
Equilibrium constant	$K \text{ or } K_{eq} = \prod_i a_{i,eq}^{v_i} \quad (2.10.8)$ $K = \frac{k_r}{k'_r}, c^\theta \text{ is used for unit consistency} \quad (2.10.9)$ $k'_r [product]_{eq}^p = k_r [reactant]_{eq}^r \quad (2.10.10)$
Arrhenius equation	Linear form: $\ln(k_r) = -\frac{E_a}{R} \times \frac{1}{T} + \ln(A) \quad (2.10.11)$ Simplification for temperature dependency calculations: $\ln\left(\frac{k_{r2}}{k_{r1}}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (2.10.12)$
Unimolecular rate law	$A \rightarrow P : -\frac{d[A]}{dt} = k_r * [A]$
Bimolecular rate law	$A + B \rightarrow P : -\frac{d[A]}{dt} = k_r * [A] * [B] \quad (2.10.13)$ $A + A \rightarrow P : -\frac{d[A]}{dt} = k_r * [A]^2 \quad (2.10.14)$
Kinetic control	If $k_{e1}, k_{e2} \ll k_{r1}, k_{r2}$: $\frac{[P_1]}{[P_2]} = \frac{k_{r1}}{k_{r2}} \quad (2.10.15)$
Thermodynamic control	If $k_{e1}, k_{e2} \gg k_{r1}, k_{r2}$:

$$\frac{[P_1]}{[P_2]} = \frac{k_{e1}}{k_{e2}} \quad (2.10.16)$$

Terms to Know:

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<https://pressbooks.bccampus.ca/chbe220/?p=1427>

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2.11: Practice Exercises

Multiple Choice Questions

✓ Exercise: Stoichiometry

Which of the following statement is true about the reaction $A + B \rightarrow P$?

- a) the stoichiometric coefficient for A is 1
- b) the stoichiometric coefficient for B is -1
- c) the reaction extent can be positive, negative
- d) the stoichiometric coefficient for P is -1

Solution

Add example text here.

b) the stoichiometric coefficient for B is -1

The stoichiometric coefficient is negative for reactants and positive for products. Since the reaction only goes forward, the reaction extent is always positive (or 0 if it doesn't happen)

✓ Exercise: Stoichiometric Expression

Which of the following statement is true about the equilibrium reaction $A + B \leftrightarrow P$?

- a) the stoichiometric coefficient for A is 1
- b) the stoichiometric coefficient for P is -1
- c) the reaction extent can be positive or negative
- d) the equilibrium constant K can be positive or negative

Solution

Add example text here.

c) the reaction extent can be positive, negative

The stoichiometric coefficient is negative for reactants and positive for products. Since it is an equilibrium reaction, if the reverse reaction happens more frequently than the forward reaction, the reaction extent can be negative. The equilibrium constant is $K = \prod_i a_{i,eq}^{v_i}$. Since the concentration of any compound must be positive, the equilibrium constant K must be positive as well.

✓ Exercise: Reaction Order

The following data shows the concentration of reactive species [A] in the system at points of time.

Time (s)	[A] (mol/L)
0	2.000
0.100	0.286
0.200	0.154
0.300	0.105

What is the reaction order of A, determined by the integrated rate law?

- a) zeroth-order

- b) first-order
- c) second-order
- d) none of the above

Solution

Add example text here.

c) second-order

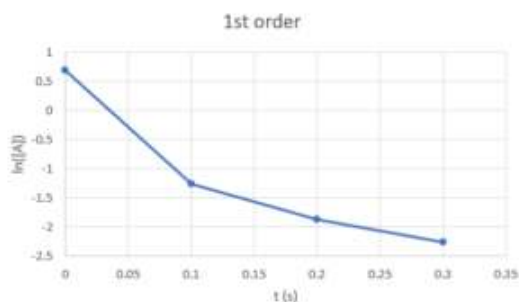
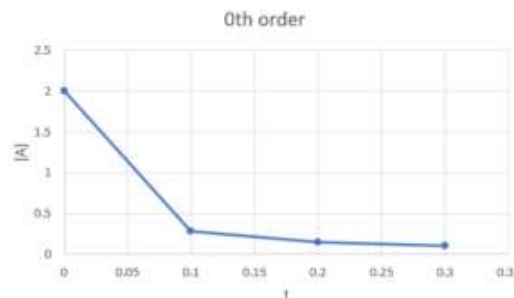
Zeroth order: $[A] - [A]_0 = -k_r \times t$, would be linear if graph $[A]$ against t

First order: $\ln[A] - \ln[A]_0 = -k_r \times t$, would be linear if graph $\ln([A])$ against t

Second order: $\frac{1}{[A]} - \frac{1}{[A]_0} = k_r \times t$, would be linear if graph $\frac{1}{[A]}$ against t So we plot $[A]$ against t , $\ln([A])$ against t , and $\frac{1}{[A]}$ against t

t	[A]	ln([A])	1/[A]
0	2	0.693147	0.5
0.1	0.286	-1.25176	3.496503
0.2	0.154	-1.8708	6.493506
0.3	0.105	-2.25379	9.52381

and see which one is linear:



We can see that only $\frac{1}{[A]}$ against t is linear, so the reaction is second order in A.

✓ Exercise: Reaction Rate Law Units



If the concentration of $[H_2O_2]$, $[I^-]$ and $[H^+]$ are measured in units of mol/L, what is the unit of the reaction rate constant k_r ?

- a) $\frac{L^2}{mol^2 \cdot s}$
- b) $\frac{mol}{L \cdot s}$
- c) $\frac{L}{mol \cdot s}$
- d) $\frac{L^5}{mol^5 \cdot s}$

Solution

Add example text here.

- c) $\frac{L}{mol \cdot s}$

Based on the unit that the reactive species are measured, we can know that the unit for r is $\frac{mol}{L \cdot s}$. So we can equate the units on both sides of the rate law:

$$\begin{aligned}\frac{\text{mol}}{\text{L} \cdot \text{s}} \times \frac{\text{L}}{\text{mol}} \times \frac{\text{L}}{\text{mol}} &= k_r \times \frac{\text{mol}}{\text{L}} \times \frac{\text{mol}}{\text{L}} \\ \frac{\text{L}}{\text{mol} \cdot \text{s}} &= k_r\end{aligned}$$

Long Answer Questions

✓ Exercices: Reaction Rates

We have the following reaction happening in a fixed reaction chamber:



The partial pressure of NH_3 was measured at each time point and shown in the table below.

Time (ms)	$[\text{NH}_3]$ (Pa)
0	1670
100	1300
200	1012
300	789
400	614
500	478

a) Calculate the initial rate of reaction

b) Calculate the initial rate of change in partial pressure for every compound involved in the reaction

*Hint: for small time intervals, we can take $\frac{d[J]}{dt} = \frac{\Delta[J]}{\Delta t}$, where J is any species involved in the reaction

Solution

Add example text here.

a)

$$\begin{aligned}r &= \frac{1}{v_j} \frac{d[J]}{dt} = \frac{1}{v_j} \frac{\Delta[J]}{\Delta t} \\ &= \frac{1}{-2} \frac{\Delta[\text{NH}_3]}{\Delta t} \\ &= \frac{1}{-2} \frac{(1300 - 1670)\text{Pa}}{(100 - 0)\text{ms} \times \frac{1\text{s}}{1000\text{ms}}} \\ &= 1850\text{Pa/s}\end{aligned}$$

b) Because is it a "fixed reaction chamber", which means the total volume of the gas chamber stays constant, so we can do the following balance using the definition of reaction rate:

$$r = \frac{1}{-2} \frac{\Delta[\text{NH}_3]}{\Delta t} = \frac{\Delta[\text{N}_2]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{H}_2]}{\Delta t} \quad (2.11.2)$$

$$\frac{\Delta[\text{NH}_3]}{\Delta t} = -2 \times r = -2 \times 1850\text{Pa/s} = -3700\text{Pa/s}$$

$$\frac{\Delta[\text{N}_2]}{\Delta t} = r = 1850\text{Pa/s}$$

$$\frac{\Delta[\text{H}_2]}{\Delta t} = 3 \times r = 5550\text{Pa/s}$$

✓ Exercise: Reaction Order and Rate Constant

$$[1] \quad (2.11.3)$$



Experimental data for the reaction at 300°C and four initial concentrations of NO₂ are listed in the following table:

Experiment	[NO ₂] ₀ (M)	Initial rate(M/s)
1	0.015	1.22×10^{-4}
2	0.010	5.40×10^{-5}
3	0.0080	3.46×10^{-5}
4	0.0050	1.35×10^{-5}

Solution

Add example text here.

Step 1: Determine the reaction order with respect to nitrogen dioxide

For example, comparing Experiments 2 and 4 shows that doubling the concentration quadruples the reaction rate

$$(5.40 \times 10^{-5}) \div (1.35 \times 10^{-5}) = 4.0 \quad (2.11.5)$$

$$[NO_2]^2 \quad (2.11.6)$$

Therefore, the reaction is second order with respect to nitrogen dioxide.

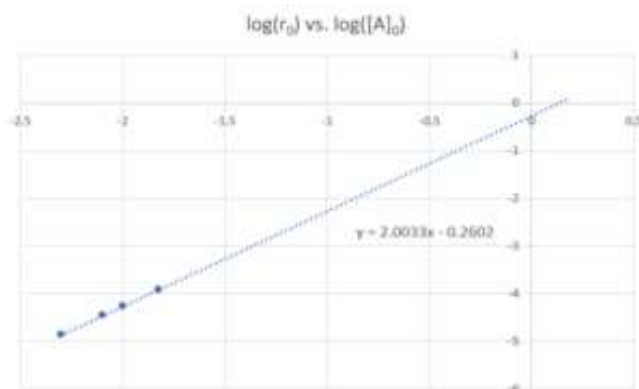
Step 2: calculate k_r

We have $rate = k_r[NO_2]^2$. We can calculate the rate constant (k_r) using data from any experiment in the table.

$$\begin{aligned} rate &= k_r[NO_2]^2 \\ 5.40 \times 10^{-5} M/s &= k_r \times (0.010 M)^2 \\ 0.54 M^{-1} s^{-1} &= k_r \end{aligned}$$

Method 2

The following graph is produced when plotting $\log(r_0)$ vs $\log([A]_0)$



From the line of best fit, we can see $a = 2$, $\log(k_r) = -0.2602$

Therefore the reaction is first order in NO₂, $k_r = 10^{-0.2602} = 0.55 M^{-1} s^{-1}$.

✓ Exercise: Rate Constant and Arrhenius Equation

Suppose a reaction has an activation energy of 85 kJ/mol. If the reaction has a reaction rate constant of 70s^{-1} at 0°C , then what is the reaction rate constant at 25°C ?

Solution

Add example text here.

We can use the rearranged Arrhenius Equation to relate the reaction rate constant to temperature. Note that the temperature should be expressed in K.

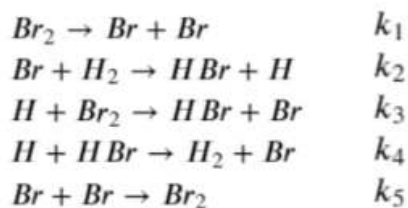
$$\begin{aligned}\ln\left(\frac{k_{r2}}{k_{r1}}\right) &= \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \\ \ln\left(\frac{k_{r2}}{70\text{s}^{-1}}\right) &= \frac{85 \times 10^3 \text{J/mol}}{8.314 \text{J/(mol} \cdot \text{K)}} \left(\frac{1}{(0 + 273.15)\text{K}} - \frac{1}{(25 + 273.15)\text{K}} \right) \\ \ln\left(\frac{k_{r2}}{70\text{s}^{-1}}\right) &= 3.138 \\ \frac{k_{r2}}{70\text{s}^{-1}} &= e^{3.138} \\ k_{r2} &= e^{3.138} \times 70\text{s}^{-1} \\ k_{r2} &= 1615\text{s}^{-1}\end{aligned}$$

✓ Exercise: Using Steady-state Approximation to Find the Rate Law Expression

Suppose we have a system with the reaction:



The elementary reactions are as follows:



Using the steady state assumption, we can prove that



This will also allow us to determine the values of k_a and k_b in terms of the elementary reaction rate constants k_1 to k_5

Solution

Add example text here.

Step 1: Start by expressing the rate of change of the intermediates Br and H , and set them equal to 0:

$$\frac{d[\text{Br}]}{dt} = 2k_1[\text{Br}_2] - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - 2k_5[\text{Br}]^2 = 0 \quad (1) \quad (2.11.8)$$

$$\frac{d[\text{H}]}{dt} = k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] = 0 \quad (2) \quad (2.11.9)$$

Step 2: Express $\frac{d[\text{HBr}]}{dt}$ based on the elementary reactions:

$$\frac{d[HBr]}{dt} = k_2[Br][H_2] + k_3[H][Br_2] - k_4[H][HBr] \quad (2.11.10)$$

We can see that to get the expression in the question statement, we need to replace $[H]$ and $[Br]$ and simplify.

Step 3: Adding equations (1) and (2) together, we can see that 3 of the terms cancel, allowing us to solve for $[Br]$:

$$\begin{aligned} 2k_1[Br_2] - 2k_5[Br]^2 &= 0 \\ 2k_1[Br_2] &= 2k_5[Br]^2 \\ \left(\frac{k_1}{k_5}\right)^{1/2}[Br_2]^{1/2} &= [Br] \end{aligned}$$

Step 4: Next, we can determine $[H]$ using equation (2) by substituting what we derived for $[Br]$:

$$\begin{aligned} k_2[Br][H_2] - k_3[H][Br_2] - k_4[H][HBr] &= 0 \\ (k_3[Br_2] + k_4[HBr])[H] &= k_2[Br][H_2] \\ [H] &= \frac{k_2[Br][H_2]}{k_3[Br_2] + k_4[HBr]} \\ [H] &= \frac{k_2\left(\frac{k_1}{k_5}\right)^{1/2}[Br_2]^{1/2}[H_2]}{k_3[Br_2] + k_4[HBr]} \end{aligned}$$

Step 5: Substitute $[H]$ and $[Br]$ into $\frac{d[HBr]}{dt}$, then simplify



Therefore, the values of k_a and k_b are:

$$k_a = 2k_2\left(\frac{k_1}{k_5}\right)^{1/2}$$

$$k_b = \frac{k_4}{k_3} \quad (2.11.11)$$

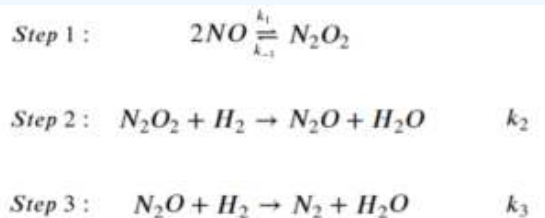
Extra Reaction Mechanism Exercises

✓ Reaction Mechanism Exercise 1

For the overall reaction



The step-wise elementary reactions are:



Express reaction rate of the overall reaction using the steady-state approximation. The expression should only include $[NO]$, $[H_2]$, and the rate constants of the elementary steps.

Solution

Add example text here.

Step 1: Steady-state approximation states that the rate of generation and consumption of intermediates sum up to 0. The intermediates in the reaction are N_2O_2 and N_2O

$$\frac{d[N_2O_2]}{dt} = k_1[NO]^2 - k_{-1}[N_2O_2] - k_2[N_2O_2][H_2] = 0 \quad (1)$$

$$\frac{d[N_2O]}{dt} = k_2[N_2O_2][H_2] - k_3[N_2O][H_2] = 0 \quad (2)$$

Step 2: Express the rate of the overall reaction. In this reaction, the rate of the overall reaction can be expressed as the rate of generation of N_2 :

$$r = \frac{d[N_2]}{dt} = k_3[N_2O][H_2] \quad (2.11.13)$$

Step 3: Use equations (1) and (2) to replace the intermediate terms in the expression for r :

From (2):

$$r = \frac{d[N_2]}{dt} = k_3[N_2O][H_2] = k_2[N_2O_2][H_2] \quad (2.11.14)$$

Then we can use equation (1) to replace $[N_2O_2]$ with an expression with $[NO]$ and $[H_2]$:

$$\begin{aligned} k_1[NO]^2 - k_{-1}[N_2O_2] - k_2[N_2O_2][H_2] &= 0 \\ k_1[NO]^2 &= k_{-1}[N_2O_2] + k_2[N_2O_2][H_2] \\ k_1[NO]^2 &= [N_2O_2] \times (k_{-1} + k_2[H_2]) \\ \frac{k_1[NO]^2}{k_{-1} + k_2[H_2]} &= [N_2O_2] \end{aligned}$$

Step 4: Substitute the result of step 3 into the expression for r :

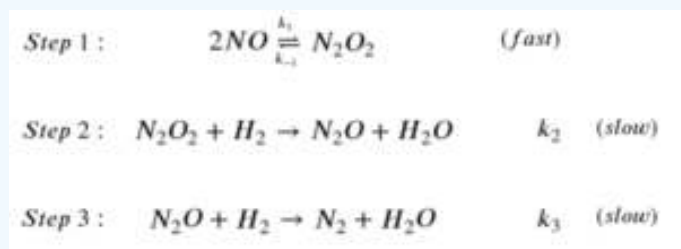
$$r = k_2[N_2O_2][H_2] = \frac{k_2 k_1 [NO]^2 [H_2]}{k_{-1} + k_2 [H_2]} \quad (2.11.15)$$

✓ Reaction Mechanism Exercise 1 - with Pre-equilibria

For the overall reaction



The step-wise elementary reactions are:



Express reaction rate of the overall reaction using the steady-state approximation and the pre-equilibrium assumption. The expression should only include $[NO]$, $[H_2]$, and the rate constants of the elementary steps.

Solution

Add example text here.

Step 1: Set the sum of the rate of generation and consumption of intermediates to 0:

$$\frac{d[N_2O_2]}{dt} = k_1[NO]^2 - k_{-1}[N_2O_2] - k_2[N_2O_2][H_2] = 0 \quad (1)$$

$$\frac{d[N_2O]}{dt} = k_2[N_2O_2][H_2] - k_3[N_2O][H_2] = 0 \quad (2)$$

Step 2: Express the rate of the overall reaction:

$$r = \frac{d[N_2]}{dt} = k_3[N_2O][H_2] \quad (2.11.17)$$

Step 3: Replace the intermediate terms:

From (2):

$$r = \frac{d[N_2]}{dt} = k_3[N_2O][H_2] = k_2[N_2O_2][H_2] \quad (2.11.18)$$

Under pre-equilibria assumptions, we assume the rate of the equilibrium reaction is much faster than the reaction that consumes the product of the equilibrium reaction. So we can express $[N_2O_2]$ using the definition of equilibrium that the rate of forward and reverse reactions in step 1 are the same:

$$\begin{aligned} k_1[NO]^2 &= k_{-1}[N_2O_2] \\ \frac{k_1[NO]^2}{k_{-1}} &= [N_2O_2] \end{aligned}$$

Step 4: Substitute the result of step 3 into the expression for r:

$$r = k_2[N_2O_2][H_2] = \frac{k_2k_1[NO]^2[H_2]}{k_{-1}} \quad (2.11.19)$$

Why are the answers different?

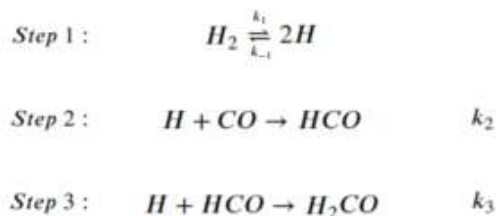
The pre-equilibria assumption states that the rate of the equilibrium reaction is much faster than the reaction that consumes the product of the equilibrium reaction, which means $k_{-1} \gg k_2$. Therefore, the $k_2[H_2]$ term is negligible comparing to the k_{-1} term in the denominator under pre-equilibria assumption.

✓ Reaction Mechanism Exercise 2

For the overall reaction to produce formaldehyde:



The step-wise elementary reactions are:



Express reaction rate of the overall reaction using the steady-state approximation. The expression can involve the concentration of the reactants of the overall reaction, $[H]$, and the rate constants of the elementary steps. Then state how to replace $[H]$ in the expression (you do not have to calculate it).

Solution

Add example text here.

Step 1: Set the sum of the rate of generation and consumption of intermediates to 0. Notice how the coefficients affect the rate law:

$$\frac{d[H]}{dt} = 2k_1[H_2] - 2k_{-1}[H]^2 - k_2[H][CO] - k_3[H][HCO] = 0 \quad (1)$$

$$\frac{d[HCO]}{dt} = k_2[H][CO] - k_3[H][HCO] = 0 \quad (2)$$

Step 2: Express the rate of the overall reaction:

$$r = \frac{d[H_2CO]}{dt} = k_3[H][HCO] \quad (2.11.21)$$

Step 3: Replace the intermediate terms:

From (2):

$$r = k_3[H][HCO] = k_2[H][CO] \quad (2.11.22)$$

We can get an expression of $[H]$ by solving for it in equation (1), also using the relationship from (2) that $k_3[H][HCO] = k_2[H][CO]$:

$$\begin{aligned} 2k_1[H_2] - 2k_{-1}[H]^2 - k_2[H][CO] - k_3[H][HCO] &= 0 \\ 2k_1[H_2] - 2k_{-1}[H]^2 - 2k_2[H][CO] &= 0 \end{aligned}$$

This is a quadratic equation about $[H]$. We can solve it using the quadratic formula:

$$[H] = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad (2.11.23)$$

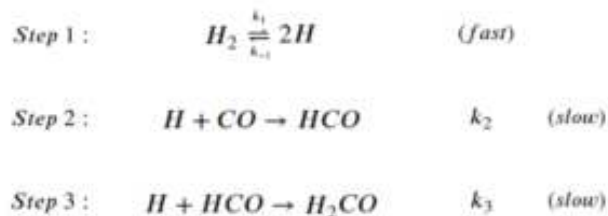
where $a = -2k_{-1}$, $b = -2k_2[CO]$, $c = 2k_1[H_2]$

✓ Reaction Mechanism Exercise 2 - with Pre-equilibria

For the overall reaction to produce formaldehyde:



The step-wise elementary reactions are:



Express reaction rate of the overall reaction using the steady-state approximation and the pre-equilibrium assumption. The expression should only include $[H_2]$, $[CO]$, and the rate constants of the elementary steps.

Solution

Add example text here.

Step 1: Set the sum of the rate of generation and consumption of intermediates to 0:

$$\begin{aligned} \frac{d[H]}{dt} &= 2k_1[H_2] - 2k_{-1}[H]^2 - k_2[H][CO] - k_3[H][HCO] = 0 \quad (1) \\ \frac{d[HCO]}{dt} &= k_2[H][CO] - k_3[H][HCO] = 0 \quad (2) \end{aligned}$$

Step 2: Express the rate of the overall reaction:

$$r = \frac{d[H_2CO]}{dt} = k_3[H][HCO] \quad (2.11.25)$$

Step 3: Replace the intermediate terms:

From (2):

$$r = k_3[H][HCO] = k_2[H][CO] \quad (2.11.26)$$

Using the pre-equilibrium assumptions to replace $[H]$:

$$k_1[H_2] = k_{-1}[H]^2$$

$$\frac{k_1}{k_{-1}} = [H]^2$$

$$\left(\frac{k_1}{k_{-1}}\right)[H_2]^{\frac{1}{2}} = [H]$$

Step 4: Substitute the result of step 3 into the expression for r:

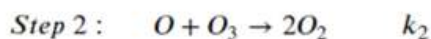
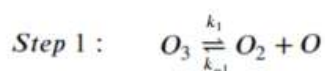
$$r = k_2[H][CO] = k_2\left(\frac{k_1}{k_{-1}}\right)[H_2]^{\frac{1}{2}}[CO] \quad (2.11.27)$$

✓ Reaction Mechanism Exercise 3

For the reaction of ozone depletion:



The step-wise elementary reactions are:



Express reaction rate of oxygen gas generation $\left(\frac{d[O_2]}{dt}\right)$ using the steady-state approximation. The expression should include $[O_3]$, $[O_2]$, and the rate constants of the elementary steps.

Solution

Add example text here.

Step 1: Set the sum of the rate of generation and consumption of intermediates to 0:

$$\frac{d[O]}{dt} = k_1[O_3] - k_{-1}[O_2][O] - k_2[O][O_3] = 0 \quad (1) \quad (2.11.29)$$

Step 2: Express $\frac{d[O_2]}{dt}$ from the elementary reactions. Notice that O_2 is generated in multiple elementary steps:

$$\frac{d[O_2]}{dt} = k_1[O_3] - k_{-1}[O_2][O] + 2k_2[O][O_3] \quad (2.11.30)$$

Step 3: Replace $[O]$ using equation (1)

$$k_1[O_3] - k_{-1}[O_2][O] - k_2[O][O_3] = 0$$

$$k_1[O_3] = k_{-1}[O_2][O] + k_2[O][O_3]$$

$$k_1[O_3] = [O](k_{-1}[O_2] + k_2[O_3])$$

$$\frac{k_1[O_3]}{k_{-1}[O_2] + k_2[O_3]} = [O]$$

$$[O] \quad (2.11.31)$$

$$\frac{d[O_2]}{dt} = k_1[O_3] - k_{-1}[O_2][O] + 2k_2[O][O_3]$$

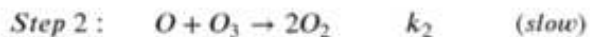
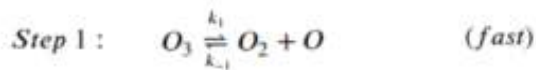
$$\frac{d[O_2]}{dt} = k_1[O_3] - \frac{k_{-1}k_1[O_3][O_2]}{k_{-1}[O_2] + k_2[O_3]} + \frac{2k_2k_1[O_3]^2}{k_{-1}[O_2] + k_2[O_3]}$$

✓ Reaction Mechanism Exercise 3 - with Pre-equilibria

For the reaction of ozone depletion:



The step-wise elementary reactions are:



Express reaction rate of oxygen gas generation ($\frac{d[O_2]}{dt}$) using the steady-state approximation and the pre-equilibrium assumption. The expression should include $[O_3]$, $[O_2]$, and the rate constants of the elementary steps.

Solution

Add example text here.

Step 1: Set the sum of the rate of generation and consumption of intermediates to 0:

$$\frac{d[O]}{dt} = k_1[O_3] - k_{-1}[O_2][O] - k_2[O][O_3] = 0 \quad (2.11.33)$$

Step 2: Express $\frac{d[O_2]}{dt}$:

$$\frac{d[O_2]}{dt} = k_1[O_3] - k_{-1}[O_2][O] + 2k_2[O][O_3] \quad (2.11.34)$$

Step 3: Using the pre-equilibrium assumptions to replace $[O]$:

$$\begin{aligned} k_1[O_3] &= k_{-1}[O_2][O] \\ \frac{k_1[O_3]}{k_{-1}[O_2]} &= [O] \end{aligned} \quad (2.11.35)$$

$$\begin{aligned} \frac{d[O_2]}{dt} &= k_1[O_3] - k_{-1}[O_2][O] + 2k_2[O][O_3] \\ &= k_1[O_3] - k_{-1}[O_2] \frac{k_1[O_3]}{k_{-1}[O_2]} + \frac{2k_2k_1[O_3]^2}{k_{-1}[O_2]} \\ &= k_1[O_3] - k_1[O_3] + \frac{2k_2k_1[O_3]^2}{k_{-1}[O_2]} \\ &= \frac{2k_2k_1[O_3]^2}{k_{-1}[O_2]} \end{aligned}$$

References

[1] Chemistry LibreTexts. 2020. 14.4: The Change Of Concentration With Time (Integrated Rate Laws). [online] Available at: <[https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_\(Brown_et_al.\)/14%3A_Chemical_Kinetics/14.4%3A_The_Change_of_Concentration_with_Time_\(Integrated_Rate_Laws\)](https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/14%3A_Chemical_Kinetics/14.4%3A_The_Change_of_Concentration_with_Time_(Integrated_Rate_Laws))> [Accessed 23 April 2020].

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CHAPTER OVERVIEW

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3.1: Pressure Definition; Absolute and Gauge Pressure

Learning Objectives

By the end of this section, you should be able to:

- **Calculate** pressure using its definition

Understand the difference between absolute & gauge pressure

Physical Properties

Physical properties are properties that can be measured without changing the molecular structure of the substance.

The three main physical properties we will introduce in this lecture are **pressure**, **temperature**, and **volume**:

Pressure – the amount of force exerted per area in a system

Temperature – a measure of the average kinetic energy of a system

Volume – the space occupied by a system

To see more about how these are related for gases, there is an interesting gas property simulator available online: <https://phet.colorado.edu/en/simulation/gas-properties>

Pressure ^[1]

When a gas molecule elastically collides with the wall of a container, it exerts a force on the wall. These forces are the source of pressure in a gas. In a sample of gas in a container, the randomness of the molecular motion causes the number of collisions to fluctuate in a given time. However, because a huge number of molecules collide with the wall in a short time, the number of collisions on the scales of time and space we measure fluctuates by only a tiny, usually unobservable fraction from the average.

As the number of molecules increases, the number of collisions, and thus the pressure, increases. If the average velocity of the molecules is higher, each collision exerts a larger force on the wall, therefore the gas pressure is higher.

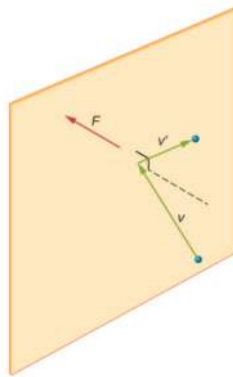


Image obtained from [OpenStax University Physics Volume 2](#) / CC BY 4.0

Calculation and Units:

$$\text{Pressure}(P) = \frac{\text{force}}{\text{area}} \quad (3.1.1)$$

$$\text{units for } P = \frac{ML}{t^2} L^{-2} = \frac{M}{LT^2} \quad (3.1.2)$$

General notation:

M – any units of mass (g, kg, lbs...)

L – any units of length (m, cm, in...)

t – any units of time (s, min, hr...)

Common units for pressure:

$$[\text{S.I.}] \frac{\text{kg}}{\text{m} \cdot \text{s}^2} = \frac{\text{N}}{\text{m}^2} = \text{Pa} \text{ (i.e. Pascal)}$$

$$[\text{cgs}] \frac{\text{g}}{\text{cm} \cdot \text{s}^2} = \frac{\text{dyne}}{\text{cm}^2}$$

$$[\text{American}] \frac{\text{lbm}}{\text{ft} \cdot \text{s}^2}$$

Other common pressure units:

$$1\text{kPa}(\text{kilo} - \text{Pascal}) = 10^3 \text{Pa} \quad (3.1.3)$$

$$1\text{MPa}(\text{mega} - \text{Pascal}) = 10^6 \text{Pa} \quad (3.1.4)$$

$$1\text{bar} = 10^5 \text{Pa} = 10^5 \text{N/m}^2$$

$$1\text{atm} = 1.013 \times 10^5 \text{Pa} = 760\text{mmHg} \quad (3.1.5)$$

✓ Exercise: Pressure Calculation

What is the force exerted from a column of air on us in mass per square metre?

Take atmosphere pressure = $1.013 \times 10^5 \text{Pa}$

Solution

Add example text here.

We can use Newton's second law $F = ma$ to find mass, with a being the acceleration of gravity. Since the mass we are looking for is "per square metre", we can also divide the force by area(in m^2), which gives us pressure on the left side of the equation.

$$\text{mass (per } \text{m}^2) = \frac{P}{a} = \frac{1.013 \times 10^5 \text{Pa}}{9.81 \frac{\text{m}}{\text{s}^2}} = \frac{1.013 \times 10^5 \frac{\text{kg}}{\text{m} \cdot \text{s}^2}}{9.81 \frac{\text{m}}{\text{s}^2}} = 10326 \frac{\text{kg}}{\text{m}^2} \quad (3.1.6)$$

Measuring Pressure (Manometers) ^[2]

A manometer can be used to determine gas pressures. The manometer is essentially a U-shaped tube containing some kind of fluid with known density, and one side is connected to the region of interest while the reference pressure is applied to the other. The difference in liquid level represents the applied pressure.

Manometer fluid – mercury was used originally (hence mmHg), but we now have a wide variety of fluids of various densities.

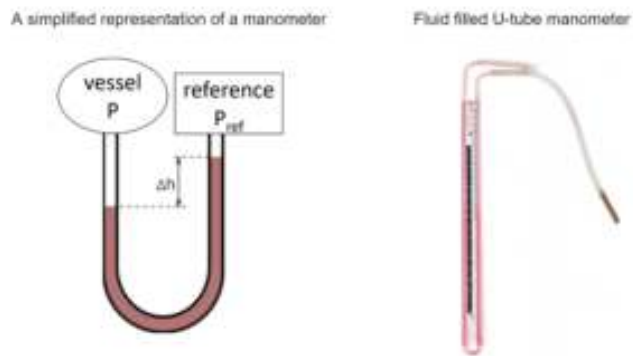
Manometer types:

1. open-ended manometer:

$$P_{\text{ref}} = P_{\text{atm}} \quad (3.1.7)$$

1. sealed-end manometer:

$$P_{\text{ref}} = \text{whatever it is set to (generally } 0, \text{ vacuum)} \quad (3.1.8)$$



Right side image obtained from [Apply Science Concepts to Trades Applications](#) / CC BY 4.0

The difference in heights of the liquid columns correlates to the difference in the pressure of the gases. The pressure of the gas in the vessel is calculated by:

$$P = P_{ref} + \rho g(h_{ref} - h) \quad (3.1.9)$$

✓ Exercise: Manometer Calculation

Compressed air has been used to transmit and store power since the 1870s. Cities such as Paris, Dresden and Buenos Aires had compressed air lines to transmit power to homes and businesses. The technology is now being applied to energy storage in former salt mines underground. One such plant in McIntosh, Alabama stores gas at 1100 psi. If a sealed end manometer with a fluid with a density of $3450 \frac{kg}{m^3}$ was used to measure this pressure, what would the height of the fluid column be? (take $g = 9.8m/s^2$)

Solution

Add example text here.

Manipulate h from the equation:

$$\begin{aligned} P &= P_{ref} + \rho g(h_{ref} - h) & (3.1.10) \\ h &= \frac{P - P_0}{\rho g} \\ h &= \frac{1100psi \times \frac{101325Pa}{14.696psi}}{3450 \frac{kg}{m^3} \times 9.8 \frac{m}{s^2}} \\ &= \frac{7.58 \times 10^6 Pa}{3.381 \times 10^4 \frac{kg}{m^2 s^2}} \\ &= 2.242 \times 10^2 \frac{Pa}{\frac{kg}{m^2 s^2}} \times \frac{1 \frac{kg}{m s^2}}{1Pa} \\ &= 2.24 \times 10^2 m \end{aligned}$$

height = $2.24 \times 10^2 m$ or 224 m, very high pressure, likely difficult to measure with a manometer.

Gauge vs. Absolute Pressure

The **absolute** pressure is the **actual pressure at the point of interest**. The absolute pressure is 0 in a vacuum and cannot be negative.

Gauge pressure is defined to be **the difference between absolute pressure and atmospheric pressure**:

$$gauge\ pressure = absolute\ pressure - atmospheric\ pressure \quad (3.1.11)$$

when gauge pressure is 0, absolute pressure = atmospheric pressure

Most measuring devices measure gauge pressure. Many measuring devices use a flexible membrane between a chamber of known pressure (the outside chamber, which is connected to the atmosphere) and a vessel with the pressure we want to measure. If there is a difference in pressure on both sides of the membrane, the membrane will expand or contract. Through this, we can relate the membrane's position to the gauge pressure of the vessel.



The units often used on the devices include:

$$psi \quad (3.1.12)$$

$$inHg \quad (3.1.13)$$

✓ Exercise: Reading Absolute and Gauge Pressures

1. If the gauge in the image reads 5 psi at the orange mark and the atmospheric pressure is 14.7 psi, which of the following are the gauge and absolute pressures?

- A – gauge = -5 psi, absolute = 9.7 psi
- B – gauge = 5 psi, absolute = 9.7 psi
- C – gauge = -5 psi, absolute = 19.7 psi
- D – gauge = 5 psi, absolute = 19.7 psi



2. If the gauge in the image reads 10 inHg at the purple mark and the atmospheric pressure is 29.9 inHg, which of the following are the gauge and absolute pressures?

- A – gauge = -10 inHg, absolute = 39.9 inHg
- B – gauge = 10 inHg, absolute = 19.9 inHg
- C – gauge = -10 inHg, absolute = 19.9 inHg
- D – gauge = 10 inHg, absolute = 39.9 inHg



Solution

Add example text here.

1. Answer: D

The arrow is on the “pressure” side, which indicates that the gauge pressure is positive. The absolute pressure is the sum of absolute pressure and gauge pressure.

$$\begin{aligned} \text{absolute pressure} &= \text{gauge pressure} + \text{atmospheric pressure} \\ &= 5\text{psi} + 14.7\text{psi} \\ &= 19.7\text{psi} \end{aligned}$$

2. Answer: C

The arrow is on the “vacuum” side, which indicates that the gauge pressure is negative. The absolute pressure is the sum of absolute pressure and gauge pressure.

$$\begin{aligned} \text{absolute pressure} &= \text{gauge pressure} + \text{atmospheric pressure} \\ &= -10\text{inHg} + 29.9\text{inHg} \\ &= 19.9\text{inHg} \end{aligned}$$

References

- [1] OpenStax University Physics Volume 2. 2016. 2.2 Pressure, Temperature, and RMS Speed. [online] <<https://openstax.org/books/university-physics-volume-2/pages/2-2-pressure-temperature-and-rms-speed>> [Accessed 11 May 2020].
- [2] Line D – Organizational Skills Competency D-2: Apply Science Concepts to Trades Applications. 2015. Manometer. [online] <<http://solr.bccampus.ca:8001/bcc/file/3654f43b-8e2b-43be-99ce-acd1b2e4d809/1/D-2.pdf>> [Accessed 11 May 2020].

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3.2: Temperature

Learning Objectives

By the end of this section, you should be able to:

- **Understand** the physical properties described by the temperature

Calculate conversions between scales of temperature

Temperature

Temperature is operationally defined as the quantity of what we measure with a thermometer. The average kinetic energy of a molecule is directly proportional to its **absolute** temperature. Differences in temperature maintain heat transfer through different systems. Heat transfer is the movement of energy from one place or material to another as a result of a difference in temperature.
[1][2]

Assigned scales are based on physical measurements:

Celsius (°C) – based on water freezing (0 °C) and boiling (100 °C) at atmospheric pressure. Absolute zero at -273.15°C.

Fahrenheit (°F) – based on water freezing (32 °F) and boiling (212 °F) at atmospheric pressure. Absolute zero at -459.67°F.

There are also other absolute scales with 0 being absolute zero:

Kelvin (K) – Same size of a degree as Celsius

Rankine (°R) – Same size of a degree as Fahrenheit

Defining Equations

Celsius to Kelvin: $T(K) = T(^{\circ}C) + 273.15$

Fahrenheit to Rankine: $T(^{\circ}R) = T(^{\circ}F) + 459.67$

Kelvin to Rankine: $T(^{\circ}R) = 1.8 \cdot T(K)$

Celsius to Fahrenheit: $T(^{\circ}F) = 1.8 \cdot T(^{\circ}C) + 32$

✓ Exercise: Temperature Conversions

Some solar plants use molten salt as a heat transfer agent that can be stored efficiently. This allows the plant to operate after the sun has set by extracting energy from the molten salt they have stored during the day. The temperature difference is important to know as it will dictate the energy obtainable from the salt. If the molten salt is heated to 1000°F on a given day and if the environment is at 25°C what is the temperature difference in Kelvin?

Solution

Add example text here.

First, convert the two temperatures to the same units. Because the question asks for the temperature difference in Kelvin, it is more convenient to compare on a Celsius scale because the sizes of 1 degree are the same for Celsius/Kelvin.

Step 1: Convert the temperature in Fahrenheit to Celsius:

$$T(^{\circ}C) = \frac{T(^{\circ}F) - 32^{\circ}F}{1.8 \frac{^{\circ}C}{^{\circ}F}} = \frac{1000^{\circ}F - 32^{\circ}F}{1.8 \frac{^{\circ}C}{^{\circ}F}} = 537.8^{\circ}C \quad (3.2.1)$$

Step 2: Calculate the difference in temperature in Celsius, which is equal to the difference in Kelvin (you can prove this to yourself if desired if you convert both temperatures above from Celsius to Kelvin).

$$\Delta T(^{\circ}C) = 537.8^{\circ}C - 25^{\circ}C = 512.8^{\circ}C \quad (3.2.2)$$

We can use Newton's second law $F = ma$ to find mass, with a being the acceleration of gravity. Since the mass we are looking for is "per square metre", we can also divide the force by area (in m^2), which gives us pressure on the left side of the equation.

$$\text{mass (per } m^2) = \frac{P}{a} = \frac{1.013 \times 10^5 Pa}{9.81 \frac{m}{s^2}} = \frac{1.013 \times 10^5 \frac{kg}{ms^2}}{9.81 \frac{m}{s^2}} = 10326 \frac{kg}{m^2} \quad (3.2.3)$$

References

- [1] OpenStax University Physics Volume 2. 2016. 1.1 *Temperature and Thermal Equilibrium*. [online] <<https://openstax.org/books/university-physics-volume-2/pages/1-1-temperature-and-thermal-equilibrium>> [Accessed 13 May 2020].
- [2] OpenStax University Physics Volume 2. 2016. 2.2 *Pressure, Temperature, and RMS Speed*. [online] <<https://openstax.org/books/university-physics-volume-2/pages/2-2-pressure-temperature-and-rms-speed>> [Accessed 13 May 2020].

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3.3: Intensive and Extensive Variables

Learning Objectives

By the end of this section, you should be able to:

- **Apply** the definitions of intensive and extensive properties to process variables

Classifying Process Variables

Extensive Variables – depend on the size of a system

Intensive Variables – do not depend on the size of a system

Are temperature, pressure, and volume extensive or intensive?

Temperature: intensive

Pressure: intensive

Volume: extensive. Instead we may use **molar volume** if we want to express volume as an intensive property. Molar volume is defined by the volume occupied by 1 mole of the substance inside the system: $\hat{V} = \frac{V}{n}$.

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3.4: Phase Diagram

Learning Objectives

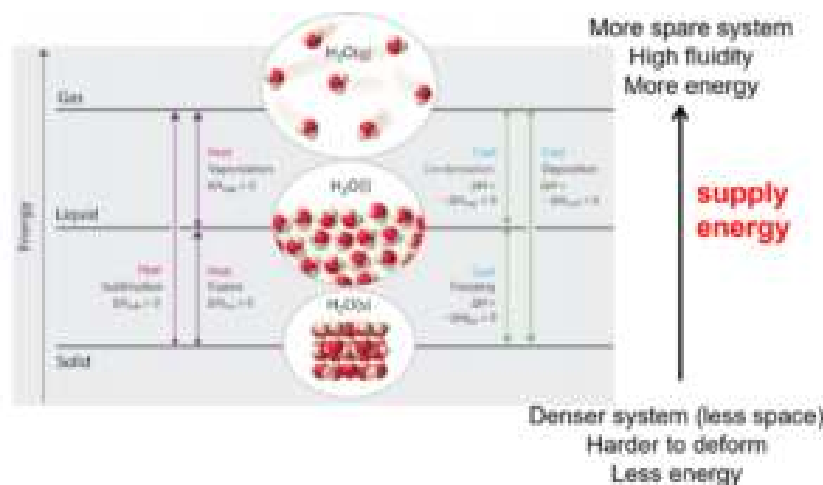
By the end of this section, you should be able to:

- **Interpret** phase diagram for relevant thermodynamic information (e.g. composition, temperature, pressure...)

Phase Transitions

The phase of a substance and separation between molecules are related to the intermolecular forces in a substance. Therefore, a source of energy needs to be supplied when the substance transitions to a higher energy state to separate the molecules in the substance.

Something similar you may recall from a previous chemistry course (say CHEM 154): Bond-breaking requires energy; Bond making releases energy. Similarly, a transition to a lower energy state releases energy.



Atkins, B.A., P. de Paula, Principles of General Chemistry (4th ed), Figure 6.1.12

image obtained from General Chemistry: Principles, Patterns, and Applications/CC BY-NC-SA

Critical Point and Reduced Properties

The phase of a given substance depends on pressure and temperature. Thus, plots of pressure versus temperature showing the phase in each region provide considerable insight into the thermal properties of substances. Such a P-T graph is called a phase diagram. ^[1]

In the phase diagram, we can observe that the boiling point curve (the line that distinguishes liquid and vapour phases) ends at a point, which is called **critical point**. Above the critical point, liquid and gas can no longer be distinguished and are classified as a supercritical fluid.

Vapour phase is a gaseous species below its critical temperature. On the other hand, a gaseous phase describes a gaseous species above its critical temperature but below its critical pressure.

Triple point is defined to be the set of pressure and temperature that solid, liquid and vapour are in equilibrium together.

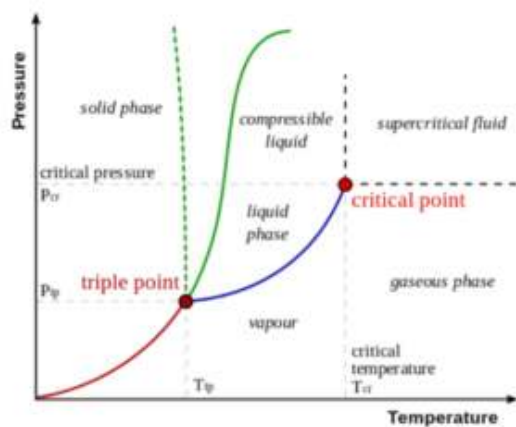


Image: Matthieumarchal CC-BY-SA-3.0 via Wikimedia Commons

Reduced properties are defined as variables (pressure, temperature) scaled by their values at the critical point. Reduced properties can be useful in coming up with general equations describing different substances.

$$T_c \quad (3.4.1)$$

$$P_c \quad (3.4.2)$$

$$\text{reduced temperature : } T_r = \frac{T}{T_c} \quad (3.4.3)$$

$$\text{reduced pressure : } P_r = \frac{P}{P_c} \quad (3.4.4)$$

Phase Diagram of Water

Critical Pressure = $P_c = 22.06 \text{ MPa}$

Critical Temperature = $T_c = 647 \text{ K}$

Triple point P with ice $I_h = 611 \text{ Pa}$

Triple point T with ice $I_h = 273.16 \text{ K}$

Ice I_h is the most common crystal structure of ice, but ice has a total of 17 known crystal forms. The latest form was discovered in 2014.

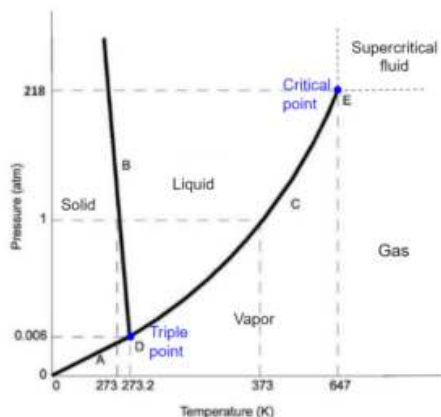


Image obtained from [Chemistry libretexts](https://eng.libretexts.org/@go/page/101159) / CC BY-NC-SA 3.0

At low temperatures, solid is the stable phase. At moderate temperatures and high pressure, liquid is the stable phase, and at high temperature and low pressure, gas/vapor is the stable phase. Lines separate these phases, representing sets of pressure/temperature for phase changes.

The melting curve or fusion curve of ice/water is very special. It has a negative slope due to the fact that when ice melts, the molar volume decreases. At higher pressure, ice actually melts at a lower temperature. When we skate, skate applies a very high pressure to the ice, so the ice below the skate melts without increasing temperature. The liquid formed between the skate and ice acts as a lubricant so that the skater moves gracefully across the ice. ^[2]

Thermodynamic Piston System

A **thermodynamic system** includes anything whose thermodynamic properties are of interest. It is embedded in its surroundings or environment; it can exchange heat with, and do work on, its environment through a boundary, which is the imagined wall that separates the system and the environment.

In reality, the immediate surroundings of the system are interacting with it directly and therefore have a much stronger influence on its behavior and properties. For our thermodynamic piston system, the gas inside the cylinder is the thermodynamic system; the cylinder, piston, and air outside form the surroundings of the system. The boundary then consists of the inner surfaces of the cylinder and piston. ^[3]

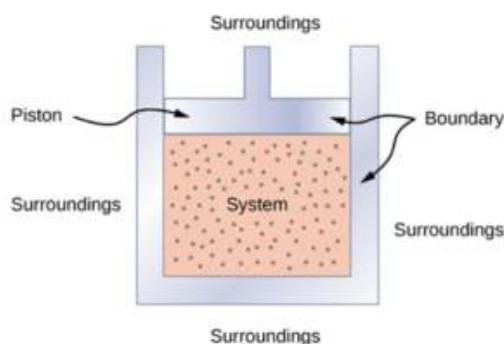
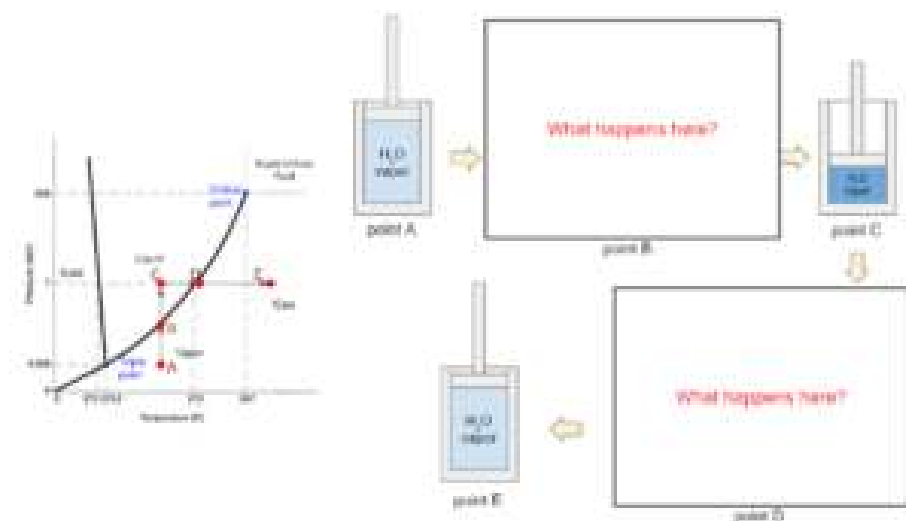


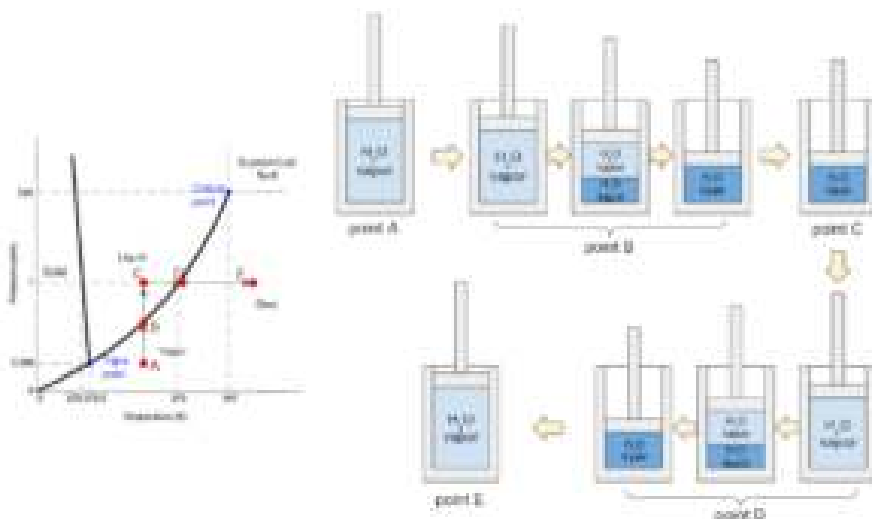
Image obtained from [OpenStax University Physics Volume 2](#) / CC BY 4.0

Phase Transitions

The path from A to E below shows a process in a thermodynamic piston system containing pure water. The water vapor (point A) in the system is first compressed under the same temperature till a certain point at liquid state (point C). Then, the water is heated under the same pressure till a certain point at vapour state (point E).



During the process, we can see that the state of water passes through the boiling curve twice (points B and D). The curve indicates a transition of state between liquid and vapor. During a boiling (point D) or condensation (point B) process, the substance does not change in temperature or pressure. Since this phase diagram does not contain information on molar volume, points B and D could be a mixture of liquid and vapor at any ratio, including pure liquid or vapor at the boiling temperature and pressure.



Types of Phase Diagram

We have seen phase diagrams with pressure and temperature on the axes from the previous chapters; this was one projection of a phase diagram. Instead, we could also have other intensive variables on the axes. As a result, a 3-dimensional phase diagram can be produced with pressure, temperature, and molar volume on separate axes. Note that we could also use other intensive variables such as enthalpy or internal energy per mole, etc.

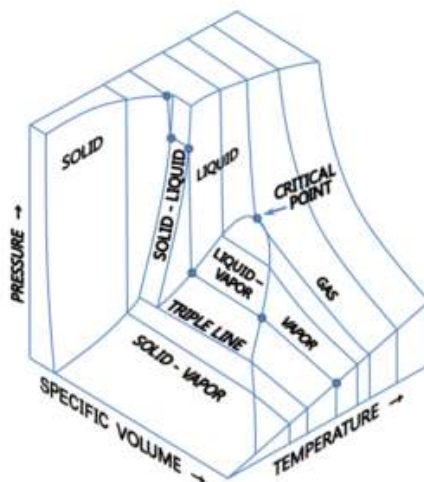


Image obtained from [Wikimedia Commons](https://commons.wikimedia.org/wiki/File:3D_Phase_Diagram.png)/ CC BY-SA 3.0

A link to a 3-D model of phase diagram to help to visualize: <http://biomodel.uah.es/Jmol/plots/phase-diagrams/>

A phase diagram can be produced with the projection on any of the planes spanned by two of the axes in the 3-dimensional phase diagram above. For example, if we project it onto the Pressure-Volume (P-V) plane we get the image below. Note that volume here appears to be written as an extrinsic variable, but should rather be a specific volume (say in $\frac{m^3}{kg}$).

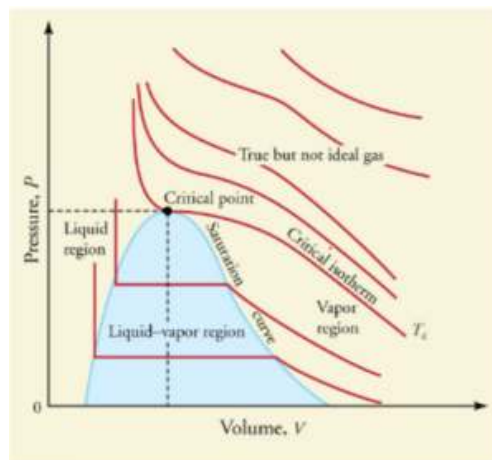


Image obtained from [College Physics](#) / CC BY 4.0

The red lines represent the substance at constant temperatures (isotherms). The isotherms have steeper slopes in the liquid region and gentler slopes in the vapour region. This agrees with what we observed before that the volume of gases experiences more significant changes due to pressure changes, but the volume of liquids is hardly affected by pressure.

The segments of isotherms in the vapour-liquid equilibrium region are horizontal, which agrees with our previous observation that the pressure is constant during the boiling process for a pure substance at a given temperature. This diagram provides information that allows us to calculate the ratio of vapour to liquid under vapour-liquid equilibrium conditions based on molar volume, which is not represented on the P-T diagram because it collapses to a point. The **vapour pressure** is represented by the y-coordinate of the horizontal segment. Note each vapour pressure will thus correspond to specific to a temperature (given by the isotherm).

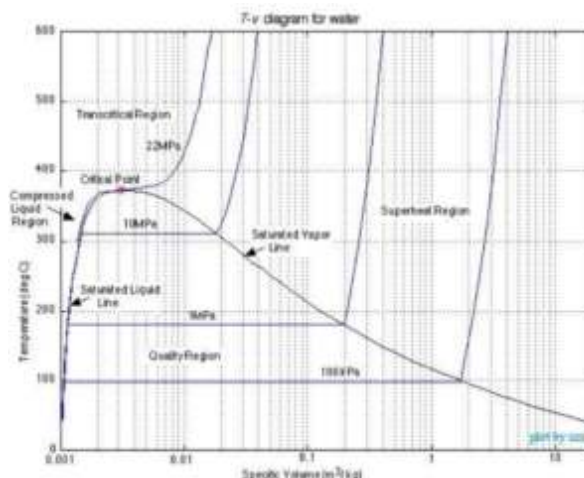


Image obtained from [Chapter 2: Pure substances](#) /CC BY-NC-SA 3.0 US

If we project the 3-dimensional phase diagram onto the temperature-volume (T-V) plane, the phase diagram will be similar to the one shown above. Each curve on the diagram represents processes with constant pressure (isobars). Similar to the P-V diagram, the pressure curve is horizontal in the region of vapour-liquid equilibrium. The vapour pressure is constant for each curve while the boiling temperature can be found as the y-coordinates on the horizontal segments. These correspond directly to the temperature and vapour pressure lines we would see on the P-V diagram.

References

[1] OpenStax University Physics Volume 2. 2016. *1.5 Phase Changes*. [online] <<https://openstax.org/books/university-physics-volume-2/pages/1-5-phase-changes>> [Accessed 14 May 2020].

[2] Chemistry Libretext. 2020. *Phase Diagrams*. [online] <[https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_\(Physical](https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical)

[_and_Theoretical_Chemistry\)/Physical_Properties_of_Matter/States_of_Matter/Phase_Transitions/Phase_Diagrams>](#) [Accessed 14 May 2020].

[3] OpenStax University Physics Volume 2. 2016. 3.1 *Thermodynamic Systems*. [online] <<https://openstax.org/books/university-physics-volume-2/pages/3-1-thermodynamic-systems>> [Accessed 15 May 2020].

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3.5: Gibb's Phase Rule

Learning Objectives

By the end of this section, you should be able to:

- **Calculate** degrees of freedom using Gibb's Phase Rule

Gibb's phase rule is used to determine the number of intensive variables required to fully specify the thermodynamic properties of a system (thermodynamic degrees of freedom).

Once this number of intensive variables is specified, we can find all the thermodynamic properties of the substance (eg. other intensive variables such as pressure, temperature, enthalpy, internal energy, etc.) at that state using previous experimental data from a table or chart.

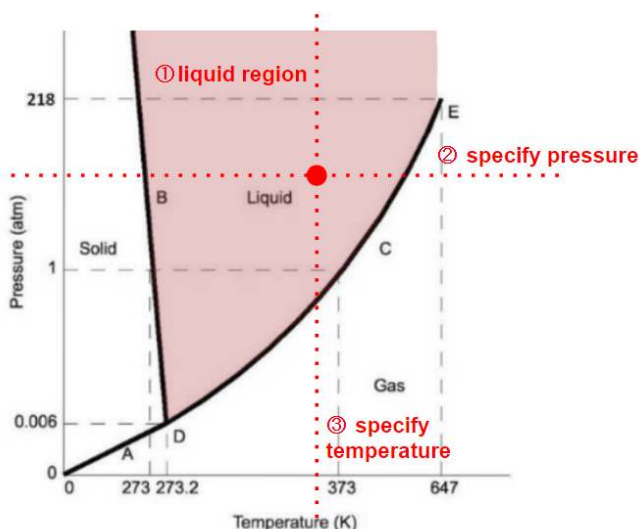
$$DF = 2 + c - \pi - r \quad (3.5.1)$$

where

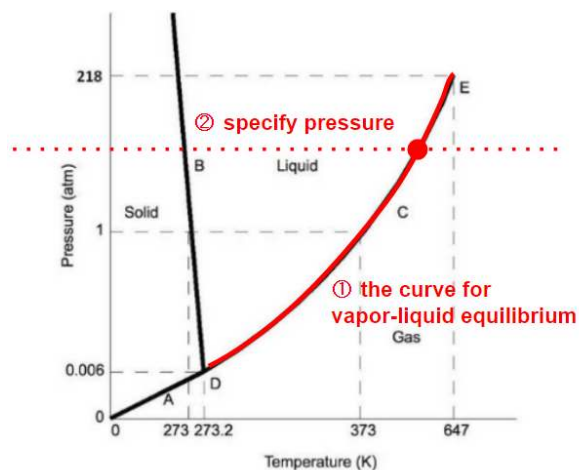
- DF = degrees of freedom (number of intensive variables that needs to be specified)
- c = number of independent chemical species
- π = number of phases in a system at equilibrium
- r = number of independent equilibrium chemical reactions among the species

One way of understanding this equation is thinking that we want to find a point (0 dimension) on the phase diagram, as this represents a single set of thermodynamic properties. If we have a single component system, the phase diagram is similar to the ones we have seen so far in this lecture. Specifying one intensive property reduces the dimension by 1. Adding a component adds another axis to the graph (to represent the composition of the mixture), which adds one dimension. Each equilibrium provides an equation that relates the composition of substances in the system, which allows us to secure a position on the composition axis.

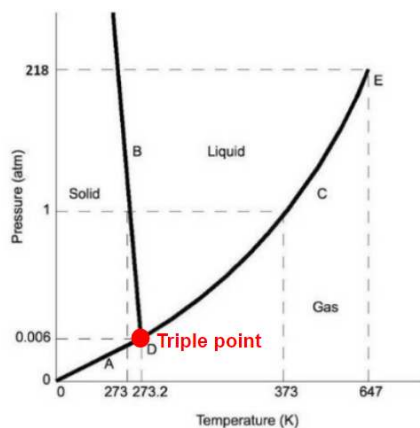
For example, if we have a pure substance in the system and we know that the state is in the liquid region (2 dimension), specifying pressure ensures the point of the state we are looking for is on a horizontal line (1 dimension). If we then also specify the temperature, it ensures the point is on a vertical line. There is only one point that satisfies both requirements of the temperature and pressure. We have reduced the dimension to 0.



In another example, if we know the state is on one of the lines indicating state transitions (eg. boiling – being vapour-liquid equilibrium), we start at 1 dimension, then we just need to specify one of the x, y coordinates (temperature or pressure) to reduce the position of the state to a point.



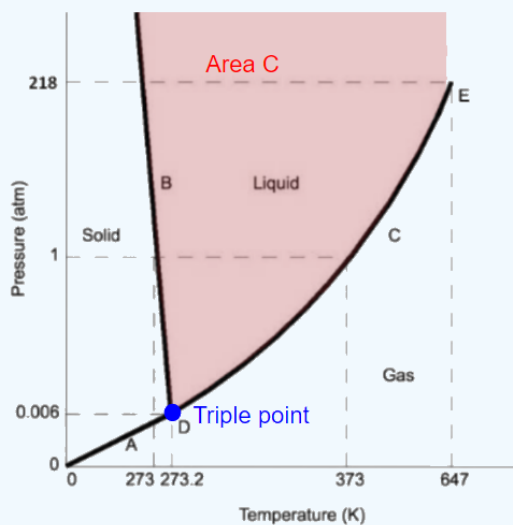
Triple point is already a point (0 dimension). No other variables need to be specified.



✓ Exercise: Gibb's Phase Rule

In a system containing pure water, how many degrees of freedom are there in the system at:

- somewhere in the liquid phase shown by area C.
- The triple point



Solution

Because we only have water in the system, $c = 1$, and there is no equilibrium chemical reaction in the system (as there is nothing to react with and no reaction specified), so $r = 0$.

a) At area C, we only have a liquid phase, so $\pi = 1$

$$DF = 2 + c - \pi - r = 2 + 1 - 1 - 0 = 2$$

This area represents pure water as a liquid. To fix this and know its thermodynamic properties we would need to know 2 intensive variables, say temperature and pressure. Knowing these two then rather than having an area, we would have a specific point.

b) At the triple point, pure vapour, liquid, and solid water exist at the same time, so $\pi = 3$

$$DF = 2 + c - \pi - r = 2 + 1 - 3 - 0 = 0$$

Specifying the water is at its triple point is equivalent to specifying the pressure and temperature, because the triple point only exists at a certain set of pressure and temperature.

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3.6: Ideal Gas Properties

Learning Objectives

By the end of this section, you should be able to:

- **Describe** the relationship between variables of state for gases

Describe gas behaviour using ideal gas law and compressibility factor using equations of state

Ideal Gas Law

Relates pressure (P), volume (V), temperature (T) and the number of moles (n) of an ideal gas species using the ideal gas constant (R):

$$PV = nRT$$

Can also relate pressure, molar volume ($\hat{V}$) and temperature:

$$P\hat{V} = RT$$

The ideal gas law is an approximation that works well under some conditions:

$$\hat{V} \text{ or } V_m = \frac{V}{n}, \text{ with units of } \frac{\text{volume}}{\text{mol}} \quad (3.6.1)$$

It is known experimentally that for gases at **low density** (such that their molecules occupy a negligible fraction of the total volume) and **at temperatures well above the boiling point**, these proportionalities hold to a good approximation. ^[1]

There are different ways to estimate how well the ideal gas approximation applies to a system. We will not go over these estimates explicitly in this course. Generally for this course, unless otherwise noted, we will assume the ideal gas law applies. However, in future thermodynamic courses, you will see when the ideal gas approximation may not be appropriate and will see other methods of relating gas properties in non-ideal scenarios.

Ideal Gas Mixtures

Dalton's Law

If two or more gases are mixed, they will come to a thermal equilibrium as a result of collisions between molecules. When the gases have the same temperature, their molecules have the same average kinetic energy. Thus, each gas obeys the ideal gas law separately and exerts the same pressure on the walls of a container that it would if it were alone.

Therefore, in a mixture of gases, **the total pressure is the sum of partial pressures of the component gases**, assuming ideal gas behavior and no chemical reactions between the components. ^[2]

$$P = \sum_{i=1}^n p_i$$

Using Dalton's law, we can calculate the partial pressure of a gas component, which is defined by the pressure that individual component in the gas mixture exerts on the wall if it were alone.

$$p_A = y_A P$$

where

$$y_A = \quad (3.6.2)$$

Amagat's Law

Amagat's Law is analogous to Dalton's Law, but is applied to the volume of the gas. The partial volume that each gas occupies will add up to the total system volume.

$$V = \sum_{i=1}^n v_i \quad (3.6.3)$$

$$v_A = y_A V \quad (3.6.4)$$

These partial volumes are proportional to the molar fraction of each gas in a system.

Standard Conditions

A word of caution that standard conditions may not always be the same in different industries or applications. This is shown below with two examples of standard conditions for gases from IUPAC (the International Union of Pure and Applied Chemistry) and NIST (the National Institute of Standards and Technology).

	IUPAC	NIST
Standard Temperature	273.15K or 0°C	20°C
Standard Pressure	1×10^5 kPa or 1 bar	1 atm or 101.325 kPa

Using the IUPAC numbers we can calculate a standard volume from the ideal gas law. This is the amount of volume a mole of gas would occupy at these standard conditions:

$$\hat{V}_s = \frac{RT_s}{P_s} = \frac{8.314 \frac{\text{m}^3 \text{Pa}}{\text{Kmol}} \times 273.15 \text{K}}{1 \times 10^5 \text{Pa}} \times \frac{1000 \text{mol}}{1 \text{kmol}} = 22.7 \frac{\text{m}^3(\text{STP})}{\text{kmol}} = 22.7 \frac{\text{L}(\text{STP})}{\text{mol}} \quad (3.6.5)$$

In some applications, gas flows may be expressed in standard cubic metres (SCM) or feet (SCF). A flow of 18.2 SCM/h means 18.2 m^3/h at standard conditions (whatever T/P these are defined to be).

We can calculate the temperature, pressure, and volume by comparing fluids at standard and non-standard conditions using the fact that R is constant. We usually use it to compare the same system under different conditions, which means the number of gas molecules (n) may be constant when we perform the calculation.

$$R = \frac{V_s \times P_s}{n \times T_s} = \frac{V \times P}{n \times T} \quad (3.6.6)$$

✓ Exercise: Natural Gas Standard Flow

Natural gas (mostly CH_4 that we might use to heat our homes) is normally measured with a correction to a certain temperature and pressure (to ensure you are always getting the same number of gas molecules). If it is a very cold winter day in Quebec City, where natural gas is entering your home at -30°C at a pressure of 2 bar and a flow of 100 L per hour. What would the standard flow (in L/hour) be if our standard conditions were 0°C and 1 bar (the IUPAC conditions)?

Solution

Add example text here.

$$\frac{V_s \times P_s}{T_s} = \frac{V \times P}{T}$$

The number of moles of gas (n) is the same in both conditions. So we can cancel n from both sides and rearrange the equation to isolate V_s . Remember that T in the equation needs to be converted to an absolute scale.

$$V_s = \frac{V \times P \times T_s}{T \times P_s} = \frac{100 \frac{L}{h} \times 2 \text{ bar} \times 273.15 K}{243.15 K \times 1 \text{ bar}} = 224.676 L/h$$

A Note on Notation

In thermodynamics, and generally in this course:

$$p_i(T) \quad (3.6.7)$$

The brackets are not for multiplication, but are for showing **what variables the variable of interest is a function of**. This is confusing, but a common notation in thermodynamics. Think of $f(x)$ you have seen in math, this means f is a function of x , rather than f is multiplied by x .

Some other examples are:

$$\rho_g(T, P) \quad (3.6.8)$$

$$\rho_l(T) \quad (3.6.9)$$

Liquid and Solid Densities

In this course, we will consider **solids and liquids incompressible**, meaning their density does not change significantly with changes in pressure. We will consider liquid density to be a weak function of temperature.

$$\rho_{liquid} \cong f(T) \neq f(P) \quad (3.6.10)$$

$$\rho_{solid} \neq f(P, T) \quad (3.6.11)$$

Density values can be found in:

- Perry's Chemical Engineers' Handbook – pp. 2-7 to 2-47 and 2-96 to 2-125, available in print as reference material in the library here:

<http://resolve.library.ubc.ca/cgi-bin/catsearch?bid=5888251> – 2008 edition

<http://resolve.library.ubc.ca/cgi-bin/catsearch?bid=9292999> – 2019 edition

Where to Find Thermodynamic Property Data:

- Introductory Chemical Engineering Thermodynamics – textbook for this course – available as an ebook through UBC library, link also available in Library course reserves on canvas:

<http://tinyurl.com/yxv3r8vy> – library ebook link

- Perry's Chemical Engineers' Handbook – pp. 2-7 to 2-47, available through UBC Library in print:

<http://resolve.library.ubc.ca/cgi-bin/catsearch?bid=5888251> – 2008 edition

<http://resolve.library.ubc.ca/cgi-bin/catsearch?bid=9292999> – 2019 edition

- Website of the National Institute of Standards and Technology (<http://webbook.nist.gov/chemistry/>)

When are Gases Non-Ideal?

- At lower temperatures: as gas molecules collide, they may experience inelastic (sticky) collisions due to intermolecular interactions.
- At high pressure: the molecules are closely packed together, so there are more chance of gas molecules experience molecular interaction or inelastic collisions.

- Intermolecular forces vary with molecular structures and polarity. Longer chain or more polar molecules usually experience more intermolecular forces.

Review: Assumptions of the ideal gas law

- The volume of gas molecules is negligible.
- Collisions between gas molecules or between gas molecules and the walls of the container are elastic, which means no energy is lost due to collisions.
- There are no attractive or repulsive forces between gas molecules.
- The average kinetic energy is proportional to the temperature.

Compressibility Factor

When rearranging the ideal gas law, we get that for ideal gases:

$$\frac{P\hat{V}}{RT} = 1 \quad (3.6.12)$$

For a real gas, we adjust the ideal gas law by the compressibility factor(Z):

$$\frac{P\hat{V}}{RT} = Z \quad (3.6.13)$$

We can generalize the value of Z based on the reduced temperature and reduced pressure, which can be obtained from charts or correlations:

$$\text{reduced temperature: } T_r = \frac{T}{T_c} \quad (3.6.14)$$

$$\text{reduced pressure: } P_r = \frac{P}{P_c} \quad (3.6.15)$$

where T_c and P_c are the temperature at the critical point.

The charts to find compressibility factor Z can be found in the “module” tab from CHBE 220 course on canvas.

✓ Exercise: Compressibility Factor

If our substance is propane at $P = 20 \text{ bar}$ and $T = 100^\circ\text{C}$, with critical parameters: $P_c = 4.23 \text{ MPa}$, $T_c = 97^\circ\text{C}$, find the compressibility factor Z.

Solution

Add example text here.

First, we calculate the reduced temperature and pressure:

Unit conversions used: $1 \text{ MPa (mega - Pascal)} = 10^6 \text{ Pa} = 10 \text{ bar}$, $T(K) = T(^{\circ}\text{C}) + 273.15$:

$$P_r = \frac{P}{P_c} = \frac{20 \text{ bar} \times \frac{1 \text{ MPa}}{10 \text{ bar}}}{4.23 \text{ MPa}} = 0.47 \quad (3.6.16)$$

$$T_r = \frac{T}{T_c} = \frac{(100 + 273.15) \text{ K}}{(97 + 273.15) \text{ K}} = 1.0 \quad (3.6.17)$$

Find the lines representing $P_r = 0.47$ on the x-axis, and $T_r = 1.0$ on the curves with solid lines. The compressibility factor Z is the y-coordinate of the intersection.

$$Z = 0.83 \quad (3.6.18)$$

References

- [1] OpenStax University Physics Volume 2. 2016. *2.1 Molecular Model of an Ideal Gas*. [online] <<https://openstax.org/books/university-physics-volume-2/pages/2-1-molecular-model-of-an-ideal-gas>> [Accessed 14 May 2020].
- [2] OpenStax University Physics Volume 2. 2016. *2.2 Pressure, Temperature and RMS Speed*. [online] <<https://openstax.org/books/university-physics-volume-2/pages/2-2-pressure-temperature-and-rms-speed>> [Accessed 14 May 2020].

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3.7: Estimating Vapour Pressure

Learning Objectives

By the end of this section, you should be able to:

- **Estimate** the vapour pressure of pure compounds at a given temperature using Antoine's equation

Vapour pressure(p^*) is defined as the pressure at which **a gas coexists with its solid or liquid phase**. Vapour pressure is created by faster molecules that break away from the liquid or solid and enter the gas phase. The vapour pressure of a substance **depends on both the substance and its temperature**—an increase in temperature increases the vapour pressure. ^[1]

One empirical method to estimate p^* is the **Antoine equation**:

$$\log_{10}(p^*) = A - \frac{B}{T + C} \quad (3.7.1)$$

where

A, B and C are constants depending on the type of substance

NOTE: Sometimes different sources of data can use different units for temperature, or used $\ln$ (base e) instead of $\log_{10}$ (base 10).

Finding Antoine Equation Parameters on NIST:

1. Search for “NIST Chemistry Webbook” or go to <https://webbook.nist.gov/chemistry/>
2. Scroll down to search options and choose, name, formula or other desired search criteria
3. Enter search criteria (e.g. methanol, CH₃OH...)
4. Leave other options as default and search for substance
5. Select desired substance from the list provided if not brought to substance homepage immediately
6. On the substance homepage scroll down to the “Other data available” section and select “phase change data”.
7. Scroll through this section to find desired data

✓ Example: Estimating Vapour Pressure for Water

text

Solution

text.

Temperature(K)	A	B	C
379-573	3.55959	643.748	-198.043
273-303	5.40221	1838.675	-31.737
304-333	5.20389	1733.926	-39.485

data obtained from [NIST](#)

Based on the data above, what is the vapour pressure of water at 100°C and 200°C?

For T=100°C: Since the temperature is given in the Kelvin scale on the chart, we convert 100°C to 373K, which is closest to the range in the first row of data, so we will use that range.

$$\begin{aligned}\log_{10}(p^*) &= A - \frac{B}{T + C} \\ p^* &= 10^{A - \frac{B}{T + C}} \\ &= 10^{3.55959 - \frac{643.748}{373 - 198.043}} \\ &= 0.76\text{bar}\end{aligned}$$

For T=200°C: We first convert the temperature to 473K, which is in the range for the first row of data.

$$\begin{aligned}\log_{10}(p^*) &= A - \frac{B}{T + C} \\ p^* &= 10^{A - \frac{B}{T + C}} \\ &= 10^{3.55959 - \frac{643.748}{473 - 198.043}} \\ &= 16.53\text{bar}\end{aligned}$$

Consider the calculated result for vapour pressure at 100 °C, compare it with your knowledge of vapour pressure of water. Does it seem accurate?

We know the vapour pressure at 100 °C should be closer to 1 bar as water would boil at 100 °C at 1 atm, this shows the error that might be present in these correlations, especially when taking them outside of their T ranges. As shown below, the value calculated at T=200 °C is more accurate, likely because it is well within the range of temperatures provided for the A, B and C parameters (although there is still some error). Remember these correlations are generalizations, meaning it is rare they are 100% accurate.

Temperature(K)	p^* calculated (bar)	p^* actual(bar)	% difference
373	0.758798	1.013	25.09403
473	16.53187	15.55	6.314304

References

[1] OpenStax University Physics Volume 2. 2016. 13.5 Phase Changes. [online] <<https://openstax.org/books/college-physics/pages/13-5-phase-changes>> [Accessed 15 May 2020].

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3.8: Multicomponent Equilibrium

Learning Objectives

By the end of this section, you should be able to:

- **Apply** properties of ideal mixtures to describe vapour-liquid separations using Raoult's law and Henry's law

An **ideal mixture** contains substances with **similar molecular interactions** (which usually means similar structures or functional groups). e.g. benzene and toluene, with both being non-polar and of a similar molecular size

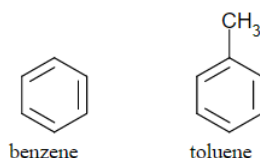


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A combination of two substances is called a **binary mixture**. For a binary mixture, there is no longer a set temperature and pressure for a boiling point. Instead, there is a range of temperature or pressure values where the mixture is in vapour-liquid equilibrium. These are bounded by two points called the **bubble point** and **dew point**. We'll explore these concepts more thoroughly when looking at diagrams for these binary mixture systems.

Vapour-Liquid Equilibrium

In a closed container, vapour-liquid equilibrium can be achieved by the same number of molecules vapourizing and condensing at any given period of time (meaning no net change in the system). The temperature and pressure have to be kept constant if we are truly at equilibrium (again, no net change in any intensive variable).

We usually denote:

$$T \quad (3.8.1)$$

$$P \quad (3.8.2)$$

$$x_i \quad (3.8.3)$$

$$y_i \quad (3.8.4)$$

Estimating the Molar Fraction of a Component at Vapour-Liquid Equilibrium

Raoult's law

Raoult's law is used when all components are in relatively significant quantities or they are chemically very similar (generally in terms of intermolecular interactions).

$$p_i = y_i \times P = x_i \times p_i^*(T) \quad (3.8.5)$$

$$p_i^*(T) \quad (3.8.6)$$

✓ Exercise: Estimating Vapour Pressure for Ethanol

At 298 K, the vapour pressure of water is 3,138 Pa and the vapour pressure of ethanol is 7,817 Pa. Suppose we have a mixture of only water and ethanol in a closed container, at 298 K, what is the mole fraction of ethanol in the vapour phase (y_{ethanol}) at equilibrium if the liquid is 50 mol% water and 50 mol% ethanol?

Solution

Add example text here.

Step 1: First note here ethanol and water both have very polar OH groups, so we will consider their intermolecular interactions similar and apply Raoult's law. Rearrange the Raoult's law to isolate y_i :

$$y_i \times P = x_i \times p_i^*(T)$$

$$y_i = \frac{x_i \times p_i^*(T)}{P}$$

Here we know both x_i , which was given to be 0.5 (50 mol%) for ethanol, and p_i^* for ethanol, again given in the question prompt. But now we need to find pressure (P).

Step 2: To find P we'll first apply the ideal gas law to the gas phase in this system. We know that for ideal gases the partial pressures (p_i) add up to the total system pressure (P). We can then use Raoult's law to express partial pressures in terms of liquid mole fractions and vapour pressures (all of which we know in this case):

$$P = p_{\text{water}} + p_{\text{ethanol}}$$

$$= x_{\text{water}} \times p_{\text{water}}^* + x_{\text{ethanol}} \times p_{\text{ethanol}}^*$$

$$= 0.5 \times 3138 \text{ Pa} + 0.5 \times 7817 \text{ Pa}$$

$$= 5477.5 \text{ Pa}$$

Step 3: Substitute P into the expression for y_{ethanol} :

$$y_{\text{ethanol}} = \frac{x_{\text{ethanol}} \times p_{\text{ethanol}}^*(298 \text{ K})}{P}$$

$$= \frac{0.5 \times 7817 \text{ Pa}}{5477.5 \text{ Pa}}$$

$$= 0.71$$

Finally we could ask ourselves, “**does this answer make sense?**”. If we look up the normal boiling point temperature of water (100 °C) and ethanol (78 °C), we see ethanol is more volatile (it boils at a lower temperature). This tells us to expect a greater mole fraction of it in the vapour phase than the liquid phase, which matches what we find with our calculations.

Henry's Law

Henry's law is used to describe the concentration of a gas (or very volatile component) dissolved in a liquid. This is typically used to describe components in a mixture that are near or above their critical temperature (think back to the difference between vapours ($T < T_c$) and gases ($T > T_c$)).

$$p_i = y_i \times P = \frac{x_i}{H_i(T)} \quad (3.8.7)$$

$$H_i(T) \quad (3.8.8)$$

The Henry's law constant $H_i(T)$ can be given in different units, such as kPa^{-1} , $\frac{\text{mol}}{\text{L} \cdot \text{kPa}}$, $\frac{\text{mol}}{\text{kg} \cdot \text{bar}}$, which will change the corresponding unit for x_i . x_i can be used to represent the solubility of the gas in per mole / per volume / per mass of solvent.

Henry's law is generally more valid when x_i is close to 0 (very dilute solutions).

✓ Exercise: Calculating Partial Pressure Using Henry's Law

[1]

(3.8.9)

Solution

Add example text here.

Step 1: Calculate Henry's law constant from data with oxygen pressure at 101.3 kPa

$$\begin{aligned}p_i &= \frac{x_i}{H_i(T)} \\H_i(T) &= \frac{x_i}{p_i} \\&= \frac{1.38 \times 10^{-3} \frac{\text{mol}}{\text{L}}}{101.3 \text{ kPa}} \\&= 1.36 \times 10^{-5} \frac{\text{mol}}{\text{L} \cdot \text{kPa}}\end{aligned}$$

Step 2: Apply Henry's law another time for an oxygen partial pressure at 20.7 kPa:

$$\begin{aligned}p_i &= \frac{x_i}{H_i(T)} \\x_i &= p_i \times H_i(T) \\&= 20.7 \text{ kPa} \times 1.36 \times 10^{-5} \frac{\text{mol}}{\text{L} \cdot \text{kPa}} \\&= 2.82 \times 10^{-4} \frac{\text{mol}}{\text{L}}\end{aligned}$$

References

[1] OpenStax Chemistry 2e. 2019 Feb. *11.3 Solubility*. [online] <<https://openstax.org/books/chemistry-atoms-first-2e/pages/11-3-solubility>> [Assessed 18 May 2020]

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3.9: Txy Diagram

Learning Objectives

By the end of this section, you should be able to:

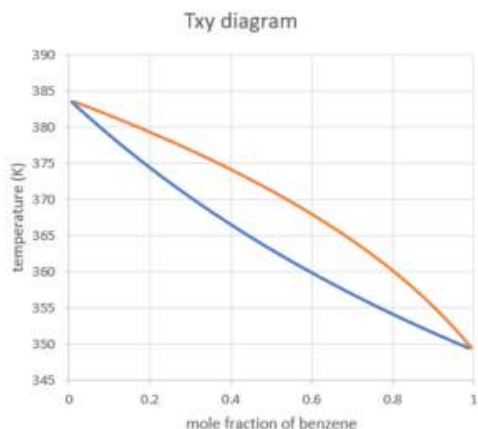
- **Read** Txy diagrams for binary mixtures

Find bubble points and dew points on a Txy diagram

Calculate the mole fraction of substances in the vapour and liquid states

The following diagram is the Txy diagram (at a constant pressure of 1 atm) for a mixture of benzene and toluene. The y-axis (ordinate) reads the temperature value, and the x-axis (abscissa) corresponds to the mole fraction of benzene. We can use the x-axis to find the mole fraction of benzene in the liquid and vapour phase.

Because this is a binary mixture, we can calculate the mole fraction of toluene as $1 - x_{\text{benzene}}$ in the liquid phase and $1 - y_{\text{benzene}}$ in the vapour phase.



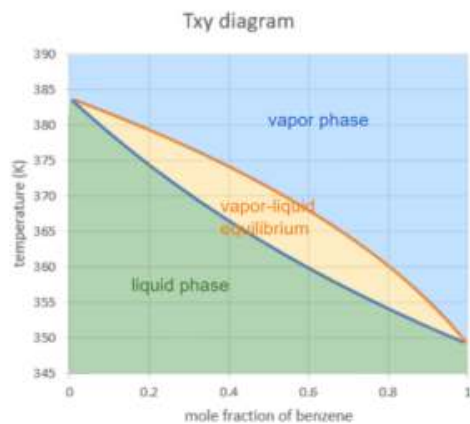
The two curves separate the diagram into 3 regions:

Liquid region: when the mixture of both components are in liquid phase, this is the lowest temperature region. This makes sense as liquid is a lower energy state than a gas, so we would expect it at lower temperatures.

Vapour region: when the mixture of both components are in vapour phase, this is the highest temperature region. Again, the higher the temperature, the more energy, and thus more likely to be a gas.

Vapour-liquid equilibrium region: when the mixture splits into a liquid and a vapour, this is the region in the middle

Given a mole fraction of benzene and temperature of this system, we can locate which of the three regions our system would be in. Note we have to ensure we are at the same pressure as the graph states when using these graphs.

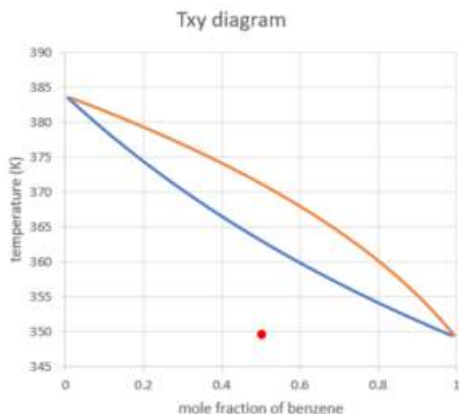


Two particular points we will analyze are when the mole fractions of benzene in the system are 1 or 0:

mole fractions of benzene = 1: $x_i = y_i = 1$, “mixture” is pure benzene. The system vapourizes/condenses at a constant temperature, which is the normal boiling point of benzene at 1 atm (~349 K in this case).

mole fractions of benzene = 0: $x_i = y_i = 0$, “mixture” is pure toluene. The system vapourizes/condenses at a constant temperature, which is the normal boiling point of toluene at 1 atm (~383 K in this case).

Let's take the following example to demonstrate how to read a Txy diagram: suppose we **start with a mixture of 0.5 mole fraction of liquid benzene in the system at 80°C and 1 atm.**

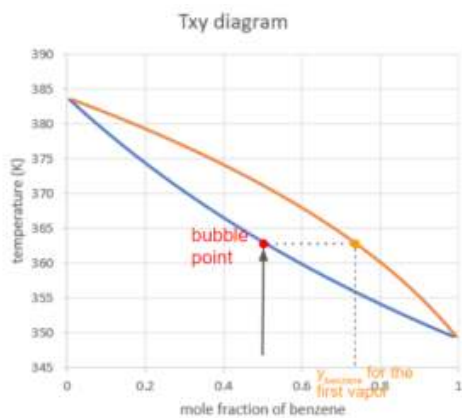


Shown above is the point we can locate on the Txy diagram. We can see that the point is completely in the liquid region, which means the mixture is completely in the liquid phase.

- In terms of phase change, the system of mixture behaves as a whole – the substance with a lower boiling point does not boil before the other, but the difference in boiling points is shown in the mole fraction of the components in each phase.

We then increase the temperature (keeping the pressure constant as defined by the diagram) until we **hit the first curve on the boundary of the liquid region:**

This point is called the **bubble point** of this mixture. At this point, we see the first bubble of vapour being formed in the liquid. The composition of this first vapour can be found at the point on the other curve at the same temperature:



Calculate the Composition of Vapour at the Bubble Point

We can also use the phase change data to calculate the composition of the first vapour. This is useful when the phase diagram is not provided:

The phase change data can be obtained from the NIST website:

substance	A	B	C
benzene	4.60362	1701.073	20.806
toluene	4.07827	1343.943	-53.773

Solution

We can also use the phase change data to calculate the composition of the first vapour. This is useful when the phase diagram is not provided:

The phase change data can be obtained from the NIST website:

Using **Raoult's law**, we can calculate the molar composition of the vapour:

$$y_i \times P = x_i \times p_i^*(T) \quad (3.9.1)$$

where

We are looking for the molar fraction of components in the vapour phase: $y_{benzene}$ and $y_{toluene}$.

P is the pressure of the system, in this case, it is kept constant at 1 atm=1.013bar

At the bubble point, there is a very small amount of vapour being formed, therefore we assume the change in the composition of the liquid is negligible. We can take $x_{benzene} = 0.5$.

$$p_i^* \quad (3.9.2)$$

$$\log_{10}(p^*) = A - \frac{B}{T + C} \quad (3.9.3)$$

However, we don't know the T for the bubble point (we are assuming the diagram is not given):

When we don't know the bubble point temperature, we use a trial and error approach: We guess a temperature and use this to find p_i^* for the substances involved. We then calculate the y_i for both substances using Raoult's law and the x_i in the liquid phase. If we are at the right temperature (the bubble point temperature) this should result in the sum of y_i being equal to 1 ($\sum_i y_i = 1$).

- If the guess results in $\sum_i y_i < 1$, that means the guess of temperature is **lower** than the bubble point. We should raise the temperature for the next trial so that the substances are more likely to vapourize.

- If the guess results in $\sum_i y_i > 1$, that means the guess of temperature is **higher** than the bubble point. We should lower the temperature for the next trial so that the substances are more likely to condense.
- You can use a software (e.g. “solver” in excel) to directly solve the bubble point temperature.

A safe place to start is taking the average of the boiling points of the two substances, but the starting point does not affect the result. It may just affect the number of iterations needed before finding the actual bubble point temperature.

From the NIST website, we can find that the boiling point of benzene at 1 atm $\approx 80^\circ\text{C}$ and the boiling point of toluene at 1 atm $\approx 110^\circ\text{C}$, so we can take $T = 95^\circ\text{C} = 368\text{K}$ for our initial guess:

Step 1: Calculate p^* for both substances using the Antoine Equation:

$$\begin{aligned}\log_{10}(p^*) &= A - \frac{B}{T + C} \\ p^* &= 10^{A - \frac{B}{T + C}} \\ p^*_{\text{benzene}} &= 10^{4.60362 - \frac{1701.073}{368 + 20.806}} = 1.692\text{bar} \\ p^*_{\text{toluene}} &= 10^{4.07827 - \frac{1343.943}{368 - 53.773}} = 0.633\text{bar}\end{aligned}$$

Step 2: Calculate the y_i for both substances using Raoult's law:

$$\begin{aligned}y_i \times P &= x_i \times p_i^*(T) \\ y_{\text{benzene}} &= \frac{x_{\text{benzene}} \times p_{\text{benzene}}^*(T)}{P} \\ &= \frac{0.50 \times 1.692\text{bar}}{1.013\text{bar}} \\ &= 0.835 \\ y_{\text{toluene}} &= \frac{x_{\text{toluene}} \times p_{\text{toluene}}^*(T)}{P} \\ &= \frac{(1 - 0.50) \times 0.633\text{bar}}{1.013\text{bar}} \\ &= 0.312\end{aligned}$$

Step 3: Check our result by adding up the y_i and adjust the guess of temperature accordingly.

$$\sum_i y_i = 0.835 + 0.312 = 1.147 > 1 \quad (3.9.4)$$

So the guess for T should be decreased for the next guess.

After several trials, we can prove that $T = 363\text{K}$ is the bubble point temperature:

Step 1: Calculate p^* for both substances using the Antoine Equation

$$\begin{aligned}\log_{10}(p^*) &= A - \frac{B}{T + C} \\ p^* &= 10^{A - \frac{B}{T + C}} \\ p^*_{\text{benzene}} &= 10^{4.60362 - \frac{1701.073}{363 + 20.806}} = 1.484\text{bar} \\ p^*_{\text{toluene}} &= 10^{4.07827 - \frac{1343.943}{363 - 53.773}} = 0.633\text{bar} = 0.540\text{bar}\end{aligned}$$

Step 2: Calculate the y_i for both substances using Raoult's law:

$$\begin{aligned}y_i \times P &= x_i \times p_i^*(T) \\ y_{\text{benzene}} &= \frac{x_{\text{benzene}} \times p_{\text{benzene}}^*(T)}{P} \\ &= \frac{0.50 \times 1.484\text{bar}}{1.013\text{bar}} = 0.732 \\ y_{\text{toluene}} &= \frac{x_{\text{toluene}} \times p_{\text{toluene}}^*(T)}{P} \\ &= \frac{(1 - 0.50) \times 0.540\text{bar}}{1.013\text{bar}} = 0.267\end{aligned}$$

Step 3: Check our result:

$$\sum_i y_i = 0.732 + 0.267 = 0.999 \quad (3.9.5)$$

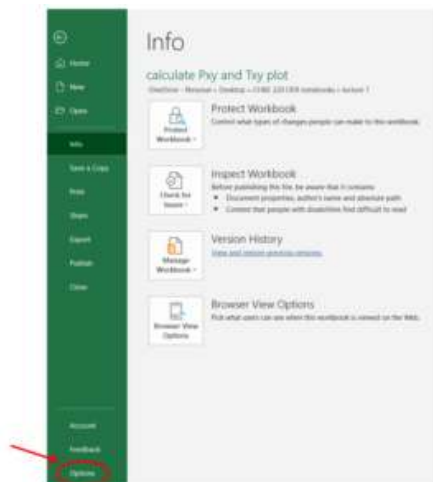
Because there are rounding errors involved in the calculations, we can say that $T=363$ K is our bubble point temperature (at least to ± 1 K).

Therefore, the molar fractions of the substances for the first vapour at the bubble point are $y_{benzene} = 0.732$ and $y_{toluene} = 0.267$. Note that this matches what we see on the diagram.

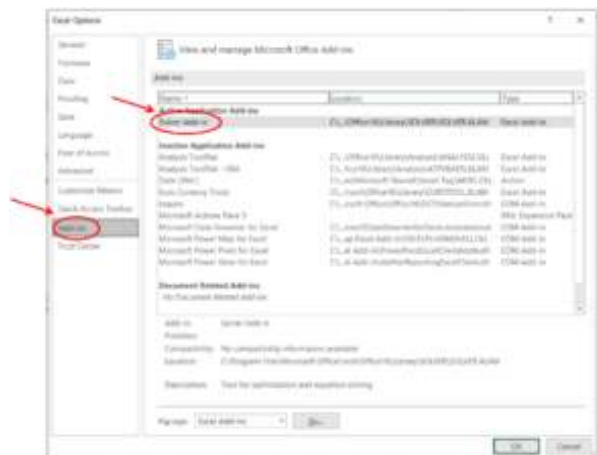
The composition of the vapour at the bubble point can also be solved with the solver add-in in excel:

How to load “Solver Add-in” in Excel:

Step 1: Click “file” in the header and open the “Options” menu:



Step 2: In the Excel Options menu, select “Solver Add-in” in the “Add-ins” section, then click “OK”.



Step 3: Then you can find the “Solver” in the “Analyze” section under the “Data” menu.



Solve for the composition of the vapour at the bubble point with the solver add-in in excel:

Step 1: To find the composition of the vapour at the bubble point, we first input all the know information for the calculation, including:

- Antoine equation parameters

- pressure, which is kept to be constant during the process
- composition of the mixture in the liquid phase
- a guess of the bubble point temperature (does not need to be accurate, again the average of the boiling points of the two pure substances is a safe place to start)

substance A			benzene	substance B			toluene
A	B	C		A	B	C	
4.60362	1701.073		20.806	4.07827	1343.943		-53.773
x (benzene) =			0.5	x (toluene) =			0.5
P(bar)=			1.013				
T(K)=			373				

Step 2: Compute the vapour pressure of both substances using the temperature we guessed:

=10^((C6-D6)/(D13+E6))							
C	D	E	F	G	H	I	
substance A			benzene	substance B			toluene
A	B	C		A	B	C	
4.60362	1701.073		20.806	4.07827	1343.943		-53.773
x (benzene) =			0.5	x (toluene) =			0.5
P(bar)=			1.013				
T(K)=			373				
p* (benzene)				p* (toluene)			
D13+E6))				y (benzene)			y (toluene)

=10^((G6-H6)/(D13+I6))							
C	D	E	F	G	H	I	
substance A			benzene	substance B			toluene
A	B	C		A	B	C	
4.60362	1701.073		20.806	4.07827	1343.943		-53.773
x (benzene) =			0.5	x (toluene) =			0.5
P(bar)=			1.013				
T(K)=			373				
p* (benzene)				p* (toluene)			
1.923308461				D13+I6))			
				y (benzene)			y (toluene)

Step 3: Compute y_i for both substances using:

$$y_i = \frac{x_i \times p_i^*(T)}{P} \quad (3.9.6)$$

=D9*C16/D11						
C	D	E	F	G	H	I
substance A		benzene	substance B		toluene	
A	B	C	A	B	C	
4.60362	1701.073	20.806	4.07827	1343.943	-53.773	
x (benzene) =		0.5	x (toluene) =		0.5	
P(bar)=		1.013				
T(K)=		373				
p*(benzene)		1.923308461	p*(toluene)		0.738377346	y (benzene)
						y (toluene)
						D11

=H9*E16/D11						
C	D	E	F	G	H	I
substance A		benzene	substance B		toluene	
A	B	C	A	B	C	
4.60362	1701.073	20.806	4.07827	1343.943	-53.773	
x (benzene) =		0.5	x (toluene) =		0.5	
P(bar)=		1.013				
T(K)=		373				
p*(benzene)		1.923308461	p*(toluene)		0.738377346	y (benzene)
						y (toluene)
						0.94931316
						=H9*E16/D11

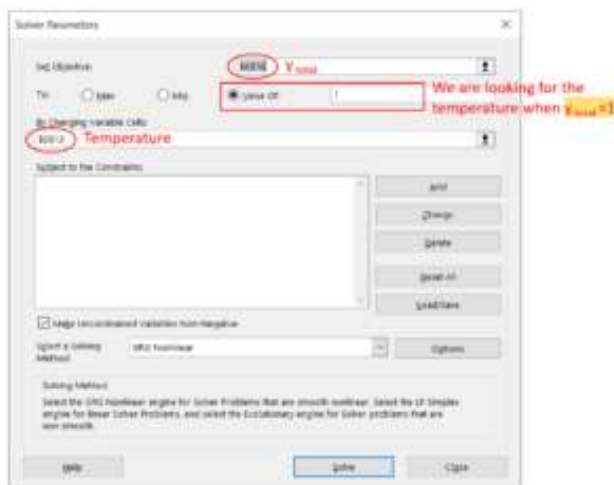
Step 4: Compute the y_{total} by adding the y_i for both substance. With our initial guess, the y_{total} we get should be close, but not equal to 1.

=G16+I16						
C	D	E	F	G	H	I
substance A		benzene	substance B		toluene	
A	B	C	A	B	C	
4.60362	1701.073	20.806	4.07827	1343.943	-53.773	
x (benzene) =		0.5	x (toluene) =		0.5	
P(bar)=		1.013				
T(K)=		373				
p*(benzene)		1.923308461	p*(toluene)		0.738377346	y (benzene)
						y (toluene)
						0.94931316
						0.28450813
						=G16+I16

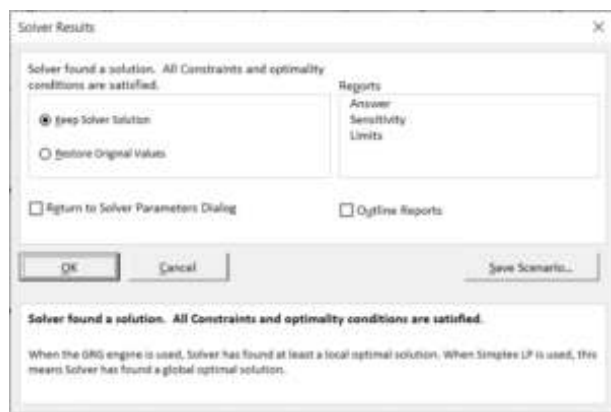
Step 5: Open the “Solver”, indicate that we want to solve for the temperature that makes our $y_{total} = 1$.

- Set objective to be the cell containing y_{total}
- To be: value of 1
- By changing variable cells containing temperature

- Click “Solve”



Step 6: Click “OK” if the window says the solver found a solution. If the solver cannot find a solution, it is maybe because our initial guess is too far away from the actual bubble point temperature, if so, we can change the temperature and try to solve it again.



Step 7: After the window closes automatically, the value for temperature and all cells affected by temperature are changed to the corresponding values calculated for the bubble point temperature found.

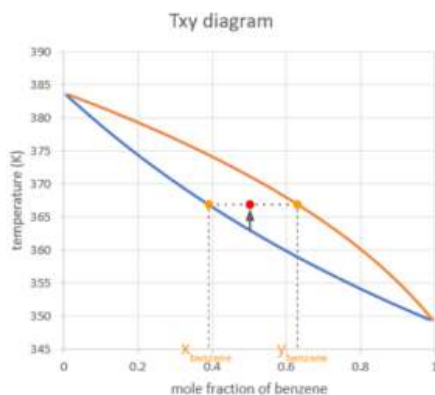
substance A			substance B		
A	B	C	A	B	C
4.80362	1.701073	20.806	4.07827	1343.943	-53.773
x (benzene) =			0.5	x (toluene) =	
P(bar) =			1.033		
T(K) =			363.0366		
p* (benzene)			1.485682589	p* (toluene)	0.540315734
y (benzene)			0.7330678	y (toluene)	0.2669321
				y (total)	0.999999961

Therefore, according to the result generated by solver:

Bubble point temperature = 363.04K

The molar fractions of the substances for the first vapour at the bubble point are $y_{benzene} = 0.733$ and $y_{toluene} = 0.267$. Note this matches what we see on the diagram and our result from the trial-and-error approach. Note, that you could also use excel without solver to make guess and check faster, we would simply guess temperatures and see the effect on y_{total} . This then uses excel to do the calculations each time we update the guess, making solving much faster. However, solver automates this process of guessing temperatures.

If we keep increasing the temperature, the system will be in the **vapour-liquid equilibrium region**. We locate the point using the total mole fraction of benzene and the temperature of the system, so the x-coordinate is 0.5 no matter what phase the system is at.



After we find the point, we draw a horizontal line (representing that the temperature of the liquid and vapour are equal under vapour-liquid equilibrium conditions), the line will hit both curves. The x-coordinates of the points where the horizontal line hits the curves are the mole fraction of benzene, with the one on the boundary of the liquid region as the mole fraction in the liquid phase and the other one as the mole fraction in the vapour phase.

At vapour-liquid equilibrium, there is always more benzene in the vapour phase compared to benzene in the liquid phase. That is because benzene is the more “volatile” compound compared to toluene, which means it has weaker intermolecular interactions, therefore it’s more likely to vapourize. A more volatile compound has a lower boiling point.

✓ Exercise: Calculate the Mole Fraction at Vapour-Liquid Equilibrium

Calculate the molar fraction of the total liquid component ($\frac{n_{liquid}}{n_{total}}$) in the system at the point shown above in the vapour-liquid region. Use values for the mole fraction of benzene in the vapour and liquid phases as read off the graph to find this.

Solution

Add example text here.

We know that the total benzene in the system is from the sum of the benzene molecules from the liquid and vapour phase, which is equal to 0.5 (as we start with a half/half mixture):

$$x_{benzene} \times n_{liquid} + y_{benzene} \times n_{vapour} = 0.5 \times n_{total} \quad (3.9.7)$$

$$x_{benzene} \times \frac{n_{liquid}}{n_{total}} + y_{benzene} \times \frac{n_{vapour}}{n_{total}} = 0.5 \quad (3.9.8)$$

We can replace the expression of $\frac{n_{vapour}}{n_{total}}$, starting from $n_{vapour} + n_{liquid} = n_{total}$ because there are only liquid phase and vapour phase present in the system:

$$\begin{aligned} \frac{n_{vapour}}{n_{total}} + \frac{n_{liquid}}{n_{total}} &= 1 \\ \frac{n_{vapour}}{n_{total}} &= 1 - \frac{n_{liquid}}{n_{total}} \end{aligned}$$

Substitute $1 - \frac{n_{liquid}}{n_{total}}$ into the $\frac{n_{vapour}}{n_{total}}$ in the equation:

$$x_{benzene} \times \frac{n_{liquid}}{n_{total}} + y_{benzene} \times (1 - \frac{n_{liquid}}{n_{total}}) = 0.5 \quad (3.9.9)$$

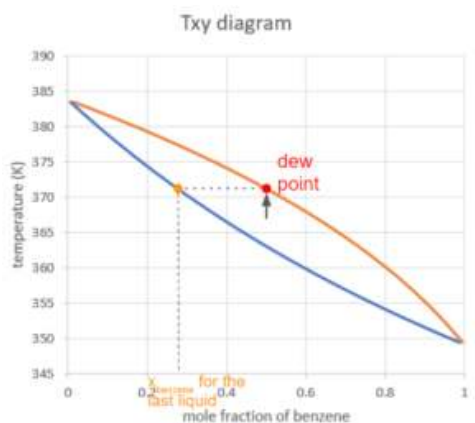
From reading the x-coordinates of the points on the curves, we can get: $x_{benzene} \approx 0.39, y_{benzene} \approx 0.62$

$$\begin{aligned}
 0.39 \times \frac{n_{\text{liquid}}}{n_{\text{total}}} + 0.62 \times \left(1 - \frac{n_{\text{liquid}}}{n_{\text{total}}}\right) &= 0.5 \\
 (0.39 - 0.62) \frac{n_{\text{liquid}}}{n_{\text{total}}} &= 0.5 - 0.62 \\
 \frac{n_{\text{liquid}}}{n_{\text{total}}} &= \frac{0.5 - 0.62}{0.39 - 0.62} \\
 &= 0.52
 \end{aligned}$$

Note this means we have roughly half vapour and half liquid. This is shown by our overall system point (red dot) being roughly between the two lines. Within the vapour-liquid region, the closer this point is to a certain line on the diagram the more of that phase will be in the system. Think back to our bubble point, where our system was almost entirely liquid (and very close to the liquid line).

If we then keep heating up the system under the same pressure, the system will hit the second curve at a certain point. We call this point the **dew point**. At this point, the last drop of liquid turns into vapour. The composition of the last drop of liquid can be found on the curve on the boundary of the liquid region at the same temperature.

In the Txy graph, the line connecting all the dew points (saturated vapour line) is always higher than the line connecting all the bubble points (saturated liquid line). Whether the slopes of the curves are positive or negative, the saturated vapour line will still be above the saturated liquid line because the system is more likely to be in the vapour phase when the temperature is higher.



✓ Exercise: Dew Point Mole Fraction

Taking a similar approach to the bubble point and using Raoult's law, calculate the x_{benzene} and x_{toluene} for the last drop of liquid at the dew point using the Antoine equation constants below.

Substance	A	B	C
benzene	4.60362	1701.073	20.806
toluene	4.07827	1343.943	-53.773

Solution

Add example text here.

Raoult's law states:

$$y_i \times P = x_i \times p_i^*(T) \quad (3.9.10)$$

We know that $P = 1.013$ bar for the system is kept constant, then we just need to calculate the p^* at the temperature of the dew point, then substitute this into the Raoult's law equation to calculate x_i .

To find p^* using the Antoine equation, we must first guess a temperature. Similar to the bubble point calculation, a safe place to start is the average of the boiling points of the pure substances $T = 368\text{K}$.

Step 1: Calculate the p_i^* for both substances:

$$\begin{aligned} \log_{10}(p^*) &= A - \frac{B}{T+C} \\ p^* &= 10^{A - \frac{B}{T+C}} \\ p^*_{benzene} &= 10^{4.60362 - \frac{1701.073}{368+20.806}} = 1.692bar \\ p^*_{toluene} &= 10^{4.07827 - \frac{1343.943}{368-53.773}} = 0.633bar \end{aligned}$$

Step 2: Substitute into the Raoult's law equation to calculate x_i for both substances:

Use $y_{benzene} = 0.5$, because when there is only very little amount of liquid left in the system, we can approximate the mole fraction of benzene in the vapour to be equal to the total mole fraction of benzene in the system.

$$\begin{aligned} y_i \times P &= x_i \times p_i^*(T) \\ x_{benzene} &= \frac{y_{benzene} \times P}{p^*_{benzene}} \\ &= \frac{0.5 \times 1.013bar}{1.692bar} \\ &= 0.299 \\ x_{toluene} &= \frac{y_{toluene} \times P}{p^*_{toluene}} \\ &= \frac{0.5 \times 1.013bar}{0.633bar} \\ &= 0.800 \end{aligned}$$

Step 3: Calculate the sum of the liquid mole fractions, and adjust the temperature guess accordingly:

$$\sum_i x_i = 0.299 + 0.800 = 1.099 > 1 \quad (3.9.11)$$

The next guess for T should be higher so that the substances tend to condense less.

After several trials, we can show that $T = 371.2K$ is the bubble point temperature:

Step 1: Calculate the p_i^* for both substances:

$$\begin{aligned} \log_{10}(p^*) &= A - \frac{B}{T+C} \\ p^* &= 10^{A - \frac{B}{T+C}} \\ p^*_{benzene} &= 10^{4.60362 - \frac{1701.073}{371.2+20.806}} = 1.837bar \\ p^*_{toluene} &= 10^{4.07827 - \frac{1343.943}{371-53.773}} = 0.699bar \end{aligned}$$

Step 2: Substitute into the Raoult's law equation to calculate x_i for both substances:

$$\begin{aligned} y_i \times P &= x_i \times p_i^*(T) \\ x_{benzene} &= \frac{y_{benzene} \times P}{p^*_{benzene}} \\ &= \frac{0.5 \times 1.013bar}{1.837bar} \\ &= 0.276 \\ x_{toluene} &= \frac{y_{toluene} \times P}{p^*_{toluene}} \\ &= \frac{0.5 \times 1.013bar}{0.695bar} \\ &= 0.725 \end{aligned}$$

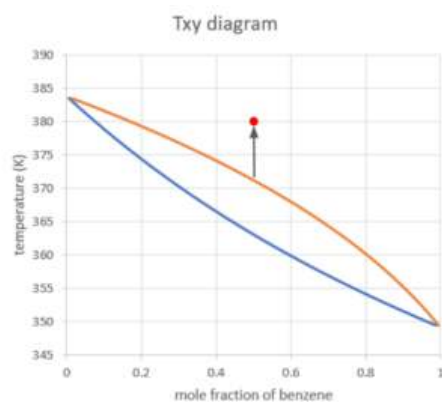
Step 3: Calculate the sum of the liquid mole fractions, and adjust the temperature guess accordingly:

$$\sum_i x_i = 0.276 + 0.725 = 1.001 \quad (3.9.12)$$

Because there are rounding errors involved in the calculations, we can say that $T=371.2K$ is our bubble point temperature.

Therefore the molar fractions of the substances in the last drop of liquid at the dew point are $x_{benzene} = 0.276$ and $y_{toluene} = 0.725$.

If we keep increasing the temperature above the dew point, the system will be in the vapour phase only. The mole fraction of benzene will still be 0.5 since it is the ratio of total benzene molecules and total molecules in the system, regardless of the state.



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3.10: Pxy Diagram

Learning Objectives

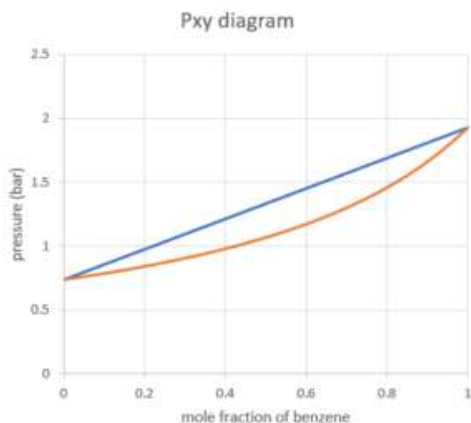
By the end of this section, you should be able to:

- **Read** Pxy diagrams for binary mixtures

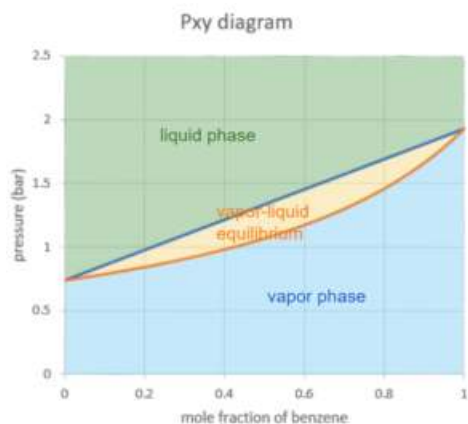
Find bubble points and dew points on a Pxy diagram

Calculate the mole fraction of substances in the vapour and liquid states

The following diagram is the Pxy diagram for a benzene-toluene mixture at a constant temperature of 373K. The y-coordinates show the pressure of the mixture and the x-coordinates show the mole fraction of benzene in liquid and/or vapour phases.

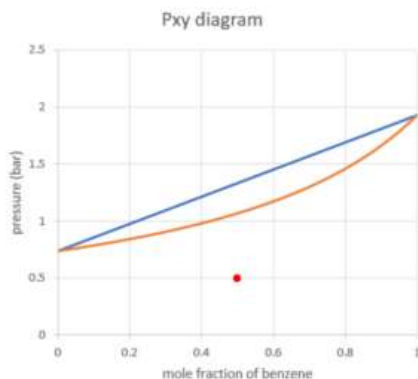


Higher pressure forces molecules to come closer together, which causes the molecules to be more likely to condense from vapour to liquid. From top to bottom, the regions are liquid region, vapour-liquid equilibrium region, vapour region, which is the opposite from the Txy diagram:



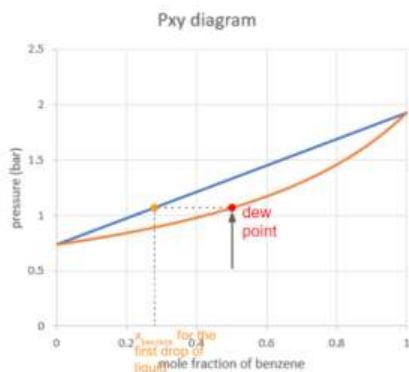
Suppose we have a mixture with **0.5 mole fraction of benzene at a pressure of 0.5 bar**, and we slowly increase the pressure while keeping the temperature constant at 373K.

We can locate our starting point using the pressure and mole fraction of benzene:

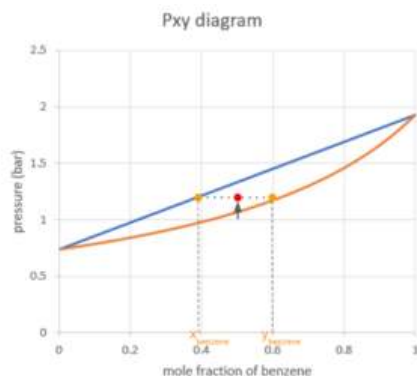


The point is fully in the vapour region, which means the mixture of benzene and toluene is in the vapour phase at a pressure of 0.5 bar and temperature of 373K.

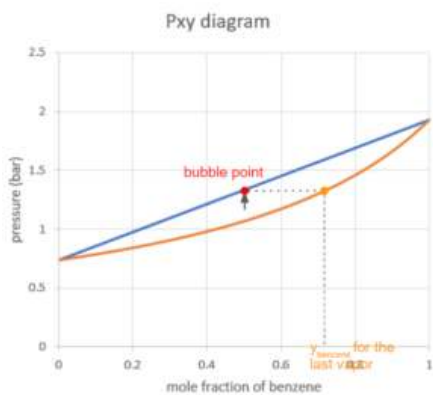
As we keep increasing the pressure, the point will hit the first curve on the boundary of the vapour region. This point is the **dew point** of the system. At the dew point, the first drop of liquid is being formed. The composition of the first liquid can be found using the x-coordinate of the point on the other curve where the pressure is the same.



If we keep increasing the pressure while keeping the temperature constant, the point will move up into the vapour-liquid equilibrium region. Similarly to the Txy diagram, we can read the mole fraction of benzene by drawing a horizontal line through the point and reading the x-coordinate where the line hits the two curves.



As the pressure goes up, the system will hit the **bubble point**, where the last drop of vapour condenses into a liquid.



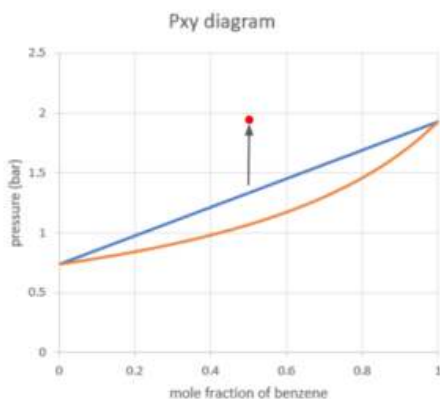
Notice that the line connecting all the bubble points at different mole fractions appears to be linear. We can show why this occurs using Raoult's law:

Starting with the total pressure in the system being the sum of individual partial pressures, we replace each partial pressure with the liquid mole fraction and vapour pressure (using Raoult's law):

$$\begin{aligned} P &= p_1 + p_2 = x_1 \times p_1^*(T) + x_2 \times p_2^*(T) \\ &= x_1 \times p_1^*(T) + (1 - x_1) \times p_2^*(T) \\ &= x_1 \times [p_1^*(T) - p_2^*(T)] + p_2^*(T) \end{aligned}$$

This equation is in a linear form, where $[p_1^*(T) - p_2^*(T)]$ is the slope and $p_2^*(T)$ is the y-intercept. Because the Pxy diagrams assume constant temperature, the vapour pressures are constant.

When we raise the pressure of the system over the dew point, the system will stay fully in the liquid region. There will be only liquid in the system and the composition of the liquid will be equal to the overall system composition.



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3.11: Phase Equilibrium Chapter Review

Important Equations

Pressure definition	$P = \frac{F}{A}$
Calculating pressure using a manometer	$P = P_{ref} + \rho g(h_{ref} - h)$
Converting gauge/absolute pressure	gauge pressure = absolute pressure – atmospheric pressure
Temperature conversions	$T(K) = T(^{\circ}C) + 273.15$ (3.11.1)
	Fahrenheit to Rankine: $T(^{\circ}R) = T(^{\circ}F) + 459.67$
	Kelvin to Rankine:
	$T(^{\circ}R) = 1.8 \cdot T(K)$ (3.11.2)
	$T(^{\circ}F) = 1.8 \cdot T(^{\circ}C) + 32$ (3.11.3)
Reduced properties	$T_r = \frac{T}{T_c}$ (3.11.4)
	$P_r = \frac{P}{P_c}$ (3.11.5)
Gibb's Phase Rule	$DF = 2 + c - \pi - r$
Ideal Gas Law	$PV = nRT$ (3.11.6)
	$P\hat{V} = RT$ (3.11.7)
Dalton's Law	$P = \sum_i^n p_i$ (3.11.8)
	$p_A = y_A P$ (3.11.9)
Amgat's Law	$V = \sum_i^n v_i$ (3.11.10)
	$v_A = y_A V$ (3.11.11)
Relating ideal gas properties	$R = \frac{V_s P_s}{n T_s} = \frac{V_s P}{n T}$
Compressibility Factor	$\frac{PV}{RT} = Z$
Antoine Equation	$\log_{10}(p^*) = A - \frac{B}{T+C}$
Raoult's Law	$p_i = y_i \cdot P = x_i \cdot p_i^*(T)$
Henry's Law	$p_i = y_i \cdot P = \frac{x_i}{H_i(T)}$

Terms to know

An interactive or media element has been excluded from this version of the text. You can view it online here:

<https://pressbooks.bccampus.ca/chbe220/?p=1753>

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3.12: Practice Exercises

Exercise: Phase Change – Carbon Dioxide

Identify the phase changes that carbon dioxide will undergo as its temperature is increased from $-100\text{ }^{\circ}\text{C}$ while holding its pressure constant at 1,000 kPa. At what approximate temperatures do these phase changes occur? The phase diagram of carbon dioxide is shown below.

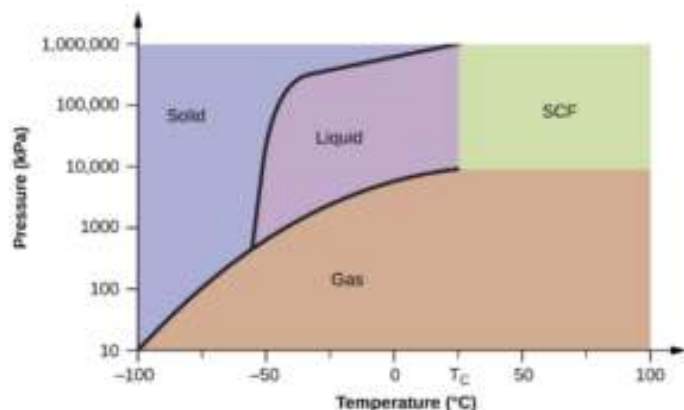


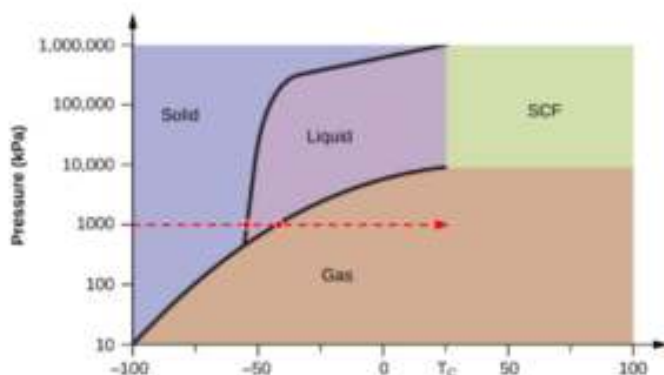
Image obtained from [OpenStax Chemistry](#)/ CC BY 4.0

Note: This diagram is missing the “vapour” phase. Usually, we call the gaseous phase under the liquid region “vapor” because it is able to condense to a liquid, while the “gas” phase is in a temperature that is too high to condense. Sometimes the terms are not strictly distinguished.

Solution

The phase change from solid to liquid at $\sim -55^{\circ}\text{C}$; from liquid to gas at $\sim -40^{\circ}\text{C}$.

To represent holding pressure constant while increasing temperature, we can draw a line moving horizontally to the right on the phase diagram.



A phase change occurs every time when the horizontal line hits a curve on the diagram.

✓ Exercise: Gibb's Phase Rule

How many degrees of freedom exist for a vapour-liquid (V-L) mixture of acetone ($(CH_3)_2CO$) and methyl ethyl ketone ($CH_3C(O)CH_2CH_3$)? Assume no chemical reaction happens.

Solution

Add example text here.

vapour-liquid mixture: $\pi = 2$

mixture of acetone and methyl ethyl ketone: $c = 2$

no chemical reactions: $r = 0$

$$DF = 2 + c - \pi - r = 2 + 2 - 2 - 0 = 2 \quad (3.12.1)$$

✓ Exercise: Ideal Gas Law

Calculate the density (mass per cubic metre) of dry air (a) under IUPAC standard conditions and (b) in a hot air balloon at a temperature of 120°C under the same pressure. Assuming ideal gas behaviour.^[1]

Take average molar mass = 29.0 mol/L for dry air. $R = 8.314 \frac{\text{J}}{\text{molK}}$

Solution

Add example text here.

a) To find the mass per cubic metre, we need the number of moles contained in a cubic metre under the IUPAC standard temperature and pressure. Calculate n by rearranging the ideal gas law:

$$\begin{aligned} PV &= nRT \\ n &= \frac{PV}{RT} \\ n &= \frac{1 \times 10^5 \text{ Pa} \times 1 \text{ m}^3}{8.314 \frac{\text{J}}{\text{molK}} \times 273.15 \text{ K}} \\ n &= 44.1 \text{ mol} \end{aligned}$$

The mass of air is equal to the number of moles contained in a cubic metre multiplied by molar mass:

$$m = n \times MW = 44.1 \text{ mol} \times 29.0 \text{ g/mol} = 1278.9 \text{ g} = 1.28 \text{ kg} \quad (3.12.2)$$

The density of air is the mass divide by volume:

$$\rho = \frac{m}{V} = \frac{1.28 \text{ kg}}{1 \text{ m}^3} = 1.28 \text{ kg/m}^3 \quad (3.12.3)$$

b) Here, we also have the same volume (1 m^3) but different temperature. We can once again find the number of moles this will hold.

$$\begin{aligned} PV &= nRT \\ n &= \frac{PV}{RT} \\ n &= \frac{1 \times 10^5 \text{ Pa} \times 1 \text{ m}^3}{8.314 \frac{\text{J}}{\text{molK}} \times (273.15 + 120) \text{ K}} \\ n &= 30.6 \text{ mol} \end{aligned}$$

We do a similar calculation as before to find the mass of the gas in the cubic metre

$$m = n \times MW = 30.6 \text{ mol} \times 29.0 \text{ g/mol} = 887.4 \text{ g} = 0.89 \text{ kg} \quad (3.12.4)$$

We can then use this to find density under this new condition:

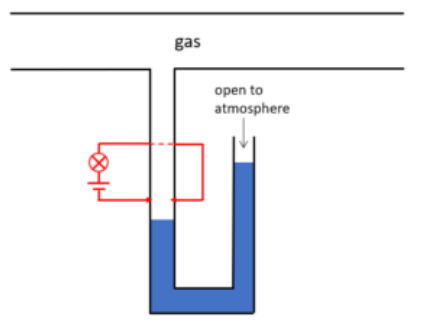
$$\rho = \frac{m}{V} = \frac{0.89\text{kg}}{1\text{m}^3} = 0.89\text{kg/m}^3 \quad (3.12.5)$$

This is less dense, which makes sense as the temperature is higher, so we would expect less gas molecules in the same volume at a similar pressure.

One other way to solve this is to observe that the density is proportional to the number of moles, which is inversely proportional to the temperature:

$$\begin{aligned} \frac{\rho_2}{\rho_1} &= \frac{T_1}{T_2} \\ \rho_2 &= \frac{T_1}{T_2} \rho_1 \\ \rho_2 &= \frac{273.15\text{K}}{(120 + 273.15)\text{K}} \times 1.28\text{kg/m}^3 \\ \rho_2 &= 0.89\text{kg/m}^3 \end{aligned}$$

✓ Exercise: Manometer in a Pressure Alarm



- The figure demonstrates the levels of the liquid at normal conditions. Is the pressure of the gas in the sealed tube higher or lower than atmospheric pressure?
- We use a circuit as shown by the red lines to report abnormal pressure in the tube. The liquid in the manometer acts as a switch: when a conductor is placed in between the red arrows, the circuit will be closed and the light bulb will be turned on. Suppose the gas in the tube is an insulator and the liquid is a conductor, the light turns on means: _____ (choose from: the tube leaks or depressurizes/ the gas in the tube is over-pressurized).

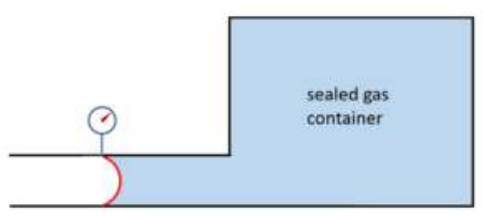
Solution

Add example text here.

- The pressure of the gas in the sealed tube is higher than atmospheric pressure.
- The tube leaks or depressurizes.

Closing the circuit requires the liquid level to rise up to the level of the red arrows. When the pressure in the gas tube decreases, the liquid level on the left side will increase to balance the pressure.

✓ Exercise: Measurement Range of a Pressure Gauge



Suppose we use a flexible membrane to measure the pressure in a sealed container. The membrane is attached to the atmosphere on one side (take $P_{atm} = 1.0 \times 10^5 Pa$) and a sealed container of gas at the other. The membrane has an area of $0.005 m^2$ and will be permanently deformed when experiencing a net force larger than 300N.

a) It is known that the absolute pressure in the gas container is 89kPa at 273K temperature. What is the range of pressure in the container that can be measured without permanently deforming the membrane?

b) Assuming the volume of the container is constant, what is the corresponding temperature range that allows the pressure in the container to be measured?

Solution

Add example text here.

a) The net force experienced by the membrane is caused by the difference of the pressure in the gas container and atmospheric pressure (gauge pressure). Using the definition of pressure $P = \frac{F}{A}$, we can calculate the range of gauge pressure we can measure with the membrane. The net force can be exerted in both directions, which means the gauge pressure may be positive to negative:

$$P = \frac{F}{A} = \frac{300N}{0.005m^2} = 60000Pa \quad (3.12.6)$$

So the range of **gauge** pressure we can measure is:

$$-60000Pa < P < 60000Pa \quad (3.12.7)$$

The range of **absolute** pressure we can measure is:

$$\begin{aligned} 1.0 \times 10^5 Pa - 60000Pa < P < 1.0 \times 10^5 Pa + 60000Pa \\ 0.4 \times 10^5 Pa < P < 1.6 \times 10^5 Pa \end{aligned}$$

b) We can calculate the corresponding temperatures by rearranging the ideal gas law:

$$n = \frac{P_1 V_1}{RT_1} = \frac{P_2 V_2}{RT_2} \quad (3.12.8)$$

Because R and the volume of the container are constant, we can simplify the equation:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad (3.12.9)$$

And we can solve for the temperature range by substituting in the range of absolute pressure and the known set of temperature and pressure:

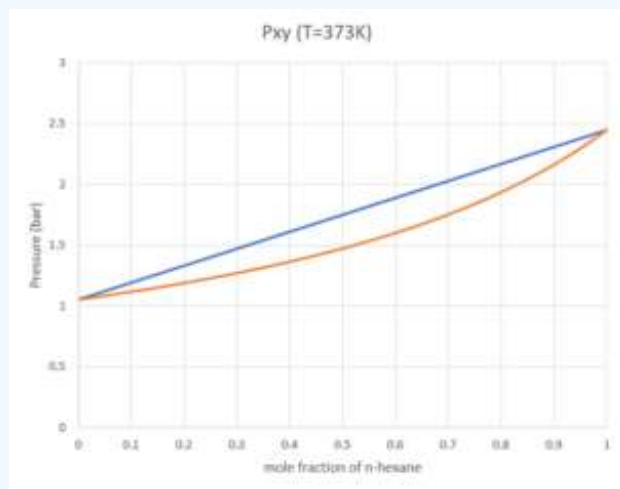
$$\begin{aligned} \frac{1.6 \times 10^5 Pa}{T_{high}} &= \frac{89 \times 10^3 Pa}{273K} \\ T_{high} &= \frac{1.6 \times 10^5 Pa \times 273K}{89 \times 10^3 Pa} \\ &= 491K \end{aligned}$$

$$\begin{aligned} \frac{0.4 \times 10^5 Pa}{T_{low}} &= \frac{89 \times 10^3 Pa}{273K} \\ T_{low} &= \frac{0.4 \times 10^5 Pa \times 273K}{89 \times 10^3 Pa} \\ &= 123K \end{aligned}$$

So the temperature range to measure the pressure in the container is

✓ Exercise: Pxy Diagram

The following graph shows the Pxy diagram for a mixture of n-hexane and n-heptane at a constant temperature of 373K.



Using the diagram above, answer the following questions:

- What is the vapour pressure of pure n-hexane at $T=373K$?
- What is the phase(s) in the system when the mole fraction of n-hexane in the system is 0.3 at a pressure of 2 bar?
- What is the dew point pressure for a mixture with 30% n-heptane?
- At vapour-liquid equilibrium, if the mole fraction of n-hexane in the liquid phase is 0.3, what is the mole fraction of n-hexane in the vapour phase?
- At vapour-liquid equilibrium, if the mole fraction of n-hexane in the vapour phase is 0.3, what is the mole fraction of n-hexane in the liquid phase?

Solution

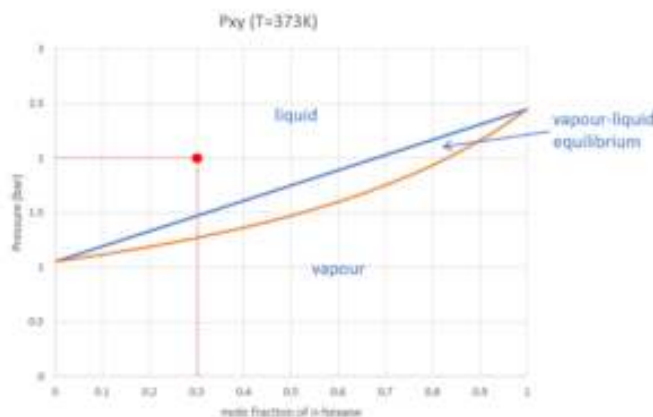
Add example text here.

(Since the answers are read from the graph, each question will allow a range of correct answers)

- 2.45 bar

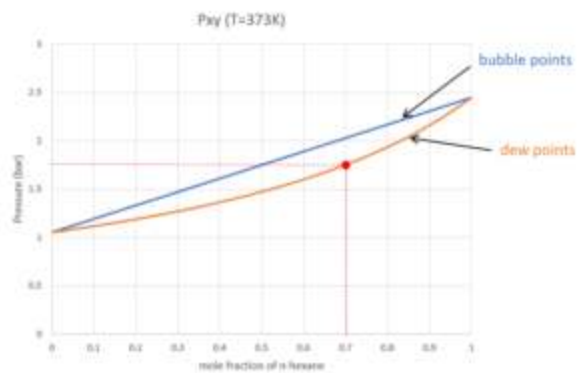
Find the y-coordinate for the point when the mole fraction of n-hexane is 1 and the two lines meet at a point.

- the system only has a liquid phase

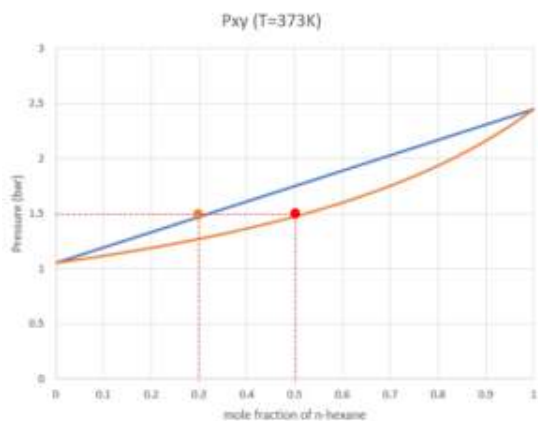


- 1.75 bar

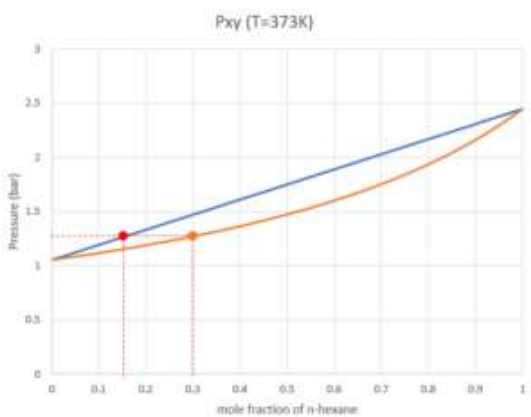
Because the x-axis represents the mole fraction of n-hexane, we need to convert 30% n-heptane to mole fraction of n-hexane=0.7:



d) $y_{n\text{-hexane}} = 0.5$

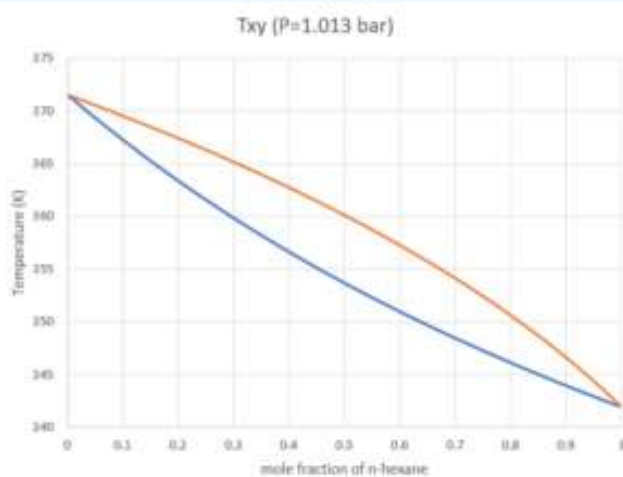


e) $x_{n\text{-hexane}} = 0.5$



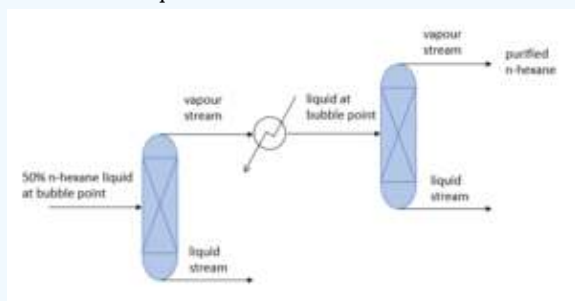
✓ Exercise: Txy Diagram

The following graph shows the Txy diagram for a mixture of n-hexane and n-heptane at a constant pressure of 1.013 bar.



Using the diagram above, answer the following questions:

- What is the boiling temperature for pure n-heptane at $P=1.013$ bar?
- What is the bubble point temperature when the mole fraction of n-hexane is 0.6?
- If the mole fraction of n-hexane is 0.4, at $T=360$ K, what is the mole fraction of n-hexane in liquid and vapour phase?
- Say we use the following process to purify the n-hexane in the stream:
 - We start with a liquid mixture of 50% n-hexane at its bubble point
 - The liquid mixture is sent to an isothermal distillation column, where the system is kept at a steady-state of vapour-liquid equilibrium at the bubble point, and we collect the vapour into the output stream as soon as the vapour is formed
 - The vapour is cooled to the bubble point
 - We send the liquid into another isothermal distillation column, where we collect the vapour formed at the bubble point



What is the mole fraction of n-hexane in the purified stream?

Solution

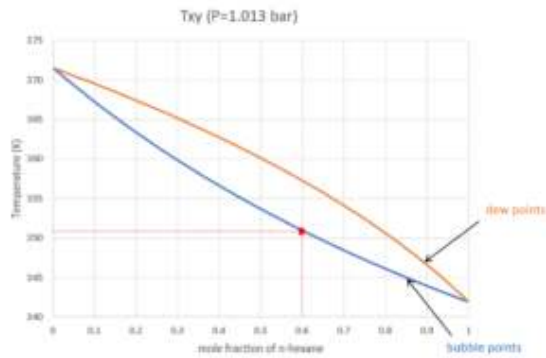
Add example text here.

(Because the answer is read from the graph, each question will allow a range of correct answers)

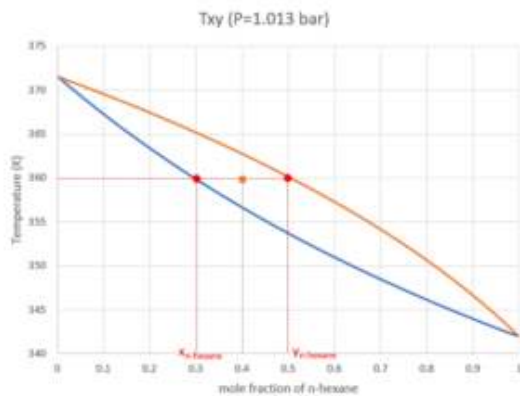
a) 372 K

Find the y-coordinate for the point when the mole fraction of n-hexane is 0 and the two lines meet at a point.

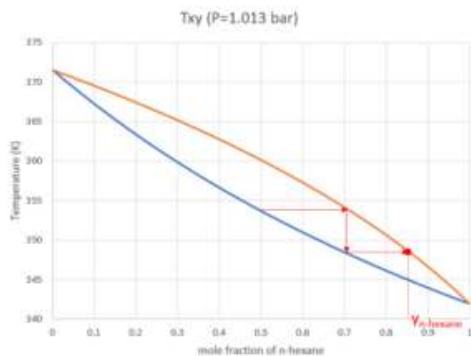
b) 351K



c) $x_{n\text{-hexane}} = 0.3$, $y_{n\text{-hexane}} = 0.5$



d) mole fraction of n-hexane in the purified stream=0.85



References

[1] OpenStax University Physics Volume 2. 2016. 2.1 Molecular Model of an Ideal Gas. [online] <<https://openstax.org/books/university-physics-volume-2/pages/2-1-molecular-model-of-an-ideal-gas>> [Accessed 14 May 2020].

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CHAPTER OVERVIEW

4: Energy Balances

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- [4.2: Phase Change and Heat Capacity](#)
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4.1: Introduction to Energy Balances

Learning Objectives

By the end of this section, you should be able to:

- **Identify** relevant terms for energy balances for open and closed systems
- **Use** thermodynamic data tables to identify enthalpy, internal energy, and other thermodynamic properties using system temperatures and pressures
- **Solve** energy balance problems using thermodynamic data

Forms of Energy

Systems are typically divided into three main categories depending on how the system interacts with its surroundings:

- **Isolated** – No energy or mass transfer between system and surroundings, energy may change form within the system
- **Closed** – Energy, but no mass transfer between system and surroundings
- **Open** – Energy and mass transfer between systems and surroundings, typically use a ' with quantities that change over time in these open systems to denote the flow rate of energy or mass.

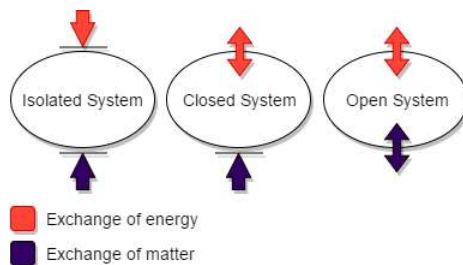


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Kinetic Energy – E_k

Kinetic Energy is energy associated with motion, which can be described as translational or rotational energy.

$$E_k = \frac{1}{2} m u^2 \quad (4.1.1)$$

$$\dot{E}_k = \frac{1}{2} \dot{m} u^2 \quad (4.1.2)$$

where m is mass and u is velocity relative to a reference. Generally we refer to earth's surface as stationary.

Potential Energy – E_p

Potential energy can be described as energy present due to position in a field, such as gravitational position or magnetic position

Usually for chemical processes, we consider the potential energy change due to the gravitational position of the process equipments.

$$E_p = m g z \quad (4.1.3)$$

$$\dot{E}_p = \dot{m} g z \quad (4.1.4)$$

$$\Delta E_p = E_{p2} - E_{p1} = m g (z_2 - z_1) \quad (4.1.5)$$

where m is mass, g is the gravitational acceleration (approximately 9.8 m/s²), and z is the height about the point of reference.

Internal Energy – U

Internal energy can be described as all other energy present in a system, including motion, and molecular interaction.

Heat – Q

- Heat is the energy flow due to temperature difference
- Heat flows from higher temperatures to lower temperatures
- Heat is generally defined as positive when it is transferred from the surroundings to the system

Work – W

- Work is energy resulting from driving forces (not temperature) such as force, torque, or voltage
- We will define work as positive when work is done by the surroundings on the system, this is a typical convention in chemistry. With this convention, we would write “ $Q + W$ ” in our energy balances. However, historically work has also been defined in physics as positive when work is done by the system on the surroundings. In this other case, the energy balance would be written with “ $Q - W$ ”. Both can be used and this is accounted for in the sign we use in front of the work term in energy balances.

Energy Transfer in Closed Systems

Closed systems are defined as systems with no mass transfer across the system’s boundaries. All the energy forms described above are applicable to closed systems.

✓ Exercise: Energy Balance Sign Conventions

Consider a system that consists of a stirred tank reactor where an exothermic reaction is taking place, where an external motor is mixing the contents in the reactors. What are the signs of Q and W for this system?

Solution

For an exothermic reaction, heat is produced by the system. Therefore, Q is **negative**.

For an external motor that is mixing the contents in the reactor, work is being done by the surroundings on the system. Therefore, W is **positive**.

Energy Balances on Closed Systems

Energy in closed systems follows the Law of Conservation of Energy

$$Accumulation = Input - Output \quad (4.1.6)$$

In terms of general energy:

$$E_{system,final} - E_{system,initial} = E_{system,transferred} \quad (4.1.7)$$

The initial energy in the system can be defined as:

$$U_i + E_{k,i} + E_{p,i} \quad (4.1.8)$$

The final energy in the system can be defined as:

$$U_f + E_{k,f} + E_{p,f} \quad (4.1.9)$$

The energy transfer of the system can be defined as:

$$Q + W \quad (4.1.10)$$

This yields the following closed system energy balance, defined as **the First Law of Thermodynamics**:

$$(U_f - U_i) + (E_{k,f} - E_{k,i}) + (E_{p,f} - E_{p,i}) = Q + W \quad (4.1.11)$$

or as commonly expressed

$$\Delta U + \Delta E_k + \Delta E_p = Q + W \quad (4.1.12)$$

Assumptions made by the First Law of Thermodynamics

- If no acceleration exists in the system, the change in the kinetic energy term will be 0, and can be omitted from the balance
- If no change in height (or other fields) exist in the system, the change in the potential energy term will be 0, and can be omitted from the balance
- Internal energy depends on chemical composition, state (solid, liquid, or gas) and temperature; Pressure's effect is negligible.
- If the system has the same temperature as its surroundings or is adiabatic, the heat term will be 0, and can be omitted from the balance
- If there are no moving parts, electrical currents, or radiation in the system, the work term will be 0 and can be omitted from the balance

Work in Open Systems

Open Systems:

Open systems are defined as systems where both mass and energy cross the system's boundaries.

Two types of work are typically observed in these systems:

- **Shaft Work** – W_s or $\dot{W}_s$
Shaft work is work done on process fluid by a moving part, such as a pump, rotor, or a stirrer.
- **Flow Work** – W_{fl} or $\dot{W}_{fl}$
Flow work is work done on process fluid (inlet minus outlet). For the work flow in, the surroundings do work on the system, therefore it is positive. For the work flow out, the system does work on the surroundings, therefore it is negative.

$$\dot{W}_{fl} = \dot{W}_{fl-in} - \dot{W}_{fl-out} = P_{in}\dot{V}_{in} - P_{out}\dot{V}_{out} \quad (4.1.13)$$

Steady-State Open-System Energy Balance

Energy Conservation for a Steady-State System

For stream 'j' in a system:

$$\Sigma_{in}\dot{E}_j + \dot{Q} + \dot{W} = \Sigma_{out}\dot{E}_j \quad (4.1.14)$$

Rearranging the energy terms, we get:

$$\dot{Q} + \dot{W} = \Sigma_{out}\dot{E}_j - \Sigma_{in}\dot{E}_j \quad (4.1.15)$$

✓ Example: Energy Flow in a System

Consider the following system:



Eg. for this system:

$$\dot{E}_1 + \dot{E}_2 + \dot{Q} + \dot{W} = \dot{E}_3 + \dot{E}_4$$

There are 2 streams with energy entering the system (streams 1 and 2), and 2 streams with energy exiting the system (streams 3 and 4).

For this system:

$$\dot{E}_1 + \dot{E}_2 + \dot{Q} + \dot{W} = \dot{E}_3 + \dot{E}_4 \quad (4.1.16)$$

Recall the three forms of energy:

$$\dot{E}_j = \dot{U}_j + \dot{E}_{k,j} + \dot{E}_{p,j} \quad (4.1.17)$$

Each energy flow term can be further separated into: $\dot{U}_j = \dot{m} * \hat{U}_j$

Specific Property “” : This denotes an intensive property obtained by dividing an extensive property by a total amount of flow rate (can be total number of moles or total mass)

$$\hat{V} = \frac{V}{n} \quad (4.1.18)$$

or

$$\hat{U} = \frac{\dot{U}}{\dot{m}} \quad (4.1.19)$$

Combining all these terms:

$$\dot{Q} + \dot{W} = \Sigma_{out} \dot{m}_j * (\hat{U}_j + \hat{E}_{k,j} + \hat{E}_{p,j}) - \Sigma_{in} \dot{m}_j * (\hat{U}_j + \hat{E}_{k,j} + \hat{E}_{p,j}) \quad (4.1.20)$$

Recall the work terms expansion:

$$\dot{W} = \dot{W}_{fl} + \dot{W}_s \quad (4.1.21)$$

where flow work is dependant on system pressure and volume

$$\dot{W}_{fl} = \Sigma_{in} \dot{m}_j P_j \hat{V}_j - \Sigma_{out} \dot{m}_j P_j \hat{V}_j \quad (4.1.22)$$

Now we have:

$$\dot{Q} + \dot{W}_s = \Sigma_{out} \dot{m}_j * (\hat{U}_j + P_j \hat{V}_j + \hat{E}_{k,j} + \hat{E}_{p,j}) - \Sigma_{in} \dot{m}_j * (\hat{U}_j + P_j \hat{V}_j + \hat{E}_{k,j} + \hat{E}_{p,j}) \quad (4.1.23)$$

Because $\hat{U} + P\hat{V}$ usually appear together in the energy balances, we define them to be "enthalpy" ($\hat{H}$):

$$\hat{H} = \hat{U} + P\hat{V} \quad (4.1.24)$$

where $\hat{U}$ is the internal energy and $P\hat{V}$ is the flow work

The following terms are defined:

- $\Delta \dot{H} = \Sigma_{out} \dot{m}_j * \hat{H}_j - \Sigma_{in} \dot{m}_j * \hat{H}_j$
- $\Delta \dot{E}_k = \Sigma_{out} \dot{m}_j * \hat{E}_{k,j} - \Sigma_{in} \dot{m}_j * \hat{E}_{k,j}$
- $\Delta \dot{E}_p = \Sigma_{out} \dot{m}_j * \hat{E}_{p,j} - \Sigma_{in} \dot{m}_j * \hat{E}_{p,j}$

Finally, an open system steady-state energy balance is defined:

$$\dot{Q} + \dot{W}_s = \Delta \dot{H} + \Delta \dot{E}_k + \Delta \dot{E}_p \quad (4.1.25)$$

✓ Exercise: Heat for an Ideal Gas

Prior to entering a furnace, air is heated from 25°C to 150°C and the change in specific enthalpy for the whole heating process is 3640 J/mol. The flow rate of air at the outlet of the heater is $1.5\text{m}^3/\text{min}$ and the air pressure at this point is 150 kPa absolute.

Calculate the heat needed for the process in kW. Assume the ideal gas behavior and that kinetic and potential energy changes from the heater inlet to the outlet are negligible.

Solution

Step 1: Calculate the molar flowrate using the ideal gas law.

$$\begin{aligned} \dot{n} &= \frac{1.5\text{m}^3}{\text{min}} * \frac{273\text{K}}{150 + 273\text{K}} * \frac{150\text{kPa}}{101.3\text{kPa}} * \frac{1\text{mol}}{22.4\text{L}} * \frac{10^3\text{L}}{1\text{m}^3} \\ \dot{n} &= 64.0 \frac{\text{mol}}{\text{min}} \end{aligned}$$

Step 2: Calculate the heat using the specific enthalpy. Since the potential and kinetic energy changes are zero, the following calculations are made

$$\begin{aligned}\dot{Q} &= \Delta \dot{H} = \dot{n} \Delta \hat{H} \\ \dot{Q} &= \frac{64.0 \text{ mol}}{\text{min}} * \frac{1 \text{ min}}{60 \text{ s}} * \frac{3640 \text{ J}}{\text{mol}} * \frac{\text{kW}}{10^3 \text{ J/s}} \\ \dot{Q} &= 3.88 \text{ kW}\end{aligned}$$

Reference States

Reference State: a substance at some pressure, temperature, and state of aggregation (solid, liquid, gas; pure or mixture).

It is much easier to estimate the energy of a system as a change from a reference state rather than the absolute energy.

✓ Exercise: Cooling in a Heat Exchanger

Water is used to cool a liquid in a heat exchanger. Water enters the heat exchanger at 10°C and exits at 100°C . Using the table below, find the change in enthalpy of water in its liquid state.

Entry #	$T(^{\circ}\text{C})$	$\hat{H}_L (\frac{\text{kJ}}{\text{kg}})$
1	5	21.02
2	10	42.02
3	100	419.17

Solution

Step 1: Determine which reference state you are going to use. In this case, we are using 10°C as the reference state.

$$\Delta \hat{H} = \hat{H}_{100^\circ\text{C}} - \hat{H}_{10^\circ\text{C}} \quad (4.1.26)$$

Step 2: Find the change in enthalpy by taking the difference of the system's specific enthalpies at different temperatures.

$$\begin{aligned}\Delta \hat{H} &= \hat{H}_3 - \hat{H}_2 \\ \Delta \hat{H} &= (419.17 - 42.02) \text{ kJ/kg} \\ \Delta \hat{H} &= 377.15 \text{ kJ/kg}\end{aligned}$$

Steam Tables

Since water is a commonly used resource in processes for heating and cooling, detailed information on its state properties at different temperatures and pressures is available.

For example, the steam table below provides $\hat{U}$, $\hat{H}$, and $\hat{V}$ at multiple sets of temperature and pressure:

$T(^{\circ}\text{C})$	$P(\text{MPa})$	$V^L (\text{m}^3/\text{kg})$	$V^V (\text{m}^3/\text{kg})$	$U^L (\text{kJ/kg})$	$\Delta U^{\text{vap}} (\text{kJ/kg})$	$U^V (\text{kJ/kg})$	$H^L (\text{kJ/kg})$	$\Delta H^{\text{vap}} (\text{kJ/kg})$	$H^V (\text{kJ/kg})$	$S^L (\text{kJ/K} \cdot \text{kg})$	$\Delta S^{\text{vap}} (\text{kJ/K} \cdot \text{kg})$	$S^V (\text{kJ/K} \cdot \text{kg})$
0.01	0.00061 2	0.00100 0	205.991 2	0.00	2374.92	2374.92	0.00	2500.92	2500.92	0.0000	9.1555	9.1555
5	0.00087 3	0.00100 0	147.011 3	21.02	2360.76	2381.78	21.02	2489.04	2510.06	0.0763	8.9485	9.0248
10	0.00122 8	0.00100 0	106.303 2	42.02	2346.63	2388.65	42.02	2477.19	2519.21	0.1511	8.7487	8.8998
15	0.00170 6	0.00100 1	77.8755	62.98	2332.51	2395.49	62.98	2465.35	2528.33	0.2245	8.5558	8.7803

How to Access Steam Tables on NIST

Steam tables can be found on [NIST](#)

- Select 'Water' from the 'Please select the species of interest:' drop-down menu
- Choose the steam table units you'd like to work with, in step 2.
- In Step 3, choose what kind of data you're looking to obtain. For an isothermal system, select 'Isothermal properties'. For a constant pressure system, select 'Isobaric properties'.
- Select the desired standard state convention. This course will most likely only use the 'Default for fluid' convention.

✓ Exercise: Steam Tables

Superheated steam at 40 bar absolute and 500°C flowing at a rate of 200kg/min is sent to an adiabatic turbine which expands to 5 bar. The turbine outputs 1250 kW . The expanded steam is then sent to a heat exchanger where isobaric heating occurs, resulting in the stream being reheated to its initial temperature. Assume no changes in kinetic energy. Write the energy balance for the turbine and determine the outlet stream temperature.

Solution

Step 1: Determine the enthalpy values for water vapor at 500°C and 40bar and 5bar. From the steam tables:

- For water vapor at 500°C and 40bar, the specific enthalpy is 3445 kJ/kg
- For water vapor at 500°C and 5bar, the specific enthalpy is 3484 kJ/kg

Step 2: Write the energy balance. Since there are no changes in potential and kinetic energy and no heat transfer, the change in enthalpy will be equal to a negative shaft work.

$$\begin{aligned}\Delta\dot{H} &= -\dot{W}_s \\ \Delta\dot{H} &= \dot{m} * (\hat{H}_2 - \hat{H}_1) \\ \hat{H}_2 &= \hat{H}_1 - \frac{\dot{W}_s}{\dot{m}} \\ &= \frac{3445\text{kJ}}{\text{kg}} - \frac{1250\text{kJ}}{\text{s}} * \frac{\text{min}}{200\text{kg}} * \frac{60\text{s}}{1\text{min}} \\ &= 3070\frac{\text{kJ}}{\text{kg}}\end{aligned}$$

Step 3: Determine the temperature of the steam corresponding to 5bar and 3070kJ/kg . From the steam tables:

$$T = 302^{\circ}\text{C}$$

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4.2: Phase Change and Heat Capacity

Learning Objectives

By the end of this section, you should be able to:

- **Evaluate** the cost of utilities in processes

Characterize energy changes in a system due to changes in temperature

Analyze energy balances on processes involving phase changes

Energy Balance Equipment

- Almost all energy exchange equipment is either a heat exchanger or jacket
- Heat exchangers and jackets often work by transferring heat with a stream of fluid
- Electrical heating elements are also available, but their high cost per unit energy may limit their use in industry

The figure below is a shell-and-tube heat exchange:

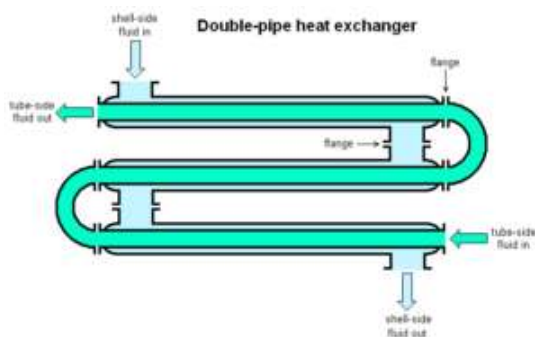


Image from [Turbojet /CC BY-SA 4.0](#)

Utilities: Utilities are services at a site such as water, electricity, and gas.

Choosing the correct utility can make a big difference in the cost of heating or cooling. For example, evaporating toluene at 190°C with a heat duty of 3,000,000 kJ/hr can be heated using the following utility options:

Utility	Inlet $T(^{\circ}\text{C})$	Outlet $T(^{\circ}\text{C})$	P (psia)	Cost (dollars/GJ)	Cost (dollars/hr)	Cost dollars/yr @ 8,000 hrs
High-pressure steam	250	249	575	5.66	16.98	135,840
Electricity	N/A	N/A	N/A	18.72	56.16	449,280

The high-pressure steam is a much cheaper option here

Phase Changes

Phase changes take place when a compound or mixture of compounds undergoes a change in their state of matter. The enthalpy changes for phase changes occur at a constant temperature and pressure and are determined experimentally.

Parameter	Phase Transition
Liquid → Gas	Heat of Vapourization ($\Delta \hat{H}_{vap}$)
Solid → Liquid	Heat of Fusion ($\Delta \hat{H}_{fus}$)
Gas → Liquid	(-) Heat of Vapourization ($-\Delta \hat{H}_{vap}$)
Liquid → Solid	(-) Heat of Fusion ($-\Delta \hat{H}_{fus}$)

Note that heat of vapourization is also referred to as latent heat

Heat Capacities

Heat capacities are physical properties that describe how much heat is needed to increase the temperature of a compound for a unit temperature per unit mass of a compound.

For a closed system where the only changing system variable is temperature:

$$T \quad (4.2.1)$$

$$C_V(T) = \left(\frac{\delta \hat{U}}{\delta T} \right)_V \quad (4.2.2)$$

Notation: $()_V$ means that the volume is kept constant during the process

This expression can be rearranged and integrated to obtain the following:

$$\begin{aligned} d\hat{U} &= C_V(T)dT \\ \Delta \hat{U} &= \int_{T_1}^{T_2} C_V dT \end{aligned} \quad (4.2.3)$$

If the C_V is constant:

$$\Delta \hat{U} = C_V * (T_2 - T_1) \quad (4.2.4)$$

For an open system, the heat capacity is defined under constant pressure conditions:

$$C_P(T) = \left(\frac{\delta \hat{H}}{\delta T} \right)_P \quad (4.2.5)$$

$$\Delta \hat{H} = \int_{T_1}^{T_2} C_P dT \quad (4.2.6)$$

If the C_P is constant:

$$\Delta \hat{H} = C_P * (T_2 - T_1) \quad (4.2.7)$$

✓ Example: Phase Changes and Heat Capacity in Energy Balances

text

Solution

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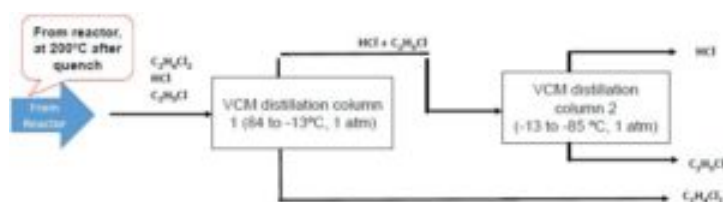
Consider a system where a mixture of dichloroethane (*EDC*), hydrogen chloride (*HCl*), and vinyl chloride (*VC*) is entering a distillation column for separation. Distillation columns work based on vapor-liquid equilibrium, and therefore the column will

generally operate at a temperature between the boiling points of all compounds.

Compound	Formula	Boiling Point at 1 atm ($^{\circ}\text{C}$)	Heat of Vapourization at 1 atm (kJ/mol)
EDC	$\text{C}_2\text{H}_4\text{Cl}_2$	84	35
HCl	HCl	-85	16
VC	$\text{C}_2\text{H}_3\text{Cl}$	-13	21

The mixture exits a reactor at 200°C and has the following properties:

Compound	Formula	Flow to Separate (tonne/hr)	Flow to Separate (tonne-mol/hr)	y_i (gas mole fraction)
EDC	$\text{C}_2\text{H}_4\text{Cl}_2$	47.5008	0.48	0.25
HCl	HCl	26.2512	0.72	0.375
VC	$\text{C}_2\text{H}_3\text{Cl}$	45	0.72	0.375

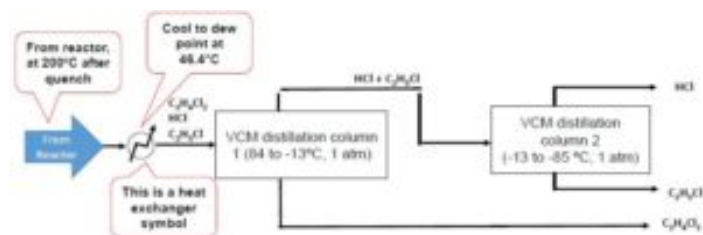


Recall **Raoult's Law**:

$$x_i = \frac{p_i^*}{y_i \times P} \quad (4.2.8)$$

Compound	Formula	Flow to Separate (tonne/hr)	Flow to Separate (tonne-mol/hr)	y_i (gas mole fraction)	x_i (liquid mole fraction)
EDC	$\text{C}_2\text{H}_4\text{Cl}_2$	47.5008	0.48	0.25	0.94
HCl	HCl	26.2512	0.72	0.375	0.005
VC	$\text{C}_2\text{H}_3\text{Cl}$	45	0.72	0.375	0.053

Suppose we operate the distillation column at the dew point of the system to separate benzene. For this system, the dew-point temperature is 46.4°C , therefore we must use a heat exchanger to bring the mixture from 200°C to 46.4°C



How much energy is removed to cool this stream from 200°C to 46.4°C ?

The *ideal gas* heat capacities for the mixture described above are listed below:

Compound	Formula	Flow to Separate (tonne/hr)	Flow to Separate (tonne-mol/hr)	C _p (J/mol-K)
EDC	$C_2H_4Cl_2$	47.5008	0.48	29
HCl	HCl	26.2512	0.72	29
VC	C_2H_3Cl	45	0.72	29

- EDC:

$$\Delta \dot{H} = \dot{n} \int_{T_1}^{T_2} C_P(T) dT \quad (4.2.9)$$

$$\Delta \dot{H} = 0.48 \frac{\text{tonne} - \text{mol}}{h} * 1,000,000 \frac{\text{mol}}{\text{tonne} - \text{mol}} * 29 \frac{J}{\text{mol} - K} * (200^\circ C - 46.4^\circ) * \frac{1K}{1^\circ} \quad (4.2.10)$$

$$\Delta \dot{H} = 2.14 \times 10^9 \frac{J}{h} \quad (4.2.11)$$

- HCl and VC:

$$\Delta \dot{H} = \dot{n} \int_{T_1}^{T_2} C_P(T) dT \quad (4.2.12)$$

$$\Delta \dot{H} = 0.72 \frac{\text{tonne} - \text{mol}}{h} * 1,000,000 \frac{\text{mol}}{\text{tonne} - \text{mol}} * 29 \frac{J}{\text{mol} - K} * (200^\circ C - 46.4^\circ) * \frac{1K}{1^\circ} \quad (4.2.13)$$

$$\Delta \dot{H} = 3.21 \times 10^9 \frac{J}{h} \quad (4.2.14)$$

There is no exchange of energy in the form of work in a heat exchanger. Therefore, the total heat removed $\dot{Q} = \Sigma \Delta \dot{H}$ is the sum of the change in enthalpy for each species:

$$\dot{Q} = \Sigma \Delta \dot{H} = 8.56 \times 10^9 \frac{J}{h} \quad (4.2.15)$$

✓ Exercise: Energy Balance for a Heat Exchanger

Consider an equimolar binary mixture of n-hexane and n-heptane at a constant pressure of 1 atm flowing at 1 kmol/h. This mixture is originally at $150^\circ C$ and needs to be cooled to $85^\circ C$ for a process in order to ensure vapor-liquid equilibrium is satisfied. The process uses a heat exchanger to achieve this cooling. The heat capacities for both compounds can be described by the following expression:

$$C_P = A + BT + CT^2 + DT^3 \quad (4.2.16)$$

where C_P is in J/mol-K and the constants A, B, C, and D are listed below:

Compound	A	B	C	D
n-Hexane	-4.413	0.528	-3.119E-04	6.494E-8
n-Heptane	-5.146	0.6762	-3.651E-04	7.658E-08

How much heat needs to be removed by the heat exchanger to reach the required temperature for the process?

Solution

Add example text here.

Step 1: Calculate the change in enthalpy for each compound using the heat capacities taking 1 kmol/hr as the molar flow.

$$\Delta \dot{H} = \dot{n} \int_{T_1}^{T_2} C_P(T) dT \quad (4.2.17)$$

where $T_1 = 150^\circ\text{C} = 423\text{K}$ and $T_2 = 85^\circ\text{C} = 358\text{K}$

$$\Delta \dot{H} = \dot{n} \int_{T_1}^{T_2} (A + BT + CT^2 + DT^3) dT \quad (4.2.18)$$

$$\Delta \dot{H} = \dot{n} \left(AT + \frac{B}{2} T^2 + \frac{C}{3} T^3 + \frac{D}{4} T^4 \right) \quad (4.2.19)$$

For n-hexane:

$$\Delta \dot{H} = 0.5 \frac{\text{kmol}}{\text{h}} * \left(-4.413 * T + \frac{0.528}{2} T^2 + \frac{-3.119E-04}{3} T^3 + \frac{6.494E-8}{4} T^4 \right) \Big|_{358\text{K}}^{423\text{K}} \quad (4.2.20)$$

$$\Delta \dot{H} = 0.5 \frac{\text{kmol}}{\text{h}} * 1000 \frac{\text{mol}}{\text{kmol}} * 1859 \frac{\text{J}}{\text{mol}} * \frac{\text{kJ}}{1000\text{J}} \quad (4.2.21)$$

$$\Delta \dot{H} = 929.5 \frac{\text{kJ}}{\text{h}} \quad (4.2.22)$$

Similarly for n-heptane:

$$\Delta \dot{H} = 0.5 \frac{\text{kmol}}{\text{h}} * 1000 \frac{\text{mol}}{\text{kmol}} * 2424 \frac{\text{J}}{\text{mol}} * \frac{\text{kJ}}{1000\text{J}} \quad (4.2.23)$$

$$\Delta \dot{H} = 1212 \frac{\text{kJ}}{\text{h}} \quad (4.2.24)$$

Step 2: Sum up the enthalpy changes for the components.

$$\begin{aligned} \dot{Q} &= \Sigma \Delta \dot{H} \\ \dot{Q} &= (929.5 + 1212) \frac{\text{kJ}}{\text{h}} \\ \dot{Q} &= 2142 \frac{\text{kJ}}{\text{h}} \end{aligned}$$

Choosing Utilities for System

For the VCM distillation system described above, we have the following utility options for cooling the stream from 200°C to 46.4°C :

Option	Utility	Inlet T ($^\circ\text{C}$)	Outlet T ($^\circ\text{C}$)	P	Cost (dollars/GJ)
A	Cooling Water	20	25	N/A	0.378
B	Refrigerated Water	5	15	N/A	4.77
C	Low T Refrigerant	-20	-5	N/A	8.49

A rule of thumb is that we want a stream we are transferring energy to have a 10°C temperature difference with the process stream. This will ensure our heat transfer occurs at an effective rate and that our heat exchanger does not need to be too big. Since our outlet temperature is only 46.4°C , all options have an inlet temperature at least 10°C below this desired outlet temperature. We could pick any but will select the cheapest option, which is cooling water.

How much will cooling this stream cost?

$$\begin{aligned} \text{Cost}\left(\frac{\text{dollars}}{h}\right) &= \dot{Q} * \text{cost}\left(\frac{\text{dollars}}{GJ}\right) \\ &= 8.56 \frac{GJ}{h} * 0.378 \frac{\text{dollars}}{GJ} \\ &= 3.24 \frac{\text{dollars}}{h} \end{aligned}$$

Process Paths

Recall that $\hat{U}$ and $\hat{H}$ are state properties. These properties depend on the state and not the path to that state.

It is easier to calculate the enthalpy change by changing one variable at a time through a hypothetical process path.

- 1 - Calculate change in enthalpy by only changing the temperature at the same state
- 2 - Calculate change in enthalpy by only changing the pressure at the same state (in the course, we usually neglect the effect of pressure on enthalpy change)
- 3 - Calculate change in enthalpy by only changing the phase

To obtain the desired change in enthalpy, add each enthalpy change where only 1 state property changes:

$$\Delta \hat{H} = \sum_i \Delta \hat{H}_i$$

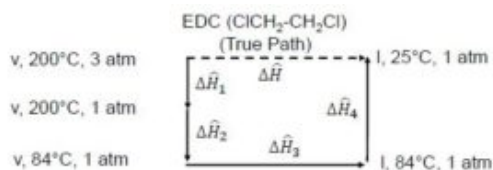
✓ Example: EDC Process Path

text

Solution

text.

Consider the enthalpy change of *EDC* transforming from vapour at 200°C and 3 atm to liquid at 25°C and 1 atm:



In this process, there are 3 variables changing:

- pressure
- temperature
- phase (vapour to liquid)

The following steps are taken in the process path and added together to get the overall change:

$$\Delta \hat{H}_1 \quad (4.2.25)$$

$$\Delta \hat{H}_2 \quad (4.2.26)$$

$$\Delta \hat{H}_3 \quad (4.2.27)$$

$$\Delta \hat{H}_4 \quad (4.2.28)$$

When we add these changes together, we can get the overall change in enthalpy:

$$\Delta \hat{H} = \Delta \hat{H}_1 + \Delta \hat{H}_2 + \Delta \hat{H}_3 + \Delta \hat{H}_4 \quad (4.2.29)$$

✓ Exercise: Process Path

What process paths can be taken to calculate the change in enthalpy for acetone going from 25°C in the liquid phase to 60°C in the vapour phase?

Solution

Add example text here.

Step 1: Bring the acetone to the boiling point temperature from 25°C without changing the phase using the C_P in the liquid phase.

Step 2: Use the latent heat (or heat of vaporization) to calculate the enthalpy of changing the phase from liquid to vapour.

Step 3: Bring the acetone to 60°C from the boiling point temperature using the C_P in the vapour phase.

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4.3: Reactive Energy Balances

Learning Objectives

By the end of this section, you should be able to:

- **Explain** heats of reaction as well as endothermic and exothermic reactions
- **Determine** the standard heat of reaction given other heats of reaction or heats of formation (Hess's Law)
- **Analyze** energy balances involving reactive systems

What happens in reactions in terms of chemical bonds?

Bonds can be formed and broken. Breaking bonds **takes** energy and forming bonds **releases** energy.

- If more energy is released in forming bonds than absorbed in breaking bonds, then the reaction is **exothermic**.
- If more energy is absorbed in breaking bonds than released in forming bonds, then the reaction is **endothermic**.

✓ Example: Chemical Bonds

Consider the simple reaction of the formation of water from hydrogen and oxygen:

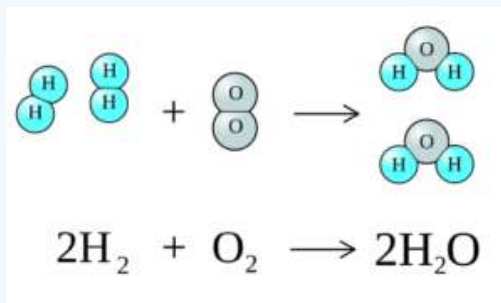
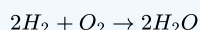


Image from すじにくシチュー / CC0

The formation of bonds takes energy while the breakage of bonds releases energy

In this reaction:

- 2 H-H bonds are broken
- 1 O-O bonds are broken
- 4 H-O bonds are formed

Heat of Reaction $\Delta H_r(T, P)$

Heat of Reaction $\Delta H_r(T, P)$: the stoichiometric enthalpy difference when reactants react completely to form products at a specified constant temperature and pressure.

$$\Delta H_r(T, P) = H_{products} - H_{reactants}$$

In **exothermic reactions**, $\Delta H_r(T, P) < 0$

- $H_{products} < H_{reactants}$

In **endothermic reactions**, $\Delta H_r(T, P) > 0$

- $H_{products} > H_{reactants}$

Heats of reaction are *directly proportional to the amount of reactants or products* in a reaction.

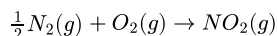
✓ Example: Formation of Nitrogen

text

Solution

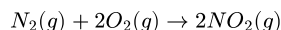
text.

Consider the formation of nitrogen dioxide



$$\Delta H_r = 33.2 kJ$$

The formation of 1 mole of NO_2 yields an enthalpy change of 33.2 kJ

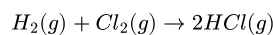


$$\Delta H_r = 66.4 kJ$$

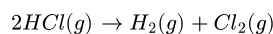
The formation of 2 moles of NO_2 yields an enthalpy change of 66.2 kJ

Heat of reactions for a reaction in the forward direction is *equal to the negative heat of reaction* for the backward reaction.

Consider the formation of hydrogen chloride (or the corresponding decomposition):



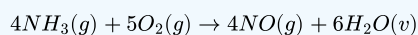
$$\Delta H_r = -184.6 kJ$$



$$\Delta H_r = +184.6 kJ$$

✓ Exercise: Heat of Reaction

Consider the oxidation of ammonia taking place in an isothermal and constant pressure reactor:



where the heat of reaction is $\Delta \hat{H}_r^\circ = -904.7 kJ$

The ammonia is fed into the reactor at $100 mol/s$ and the oxygen enters at $200 mol/s$. Assuming the limiting reactant is completely consumed, what is the enthalpy change for this reaction?

Solution

Add example text here.

Step 1: Find the limiting reactant by finding the smallest reactant extent if all of a reactant is consumed.



$$NH_3 \tag{4.3.1}$$

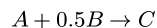
Step 2: Multiply the reaction extent by the $\Delta \hat{H}_r^\circ = -904.7 \frac{kJ}{mol NH_3}$ to obtain $\Delta \dot{H}_r$

$$\begin{aligned} \Delta \dot{H}_r &= \xi * \Delta \hat{H}_r^\circ \\ \Delta \dot{H}_r &= 25 \frac{mol}{s} * -904.7 \frac{kJ}{mol} \\ \Delta \dot{H}_r &= -22620 \frac{kJ}{s} \end{aligned}$$

Hess's Law

Some reactions may be difficult to reproduce in a laboratory setting. Instead, for analyzing a certain overall reaction, we may break the reaction down in multiple steps:

For example, say we want to find the standard heat of reaction for the following hypothetical reaction:

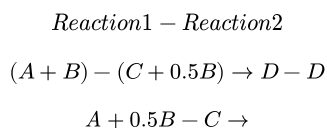


If this reaction is difficult to carry out in a laboratory, we might break it up into 2 reactions, that are easier to carry out and where we can determine specified standard heats of reaction:

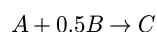
Reaction 1: $A + B \rightarrow D$ with ΔH_{rxn1}°

Reaction 2: $C + 0.5B \rightarrow D$ with ΔH_{rxn2}°

We can combine reactions 1 and 2 to obtain our desired reaction by subtracting reaction 2 from reaction 1:



We obtain our desired reaction:

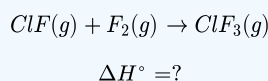


Therefore, the heat of reaction of the desired reaction will be:

$$\Delta H^\circ = \Delta H_{rxn1}^\circ - \Delta H_{rxn2}^\circ$$

✓ Exercise: Hess's Law

Consider the formation of chlorine trifluoride from chlorine monofluoride and fluorine:



Data on the following reactions are available:

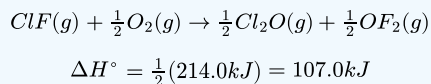
Number	Reaction	ΔH° (kJ)
1	$2OF_2(g) \rightarrow O_2(g) + 2F_2(g)$	-49.4
2	$2ClF(g) + O_2(g) \rightarrow Cl_2O(g) + OF_2(g)$	214.0
3	$ClF_3(g) + O_2(g) \rightarrow \frac{1}{2}Cl_2O(g) + \frac{3}{2}OF_2(g)$	236.2

What is the ΔH° for the desired reaction?

Solution

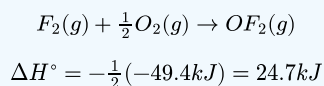
Step 1: Determine what reaction will give us ClF in the reactants.

Since $ClF(g)$ is needed as a reactant, we can multiply reaction 2 by $\frac{1}{2}$ to obtain:



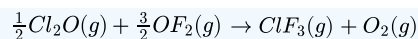
Step 2: Determine what reaction will give us F_2 in the reactants.

Since F_2 is needed as a reactant, we can multiply reaction 1 by $-\frac{1}{2}$ to obtain:



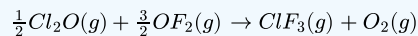
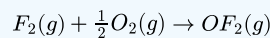
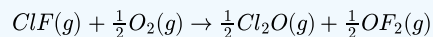
Step 3: Determine what reaction will give us ClF_3 as a product.

Since ClF_3 is needed as a product, we can multiply reaction 3 by -1 to obtain:

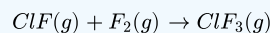


$$\Delta H^\circ = -(236.2kJ) = -236.2kJ$$

Step 4: Add the reactions up to ensure that the desired reaction is obtained:



↓ (+)



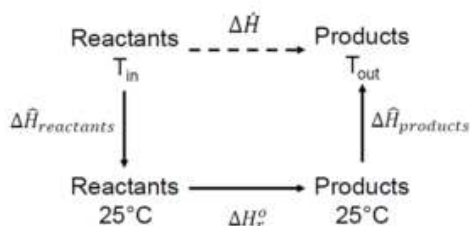
Step 5: Add up all the manipulated heat of reactions to obtain the desired ΔH°

$$\Delta H^\circ = (107.0 + 24.7 + -236.2)kJ$$

$$\Delta H^\circ = -104.5kJ$$

Heat of Reaction Method for Analyzing Energy Use in a Process

Now let's try applying the heat of reaction to determine energy use in a process, where reactants and products are coming in and exiting at a given temperature. The following process path is taken for the heat of reaction method, where the reference state is at $25^\circ C$:



Generally, ΔH_r° refers to standard state conditions at $25^\circ C$ and 1 atm, but always double-check whether a different standard state condition is used.

In this process path, the enthalpy calculations are done in three steps:

1. Temperature change: calculate the $\Delta \hat{H}_{reactants}$ using the heat capacities. The temperature change will be the difference between the inlet temperature of the reactants and the standard or reference temperature ($25^\circ C$ in this case).
2. Reaction enthalpy: calculate the enthalpy of the reaction ΔH_r° . This can be done using Hess's Law or the Heat of Formation method (discussed below).
3. Temperature change: calculate the $\Delta \hat{H}_{products}$ using the heat capacities. The temperature change will be the difference between the outlet temperature of the products and the standard or reference temperature ($25^\circ C$ in this case).

The calculated enthalpy changes for each step are then added to obtain $\Delta \hat{H}$.

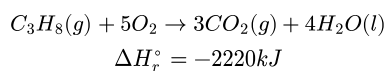
✓ Example: Heat of Reaction Method for Energy Use

text

Solution

text.

Consider a propane combustion chamber, where $100mol/s$ of propane are feed to the chamber at $25^\circ C$ and air is fed at $300^\circ C$ ($600mol/sO_2(g)$ and $2256mol/sN_2(g)$). The products stream exits at $1000^\circ C$ and consists of $100mol/sO_2(g)$, $2256mol/sN_2(g)$, $300mol/sCO_2(g)$, and $400mol/sH_2O(v)$. How much heat is released by this combustion chamber? Assuming atmosphere pressure, so water boils at $100^\circ C$.



The following information is provided:

The values listed under each compound are specific enthalpies in kJ/mol

Temperature ($^{\circ}C$)	O_2	N_2	CO_2	H_2O
25	0	0	0	0
100	2.24	2.19	2.90	2.54
300	8.47	8.12	11.58	9.57
1000	32.47	30.56	48.60	37.69

- $C_{P,l}(H_2O) = 75.4 * 10^{-3} \frac{\text{kJ}}{\text{molK}}$
- $C_{P,v}(H_2O) = 33.46 * 10^{-3} + 0.688 * 10^{-5} * T + 0.7604 * 10^{-8} * T^2 - 3.593 * 10^{-12} * T^3 (\text{J/molK})$
- $\Delta \hat{H}_{\text{vap}}(100^{\circ}C) = 40.66 \text{ kJ/mol}$

How can we solve the system's energy balance?

1 – Solve material balances as much as possible

This example already has the material balances solved

2 – Choose reference states for energy calculations. Like we say in the previous figure we want to calculate the changes in energy associated with bringing our reactants to our reference state, calculating the energy of the reaction at the reference state, and then the energy associated with bringing the products to their final state. We will choose reference states based on the information we have to try to make these calculations as easy as possible.

For reacting species:

Since ΔH_r° is given, we will assume this is at $25^{\circ}C$ and 1 atm (as there is nothing indicating otherwise), and we will use this as our reference state.

For non-reacting species:

We can use any convenient temperature and pressure as a reference state (inlet temperature, outlet temperature, temperature in enthalpy table). With this example, the enthalpy table given uses a reference state of $25^{\circ}C$, and we will assume everything is at 1 atm (as no other values for pressure are given).

3 – Calculate the extent of reaction for all reactions (in this case we just have the one reaction)

$$\xi = \frac{(\dot{n}_i)_{\text{out}} - (\dot{n}_i)_{\text{in}}}{\nu_i}$$

$$\xi = \frac{(\dot{n}_{CO_2})_{\text{out}} - (\dot{n}_{CO_2})_{\text{in}}}{\nu_{CO_2}}$$

$$\xi = \frac{300 \frac{\text{mol}}{\text{s}} - 0 \frac{\text{mol}}{\text{s}}}{3} = 100 \text{ mol/s}$$

4 – Prepare an inlet-out enthalpy table (this will show what enthalpies we need to calculate associated with energy changes in the reactants or products)

Substance	$\dot{n}_{in}(\text{mol/s})$	$\hat{H}_{in}(\text{kJ/mol})$	$\dot{n}_{out}(\text{mol/s})$	$\hat{H}_{out}(\text{kJ/mol})$
C_3H_8	100	$\hat{H}_1$	–	–
O_2	600	$\hat{H}_2$	100	$\hat{H}_4$
N_2	2256	$\hat{H}_3$	2256	$\hat{H}_5$
CO_2	–	–	300	$\hat{H}_6$
H_2O	–	–	400	$\hat{H}_7$

5 – Calculate all the enthalpies. For $\hat{H}_1$ to $\hat{H}_6$, the specific enthalpies at different temperatures are given as the difference in enthalpy from the reference state (25°C, 1atm, which is the same as what we choose as reference state):

$$\hat{H}_1 = \Delta \hat{H}_{C_3H_8}(25^\circ C \rightarrow 25^\circ C) = 0 \text{ kJ/mol}$$

$$\hat{H}_2 = \Delta \hat{H}_{O_2}(25^\circ C \rightarrow 300^\circ C) = (8.47 - 0) \text{ kJ/mol}$$

$$\hat{H}_3 = \Delta \hat{H}_{N_2}(25^\circ C \rightarrow 300^\circ C) = (8.12 - 0) \text{ kJ/mol}$$

$$\hat{H}_4 = \Delta \hat{H}_{O_2}(25^\circ C \rightarrow 1000^\circ C) = (32.47 - 0) \text{ kJ/mol}$$

$$\hat{H}_5 = \Delta \hat{H}_{N_2}(25^\circ C \rightarrow 1000^\circ C) = (30.56 - 0) \text{ kJ/mol}$$

$$\hat{H}_6 = \Delta \hat{H}_{CO_2}(25^\circ C \rightarrow 1000^\circ C) = (48.60 - 0) \text{ kJ/mol}$$

$$\hat{H}_7 = \Delta \hat{H}_{H_2O}(l, 25^\circ C \rightarrow H_2O(v, 1000^\circ C))$$

6 – For $\hat{H}_7$, the specific enthalpy for water is calculated. From the reference state of 25°C to the stream temperature of 1000°C, water is first heated to 100°C, which is its natural boiling point at 1atm, then vaporized, then heated in vapor phase to 1000°C. The enthalpy change of each process is calculated separately and added together to get $\hat{H}_7$.

Note: The T in the formulas to calculate C_P is given in kelvin. This doesn't make a difference when C_P is given as a number, as the scales for one degree of Celcius and kelvin are the same, but the temperature must be converted to kelvin when T^2 is higher power of T is used in calculation.

$$100^\circ C = 373K, 1000^\circ C = 1273K$$

$$\begin{aligned}
 \hat{H}_7 &= \int_{25^\circ C}^{100^\circ C} C_{P,l} dT + \Delta \hat{H}_{vap}(100^\circ C) + \int_{100^\circ C}^{1000^\circ C} C_{P,v} dT \\
 &= \int_{25^\circ C}^{100^\circ C} 75.4 * 10^{-3} dT + \Delta \hat{H}_{vap}(100^\circ C) \\
 &\quad + \int_{373K}^{1273K} (33.46 * 10^{-3} + 0.688 * 10^{-5} * T + 0.7604 * 10^{-8} * T^2 - 3.593 * 10^{-12} * T^3) dT \\
 &= 75.4 * 10^{-3} * (100 - 25) + 40.66 \\
 &\quad + (33.46 * 10^{-3} * T + \frac{1}{2} * 0.688 * 10^{-5} * T^2 + \frac{1}{3} * 0.7604 * 10^{-8} * T^3 \\
 &\quad - \frac{1}{4} * 3.593 * 10^{-12} * T^4) \Big|_{373K}^{1273K} \\
 &= (5.65 + 40.66 + 35.1) \text{ kJ/mol} \\
 &= 81.46 \text{ kJ/mol}
 \end{aligned}$$



Therefore, we have calculated all the specific enthalpy for the reactants and products:

Substance	$\dot{n}_{in}$ (mol/s)	$\hat{H}_{in}$ (kJ/mol)	$\dot{n}_{out}$ (mol/s)	$\hat{H}_{out}$ (kJ/mol)
C_3H_8	100	0	—	—
O_2	600	8.47	100	32.47
N_2	2256	8.12	2256	30.56
CO_2	—	—	300	48.60
H_2O	—	—	400	81.46

8 – Finally, solve the energy balance

$$\Delta\dot{H}_{in} + \Delta\dot{H}_{E,k} + \Delta\dot{H}_{E,p} = \dot{Q} + \dot{W}_{s}$$

$$\Delta\dot{E}_k \quad (4.3.2)$$

$$\dot{Q} = \Delta\dot{H}$$

$$\dot{Q} = -126MW$$

The combustion chamber releases 126MW of heat to the environment

Heat of Formation ΔH_f°

Formation Reaction: a reaction in which the compound is formed from its elemental constituents as they would normally occur in nature (eg. O_2 rather than O).

For elemental constituents, the energy of formation is $\Delta H_f^\circ = 0$, since they would be forming themselves: $O_2 \rightarrow O_2$

Standard specific heat of formation ΔH_f° : the enthalpy change associated with forming 1 mole of the compound of interest at standard temperature ($25^\circ C$) and pressure (1 atm)

Compound	Reaction	$\Delta\hat{H}_{f,i}^\circ$ (kJ/mol)
Water	$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$	-285.83
Methane	$C(s) + 2H_2(g) \rightarrow CH_4(g)$	-74.8936
Ethane	$2C(s) + 3H_2(g) \rightarrow C_2H_6(g)$	-83.82
Propane	$3C(s) + 4H_2(g) \rightarrow C_3H_8(g)$	-104.68
Benzene	$6C(s) + 3H_2(g) \rightarrow C_6H_6(l)$	82.88
Toluene	$7C(s) + 4H_2(g) \rightarrow C_7H_8(l)$	50.17
Oxygen	$O_2(g) \rightarrow O_2(g)$	0
Nitrogen	$N_2(g) \rightarrow N_2(g)$	0

We can use these heats of formation and Hess's law to find the heat of reaction for a given reaction:

$$\Delta H_r^\circ = \sum_i \nu_i \Delta\hat{H}_{f,i}^\circ = \sum_{products} |\nu_i| \Delta\hat{H}_{f,i}^\circ - \sum_{reactants} |\nu_i| \Delta\hat{H}_{f,i}^\circ$$

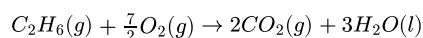
✓ Example: Heat of Formation

text

Solution

text.

Consider the combustion of ethane:



where $\Delta H_r^\circ = -1560 \text{ kJ/mol}$

To calculate the enthalpy using the heat of formation method, the following steps are taken:

$$\Delta H_r^\circ = (3 * \Delta \hat{H}_{f,H_2O}^\circ + 2 * \Delta \hat{H}_{f,CO_2}^\circ) - (1 * \Delta \hat{H}_{f,C_2H_6}^\circ + \frac{7}{2} * \Delta \hat{H}_{f,O_2}^\circ)$$

$$\Delta H_r^\circ = (3 * -285.83 + 2 * -393.51) \text{ kJ/mol} - (1 * -83.82 + \frac{7}{2} * 0) \text{ kJ/mol}$$

$$\Delta H_r^\circ = -1561 \text{ kJ/mol}$$

The enthalpy of reaction using the heat of formation method is very close to the enthalpy of reaction (combustion).

Where to find Heat of Formation Data

One source of heat of formation data is the [National Institute of Standards and Technology \(NIST\) Webbook NIST](#)

To find the heat of formation data at this site:

1 – Look up the compound of interest

2 – Heat of formation data will be under “condensed phase thermochemistry data” (for liquids or solids) or “gas phase thermochemistry data” (for gases).

Heats of formation can also be found in Appendix E of “Introductory Chemical Engineering Thermodynamics” by J. Richard Elliot and Carl T. Lira.

Heat of Formation Method for Analyzing Energy Use in a Process

1. Solve the material balance as much as possible: this can include solving for mass or molar flows using stoichiometry or mass balances
2. Choose reference states for energy calculations: reference states provide a basis for enthalpy calculations. Choose reference states that make your calculations convenient or reference states that match the available data. Most data is provided at 25°C and 1 atm, therefore this is a common reference state.
3. Prepare an inlet-outlet enthalpy table: this table will include all the compounds involved in the system, the inlet molar flow, the inlet enthalpy values, the outlet molar flow, and the outlet enthalpy values. Fill out the table with all the known values and number the enthalpy values accordingly.
4. Calculate all the enthalpies: use process paths to calculate the enthalpies listed in the table in step 3. The enthalpy change of each compound is calculated by summing the heat of formation, enthalpy change due to temperature change in the same state (which can be calculated using the C_P values), and enthalpy change due to phase change when phase change is involved.
5. Calculate the $\Delta \dot{H}$ for the system: this is done by multiplying each molar flow by the corresponding enthalpy and using the following expression. Remember that the stoichiometric coefficients are negative for reactants and positive for products: $\Delta \dot{H} = \sum \dot{n}_{out} * \hat{H}_{out} - \sum \dot{n}_{in} * \hat{H}_{in}$
6. Solve the energy balance: determine which energy terms are present in the system and solve accordingly.

✓ Example: Heat of Formation Method for Energy Use

text

Solution

text.

Let's consider the propane combustion chamber problem we analyzed before with the heat of reaction method, and let's see if we can get a similar answer using the heat of formation method.

1 – Solve the material balance as much as possible

This example already has the material balances solved

2 – Choose reference states for energy calculations

For reacting species: elemental species that make up reacting species at standard conditions; we will choose 25°C at 1 atm with $\text{C}(s)$, $\text{H}_2(g)$, and $\text{O}_2(g)$.

For non-reacting species (same as ΔH_r): Use any convenient temperature (inlet temperature, outlet temperature, temperature in enthalpy table) Here, 25°C and 1 atm works because of our enthalpy table values

3 – Prepare an inlet-outlet enthalpy table

Substance	$\dot{n}_{in}(\text{mol/s})$	$\hat{H}_{in}(\text{kJ/mol})$	$\dot{n}_{out}(\text{mol/s})$	$\hat{H}_{out}(\text{kJ/mol})$
C_3H_8	100	$\hat{H}_1$	—	—
O_2	600	$\hat{H}_2$	100	$\hat{H}_4$
N_2	2256	$\hat{H}_3$	2256	$\hat{H}_5$
CO_2	—	—	300	$\hat{H}_6$
H_2O	—	—	400	$\hat{H}_7$

4 – Calculate all the enthalpies

Substance	$\Delta H_f^\circ(\text{kJ/mol})$
C_3H_8	-103.8
O_2	0
N_2	0
CO_2	-393.51
$\text{H}_2\text{O}(v)$	-241.835

$$\hat{H}_1 = \Delta \hat{H}_{f, \text{C}_3\text{H}_8(g)}^\circ = -103.8 \text{ kJ/mol}$$

$$\hat{H}_2 = \Delta \hat{H}(\text{O}_2(25^\circ\text{C} \rightarrow 300^\circ\text{C})) = (8.47 - 0) \text{ kJ/mol}$$

$$\hat{H}_3 = \Delta \hat{H}(\text{N}_2(25^\circ\text{C} \rightarrow 300^\circ\text{C})) = (8.12 - 0) \text{ kJ/mol}$$

$$\hat{H}_4 = \Delta \hat{H}(\text{O}_2(25^\circ\text{C} \rightarrow 1000^\circ\text{C})) = (32.47 - 0) \text{ kJ/mol}$$

$$\hat{H}_5 = \Delta \hat{H}(\text{N}_2(25^\circ\text{C} \rightarrow 1000^\circ\text{C})) = (30.56 - 0) \text{ kJ/mol}$$

$$\hat{H}_6 = \Delta \hat{H}_{f, \text{CO}_2(g)}^\circ + \int_{25^\circ\text{C}}^{1000^\circ\text{C}} C_{p, \text{CO}_2(g)} dT = -344.9 \text{ kJ/mol}$$

$$\hat{H}_7 = \Delta \hat{H}_{f, \text{H}_2\text{O}(v)}^\circ + \int_{25^\circ\text{C}}^{1000^\circ\text{C}} C_{p, \text{H}_2\text{O}(v)} dT = -204.1 \text{ kJ/mol}$$

Here, you assume that water forms as vapor directly in the reaction. Therefore, there is no need to account for heat of vaporization.

Substance	$\dot{n}_{in}$ (mol/s)	$\hat{H}_{in}$ (kJ/mol)	$\dot{n}_{out}$ (mol/s)	$\hat{H}_{out}$ (kJ/mol)
C_3H_8	100	-103.8	—	—
O_2	600	8.47	100	32.47
N_2	2256	8.12	2256	30.56
CO_2	—	—	300	-344.9
H_2O	—	—	400	-204.1

5 – Calculate $\Delta\dot{H}$ for the reactor

$$\Delta\dot{H} = \sum \dot{n}_{out} * \hat{H}_{out} - \sum \dot{n}_{in} * \hat{H}_{in} = 1.26 \times 10^5 \text{ kJ/s}$$

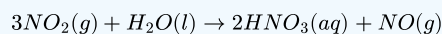
6 – Finally, solve the energy balance

$$\dot{Q} = \Delta\dot{H}$$

$$\dot{Q} = -126 \text{ MW}$$

✓ Exercise: Heat of Formation

Consider a reactor where the following reaction takes place :



$$\Delta H^\circ = ?$$

The reactor uses an 0.8 kW impeller (mixer for liquids) that mixes the reactor contents. The reaction occurs at standard temperature and pressure. A feed consisting of 100 mol/s and 300 mol/s of water and NO_2 , respectively, enters the reactor. The reaction goes to completion and the products stream consists of 200 mol/s of HNO_3 and 100 mol/s of NO .

The following heats of formation are available:

Number	Reaction	$\Delta H_{f,i}^\circ$ (kJ/mol)
1	$\frac{1}{2} N_2(g) + O_2(g) \rightarrow NO_2(g)$	33.2
2	$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$	-285.8
3	$\frac{1}{2} H_2(g) + \frac{1}{2} N_2(g) + \frac{3}{2} O_2(g) \rightarrow HNO_3(aq)$	-207.4
4	$\frac{1}{2} N_2(g) + \frac{1}{2} O_2(g) \rightarrow NO(g)$	90.2

How much heat must be removed from the reactor in one day for it to remain at standard temperature?

[Click here to see the solution!](#)

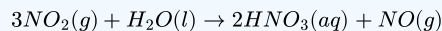
Solution

Step 1: Determine what combination of the given reactions will give the desired reaction (Hess's Law)

For this desired reaction:

$$\begin{aligned}
 &- 3 * \text{Reaction1} \\
 &- 1 * \text{Reaction2} \\
 &+ 2 * \text{Reaction3} \\
 &+ 1 * \text{Reaction4}
 \end{aligned}$$

Summing all the reactions above yields:



Step 2: Add all the individual reaction enthalpies:

$$\begin{aligned}
 \Delta H_r^\circ &= -3 * \Delta H_1^\circ - 1 * \Delta H_2^\circ + 2 * \Delta H_3^\circ + \Delta H_4^\circ \\
 \Delta H_r^\circ &= -3 * 33.2 \text{ kJ/mol} - 1 * -285.8 \text{ kJ/mol} + 2 * -207.4 \text{ kJ/mol} + 90.2 \text{ kJ/mol} \\
 \Delta H_r^\circ &= (-99.6 + 285.8 - 414.8 + 90.2) \text{ kJ/mol} = -138.4 \text{ kJ/mol}
 \end{aligned}$$

Step 3: Calculate the overall change in enthalpy using the extent of the reaction:

$$\begin{aligned}
 \xi &= \frac{|(\dot{n}_i)_{out} - (\dot{n}_i)_{in}|}{|\dot{V}_i|} \text{ hat} \\
 &= \frac{|(\dot{n}_{\text{H}_2\text{O}})_{out} - (\dot{n}_{\text{H}_2\text{O}})_{in}|}{|\dot{V}_{\text{H}_2\text{O}}|} \\
 &= \frac{|0 \frac{\text{mol}}{\text{s}} - 100 \frac{\text{mol}}{\text{s}}|}{|-1|} \\
 &= 100 \text{ mol/s} \\
 \Delta \dot{H} &= \xi * \Delta H_r^\circ \\
 \Delta \dot{H} &= 100 \frac{\text{mol}}{\text{s}} * -138.4 \frac{\text{kJ}}{\text{mol}} = -138400 \frac{\text{kJ}}{\text{s}}
 \end{aligned}$$

Step 4: Calculate how much work is done on the reactor by the impeller in one day:

$$\begin{aligned}
 W_s &= 0.8 \frac{\text{kJ}}{\text{s}} * 3600 \frac{\text{s}}{\text{hr}} * 24 \text{ hr} \\
 W_s &= 69120 \text{ kJ}
 \end{aligned}$$

Step 5: Perform an energy balance on the reactor

$$\begin{aligned}
 \dot{Q} &= \Delta H^\circ - W_s \\
 \dot{Q} &= (-138400 - 69120) \text{ kJ} = -207520 \text{ kJ}
 \end{aligned}$$

Solution

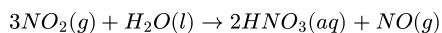
Add example text here.

Step 1: Determine what combination of the given reactions will give the desired reaction (Hess's Law)

For this desired reaction:

$$\begin{aligned}
 &- 3 * \text{Reaction1} \\
 &- 1 * \text{Reaction2} \\
 &+ 2 * \text{Reaction3} \\
 &+ 1 * \text{Reaction4}
 \end{aligned}$$

Summing all the reactions above yields:



Step 2: Add all the individual reaction enthalpies:

$$\begin{aligned}
 \Delta H_r^\circ &= -3 * \Delta H_1^\circ - 1 * \Delta H_2^\circ + 2 * \Delta H_3^\circ + \Delta H_4^\circ \\
 \Delta H_r^\circ &= -3 * 33.2 \text{ kJ/mol} - 1 * -285.8 \text{ kJ/mol} + 2 * -207.4 \text{ kJ/mol} + 90.2 \text{ kJ/mol} \\
 \Delta H_r^\circ &= (-99.6 + 285.8 - 414.8 + 90.2) \text{ kJ/mol} = -138.4 \text{ kJ/mol}
 \end{aligned}$$

Step 3: Calculate the overall change in enthalpy using the extent of the reaction:

$$\begin{aligned}\xi &= \frac{|(\dot{n}_i)_{out} - (\dot{n}_i)_{in}|}{|(\dot{V}_i)|} \text{ hat} \\ &= \frac{|(\dot{n}_{H_2O})_{out} - (\dot{n}_{H_2O})_{in}|}{|(\dot{V}_{H_2O})|} \\ &= \frac{|0 \frac{\text{mol}}{\text{s}} - 100 \frac{\text{mol}}{\text{s}}|}{|-1|} \\ &= 100 \text{ mol/s}\end{aligned}$$

$$\Delta \dot{H} = \xi * \Delta H_r^\circ$$

$$\Delta \dot{H} = 100 \frac{\text{mol}}{\text{s}} * -138.4 \frac{\text{kJ}}{\text{mol}} = -138400 \frac{\text{kJ}}{\text{s}}$$

Step 4: Calculate how much work is done on the reactor by the impeller in one day:

$$W_s = 0.8 \frac{\text{kJ}}{\text{s}} * 3600 \frac{\text{s}}{\text{hr}} * 24 \text{ hr}$$

$$W_s = 69120 \text{ kJ}$$

Step 5: Perform an energy balance on the reactor

$$\dot{Q} = \Delta H^\circ - W_s$$

$$\dot{Q} = (-138400 - 69120) \text{ kJ} = -207520 \text{ kJ}$$

Summary of Heat of Reaction and Formation Methods

Heat of Reaction Method

$$\Delta \dot{H} = \xi \Delta \dot{H}_r^\circ + \Sigma \dot{n}_{out} * \hat{H}_{out} - \Sigma \dot{n}_{in} * \hat{H}_{in}$$

where $\hat{H}_i = \int_{T_{ref}}^T C_P dT$ assuming there are no phase changes

If a phase change occurs, an additional heat term (i.e. heat of vapourization) will be added to the $\hat{H}_i$ term in both methods

$$\Delta \dot{H} = \xi \Delta \dot{H}_r + \Sigma \dot{n}_{out} * \int_{T_{ref}}^{T_{out}} C_P dT - \Sigma \dot{n}_{in} * \int_{T_{ref}}^{T_{in}} C_P dT$$

Heat of Formation Method

$$\Delta \dot{H} = \Sigma \dot{n}_{out} * \hat{H}_{out} - \Sigma \dot{n}_{in} * \hat{H}_{in}$$

where $\hat{H}_i = \hat{H}_{f,i}^\circ + \int_{T_{ref}}^T C_P dT$ assuming there are no phase changes

$$\Delta \dot{H} = \Sigma \dot{n}_{out} * (\hat{H}_{f,i}^\circ + \int_{T_{ref}}^{T_{out}} C_P dT) - \Sigma \dot{n}_{in} * (\hat{H}_{f,i}^\circ + \int_{T_{ref}}^{T_{in}} C_P dT)$$

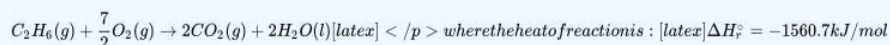
For the same system, equating $\Delta \dot{H}$ for both methods, we can see that the C_P terms cancel. We obtain the following:

$$\xi \Delta \dot{H}_r^\circ = \Sigma \dot{n}_{out} * \hat{H}_{f,i}^\circ - \Sigma \dot{n}_{in} * \hat{H}_{f,i}^\circ$$

Overall, the final $\Delta \dot{H}$ for both methods will be the **same**. This means we can choose either method based on which is easiest to use with the information we have available.

✓ Exercise: Comparing Both Methods

Ethane and oxygen are fed into a furnace at 100 kmol/hr and 500 kmol/hr, respectively. Ethane goes through complete combustion in the furnace. Oxygen, carbon dioxide, and water exit the furnace at 150 kmol/hr, 200 kmol/hr, and 300 kmol/hr, respectively.



The following data on heats of formations is available:

Compound	$\Delta H_{f,i}^\circ$ (kJ/mol)
Ethane	-83.82
Oxygen	0
Carbon Dioxide	-393.51
Water (liquid)	-285.83

Assume the reaction takes place in the furnace at standard temperature and pressure. What is the ΔH° for the desired reaction? Calculate the change in enthalpy using both the heat of reaction and heat of formation method

Solution

Add example text here.

Heat of Reaction Method

Step 1: Determine the extent of the reaction:

$$\begin{aligned}\xi &= \frac{|\dot{n}_i|_{out} - |\dot{n}_i|_{in}}{|\dot{\nu}_i|} \text{ hat} \\ &= \frac{|\dot{n}_{C_2H_6}|_{out} - |\dot{n}_{C_2H_6}|_{in}}{|\dot{\nu}_{C_2H_6}|} \\ &= \frac{|0 \frac{\text{kmol}}{\text{hr}} - 100 \frac{\text{kmol}}{\text{hr}}|}{|-1|} \\ &= 100 \text{ kmol/hr}\end{aligned}$$

Step 2: Multiply the extent of the reaction by the heat of reaction for combustion

$$\begin{aligned}\Delta \dot{H} &= \xi * \Delta H_r^\circ \\ \Delta \dot{H} &= 100 \frac{\text{kmol}}{\text{hr}} * -1560.7 \frac{\text{kJ}}{\text{mol}} * 1000 \frac{\text{mol}}{\text{kmol}} \\ \Delta \dot{H} &= -156 \text{ MJ/hr}\end{aligned}$$

Heat of Formation Method

Step 1: Set up the heat of formation formula

$$\begin{aligned}\Delta \dot{H} &= \sum \dot{n}_{out} * \hat{H}_{out} - \sum \dot{n}_{in} * \hat{H}_{in} \\ \Delta \dot{H} &= (\dot{n}_{out,ethane} * \hat{H}_{ethane}) + (\dot{n}_{out,oxygen} * \hat{H}_{oxygen}) + (\dot{n}_{out,water} * \hat{H}_{water}) + (\dot{n}_{out,carbondioxide} * \hat{H}_{carbondioxide}) - (\dot{n}_{in,ethane} * \hat{H}_{ethane}) \\ &\quad + (\dot{n}_{in,oxygen} * \hat{H}_{oxygen}) + (\dot{n}_{in,water} * \hat{H}_{water}) + (\dot{n}_{in,carbondioxide} * \hat{H}_{carbondioxide})\end{aligned}$$

Step 2: Plug in the enthalpies of formation and calculate the change in enthalpy

Compound	n_{in} (kmol/hr)	n_{out} (kmol/hr)
Ethane	100	0
Oxygen	500	150
Carbon Dioxide	0	200
Water	0	300

$$\begin{aligned}\Delta \dot{H} &= ((0 \frac{\text{kmol}}{\text{hr}} * -83.82 \frac{\text{kJ}}{\text{mol}}) + (150 \frac{\text{kmol}}{\text{hr}} * 0 \frac{\text{kJ}}{\text{mol}}) + (200 \frac{\text{kmol}}{\text{hr}} * -393.51 \frac{\text{kJ}}{\text{mol}}) + (300 \frac{\text{kmol}}{\text{hr}} * -285.83 \frac{\text{kJ}}{\text{mol}}) - (100 \frac{\text{kmol}}{\text{hr}} * -83.82 \frac{\text{kJ}}{\text{mol}}) \\ &\quad - (500 \frac{\text{kmol}}{\text{hr}} * 0 \frac{\text{kJ}}{\text{mol}}) - (0 \frac{\text{kmol}}{\text{hr}} * -393.51 \frac{\text{kJ}}{\text{mol}}) - (0 \frac{\text{kmol}}{\text{hr}} * -285.83 \frac{\text{kJ}}{\text{mol}})) * 1000 \frac{\text{mol}}{\text{kmol}} \\ \Delta \dot{H} &= -150 \text{ MJ}\end{aligned}$$

Notice that the methods aren't exactly equal. This is due to slight differences in available enthalpy data and assumptions made regarding temperature

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4.4: Energy Balances Review

Important Equations

Kinetic Energy	$E_k = \frac{1}{2}mu^2 \quad (4.4.1)$ $\dot{E}_k = \frac{1}{2}\dot{m}u^2 \quad (4.4.2)$
Potential Energy	$E_p = mgz \quad (4.4.3)$ $\dot{E}_p = \dot{m}gz \quad (4.4.4)$
Flow Work	$\dot{W}_{fl} = \dot{W}_{fl-in} - \dot{W}_{fl-out} = P_{in}\dot{V}_{in} - P_{out}\dot{V}_{out}$
Steady-state Open System Energy Balance	$\dot{Q} + \dot{W} = \sum_{out}\dot{E}_j - \sum_{in}\dot{E}_j \quad (4.4.5)$ $\dot{Q} + \dot{W}_s = \Delta\dot{H} + \Delta\dot{E}_k + \Delta\dot{E}_p \quad (4.4.6)$
Enthalpy	$\hat{H} = \hat{U} + P\hat{V} \quad (4.4.7)$ $\Delta\hat{H} = \sum_i\Delta\hat{H}_i \quad (4.4.8)$
Heat Capacity (closed system)	$C_V(T) = \left(\frac{\delta\hat{U}}{\delta T}\right)_V$
Internal Energy (closed system)	$d\hat{U} = C_V(T)dT$ $\Delta\hat{U} = \int_{T_1}^{T_2} C_V dT \quad (4.4.9)$
Heat Capacity (open system)	$C_P(T) = \left(\frac{\delta\hat{H}}{\delta T}\right)_P$
Enthalpy (open system)	$\Delta\hat{H} = \int_{T_1}^{T_2} C_P dT$
Heat of Reaction Method	$\Delta\dot{H} = \xi\Delta\dot{H}_r + \sum\dot{n}_{out} * \int_{T_{ref}}^{T_{out}} C_P dT - \sum\dot{n}_{in} * \int_{T_{ref}}^{T_{in}} C_P dT$
Heat of Formation Method	$\xi\Delta\dot{H}_r^\circ = \sum\dot{n}_{out} * \hat{H}_{f,i}^\circ - \sum\dot{n}_{in} * \hat{H}_{f,i}^\circ$

Terms to Know

An interactive or media element has been excluded from this version of the text. You can view it online here:

<https://pressbooks.bccampus.ca/chbe220/?p=1783>

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4.5: Practice Exercises

Multiple Choice Questions

✓ Exercise: Endothermic Energy Balance

Consider a reactor in which an endothermic reaction takes place and 15.8 kJ are absorbed. A mixer is used in the reactor and provides 6.3 kJ of work on the system. What is the overall heat that needs to be provided to the system?

- a. -22.1 kJ
- b. 9.5 kJ
- c. 22.1 kJ
- d. -9.5 kJ

Solution

b) 9.5 kJ

Performing an energy balance on the system, we know that $\Delta H = Q + W$. Since this is an endothermic reaction and work is done on the system, both the enthalpy of the reaction and the work are positive:

$$\begin{aligned} Q &= \Delta H - W \\ &= 15.8 \text{ kJ} - 6.3 \text{ kJ} \\ &= 9.5 \text{ kJ} \end{aligned}$$

✓ Exercise: Heat Capacity

A heat exchanger heats methanol from 25°C to 100°C at a pressure of 1 atm. The methanol is entering and exiting the heat exchanger at a molar flow rate of 500 mol/s. The following data is available:

Cp (liquid) [J/molK]	80
Cp (vapour) [J/molK]	40
Heat of Vapourization [kJ/mol]	40
Normal Boiling Point Temperature [$^\circ\text{C}$]	65

What is the rate of change in enthalpy for the heat exchange?

- a. 22.3 MW
- b. 2.3 MW
- c. 2.3 kW
- d. 22.3 kW

Solution

a) 22.3 MW

Recall that $\Delta \dot{H} = \dot{n} \int_{T_1}^{T_2} Cp dT$. We can expand this expression in order to include phase changes:

$$\Delta \dot{H} = \dot{n} \left(\int_{T_1}^{T_{\text{boiling}}} Cp(\text{liquid}) dT + \Delta H_{\text{vap}} + \int_{T_{\text{boiling}}}^{T_2} Cp(\text{vapour}) dT \right) \quad (4.5.1)$$

Plugging in our values, we get:

$$\Delta \dot{H} = (500 \text{ mol/s}) \left(\int_{25^\circ\text{C}}^{65^\circ\text{C}} 80 \text{ J/molK} dT + 40,000 \text{ J/mol} + \int_{65^\circ\text{C}}^{100^\circ\text{C}} 40 \text{ J/molK} dT \right)$$

$$\Delta \dot{H} = (500 \text{ mol/s}) (80 \text{ J/molK} (65 - 25) \text{ K} + 40,000 \text{ J/mol} + 40 \text{ J/molK} (100 - 65) \text{ K})$$

$$\Delta \dot{H} = (500 \text{ mol/s}) (44,600 \text{ J/mol})$$

$$\Delta \dot{H} = 22,300,000 \text{ J/s} = 22,300,000 \text{ W} = 22.3 \text{ MW}$$

✓ Exercise: Utilities

We have the following utility options for heating toluene from 10°C to 60°C .

Utility	Inlet T($^\circ\text{C}$)	Outlet T($^\circ\text{C}$)	Cost (\$/GJ)
Cooling Water	20	25	0.378
Refrigerated Water	5	15	4.77
Low-pressure Steam	125	124	4.54
Medium-pressure Steam	175	174	4.77

Which utility would be the best option for this scenario?

- Cooling water
- Refrigerated water
- Low-pressure steam
- medium-pressure steam

Solution

c) Low-pressure steam

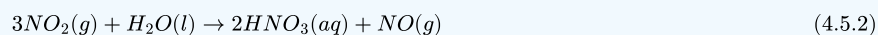
A minimum of 10°C of difference in temperature is required for efficient heat exchange.

The cooling and refrigerated water are not hot enough to heat the toluene. Both the low and medium pressure steam are hot enough to heat the toluene to 60°C , but low-pressure steam is the cheaper option.

Short Answer Questions

✓ Exercise: Hess's Law

Consider the following desired reaction:

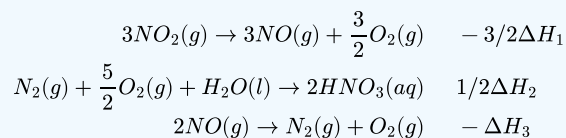


Express the enthalpy change of the desired reaction using the following reactions' enthalpies:

- Reaction 1: $2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)$ with ΔH_1
- Reaction 2: $2\text{N}_2(g) + 5\text{O}_2(g) + 2\text{H}_2\text{O}(l) \rightarrow 4\text{HNO}_3(aq)$ with ΔH_2
- Reaction 3: $\text{N}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}(g)$ with ΔH_3

Solution

Using Hess's Law we can multiply reaction 1 by $-3/2$, reaction 2 by $1/2$, and reaction 3 by -1 to obtain our desired reaction:

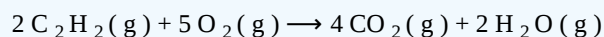


Therefore, our change in enthalpy can be represented by:



✓ Exercise: Heat of Formation

Consider the combustion of acetylene. Find the enthalpy of combustion using the heats of formation at 25°C:



Compound	ΔH_f° (kJ/mol)
$\text{C}_2\text{H}_2(\text{g})$	226.7
$\text{O}_2(\text{g})$	0
$\text{CO}_2(\text{g})$	-393.5
$\text{H}_2\text{O}(\text{g})$	-241.8

Solution

Recall that

$$\Delta H_r^\circ = \sum_i \nu_i \Delta \hat{H}_{f,i}^\circ = \sum_{\text{products}} |\nu_i| \Delta \hat{H}_{f,i}^\circ - \sum_{\text{reactants}} |\nu_i| \Delta \hat{H}_{f,i}^\circ \quad (4.5.3)$$

Using the data provided and the reaction's stoichiometry:

$$\Delta H_r^\circ = 4 \text{mol}(-393.5 \text{kJ/mol}) + 2 \text{mol}(-241.8 \text{kJ/mol}) - 2 \text{mol}(226.7 \text{kJ/mol}) - 5 \text{mol}(0 \text{kJ/mol})$$

$$\Delta H_r^\circ = -2511 \text{kJ} \quad (4.5.4)$$

✓ Exercise: Process Paths

You have a feed stream of methanol at 1 atm and 25°C. You'd like to bring it to a temperature of 100°C so that it enters a reactor as a gas. The boiling point of methanol is 65°C at 1 atm. What process path (with enthalpy changes) can you take to achieve this change and calculate the overall enthalpy?

Solution

The following steps can be taken to calculate the overall change in enthalpy of going from liquid methanol at 1 atm and 25°C to gas methanol at 1 atm and 100°C.

1. Enthalpy change from 25°C to 65°C using the liquid state heat capacity of methanol
2. Heat of vapourization of methanol at a constant temperature of 65°C
3. Enthalpy change from 65°C to 100°C using the gas state heat capacity of methanol

The enthalpy change of the process will be the sum of steps 1-3.

Long Answer Questions

✓ Exercise: Energy Balance on Heat Exchanger

A heat exchanger uses superheated steam to heat up a stream of pure benzene at 1 MPa.



The heat capacity of benzene can be represented using the following expression:

$$C_p = A + BT + CT^2 + DT^3 \quad (4.5.5)$$

where T is in K and C_p is given in J/mol K.

	A	B	C	D
Benzene	-6.211	5.65×10^{-1}	-3.141×10^{-4}	0

The enthalpy change for steam can be found using data from the steam table:

	300°C, 0.1 MPa	350°C, 0.1 MPa
$\hat{H}$ (kJ/kg)	3074.5	3175.8

The benzene's boiling point temperature is 80.1°C at 1 atm, and its heat of vaporization is 30.765 kJ/mol.

Does the benzene vapourize in the heat exchanger? What is the final temperature of the benzene exiting the heat exchanger? Assume there is no energy loss due to heat transfer.

Solution

Because there are no other forms of energy transfer other than the heat transfer between the streams, the energy balance simplifies to:

$$\Delta \dot{H}_{water} + \Delta \dot{H}_{acetic\ acid} = 0 \quad (4.5.6)$$

The enthalpy change for steam $\Delta \dot{H}$ in the energy balance can be expanded to:

$$\Delta \dot{H}_{water} = \dot{H}_f - \dot{H}_i \quad (4.5.7)$$

$$\begin{aligned} \Delta \dot{H}_{benzene} &= \int_{T_i}^{T_f} C_p dT \\ &= \int_{T_i}^{T_f} A + BT + CT^2 + DT^3 dT \\ &= AT + \frac{1}{2}BT^2 + \frac{1}{3}CT^3 + \frac{1}{4}DT^4 \Big|_{T_i}^{T_f} \\ &= A(T_f - T_i) + \frac{1}{2}B(T_f - T_i)^2 + \frac{1}{3}C(T_f - T_i)^3 + \frac{1}{4}D(T_f - T_i)^4 \end{aligned}$$

Step 1: Input given information that will be used in the calculation. This includes the given data to calculate enthalpy change, the molar flow rate of both substances, molecular weights, and the initial temperature of the benzene stream.

A	B	C	D	E	F	G	H	I	J
Cp Constants						Molecular Weight			
Benzene	A	B	C	D		Benzene	78.11	g/mol	kg/kmol
	-6.211	0.565	-0.0003343	0		Water	18	g/mol	kg/kmol
Water	H	300°C	350°C						
	(kJ/kg)	3074.5	3175.8						
	(kJ/kmol)	55381	57168.4						
	Benzene	Water							
Flow (kmol/min)	50	10							
Ti (K)	293	623							
Tf (K)		573							

LINEST $\rightarrow$ $=\text{G1}*\text{B13-B12}+\text{C12}*\text{B13-B12}*\text{C13}*\text{B13-B12}*\text{C13}$

	A	B	C	D	E	F	G	H	I	J
1		Cp Constants					Molecular Weight			
2	Benzene	A	B	C	D		Benzene	78.11	g/mol	kg/mol
3		-4.211	0.565	-0.0009142			Water	18	g/mol	kg/mol
4										
5										
6										
7	Water	H	300 °C	350 °C						
8		(J/kg)	3074.3	3173.8						
9		(kJ/kmol)	35541	37164.4						
10										
11		Benzene	Water							
12	Flow (kmol/min)		50	110						
13	Ti (K)		295	623						
14	Tf (K)		400	573						
15	ΔH (kJ/kmol)		23517853	1822.4						

1	Cp Constants					Molecular Weight				
2	Benzene	A	B	C	D		Benzene	78.11	g/mol	kg/kmol
3			-2.213	0.565	-0.0003141		Water	18	g/mol	kg/kmol
4										
5										
6										
7	Water	H	300 °C	350 °C						
8		(kJ/kg)	3074.3	3175.9						
9		(kJ/kmol)	55341	57164.4						
10										
11		Benzene	Water							
12	Flow (kmol/min)		50	10						
13	T (K)		293	623						
14	H (K)		400	573						
15	ΔH (kJ/kmol)		3443	303498	-428.08					

Step 3: Calculate the total enthalpy change for both substances by multiplying the molar flow rate by the molar enthalpy change.

	A	B	C	D	E	F	G	H	I	J	
1	Cp Constants						Molecular Weight				
2	Benzene	A	B	C	D		Benzene	78.11	g/mol	kg/mol	
3		-6.211	0.265	-0.0003242	0		Water	18	g/mol	kg/mol	
4											
5											
6											
7											
8	Water	H	300 °C	350 °C							
9		(kJ/kg)	3074.5	3175.9							
10		(kJ/kmol)	55241	57284.4							
11											
12											
13											
14											
15											
16											
17											
18											
19											
20											
21	Flow (kmol/min)	50									
22	Ti (K)	293	623								
23	Tf (K)	400	573								
24	ΔH (kJ/kmol)	2441.302688	-1812.4								
25	QH (kJ/min)	-812.912	18238								

Step 4: Use a cell to represent the sum of enthalpy change. If we have guessed the correct final temperature, the value of this cell should be 0. We will use Solver to let excel perform the guess-and-check process for us.

LINEST =SUM(B5:C15)

C ₂ Constants				Molecular Weight		
	A	B	C	D		
Benzene	-0.211	0.540	0.000342	0	Benzene	78.11 g/mol kg/kmol
Water					Water	18 g/mol kg/kmol

	H	300 °C	350 °C
Water		8074.5	3175.8
	(kJ/kg)		
	(kJ/kmol)	55341	57364.6

	Benzene	Water
Flow (kmol/min)	30	10
T (K)	293	622
T (°C)	490	573
ΔH (kJ/kmol)	2441, 502498	-5823.4
ΔH (kJ/min)	332205, 1249	-1823.9
Sum ΔH (kJ/min)	=SUM(B5:C15)	

Step 5: Select “Solver” from the “Data” menu in the header, and indicate that we want to solve for the final temperature of benzene that makes our sum of $\Delta H = 0$:

- Set objective to be the cell containing sum of ΔH
- To: value of 0
- By changing variable cells containing the final temperature of benzene
- Click “Solve”

Step 6: Click “OK” if Solver finds a solution. If the solver cannot find a solution, it is maybe because our initial guess is too far away from the actual final temperature, if so, we can change the temperature and try to solve it again.

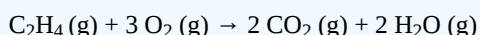
Step 7: After the window closes, the value of the final temperature of benzene and all cells affected by that temperature are changed to the corresponding values calculated with the actual final temperature.

	A	B	C	D	E	F	G	H	I	J
1		Cp Constants					Molecular Weight			
2	Benzene	A	B	C	D		Benzene	78.11	g/mol	kg/kmol
3			-6.211	0.965	-0.0003141		Water	18	g/mol	kg/kmol
4										
5										
6	Water	H		300°C	350°C					
7		(kJ/kg)		3074.5	3175.8					
8		(kJ/kmol)		55341	57104.4					
9										
10										
11	Flow (kmol/min)			50	10					
12	Ti (K)			298	623					
13	Tf (K)			342.1479888	373					
14	ΔH (kJ/kmol)			3046.790821	-1823.4					
15	ΔH (kJ/min)			18233.85411	-1823.4					
16	Sum ΔH (kJ/min)			-0.045894253						

Therefore, the final temperature of the benzene stream is 342.1K, which is equal to 69.1°C. This temperature is lower than the boiling temperature of benzene at 1 atm, so the stream will not start to vapourize.

✓ Exercise: Heat of Combustion of Ethylene

Consider the combustion of ethylene:



The enthalpy of combustion can be determined using the enthalpies of the following reactions:

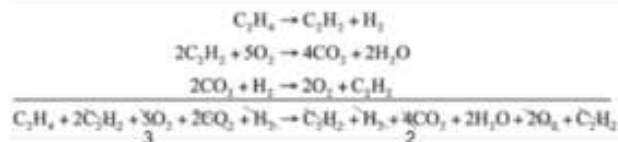
- Reaction 1: $\text{C}_2\text{H}_2 + \text{H}_2 \rightarrow \text{C}_2\text{H}_4 \Delta H_{r1} = -174.19 \text{ kJ}$
- Reaction 2: $2 \text{C}_2\text{H}_2 + 5 \text{O}_2 \rightarrow 4 \text{CO}_2 + 2 \text{H}_2\text{O} \Delta H_{r2} = -2511 \text{ kJ}$
- Reaction 3: $2 \text{CO}_2 + \text{H}_2 \rightarrow 2 \text{O}_2 + \text{C}_2\text{H}_2 \Delta H_{r3} = 1013.7 \text{ kJ}$

Determine the enthalpy of the combustion of ethylene from reactions 1, 2, and 3 using Hess’s Law at standard temperature and pressure.

Solution

Step 1: Determine the combination of reactions that will give us the desired combustion reaction.

We know that we need C_2H_4 in the reactants, so we multiply reaction 1 by -1. We notice that by adding the other 2 reactions to reaction 1 (multiplied by -1), we get our desired reaction:



Step 2: Calculate the heat of combustion from the reaction enthalpies.

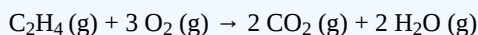
$$\Delta H^\circ = -1 * \Delta H_{r1}^\circ + \Delta H_{r2}^\circ + \Delta H_{r3}^\circ \quad (4.5.8)$$

$$\Delta H^\circ = -1 * (-174.19 kJ) + (-2511 kJ) + 1013.7 kJ \quad (4.5.9)$$

$$\Delta H^\circ = -1323.11 kJ \quad (4.5.10)$$

✓ Exercise: Enthalpy of Formation of Ethylene Combustion

Consider the combustion of ethylene:



Using the enthalpies of formation listed below, determine the enthalpy of combustion for ethylene at standard temperature and pressure. Compare the enthalpy of combustion to the one found in the previous exercise found using Hess's Law.

Compound	ΔH_f° (kJ/mol)
$C_2H_2(g)$	226.7
$C_2H_4(g)$	52.51
$O_2(g)$	0
$CO_2(g)$	-393.5
$H_2O(g)$	-241.8
$H_2(g)$	0

Solution

Step1: Calculate the enthalpy of reaction for each of the reactions using the enthalpy of formation of the reactants and products.

$$\Delta H_r^\circ = \sum_i \nu_i \Delta \hat{H}_{f,i}^\circ = \sum_{products} |\nu_i| \Delta \hat{H}_{f,i}^\circ - \sum_{reactants} |\nu_i| \Delta \hat{H}_{f,i}^\circ \quad (4.5.11)$$

Step2: Compare the calculated enthalpy of combustion using heats of formation to the enthalpy of combustion using Hess's Law from the previous exercise.

They are both equal to -1323.11 kJ!

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CHAPTER OVERVIEW

5: Unsteady-state Operations and Process Control

- [5.1: Introduction to Unsteady-state Operations](#)
- [5.2: Separable Differential Equations](#)
- [5.3: Non-separable Differential Equations](#)
- [5.4: Process Control](#)
- [5.5: Unsteady-state Operations and Process Control Review](#)
- [5.6: Practice Exercises](#)

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5.1: Introduction to Unsteady-state Operations

Learning Objectives

By the end of this section, you should be able to:

- **Recognize** unsteady-state balance systems

Derive material balance equations

Introduction to Unsteady-State Balances

Unsteady-State: in unsteady-state processes, mass and energy in the system are changing with time (not constant).

Understanding and modeling these systems allow us to:

- Control system variables by adjusting parameters
- Predict the system's behavior during start-up and shutdown

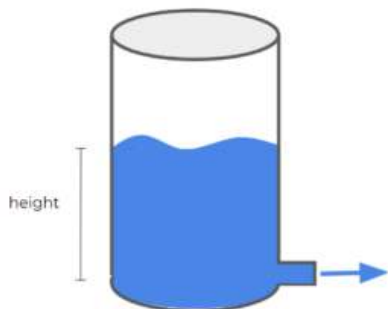
✓ Example: Draining Tank

text

Solution

text.

Consider the following draining tank:



This tank demonstrates a very simple unsteady-state system. Taking the tank as our system of interest, as the water drains from the tank, the system's overall mass changes. The height of the liquid in the tank also changes as the liquid drains out of the tank.

General Balance Equation

To characterize systems (generally process units), we can do a balance on any quantity (total mass, energy, moles, etc.). For this class, we will focus on mass, energy, and mole balances, but we could do these balances on any quantity.

$$Input - Output + Generation - Consumption = Accumulation \quad (5.1.1)$$

- Input: Enters through the system boundaries (*IN*)
- Output: Exits through the system boundaries (*OUT*)
- Generation: Produced in the system (*GEN*)
- Consumption: Consumed in the system (*CON*)
- Accumulation: Build-up or overall loss in the system (*ACC*)

Note that the generation and consumption terms are often associated with chemical reactions

$$IN - OUT + GEN - CON = ACC \quad (5.1.2)$$

✓ Exercise: Balance Terms

Consider a reactor with continuous inlet and exit streams. A reaction occurs in the reactor that is first order:



The inlet stream only contains species A and the reaction goes to completion in the reactor. The reactor is initially filled entirely with A. What terms in the following expression are considered (i.e. non-zero) for this system when assessing the moles of species A as the reaction starts occurring?

$$IN - OUT + GEN - CON = ACC \quad (5.1.4)$$

Solution

Add example text here.

Since the reaction goes to completion in the reactor, there is no A exiting in the outlet stream. Therefore, *OUT* will be omitted from the expression. This reaction is a non-reversible reaction, so no A is generated in the system ($GEN = 0$). All the other terms are present, A is fed in (*IN*), A is consumed or reacted (*CON*) and the amount of A in the reactor will change with time as B is produced (*ACC*).

$$IN - CON = ACC \quad (5.1.5)$$

Because we start with a reactor filled with A initially, the moles of A decreases in the reactor during start-up, and approaches a steady-state, as shown in the image below. The change in moles of A in the reactor represents the *ACC* term in the balance.

Transient Balances

Transient balances are any balances that where some quantities involved in the balance are functions with time. If we have a continuous process, we can analyze what happens to a given quantity for a given change in time Δt . As an example, let's take the mass of a given species (we'll call species A) to be our quantity of interest:

$$IN - OUT + GEN - CON = ACC \quad (5.1.6)$$

$$\dot{m}_{in,A} * \Delta t - \dot{m}_{out,A} * \Delta t + \dot{r}_{gen,A} * \Delta t - \dot{r}_{con,A} * \Delta t = \Delta M_A \quad (5.1.7)$$

Where:

- $\dot{m}_{in,A}$, $\dot{m}_{out,A}$ are the mass flows in and out of the system of species A
- $\dot{r}_{gen,A}$, $\dot{r}_{con,A}$ are the rates of generation and consumption of A in the system
- M_A is the total mass of A in the system at a given time

If we want to turn this into a differential balance, we will isolate Δt and let it approach to 0 (just like in calculus classes):

$$\dot{m}_{in,A} * \Delta t - \dot{m}_{out,A} * \Delta t + \dot{r}_{gen,A} * \Delta t - \dot{r}_{con,A} * \Delta t = \Delta M_A \quad (5.1.8)$$

$$(\dot{m}_{in,A} - \dot{m}_{out,A} + \dot{r}_{gen,A} - \dot{r}_{con,A}) * \Delta t = \Delta M_A \quad (5.1.9)$$

$$(\dot{m}_{in,A} - \dot{m}_{out,A} + \dot{r}_{gen,A} - \dot{r}_{con,A}) = \frac{\Delta M_A}{\Delta t} \quad (5.1.10)$$

$$(\dot{m}_{in,A} - \dot{m}_{out,A} + \dot{r}_{gen,A} - \dot{r}_{con,A}) = \frac{dM_A}{dt} \quad (5.1.11)$$

We can multiply dt on both sides, and take the integral of each term to calculate the change of each term over time:

$$\dot{m}_{in,A} dt - \dot{m}_{out,A} dt + \dot{r}_{gen,A} dt - \dot{r}_{con,A} dt = dM_A \quad (5.1.12)$$

$$\int_{t_i}^{t_f} \dot{m}_{in,A} dt - \int_{t_i}^{t_f} \dot{m}_{out,A} dt + \int_{t_i}^{t_f} \dot{r}_{gen,A} dt - \int_{t_i}^{t_f} \dot{r}_{con,A} dt = \int_{M_i}^{M_f} dM_A \quad (5.1.13)$$

For steady-state processes, the $\frac{dM_A}{dt}$ term goes to 0, as there would be no change in the total mass of A in the system over time. For unsteady-state processes, this differential equation must be solved using **boundary conditions**.

An example of a boundary condition is $M_A(t = 0) = M_i$

This equation says that the mass of A in the system at time ($t = 0$) is equal to M_i . This mass can be equal to 0, meaning that there is no A in our system at time zero. It can also be equal to a specific value, meaning that our system starts with an initial mass of A.

Differential Balances General Procedure

1. Omit any terms that are equal to zero or negligible from the mass, energy, or mole balances.
2. Write an expression for the total amount of the quantity of interest (mass, energy, moles) using the remaining terms in the balance
3. Determine the initial conditions of the system and solve accordingly

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5.2: Separable Differential Equations

Learning Objectives

By the end of this section, you should be able to:

- **Provide** initial conditions for well-mixed separable transient single-unit processes.

Solve separable transient balances to find a property of a system at any given time.

Separable Differential Equations

Separable differential equations are differential equations where the variables can be isolated to one side of the equation. Take the following differential equations:

$$1 - \frac{dx}{dy} = (x^3 + x) * (y - y^2)$$

This equation is *separable* because you can completely isolate the x and y variables as follows:

$$\frac{dx}{x^3 + x} = dy * (y - y^2) \quad (5.2.1)$$

$$2 - \frac{dx}{dy} = \frac{x}{x+y}$$

This equation is *non-separable* because you cannot completely isolate the x and y variables:

$$dy * (x + y) = dx * x \quad (5.2.2)$$

These non-separable equations we will discuss later.

✓ Example: Chemical Reactor

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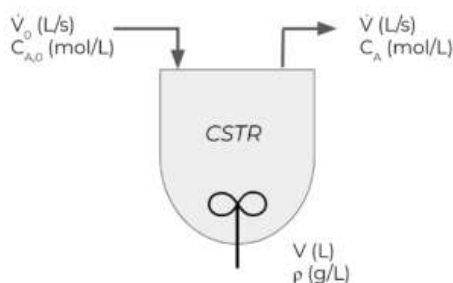
Solution

text.

Consider a “continuous stirred-tank reactor” (CSTR). CSTRs are reactors with continuous feed and exit streams and some kind of mixer.

Say we know the following information about this CSTR:

- The feed enters at a constant volumetric flowrate of $\dot{V}_0$ in L/s
- The volume of the tank is V in L.
- Initially ($t = 0$), the tank is filled to V_i in L
- The exit stream flows at a constant rate of $\dot{V}$ in L/s
- We can assume that the density of all streams in the system is constant at ρ in g/L



We want to write a balance for the total (overall) mass in the system under transient conditions.

We start off by writing out the overall balance:

$$IN - OUT + GEN - CON = ACC \quad (5.2.3)$$

Mass is not being consumed or generated, just changed from one substance to another. This means the *GEN* and *CON* terms are negligible. We get:

$$IN = \dot{V}_0 * \rho \quad (5.2.4)$$

$$OUT = \dot{V} * \rho \quad (5.2.5)$$

$$ACC = \frac{dM}{dt} = \frac{d(V * \rho)}{dt} = \rho * \frac{dV}{dt} \quad (5.2.6)$$

The units for the *IN*, *OUT*, and *ACC* terms are kg/s. Simplifying the balance, we get:

$$\dot{V}_0 * \rho - \dot{V} * \rho = \rho * \frac{dV}{dt} \quad (5.2.7)$$

Since the densities are all constant, we can cancel them out:

$$\dot{V}_0 - \dot{V} = \frac{dV}{dt} \quad (5.2.8)$$

Using separation of variables (from calculus), we can integrate both sides. We want to find a given value about our system at a specific final time (t_f), starting from an initial time (say $t_0 = 0$). We know the initial volume V_i and want to find the final volume V_f .

$$(\dot{V}_0 - \dot{V})dt = dV \quad (5.2.9)$$

$$\int_{t_0}^{t_f} (\dot{V}_0 - \dot{V})dt = \int_{V_i}^{V_f} dV \quad (5.2.10)$$

$$(\dot{V}_0 - \dot{V}) * (t_f - t_0) = V_f - V_i \quad (5.2.11)$$

$$V_f = V_i + (\dot{V}_0 - \dot{V}) * (t_f - t_0) \quad (5.2.12)$$

Let's try substituting in some numbers to this equation. Say the rate of flow in is 5 L/min, and the flow out is 6 L/min with 300 L initially in the tank. How much water remains in the tank after 1 hour? Using the formula we derived, we can find this:

$$V_f = V_i + (\dot{V}_0 - \dot{V}) * (t_f - t_0) \quad (5.2.13)$$

Formula does not parse. What is the height of the tank at 10 minutes?

Solution

Step 1: Determine what terms in the general balance are zero or negligible.

$$IN - OUT + GEN - CON = ACC \quad (5.2.14)$$

Since there are no feed streams and no reactions (no mass generated or consumed), the *IN*, *GEN*, and *CON* terms can be omitted from the balance.

$$-OUT = ACC \quad (5.2.15)$$

Step 2: Write out the mass balance for species A in the system.

$$(-\dot{m}_{out,A}) = \frac{dM_A}{dt} \quad (5.2.16)$$

Step 3: Expand the mass terms.

Recall that *Mass* = *Volume* * *density*, so we can use that to express both terms in the mass balance:

$$(-\dot{V}_{out,A} * \rho) = \rho * \frac{dV_A}{dt} \quad (5.2.17)$$

Since the density is constant, the density terms on both sides cancel each other out

$$(-\dot{V}_{out,A}) = \frac{dV_A}{dt} \quad (5.2.18)$$

The volume terms can be further expanded. Recall that the volume of a cylinder $Area * Height$ or $A * h$. In differential terms, $\frac{dV}{dt} = A \frac{dh}{dt} + h \frac{dA}{dt}$. Since the area is constant in this case, this simplifies to: $\frac{dV}{dt} = A \frac{dh}{dt}$.

$$(-\dot{V}_{out,A}) = A_{tank} * \frac{dh}{dt} \quad (5.2.19)$$

$$A_{tank} = \frac{\pi}{4} * D_{tank}^2 = \frac{\pi}{4} * 2m^2 = 3.14m^2 \quad (5.2.20)$$

Step 4: Solve the integral from $t = 0$ to $t = 10$ mins

$$(-\dot{V}_{out,A})dt = A_{tank} * dh \quad (5.2.21)$$

$$\int_{0min}^{t=10min} (-\dot{V}_{out,A})dt = \int_{h_{initial}}^{h_{final}} A_{tank} * dh \quad (5.2.22)$$

$$\int_{0min}^{t=10min} (-0.10 \frac{m^3}{min})dt = \int_{h_{initial}}^{h_{final}} 3.14m^2 * dh \quad (5.2.23)$$

$$(-0.1 \frac{m^3}{min}) * t \Big|_{0min}^{t=10min} = (3.14m^2) * h \Big|_{5m}^{h_{final}} \quad (5.2.24)$$

$$(-0.1 \frac{m^3}{min}) * (10min - 0min) = (3.14m^2) * (h_{final} - 5m) \quad (5.2.25)$$

$$-1m^3 * \frac{1}{3.14m^2} = h_{final} - 5m \quad (5.2.26)$$

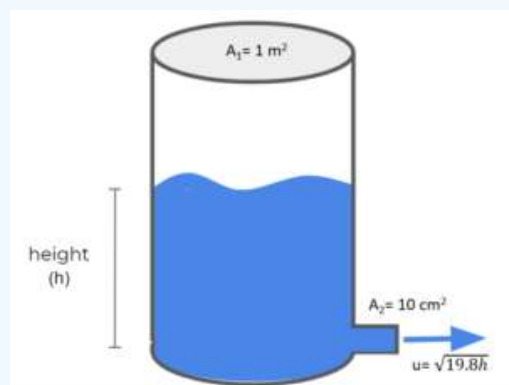
$$-0.32m = h_{final} - 5m \quad (5.2.27)$$

$$(-.32 + 5)m = h_{final} \quad (5.2.28)$$

$$h_{final} = 4.68m \quad (5.2.29)$$

✓ Exercise: Transient Mass Balance

Suppose we have a tank with an outlet at the bottom as shown below. Water is the only thing in the tank (we'll call this species A). The water flows out of the tank at a rate of $\sqrt{19.6 * h} \text{ m/s}$, where h is the height of water in m at any specific time (note that expression like this for outlet flow come from conservation of energy in a tank with gravity driving flow out of the tank). The tank has a cross-sectional area of $1m^2$ and the outlet pipe has a cross-sectional area $10cm^2$. If the initial height of the water in the tank is 1 m, using a transient mass balance, calculate the height of water in the tank after 5 mins.



Solution

Add example text here.

Step 1: Determine what terms in the general balance are zero or negligible.

$$IN - OUT + GEN - CON = ACC \quad (5.2.30)$$

Since there is no inlet stream and no chemical reactions in the tank, there is no IN , GEN or CON terms:

$$-OUT = ACC \quad (5.2.31)$$

Step 2: Write out the mass balance for species A in the system.

$$(-\dot{m}_{out}) = \frac{dM}{dt} \quad (5.2.32)$$

Step 3: Express each term using the given quantities:

Replace Mass by Volume $\times$ density for both terms:

$$(-\dot{V}_{out} \times \rho) = \frac{dV \times \rho}{dt} \quad (5.2.33)$$

Because ρ are multiplied by both sides and we assume it is constant throughout the system, we can cancel ρ in this step:

$$(-\dot{V}_{out}) = \frac{dV}{dt} \quad (5.2.34)$$

The volume of fluid flowing out of a pipe at any instant can be calculated using $\dot{V} = u \times A$, where u is the instantaneous velocity of the fluid and A is the cross-sectional area of the pipe. We can use this to express the outlet flow. For the accumulation term, it is not beneficial to do this because we don't know the expression for u .

For the accumulation term, we can express dV as $A_1 \times dh$ because we know that A_1 is constant, and this leaves only one variable (h) for us to solve for in the mass balance:

$$-u \times A_2 = \frac{A_1 dh}{dt} \quad (5.2.35)$$

We can replace u using $u = \sqrt{19.6 \times h}$ given in the question. T

$$-\sqrt{19.6 \times h} \times A_2 = \frac{A_1 dh}{dt} \quad (5.2.36)$$

Step 4: Solve the integral to find h_f :

$$\int_{t_0}^{t_f} -\sqrt{19.6 \times h} \times A_2 dt = \int_{h_0}^{h_f} A_1 dh \quad (5.2.37)$$

Separate the equation by moving all terms involving h to one side:

$$\int_{t_0}^{t_f} -\frac{A_2}{A_1} dt = \int_{h_0}^{h_f} \frac{1}{\sqrt{19.6 \times h}} dh \quad (5.2.38)$$

Replace the variables by the given information: $A_2 = 10\text{cm}^2 = 10 \times 10^{-4}\text{m}^2$, $A_1 = 1\text{m}^2$, $t_0 = 0\text{s}$, $t_f = 5\text{min} = 300\text{s}$.

$$\begin{aligned} \int_0^{t=300} -\frac{10 \times 10^{-4}}{1} dt &= \int_{h_0=1}^{h_f} \frac{1}{\sqrt{19.6}} \times h^{-\frac{1}{2}} dh \\ -10 \times 10^{-4} \times t \Big|_0^{t=300} &= \frac{2}{\sqrt{19.6}} \times h^{\frac{1}{2}} \Big|_{h_0=1}^{h_f} \\ -10 \times 10^{-4} \times (300 - 0) &= \frac{2}{\sqrt{19.6}} \times h_f^{\frac{1}{2}} - \frac{2}{\sqrt{19.6}} \times (1)^{\frac{1}{2}} \\ \left(\frac{-10 \times 10^{-4} \times (300 - 0) + \frac{2}{\sqrt{19.6}} \times (1)^{\frac{1}{2}}}{\frac{2}{\sqrt{19.6}}} \right)^2 &= h_f \\ h_f &= 0.11\text{m} \end{aligned}$$

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5.3: Non-separable Differential Equations

Learning Objectives

By the end of this section, you should be able to:

- **Provide** initial conditions for well-mixed non-separable transient single-unit processes.

Set-up separable transient balances.

Non-Separable Differential Equations

Non-separable differential equations are differential equations where the variables cannot be isolated. These equations cannot be easily solved and require numerical or analytical methods that will be taught in future courses. You will learn some methods to solve non-separable equations in CHBE 230 (numerical methods) and MATH 256 (differential equations).

$$\frac{dy}{dx} = \frac{y}{x} + 1 \quad (5.3.1)$$

You cannot isolate the x and y variables in this differential equation, making it a non-separable ordinary differential equation. Without separation you cannot use the integration techniques you learned in your calculus courses to solve this equation for y as a function of x .

In this class, we will only formulate non-separable differential equations without solving them. We will use general balance equations to come up with differential equations and identify the initial conditions, but we will not find the solutions.

✓ Example: Chemical Reactor

text

Solution

text.

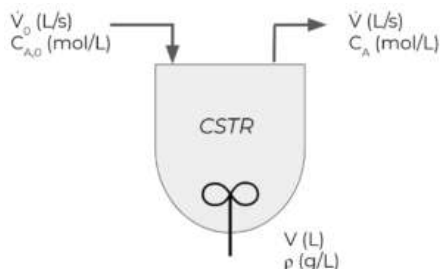
Consider a “continuous stirred-tank reactor” (CSTR). CSTRs are reactors with continuous feed and exit streams and some kind of mixer. Let’s say the following first-order reaction takes place in our CSTR:



Say the units of the rate of consumption of A are $\frac{\text{mol}}{\text{s} \cdot \text{L}}$.

Say we know the following information about this CSTR:

- The feed enters at a volumetric flowrate of $\dot{V}_0$ in L/s and a concentration of $C_{A,0}$ in mol/L
- The volume of the tank is constant at V in L and it is perfectly mixed. This means that the concentration of A is uniform within the tank and matches the exit concentration.
- We will assume that the density of all streams in the system is constant at ρ in g/L
- Initially ($t = 0$), the tank has an initial concentration of $C_{A,i}$ in mol/L
- The exit stream flows at a rate of $\dot{V}$ in L/s, which is the same as $\dot{V}_0$ to ensure our volume stays constant



We want to write a balance for the moles of A in the system under transient conditions.

We start off by writing out the general balance for the moles of A for a CSTR:

$$IN - OUT + GEN - CON = ACC \quad (5.3.3)$$

For this example, we can assume that the reaction is irreversible, indicated by the one-way arrow in the reaction. Therefore, there will be no \$GEN\$ term in the mole balance for A. We get the following terms:

$$IN = \dot{V}_0 * C_{A,0} \quad (5.3.4)$$

$$OUT = \dot{V} * C_A \quad (5.3.5)$$

$$GEN = 0 \quad (5.3.6)$$

$$CON = k * C_A * V \quad (5.3.7)$$

$$\frac{dN_A}{dt} = \frac{d(V * C_A)}{dt} = V * \frac{dC_A}{dt} \quad (5.3.8)$$

The units for all these terms are mol/s. Simplifying the balance, we get:

$$\dot{V}_0 * C_{A,0} - \dot{V} * C_A - k * C_A * V = V * \frac{dC_A}{dt} \quad (5.3.9)$$

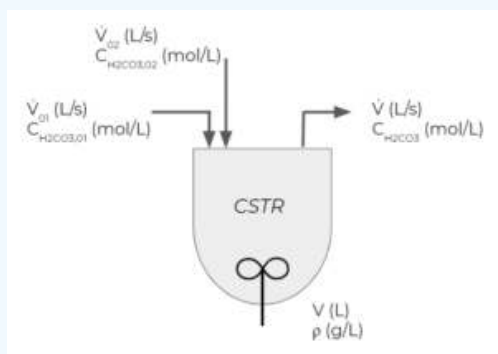
$$\frac{\dot{V}_0 * C_{A,0}}{V} - \frac{\dot{V} * C_A}{V} - k * C_A = \frac{dC_A}{dt} \quad (5.3.10)$$

with initial conditions: $C_A = C_{A,i}$ when $t = 0$

For this course, formulating this differential equation and listing initial conditions without solving it is sufficient. You will learn how to solve these different equations in future classes.

✓ Exercise: Transient Mole Balance

Consider a CSTR where carbonic acid irreversibly decomposes to form water and carbon dioxide as follows:



There are two streams entering the CSTR that both contain carbonic acid. The first stream has a concentration of $C_{H_2CO_3,01}$ and a volumetric flowrate of $\dot{V}_{01}$, while the second stream has a concentration of $C_{H_2CO_3,02}$ and a volumetric flowrate of $\dot{V}_{02}$. The volume of the reactor is constant V . The concentration of the exit stream is $C_{H_2CO_3,i} = 0.5M$ at 0 minutes. If the reaction is first order with the following rate of reaction:

$$-r_{H_2CO_3} = k * C_{H_2CO_3} \quad (5.3.12)$$

What is the transient mole balance on carbonic acid? Set up the ordinary differential equation and initial conditions for this system without solving the differential equation.

Solution

Add example text here.

Step 1: Determine what terms are present in the mole balance.



$$OUT = \dot{V} * C_{H_2CO_3} \quad (5.3.13)$$

$$GEN = 0 \quad (5.3.14)$$

$$CON = -r_{H_2CO_3} * V = k * C_{H_2CO_3} * V \quad (5.3.15)$$

$$ACC = \frac{dN_{H_2CO_3}}{dt} = \frac{d(V * C_{H_2CO_3})}{dt} \quad (5.3.16)$$

Step 2: Write out the mole balance with the derived terms and determine the initial conditions.

$$\dot{V}_{01} * C_{H_2CO_3,01} + \dot{V}_{02} * C_{H_2CO_3,02} - \dot{V} * C_{H_2CO_3} - k * C_{H_2CO_3} * V = \frac{d(V * C_{H_2CO_3})}{dt} \quad (5.3.17)$$

The initial conditions are $C_{H_2CO_3}(t = 0min) = 0.5M$

Note you can see from this equation that $V * C_{H_2CO_3}$ cannot be isolated. When we try to put all terms containing $C_{H_2CO_3}$ to the right side by dividing it, it induced $C_{H_2CO_3}$ terms into the first and second term on the left. and thus we cannot use separation of variables. You will learn to solve these equations in your ordinary differential equations class.

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5.4: Process Control

Learning Objectives

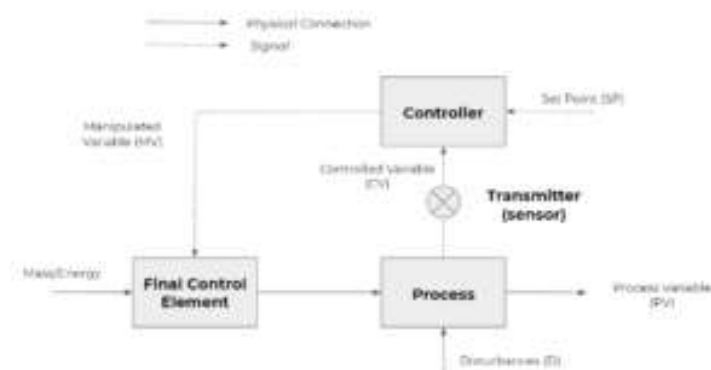
By the end of this section, you should be able to:

- **Apply** control strategies to control common process variables: flow, liquid pressure, liquid level, and temperature of endothermic process streams.

Control System Elements

Some common terms used in process control:

- **Set-Point:** this is a target or desired value of a variable in the system (such as flowrate, temperature, etc.)
- **Disturbance Variable:** a variable that we have no control over in the process but affects the material or heat flow of the process.
- **Manipulated Variable:** a variable that we can control in the process and directly affects the output of the process.
- **Process Variable:** the variable in the system or process that we desire to control.
- **Controlled Variable:** the output process variable we compare to the set-point.



✓ Exercise: Control System Variables

You are driving a car and are approaching a hill. Assume there are three variables in this system:

1. gas pedal
2. the hill
3. the car's speed

Classify each of these variables as process/controlled variable, manipulated variable, or disturbance variable.

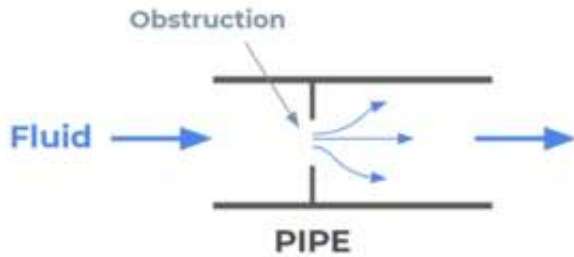
Solution

Add example text here.

The gas pedal will be the manipulated variable since you have direct control on the gas pedal. The hill will be the disturbance variable, because you cannot control the hill's steepness and how this will affect the system. Finally, the car's speed is the process or controlled variable, since it is the system's output variable.

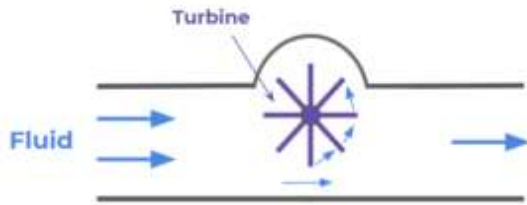
Flow Measurement

1 – Obstruction Meter

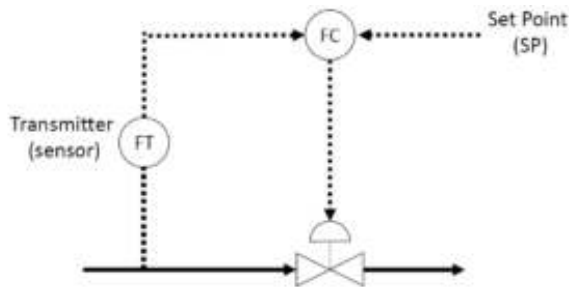


An obstruction meter measures the change in pressure ΔP and correlates it to flow.

2 – Rotational or Turbine Flowmeter



A rotational or turbine flowmeter measures the speed of the rotation of the turbine and correlates it to flow.



For the flow control loop depicted above:

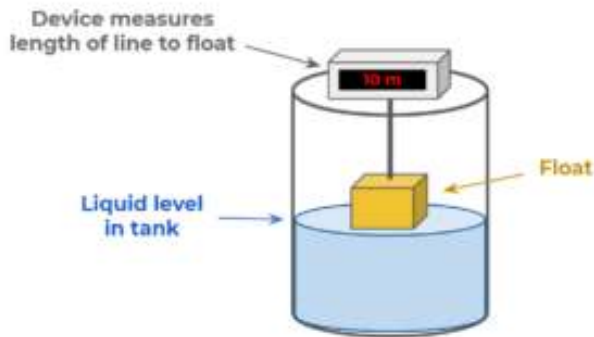
- If the flow is too low → open the valve
- If the flow is too high → close the valve

The transmitter is generally placed sufficiently upstream of the valve so that the flow reading is typically not affected by the valve.

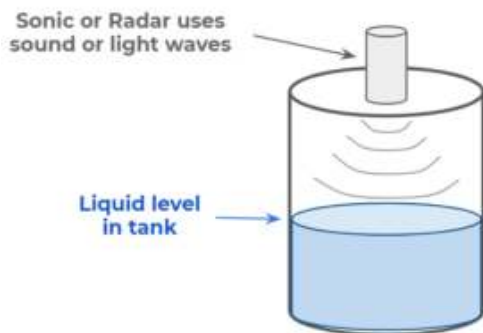
Level Measurement

Many level measurement devices are available (pressure, weight, thermal), but float and sonic/radar level measures are the most common.

1 – Float

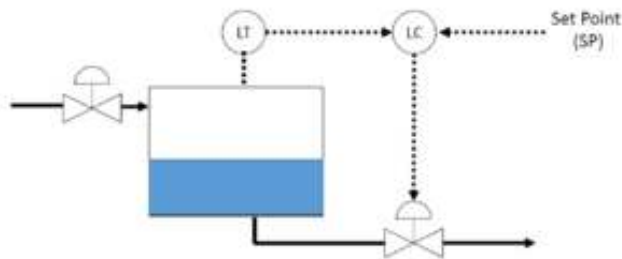


2 – Sonic/Radar



A sonic or radar device measures the level of the tank by measuring the time for wave to reach the liquid-gas interphase and reflect back to the device, and correlating the time to distance. The sonic or radar device can be installed from the top or bottom of the tank.

A typical level control loop is depicted:



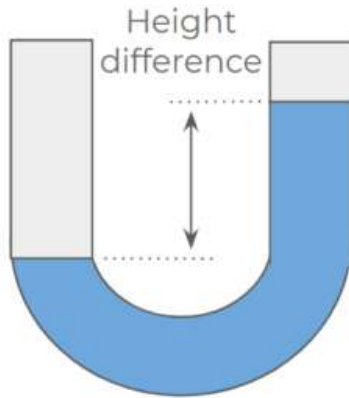
For the level control loop depicted above:

- If the level is too low → close the valve below the tank (outlet valve)
- If the level is too high → open the valve below the tank (outlet valve)

Note that we could also manipulate the inlet valve to affect the tank level, but typically in these systems, the outlet valve is used to control the level. We will stick with this convention in this class.

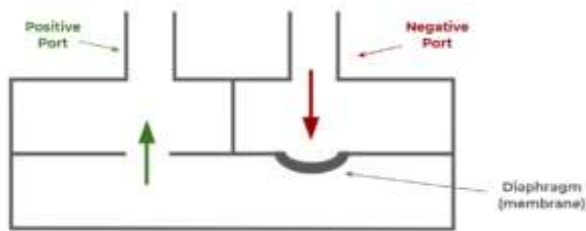
Pressure Measurement

1 – Manometer



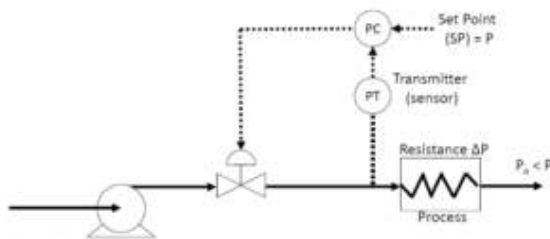
Manometers measure difference in fluid height and correlate it to pressure.

2 – Differential Pressure Cells



A differential pressure cell measures the deflection of the membrane and correlates it to change in pressure ΔP .

A typical liquid pressure control loop is depicted:



For the level control loop depicted above:

- If the pressure is too low → open the valve
- If the pressure is too high → close the valve

For a centrifugal pump (least expensive and most common for liquids), the line can be closed without immediate damage to the pump. Other pumps (positive displacement pumps) will use other strategies.

Temperature Measurement

1 – Expansion-based

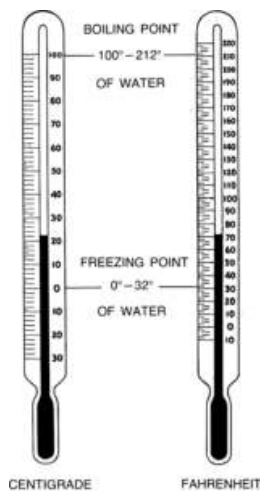


Image from [Pearson Scott Foresman](#) / Public domain

Expansion-based thermometers measure fluid expansion and correlate it to temperature.

2 – Electrical

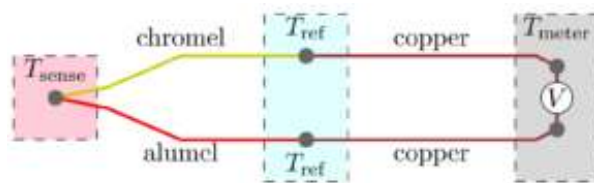
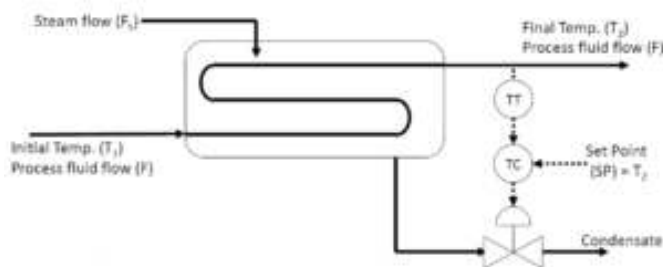


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Thermocouples or resistance temperature devices measure changes in electrical properties and correlate them to temperature. Electrical temperature measurements are the most commonly used in plants as switching combination of metals can adopt to a wide range on temperature.

A typical slow-response endothermic temperature control loop is depicted:

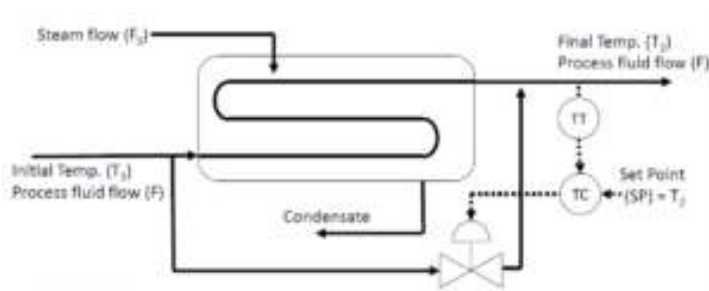


For the temperature control loop depicted above:

- if the temperature (T_2) is too high → close the valve, because it allows more condensate to be stored in the heat exchanger, therefore allow less steam in the heat exchanger and lower the amount of heat released by condensation of steam
- if the temperature (T_2) is too low → open the valve

A slow-response endothermic temperature control loop is classified as **slow** because it takes a longer time to see a temperature change. The response of the system is dependant on the amount of steam that condenses in the heat exchanger. When the outflow of condensate is manipulated, the vapour-liquid equilibrium point is shifted, which affects the rate of condensation/vaporization. The equilibrium shift speed causes a delay in the response time of temperature control.

A typical critical endothermic temperature control loop is depicted:



For the temperature control loop depicted above:

- if the temperature (T_2) is too high → open the valve, because it allows the bypass of the process fluid that does not go through the heat exchanger to mix with the outlet process fluid
- if the temperature (T_2) is too low → close the valve

A critical endothermic temperature control loop is **faster** than a slow-response endothermic control loop because the temperature of the process fluid is directly changed. This eliminates the lag that would be present from manipulating the steam temperature.

✓ Example: Endothermic Temperature Control Loops

text

Solution

text.

Consider a heat exchanger where an endothermic temperature control loop is present in the system (which means the process stream absorbs heat from the utilities). There is a 5°C (from the set-point) increase in the outlet temperature of the process fluid. Which endothermic control loop will decrease the temperature back to its original set-point faster and why?

For a **slow-response endothermic temperature control loop** :

When the temperature change is detected, the controller will close the valve slightly to allow for less condensate to flow out of the heat exchanger. This will allow less steam in the heat exchanger to provide heat through condensation, and eventually cause the outlet process fluid temperature to decrease to the set-point temperature

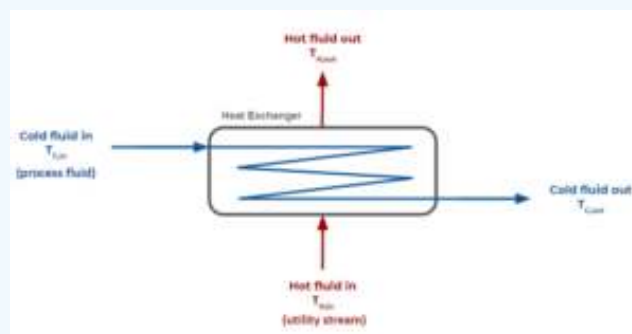
For a **critical endothermic temperature control loop** :

When the temperature change is detected, the controller will open the valve of the cold process fluid. This will directly add cold process fluid to the outlet process fluid and directly decrease the temperature back to its set-point, without any delay.

Therefore, a critical endothermic temperature control loop is going to decrease the temperature back to its original set-point faster.

✓ Exercise: Heat Exchanger Control

Consider the following heat exchanger system. We'd like to control the outlet cold temperature $T_{C,out}$.

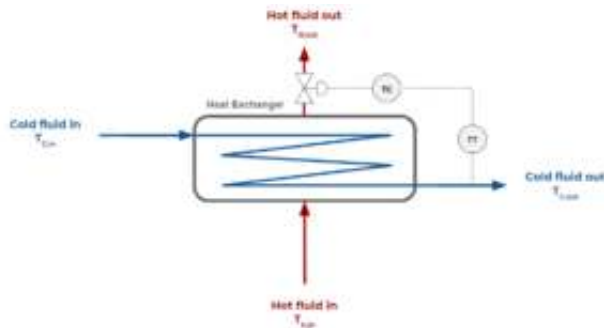


Suggest 2 different control loops that we can implement to this system.

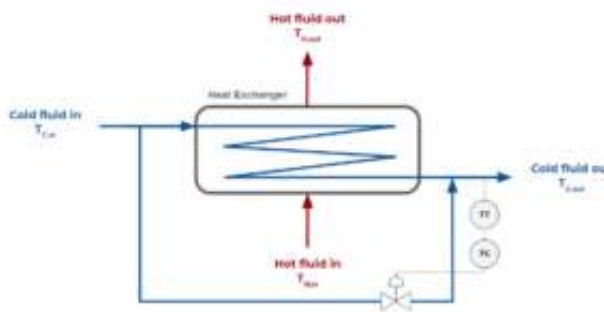
Solution

Add example text here.

The first control strategy measures the process variable ($T_{C,out}$) and adjusts the outlet hot stream's temperature ($T_{H,out}$) by manipulating the outlet flowrate of the hot fluid. This control strategy is known as the slow-response endothermic control loop.



The second control strategy measures the process variable ($T_{C,out}$) and adjusts the inlet cold stream's temperature ($T_{C,in}$) by adding more cold process fluid to the outlet cold stream. This control strategy is known as the critical endothermic control loop.



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5.5: Unsteady-state Operations and Process Control Review

Important Equations

General balance	$IN - OUT + GEN - CON = ACC$
General mass balance	$\int_{t_i}^{t_f} \dot{m}_{in,A} dt - \int_{t_i}^{t_f} \dot{m}_{out,A} dt + \int_{t_i}^{t_f} \dot{r}_{gen,A} dt - \int_{t_i}^{t_f} \dot{r}_{con,A} dt = \int_{M_i}^{M_f} dM_A$

Terms to Know

An interactive or media element has been excluded from this version of the text. You can view it online here:

<https://pressbooks.bccampus.ca/chbe220/?p=1804>

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5.6: Practice Exercises

Multiple Choice Questions

✓ Exercise: Separable Differential Equations

Which of the following is not a separable differential equation?

- a) $\frac{t^2}{C_A} = 4 * C_A \frac{dC_A}{dt}$
- b) $\frac{t^2}{T} = 3 * T \frac{dT}{dt}$
- c) $\frac{dM_A}{dt} + e^{M_A+t} = 0$
- d) $\frac{-2t+T^2}{2*T*t} = \frac{dT}{dt}$

Solution

Add example text here.

d) $\frac{-2t+T^2}{2*T*t} = \frac{dT}{dt}$

If you try to separate this equation, you get: $2 * t + T^2 + 2 * T * t * \frac{dT}{dt} = 0$. There is no way to isolate the T and t variables further.

How to separate the other choices:

a)

$$\begin{aligned}\frac{t^2}{C_A} &= 4 * C_A \frac{dC_A}{dt} \\ t^2 dt &= 4 * C_A^2 dC_A\end{aligned}$$

b)

$$\begin{aligned}\frac{t^2}{T} &= 3 * T \frac{dT}{dt} \\ t^2 dt &= 3 * T^2 dT\end{aligned}$$

c)

$$\begin{aligned}\frac{dM_A}{dt} + e^{M_A+t} &= 0 \\ \frac{dM_A}{dt} + e^{M_A} \cdot e^t &= 0 \\ e^{M_A} \cdot e^t &= -\frac{dM_A}{dt} \\ e^t dt &= -\frac{1}{e^{M_A}} dM_A\end{aligned}$$

✓ Exercise: Process Control Variables

Consider a mixing tank with 2 inlet streams and 1 outlet stream. Stream 1 is feeding the tank with a solution with a concentration of species A. We can change the flowrate of stream 1 using a valve. Stream 2 is feeding the tank with a solution with a concentration of species B, but we do not have control over stream 2's flowrate or concentration (species B concentration fluctuates and is decided by an upstream process). We measure the concentration of the outlet stream and adjust our system accordingly. Which of the following variables is the *disturbance variable*?

- a) Stream 1 flowrate
- b) Stream 2 flowrate
- c) Outlet stream flowrate
- d) Outlet stream concentration

Solution

Add example text here.

b) Stream 2 flowrate

The flowrate of stream 2 is the best answer here because it is an input variable that is affecting our controlled variable (outlet stream concentration), but we do not have control over it. We must adjust our manipulated variable (stream 1 flowrate) to achieve our desired outlet flowrate or concentration.

✓ Exercise: Unsteady-state Systems

Which of the following is not a steady-state system?

- a) CSTR (continuous stirred-tank reactor) with constant flow in and out of all species
- b) A filtration system that has fluid entering and exiting the system at constant volumetric flowrates
- c) A bathtub filling up with water at the same rate as the drain empties the water
- d) Heat exchanger in a process that maintains the process fluid at 50°C

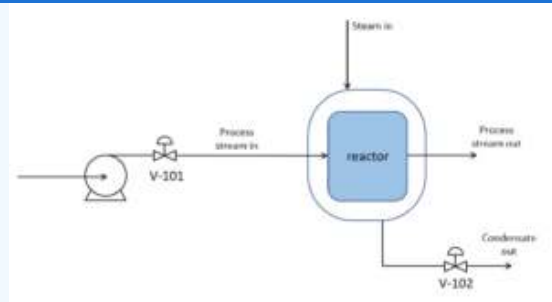
Solution

Add example text here.

b) A filtration system that has fluid entering and exiting the system at the same rate

This system will accumulate a build-up of the filtered product. Although the flowrates entering and exiting the system are constant, the concentration will change over time due to the filter present.

✓ Exercise: Methods to Decrease Reactor Temperature



We have the following reactor with an **endothermic** reaction taking place inside the reactor. There is a heating jacket outside of the reactor that acts in a similar manner to a heat exchanger with steam as the utility stream. If the reactor temperature is currently lower than the desired temperature that is required to achieve the optimum yield from the reaction, how should we manipulate both valves to increase the temperature in the reactor?

- a) V-101 and V-102 both open
- b) V-101 and V-102 both close
- c) V-101 opens; V-102 closes
- d) V-101 closes; V-102 opens

Solution

Add example text here.

d) V-101 closes; V-102 opens

Since the reaction is endothermic, we want to slow down the reaction rate inside the reactor to increase the temperature, which can be achieved by closing V-101 to slow down the inlet flow of the reactant.

The heating jacket releases more heat into the reactor when there is more steam and less condensate in the jacket, due to most of the heat released comes from the condensation process. This can be achieved by opening V-102 to let out some of the condensates in the heating jacket.

Short Answer Questions

✓ Exercise: General Balance for Semi-Batch Reactor

Consider a semi-batch reactor that is initially filled with species A prior to the startup of the reactor. Species B is added to the reactor slowly until a stoichiometrically balanced (species A and B) amount is reached. There is a continuous outlet stream in the reactor. Species B reacts with species A with a conversion of 75% at the end of the process. The reaction is reversible.



What terms in the general balance ($IN - OUT + GEN - CON = ACC$) are considered for species A in this system?

Solution

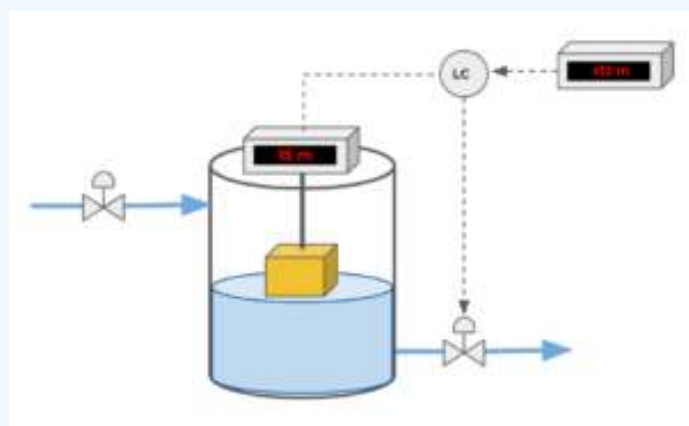
Add example text here.

- IN = 0: there is no A entering the reactor (it is already in the reactor prior to startup)
- OUT: some of reactant A does not react (75% conversion) or is produced from the reverse reaction, and therefore exits the system
- GEN: species A generated will come from the reversible reaction, where species C will form species A and B
- CON: species A will react and will be consumed along with species B to form species C

$$GEN - OUT - CON = ACC$$

✓ Exercise: Level Control Loop

Consider the following control loop. The number indicated by the reader is the level of water (height of the water inside the tank), not the height from the top of the tank to the surface of the water. The exit valve is initially closed.



What action will the level control take on the valve and why?

Solution

Add example text here.

The level controller will signal the valve to open to drain some of the water in the tank. The setpoint height in the tank is less than or equal to 12 m. Given that the tank water level is at 15 m, we must drain some of the water in the tank to bring the water level back to an acceptable range.

✓ Exercise: Temperature Boundary Conditions

The change in temperature with respect to time for a system can be described by the following function, where the temperature(T) is in K and time(t) is in mins:

$$\frac{dT}{dt} = 20e^{-0.2t} \quad (5.6.2)$$

The temperature of the system is initially at 270 K. Solve for the time when the temperature change is equal to 95% of the temperature change $t = 0$ minutes to $t \rightarrow \infty$

Solution

Add example text here.

$$T(t) = \int 20e^{-0.2t} dt$$

$$T(t) = -100e^{-0.2t} + C$$

Our boundary condition is $T(t=0) = 270$ K. We can use this to solve for the constant in the temperature function.

$$270 = -100e^{-0.2*0} + C$$

$$270 = -100 + C$$

$$C = 370K$$

Find the system temperature when time goes to infinity:

$$T(t = \infty) = -100 * 0 + 370K$$

$$T(t = \infty) = 370K$$

Our temperature T_2 is going to be 95% of temperature change $T_{\infty} - T_{t=0}$ plus $T_{t=0}$:

$$T_2 = 0.95(370K - 270K) + 270K$$

$$T_2 = 365K$$

Now, to find the time, we plug in our temperature T_2 :

$$365 = -100e^{-0.2t_2} + 370$$

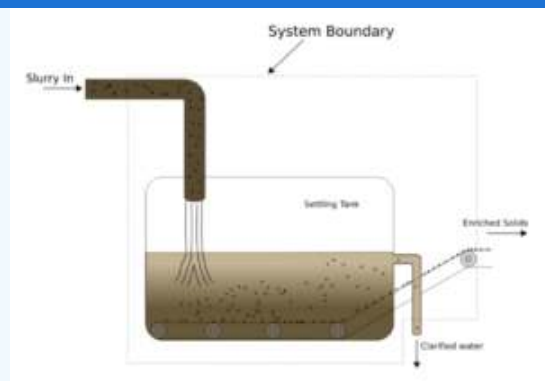
$$-5 = -100e^{-0.2t_2}$$

$$0.05 = e^{-0.2t_2}$$

$$t_2 = \frac{\ln(0.05)}{-0.2} = 15mins$$

Long Answer Questions

✓ Exercise: Mass Balance in a Filtration System



Suppose we have the settling tank system above to separate solid particles from a waste stream. Given the following information:

- The slurry flows into the tank at a rate of 30 kg/hr with 10% solids
- The enriched solid stream carries solid out of the system at a rate of 2.5 kg/hr and contains 100% solids
- The clarified water stream flows out of the system at a rate of 27.5 kg/hr and contains 1% solids

We know that we need to stop the process and clean the tank when there is 500 kg of solids accumulated in the tank. If the tank is initially empty, what is the maximum time before we must clean the tank up?

Solution

Add example text here.

We write each term in the mass balance in terms of the slurry and simplify the mass balance:

- $IN = 30 \frac{kg}{hr} \times 10 = 3 \frac{kg}{hr}$
- $OUT = 2.5 \frac{kg}{hr} \times 100 + 27.5 \frac{kg}{hr} \times 1 = 2.775 \frac{kg}{hr}$
- $GEN = 0$
- $CON = 0$
- $ACC = IN - OUT$

Since the tank is initially empty, we know that the $M_i = 0kg$ when $t=0$ hr, so we can solve the mass balance to find t when $M_i = 500kg$.

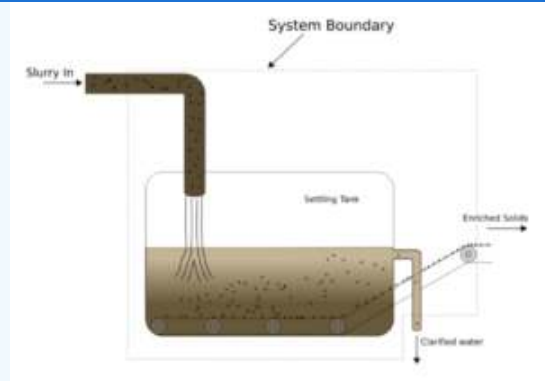
$$\int_{t_i=0hr}^{t_f} 3 \frac{kg}{hr} dt - \int_{t_i=0hr}^{t_f} 2.775 \frac{kg}{hr} dt = \int_{M_i=0kg}^{M_f=500kg} dM$$

$$3 \frac{kg}{hr} \times (t_f - 0)hr - 2.775 \frac{kg}{hr} \times (t_f - 0)hr = (500 - 0)kg$$

$$t_f \times 0.225 \frac{kg}{hr} = 500kg$$

$$t_f = 2222hr (\cong 93days)$$

✓ Exercise: Mass Balance in a Filtration System



For the same settling tank system, suppose we have the following information instead:

- The slurry flows into the tank at a rate of 30kg/hr with 10% solids
- The enriched solid stream carries solid out of the system at a rate of 2.5 kg/hr and contains 100% solids
- The clarified water stream carries out 0.1% of the total mass of solids in the tank every hour

Express each term in the mass balance for the mass of the solids inside the tank. Construct the balance equation to solve for the time when 500kg of solids accumulated in the tank. You do not need to solve the equation.

Solution

Add example text here.

Let M be the total mass of solids in the tank. We write each term in the mass balance in terms of the slurry and simplify the mass balance:

- $IN = 30 \frac{kg}{hr} \times 10 = 3 \frac{kg}{hr}$
- $OUT = 2.5 \frac{kg}{hr} \times 100\% + 0.1M \frac{kg}{hr} = (2.5 + 0.1M) \frac{kg}{hr}$
- $GEN = 0$
- $CON = 0$
- $ACC = IN - OUT$

Since the tank is initially empty, we know that the $M_i = 0kg$ when $t=0hr$, so we can solve the mass balance to find t when $M_i = 500kg$.

$$\int_{t_i=0hr}^{t_f} 3 \frac{kg}{hr} dt - \int_{t_i=0hr}^{t_f} (2.5 + 0.1M) \frac{kg}{hr} dt = \int_{M_i=0kg}^{M_f=500kg} dM$$

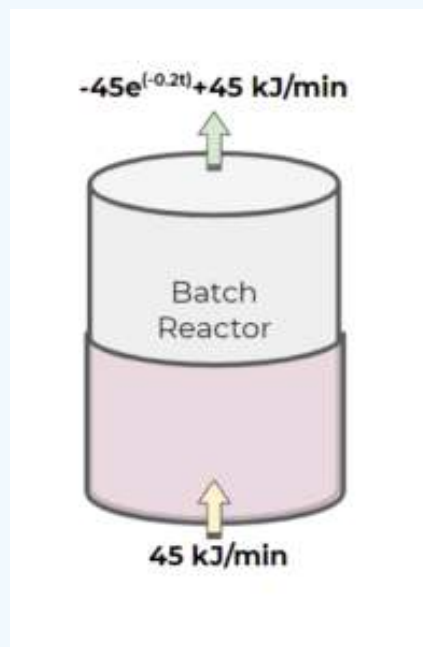
Because M is also a function of t , this equation is not separable, so we don't need to solve it in this course.

✓ Exercise: Batch Reactor with Unsteady-state Energy Balance

A batch reactor is used for a reaction that requires a high temperature prior to adding a catalyst to the system. A heated jacket is used to heat the batch reactor. The heat jacket provides heat to the batch reactor at a rate of $45 \frac{kJ}{min}$. The batch reactor vessel is losing energy at a rate described by the following function, where energy is in $\frac{kJ}{min}$ and time is in mins:

$$-45e^{-0.2t} + 45 \quad (5.6.3)$$

The accumulation of heat in the system (batch reactor) can be described by $C_P * m \frac{dT}{dt}$, where $C_P = 0.38 \frac{kJ}{kg \cdot K}$ and the mass of the reactor is $10kg$. The reactor is initially at $300 K$.



- Write out the overall energy balance, with each of the terms in the $IN-OUT+GEN-CON=ACC$ formula.
- At what time will the reactor reach a temperature of $350 K$?

Solution

Add example text here.

- For each of the energy balance terms, we have:

- $IN = 45 \frac{kJ}{min}$
- $OUT = (-45e^{-0.2t} + 45) \frac{kJ}{min}$

- $GEN = 0$
- $CON = 0$
- $ACC = C_P * m \frac{dT}{dt} = 0.38 \frac{kJ}{kg \cdot K} * 10kg * \frac{dT}{dt}$

b) Once again, we solve the energy balance:

$$\begin{aligned}
 45 \frac{kJ}{min} - (-45e^{-0.2t} + 45) \frac{kJ}{min} &= C_P * m \frac{dT}{dt} \\
 45 \frac{kJ}{min} + (45e^{-0.2t} - 45) \frac{kJ}{min} &= 0.38 \frac{kJ}{kg \cdot K} * 10kg * \frac{dT}{dt} \\
 45e^{-0.2t} \frac{kJ}{min} &= 0.38 \frac{kJ}{kg \cdot K} * 10kg * \frac{dT}{dt} \\
 45e^{-0.2t} \frac{kJ}{min} &= 3.8 \frac{kJ}{K} * \frac{dT}{dt}
 \end{aligned}$$

We know that the temperature of the batch reactor is initially at 300 K. Therefore, our first boundary condition is ($t_1=0$ mins, 300 K). Our second boundary condition will be (t_2 , 350 K). We can now separate our differential equation and take the integral of both sides:

$$\begin{aligned}
 \int_{0 \text{ mins}}^{t_2 \text{ mins}} 45e^{-0.2t} \frac{kJ}{min} * dt &= \int_{300K}^{350K} 3.8 \frac{kJ}{K} * dT \\
 \left(\frac{-45}{0.2} e^{-0.2t_2} + \frac{45}{0.2} e^{-0.2*0} \right) \frac{kJ}{min} &= 3.8 \frac{kJ}{K} * (350K - 300K) \\
 \frac{45}{0.2} (1 - e^{-0.2*t_2}) \frac{kJ}{min} &= 190kJ \\
 225(1 - e^{-0.2*t_2}) \frac{kJ}{min} &= 190kJ \\
 (1 - e^{-0.2*t_2}) &= \frac{190kJ}{225 \frac{kJ}{min}} \\
 (1 - e^{-0.2*t_2}) &= 0.84 \\
 e^{-0.2*t_2} &= 0.16 \\
 -0.2 * t_2 &= \ln(0.16) \\
 t_2 &= \frac{\ln(0.16)}{-0.2} \\
 t_2 &= 9.2 \text{ minutes}
 \end{aligned}$$

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CHAPTER OVERVIEW

6: Process Economics

- [6.1: Plant Capital Cost](#)
- [6.2: Purchased Equipment \(PE\) Cost](#)
- [6.3: Lang Factor and Return on Investment](#)
- [6.4: Cost of Operating Labour](#)
- [6.5: Costs of Manufacturing](#)
- [6.6: Process Economics Review](#)
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6.1: Plant Capital Cost

Learning Objectives

By the end of this section, you should be able to:

- **Understand** The elements that contribute to the capital cost for a plant

Total Capital Investment (TCI)

Total Capital Investment (TCI) is the amount of money (A.K.A. capital) needed for a project to proceed. TCI is the total amount of funds needed to build and start a chemical plant, including the testing and troubleshooting stages before the actual production. It does not include operating expenses or maintenance during the production process. This is further divided into 2 types of capital:

- Fixed Capital Investment (FCI)
- Working Capital (WC)

$$TCI = FCI + WC \quad (6.1.1)$$

Fixed Capital Investment (FCI)

Fixed capital investment is the total price to purchase equipment, get it installed and tested.

FCI is made up of direct costs and indirect costs. These are described below and common direct and indirect cost categories are listed in the table below.

- Direct costs: related to tangible things or products such as process equipment.
- Indirect costs: related to intangible items, these won't stay at the end of building the plant. For example, supervision and project management expenses are indirect costs.

Table 1: Examples of Direct and Indirect Costs that Contribute to FCI

Directs costs	Indirect costs
1. purchased equipment (PE) cost	1. Engineering and supervision
2. PE installation	2. Construction expenses
3. Instrumentation and controls	3. Contractor's fee
4. Piping	4. Contingency
5. Electrical equipment and materials	
6. Buildings	
7. Yard improvements	
8. Service facilities	
9. Land	

Working Capital (WC)

The Working Capital is the initial money required to start the plant. You can think of this like a float (initial money in a cash box) when selling something like samosas or baked goods in CHBE. It is money needed for supplies or people that is not recovered until after the plant closes. Since this is generally a long-time in the future, it is considered a capital investment rather than a manufacturing cost.

WC includes capital invested in:

1. Raw materials and supplies in stock

2. Finished product in stock
3. Cash for monthly operating expenses such as wages, utility bills, etc.
4. Accounts receivable
5. Accounts payable
6. Taxes payable

Typically the WC is 10-20% of the TCI for most chemical plants

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6.2: Purchased Equipment (PE) Cost

Learning Objectives

By the end of this section, you should be able to:

- **Estimate** the purchased equipment price based on baseline data using the effect of capacity and time

PE is the purchased price of equipment from a vendor (someone selling the equipment). It is one of the major factors in the TCI direct costs.

It includes the cost to build the equipment but does not include the cost associated with transportation of that equipment to the site, and installation, etc.

Many times we may estimate PE costs based on costs of PE from previous projects. We will usually use factors to adjust the cost for **capacity** or changes in prices over **time**.

Effect of Capacity

There are a variety of ways to adjust PE pricing to account for different equipment capacity (bigger or smaller equipment). The most common, simple relationship, and the one we'll use in this class, is shown below:

$$\frac{C_a}{C_b} = \left(\frac{A_a}{A_b} \right)^n \quad (6.2.1)$$

Where

$$C_a \quad (6.2.2)$$

$$C_b \quad (6.2.3)$$

$$A_a \quad (6.2.4)$$

$$A_b \quad (6.2.5)$$

$$n \quad (6.2.6)$$

We can rearrange this equation and plot it in a linear form as well (many times you may see log-based plots comparing equipment capacity and cost):

$$\ln(C_a) = \ln(K) + n \ln(A_a) \quad (6.2.7)$$

Where

$$K = \frac{C_b}{A_b^n} \quad (6.2.8)$$

If you are curious, we show how this equation is derived below:

Since C_b and A_b are known values for equipment, we can treat them as constants and take use K to represent $\frac{C_b}{A_b^n}$, and take the $\ln$ of both sides of the equation.

$$\begin{aligned} \frac{C_a}{C_b} &= \left(\frac{A_a}{A_b} \right)^n \\ C_a &= \frac{C_b}{A_b^n} \times A_a^n \\ C_a &= K \times A_a^n \\ \ln(C_a) &= \ln(K) + n \ln(A_a) \end{aligned}$$

Table 1: Examples of Cost Exponents for Process Equipment

Equipment Type	Range of Correlation	Capacity Units	Cost Exponent (n)
Air compressor, multiple stages	1 -1500	kW	0.85
Shell and tube heat exchanger stainless steel	1.9 – 1860	m^2	0.60
Horizontal tank carbon steel	0.5-74	m^3	0.30
centrifugal pump stainless steel	1-70	hp	0.67
Crystalizer	0.2-3.8	m^3	0.47

Note: heat exchanger capacities are measured by the area of heat exchange, thus the unit is m^2 .

Analogous exponent values are shown due to copyright considerations. You can find the updated values in [Analysis, Synthesis and Design of Chemical Processes, fifth edition, Section 2, Chapter 7.2, Table 7.3.](#)^[1]

A general rule for cost exponents is called the six-tenths rule. This is a generalization that for many processes, the exponent will be close to six-tenth's (0.60). You can see this applies better to certain equipment more than others based on the table above.

✓ Exercise: Using Capacity Correlation to Estimate Purchased Equipment Cost

If a 0.8 m^3 crystalizer costs \$35,000, how much does a piece of similar equipment with a capacity of 3.0 m^3 ? Compare the results using the given cost exponent and the six-tenth rule.

Solution

Add example text here.

Using $n=0.48$ given by the cost exponent:

$$\begin{aligned}\frac{C_a}{C_b} &= \left(\frac{A_a}{A_b} \right)^n \\ C_a &= C_b \times \left(\frac{A_a}{A_b} \right)^n \\ C_a &= \$35000 \times \left(\frac{3.0}{0.8} \right)^{0.47} \\ C_a &\approx \$65,100\end{aligned}$$

Using $n=0.60$ given by the six-tenth rule:

$$\begin{aligned}\frac{C_a}{C_b} &= \left(\frac{A_a}{A_b} \right)^n \\ C_a &= C_b \times \left(\frac{A_a}{A_b} \right)^n \\ C_a &= \$35000 \times \left(\frac{3.0}{0.8} \right)^{0.60} \\ C_a &\approx \$77,400\end{aligned}$$

This shows the difference these factors can make, so we want to try to use factors that are as accurate as possible (or be clear about our uncertainties).

Effect of Time

As you may know, the value of money changes with time due to factors such as inflation. Cost indexes give us an estimate of what a common item costs at different points in time.

$$C_2 = C_1 \left(\frac{I_2}{I_1} \right) \quad (6.2.9)$$

where

$$C_1 \quad (6.2.10)$$

$$C_2 \quad (6.2.11)$$

$$I_1 \quad (6.2.12)$$

$$I_2 \quad (6.2.13)$$

Table 2: Cost indexes for 1996-2020

Year	Marshall and Swift Equipment cost index	Chemical Engineering Plant Cost Index
1996	211.7	154.7
2000	264.8	169.3
2004	301.7	186.3
2008	339.2	212.8
2012	391.5	227.8
2016	418.9	237.8
2020	458.3	258.8

Analogous time indexes are shown due to copyright considerations. You can find the updated values in [Analysis, Synthesis and Design of Chemical Processes, fifth edition, Section 2, Chapter 7.2.2, Table 7.4.](#)^[1]

Marshall and Swift Equipment cost index and **Chemical Engineering Plant Cost Index** are two common types of cost indexes that we will use for this course.

Note the Marshall and Swift is used for equipment, whereas the plant cost index is for an overall plant cost including installation, piping, etc.

✓ Exercise: Estimation of Equipment Price Over Time

If a stainless steel shell-and-tube heat exchanger costs \$18,000 in 1996, what is the cost of a shell-and-tube heat exchanger with the same capacity in 2020?

Solution

Add example text here.

Marshall and Swift Equipment cost index is used because we are considering the cost for a heat exchanger, which is a single piece of equipment.

$$C_2 = C_1 \left(\frac{I_2}{I_1} \right)$$

$$C_2 = \$18000 \times \left(\frac{458.3}{211.7} \right)$$

$$C_2 \approx \$39,000$$

✓ Exercise: Estimation of Plant Price Over Time

If a plant producing 200,000 tons of ammonia per year costs \$25,000,000 to build in 2000, what would the cost of such a plant be in 2020?

Solution

Add example text here.

Since we are interested in the cost for the whole plant, we can use the Chemical Engineering Plant Cost Index.

$$C_2 = C_1 \left(\frac{I_2}{I_1} \right)$$
$$C_2 = \$25,000,000 \times \left(\frac{258.8}{169.3} \right)$$
$$C_2 \approx \$38,000,000$$

✓ Exercise: Combining the Effect of Time and Capacity for Equipment Cost

If a 150kW multiple-stage air compressor costs \$80,000 in 2004, how much does the same type compressor with 500kW compacity cost in 2020?

Solution

Add example text here.

We use Marshall and Swift Equipment cost index to solve for effect of time and cost exponent to solve for the effect of capacity. Both factors are multiplied so the order does not matter.

$$C_2 = C_1 \times \left(\frac{A_a}{A_b} \right)^n \times \left(\frac{I_2}{I_1} \right)$$
$$C_2 = \$80,000 \times \left(\frac{500}{150} \right)^{0.85} \times \left(\frac{458.3}{301.7} \right)$$
$$C_2 \approx \$340,000$$

References

[1] Joseph A. Shaeiwitz; Debangsu Bhattacharyya; Wallace B. Whiting; Richard C. Bailie; Richard Turton. *Analysis, Synthesis and Design of Chemical Processes*, fifth edition. [online]<<https://gw2jh3xr2c.search.serialsol...al%20processes>> [Accessed 11 June, 2020].

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6.3: Lang Factor and Return on Investment

Learning Objectives

By the end of this section, you should be able to:

- **Estimate** the total capital investment (TCI) and fixed capital investment (FCI) based on the lang factor

Lang Factor

Lang factor relates purchased equipment cost to total capital investment (TCI) and fixed capital investment (FCI). This factor represents the cost of building a major expansion onto an existing chemical plant, including other costs such as piping, control, etc.

$$C_{TM} = F_{lang} \sum_{i=1}^n C_{p,i} \quad (6.3.1)$$

where C_{TM} is the total plant cost, F_{lang} is the lang factor, and $\sum_{i=1}^n C_{p,i}$ is the sum of the cost of all purchased equipment.

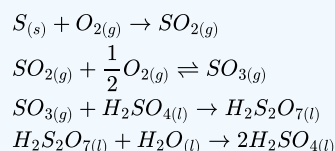
Lang factors for common plant types are given below. Note that fluid processing means plants processing liquids and/or gasses.

Table 1: Lang Factors for Common Plant Types ^[1]

type of plant	FCI	TCI
solid processing plant	3.8	4.5
solid-fluid processing plant	4.3	4.8
fluid processing plant	5.0	5.8

✓ Exercise: Estimating FCI Using the Lang Factor

Suppose we want to build a sulfuric acid production plant. Say the reaction mechanism for the process is as follows:



The purchased price for all equipment is shown below:

Equipment categories	Purchased price
pre-treatment	\$3,000,000
reactors	\$8,000,000
absorption tower (for separation)	\$5,000,000
tanks	\$2,000,000
pumps and compressors	\$4,000,000

Estimate the total capital investment for the plant.

Solution

From the reaction mechanisms, we see solid, liquid, and gaseous phases in the process streams, so we select the lang factor to calculate TCI for solid-fluid processing plant ($F_{lang} = 4.9$).

$$TCI = F_{lang} \sum_{i=1}^n C_{p,i}$$

$$TCI = 4.9 \times (\$3,000,000 + \$8,000,000 + \$5,000,000 + \$2,000,000 + \$4,000,000)$$

$$TCI = \$107,800,000$$

Return on Investment (ROI)

Return on investment is the ratio of the net profit and total capital investment (TCI). The net profit can be calculated by the total revenue minus cost of manufacturing (COM). It provides a measure of how favourable the investment is.

Typically ROI ranges from 10%-20%. An ROI over 30% for a plant is considered very desirable.

$$ROI = \frac{(revenue - COM)}{TCI} \times 100 \quad (6.3.2)$$

Revenue is the total profit we generated from selling the product without deducting the cost of production:

$$revenue = \text{unit price of product} \times \text{sales} \quad (6.3.3)$$

COM is the total cost of operating the plant, including raw materials, utilities, labours, etc. We are going to learn about how to estimate COM later.

✓ Exercise: Estimating ROI

Suppose we want to build a solid-fluid processing plant that produces soda ash ($NaCO_3$), and it also produces HCl and $(NH_4)_2SO_4$ as profitable by-products. The annual production rates and market prices for our products are shown below:

product	production rate (tonne/year)	price per tonne
$NaCO_3$	120,000	\$220
HCl	95,000	\$145
$(NH_4)_2SO_4$	90,000	\$150

Suppose the cost for the total purchased equipment is 18,000,000 dollars and the annual cost of manufacturing is 60,000,000 (which includes the cost of raw materials). Assuming all the products are sold, what is the return on investment for our plant? Based on this estimate would it be economically feasible?

Solution

Step 1: Calculate the total revenue generated by all types of products:

$$\begin{aligned} \text{revenue} &= \sum_i \text{unit price of product } i \times \text{sales} \\ &= 120,000 \times \$220 + 95,000 \times \$145 + 90,000 \times \$150 \\ &= \$53,675,000 \end{aligned}$$

Step 2: Estimate TCI using the lang factor:

We select the lang factor to calculate TCI for solid-fluid processing plants ($F_{lang} = 4.9$) as stated in the question.

$$TCI = 4.9 \times \$18,000,000 = \$88,200,000 \quad (6.3.4)$$

Step 3: Calculate ROI using the values we calculated in the previous steps:

$$\begin{aligned} ROI &= \frac{(revenue - COM)}{TCI} \times 100 \\ &= \frac{(\$53,675,000 - \$60,000,000)}{\$88,200,000} \times 100 \\ &= -7.17 \end{aligned}$$

The project is not feasible because the return on investment is negative, which means we are deficient even if we assume we sold all of the products.

Other Useful Resources for Capital Cost Estimation

Chemical Engineering Magazine; Accessible from UBC library at <http://tinyurl.com/ybaf56kt>

G. P. Towler and R. K. Sinnott, Chemical Engineering Design: Principles, Practice, and Economics of Plant and Process Design. (2nd ed.) Waltham, MA; Oxford; Butterworth-Heinemann, 2013; Accessible from UBC library at <http://tinyurl.com/y9oubo7n>

References

[1] Joseph A. Shaeiwitz; Debangsu Bhattacharyya; Wallace B. Whiting; Richard C. Bailie; Richard Turton. *Analysis, Synthesis and Design of Chemical Processes*, fifth edition. [online]<https://gw2jh3xr2c.search.serialssolutions.com/?sid=sersol&SS_jc=TC0002267093&title=Analysis%2C%20synthesis%20and%20design%20of%20chemical%20processes> [Accessed 11 June, 2020].

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6.4: Cost of Operating Labour

Learning Objectives

By the end of this section, you should be able to:

- **Understand** the components of manufacturing costs
- **Estimate** the cost of operating labour

Manufacturing Costs

Typically divided into three main elements:

1. **Direct manufacturing costs:** Factors that vary directly with the rate of production
e.g. raw materials, plant operators
2. **Fixed manufacturing costs:** Factors not affected by the level of production, but related to manufacturing
e.g. taxes and insurance
3. **General expenses:** Management and administrative expenses not related to manufacturing

$$\text{Cost of Manufacturing (COM)} = \text{direct cost} + \text{fixed cost} + \text{general expenses} \quad (6.4.1)$$

Useful Entities for Estimating Costs

- **Fixed capital investment (FCI):** We saw this previously and saw how to estimate this using the Lang factor and purchased equipment cost.
- **Cost of raw materials (CRM):** We saw how to estimate these previously using chemical pricing data (recall estimating GEP).
- **Cost of utilities (C_{UT}):** Previously saw how to calculate our utility needs for a unit and assess costs associated with this (recall from the energy balance section).
- **Cost of operating Labor (C_{OL}):** Cost of operators – we will see how to estimate this.
- **Cost of waste treatment (C_{WT}):** Harder to estimate – there are ways to assess this, but it is beyond the scope of this class. For now, we will need to be given this for a process.

Number of Operating Labour

$$N_{OL} \quad (6.4.2)$$

The number of operators (N_{OL}) needed per shift can be estimated from a correlation by Alkhatat and Gerrard^[1] which is based on data from five major chemical companies.

$$N_{OL} = (6.29 + 31.7P^2 + 0.23N_{np})^{0.5} \quad (6.4.3)$$

where

$$N_{OL} \quad (6.4.4)$$

$$P \quad (6.4.5)$$

$$N_{np} \quad (6.4.6)$$

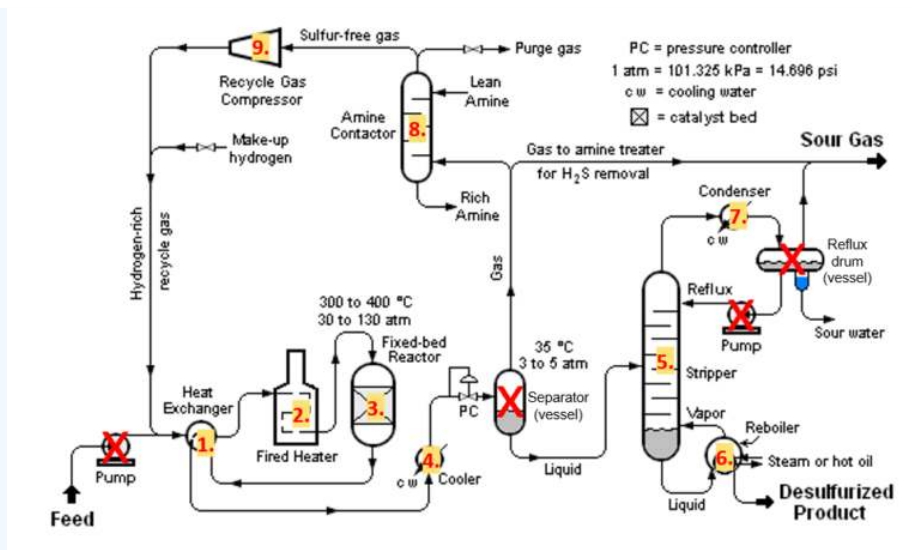
We will take the convention of **rounding up to the nearest integer** to ensure there is enough labour to operate the plant, although in practice there may be ways to have part-time staff etc.

Cost of Operating Labour

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The number of operators is **rounded up to the nearest integer** when the calculation does not result in a whole number.

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So $P = 0$; $N_{np} = 9$. Substituting this into the formula for the number of operators:

$$\begin{aligned}
 N_{OL} &= (6.29 + 31.7 \times (0)^2 + 0.23 \times 9)^{0.5} \\
 &= 2.89 \\
 &\approx 3
 \end{aligned}$$

Therefore, each shift needs 3 operators.

Step 2: Calculate the number of operators needed to fill a position that needs one operator at a time:

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Step 3: Calculate the total number of operators needs to be hired for the plant:

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Step 4: Calculate the total cost of operating labours:

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References

[1] Alkhatat, W. A., and A. M. Gerrard, *Estimating Manning Levels for Process Plants*, AACE Transactions, I.2.1–I.2.4, 1984.

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6.5: Costs of Manufacturing

Learning Objectives

By the end of this section, you should be able to:

- **Calculate** the cost of manufacturing based on a few known process costs

Direct Costs of Manufacturing

Direct Costs of Manufacturing are costs that are directly impacted by the manufacturing rate. To assess the impacts of some of the main elements of the direct costs, we will use multiplication factors based on certain known costs.

Direct manufacturing costs	Symbol or Range of multiplying factors	Avg. factor used
1. Raw Materials	C_{RM}	
2. Utilities	C_{UT}	
3. Operating Labour	C_{OL}	
4. Waste Treatment	C_{WT}	
5. Direct Supervisory and clerical labour	$(0.1 - 0.25)C_{OL}$	$0.18C_{OL}$
6. Maintenance and repairs	$(0.02 - 0.1)FCI$	$0.06FCI$
7. Operating supplies	$(0.006 - 0.012)FCI$	$0.009FCI$
8. Laboratory charges	$(0.1 - 0.2)C_{OL}$	$0.15C_{OL}$
9. Patents and Royalties	$(0 - 0.06)COM(\text{cost of manufacturing})$	$0.03COM$
Total direct costs of manufacturing	$C_{RM} + C_{WT} + C_{UT} + 1.33C_{OL} + 0.03COM + 0.069FCI$	

Fixed Costs of Manufacturing

Fixed Costs of Manufacturing are costs that are not directly impacted by the manufacturing rate. To assess the impacts of some of the main elements of the fixed costs, we will use multiplication factors based on certain known costs.

Fixed manufacturing costs	Range of multiplication factors	Avg. factor used
1. Depreciation – costs associated with buildings and plant equipment. Note that this is not an actual expense, but just accounted for in terms of tax purposes	0.1 FCI (Note there are a variety of ways depreciation can be calculated, this is a very crude approximation)	$0.1FCI$
2. Local taxes and insurance	$(0.014 - 0.05)FCI$	$0.031FCI$
3. Plant overhead costs (referring to the costs related to running the business but not directly related to the process of making the product)	$(0.59 - 0.826)C_{OL} + (0.030 - 0.42)FCI$	$0.708C_{OL} + 0.036FCI$
Total fixed costs of manufacturing	$0.708C_{OL} + 0.068FCI + depreciation(0.1FCI)$	

Depreciation

Governments will not let companies write off all expenses to build a plant immediately. Instead, they are written off over time, in what is known as depreciation.

Depreciation is calculated based on the purchase value of equipment minus the salvage value and evaluated over a number of years specified. This does not include land costs, since land generally retains its value, whereas equipment and buildings tend to lose their value over time.

$$\text{Depreciation} = \frac{\text{purchased value (FCIL)} - \text{salvage value}}{\text{life of equipment (n)}} \quad (6.5.1)$$

✓ Exercise: Estimate Depreciation Value

The following information is the purchased cost for categories of equipment at a small waste treatment facility.

Equipment categories	Purchased price
pre-treatment	\$2,000,000
reactors	\$5,500,000
tanks	\$4,000,000
pumps and compressors	\$3,500,000
sensor and control devices	\$1,000,000

If the life of all of the equipment shown in the table above is 8 years, and the total salvage value of all the equipment is \$89,000. Calculate the depreciation per year using the straight-line method.

Solution

$$\begin{aligned}
 \text{Depreciation} &= \frac{\text{purchased value (FCIL)} - \text{salvage value}}{\text{life of equipment (n)}} \\
 &= \frac{(\$2,000,000 + \$5,500,000 + \$4,000,000 + \$3,500,000 + \$1,000,000) - \$89,000}{8} \\
 &\approx \$2,000,000
 \end{aligned}$$

✓ Exercise: Estimating Depreciation Using FCI

Calculate the yearly straight-line depreciation based on the following information about a hydrodesulphurization plant:

Item	Value (dollars or in units specified)
Fixed Capital Investment	\$87,000,000
land cost	\$1,000,000
salvage value	\$3,200,000
life of equipment	12 years

Solution

The purchased equipment cost can be calculated using **the Fixed Capital Investment excluding the land cost**:

$$\begin{aligned}
 \text{Depreciation} &= \frac{\text{purchased value (FCIL)} - \text{salvage value}}{\text{life of equipment (n)}} \\
 &= \frac{(\$87,000,000 - \$1,000,000) - \$3,200,000}{12} \\
 &= \$6,900,000
 \end{aligned}$$

General Expenses

General expenses are overhead costs related to carrying out business functions. To assess the impacts of some of the main elements of general expenses we will use multiplication factors based on certain known costs.

General expenses	Range of multiplication factors	Avg. factor used
1. Administrative costs	$(0.147 - 0.207)C_{OL} + (0.0075 - 0.0105)FCI$	$0.177C_{OL} + 0.009FCI$
2. Product distribution and selling costs	$(0.02 - 0.2)COM$	$0.11COM$
3. Research and development	$0.05COM$	$0.05COM$
Total general expenses	$0.177C_{OL} + 0.009FCI + 0.16COM$	

Overall Manufacturing Costs

Summing together the Direct Costs of Manufacturing, Fixed Costs of Manufacturing, and General Expenses, we can get a general formula to estimate the total cost of manufacturing.

Direct Cost of Manufacturing: $C_{RM} + C_{WT} + C_{UT} + 1.33C_{OL} + 0.03COM + 0.069FCI$

Fixed Cost of Manufacturing: $0.708C_{OL} + 0.068FCI + depreciation(0.1FCI)$

General Expenses: $0.177C_{OL} + 0.009FCI + 0.16COM$

Cost of Manufacturing: $0.180FCI + 1.23(C_{RM} + C_{WT} + C_{UT}) + 2.73C_{OL} + depreciation(0.1FCI)$

Depreciation is not included in most of the calculations we perform – depreciation is not a real cost that we need to pay, but it is part of the money we lose for tax purposes.

✓ Exercise: Estimating the Cost of Manufacturing

Suppose the following information is obtained from a plant producing 100,000 tonnes of ethylene oxide annually.

Item	Value (dollars)
Fixed Capital Investment	\$46,000,000
Raw Material Cost	\$27,600,000
Waste Treatment Cost	\$5,000,000
Utility Cost	\$800,000
Direct Labour Cost	\$840,000

- What is the cost of manufacturing?
- Calculate the percentage of each element (Direct Cost of Manufacturing, Fixed Cost of Manufacturing, and General Expenses) as a portion of the Cost of Manufacturing.

Do not include depreciation in the calculations above.

Solution

a. Cost of Manufacturing (COM):

$$\begin{aligned}
 &0.180FCI + 1.23(C_{RM} + C_{WT} + C_{UT}) + 2.73C_{OL} \\
 &= 0.180 \times 46,000,000 + 1.23 \times (27,600,000 + 5,000,000 + 800,000) + 2.73 \times 840,000 \\
 &\approx 51,700,000
 \end{aligned}$$

b.

Direct Cost of Manufacturing

$$\begin{aligned}
 & C_{RM} + C_{WT} + C_{UT} + 1.33C_{OL} + 0.03COM + 0.069FCI \\
 &= 27,600,000 + 5,000,000 + 800,000 + 1.33 \times 840, \\
 & \quad 000 + 0.03 \times 51,700,000 + 0.069 \times 46,000,000 \\
 & \approx 39,200,000
 \end{aligned}$$

$$\frac{\text{Direct Cost of Manufacturing}}{\text{Cost of Manufacturing}} \times 100 = \frac{39,200,000}{51,700,000} \times 100 \approx 75.8$$

Fixed Cost of Manufacturing

$$\begin{aligned}
 & 0.708C_{OL} + 0.068FCI \\
 &= 0.708 \times 840,000 + 0.068 \times 46,000,000 \\
 & \approx 3,700,000
 \end{aligned}$$

$$\frac{\text{Fixed Cost of Manufacturing}}{\text{Cost of Manufacturing}} \times 100 = \frac{3,700,000}{51,700,000} \times 100 \approx 7.2$$

General Expenses

$$\begin{aligned}
 & 0.177C_{OL} + 0.009FCI + 0.16COM \\
 &= 0.177 \times 840,000 + 0.009 \times 46,000,000 + 0.16 \times 51,700,000 \\
 & \approx 8,800,000
 \end{aligned}$$

$$\frac{\text{General Expenses}}{\text{Cost of Manufacturing}} \times 100 = \frac{8,800,000}{51,700,000} \times 100 \approx 17.0$$

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6.6: Process Economics Review

Important Equations

Total Capital Investment	$TCI = FCI + WC$
Effect of capacity on equipment prices	$\frac{C_a}{C_b} = \left(\frac{A_a}{A_b} \right)^n$ $\ln(Ca) = \ln(K) + n \ln(A_a) \quad (6.6.1)$
Effect of time on equipment prices	$C_2 = C_1 \left(\frac{I_2}{I_1} \right)$
Preliminary Estimation of Purchased Equipment Costs	$C_e = a + bS^n$
Lang Factor	$C_{TM} = F_{lang} \sum_{i=1}^n C_{p,i}$
Return on Investment	$ROI = \frac{\text{revenue} - COM}{TCI} \times 100$
Revenue	$\text{revenue} = \text{unit price of product} \times \text{sales}$
Cost of manufacturing	$\begin{aligned} \text{cost of manufacturing} \\ &= \text{direct cost} + \text{fixed cost} \\ &\quad + \text{general expenses} \end{aligned}$
Number of operating labour	$N_{OL} = (6.29 + 31.7P^2 + 0.23N_{np})^{0.5}$
Cost of operating labour	Misplaced '#' Misplaced '#'
Total direct cost of manufacturing	$\begin{aligned} \text{total direct cost of manufacturing} \\ &= C_{RM} + C_{WT} + C_{UT} + 1.33C_{OL} \\ &\quad + 0.03COM + 0.069FCI \end{aligned}$
Total fixed cost of manufacturing	$\begin{aligned} \text{total fixed cost of manufacturing} \\ &= 0.708C_{OL} + 0.068FCI + \text{depreciation}(0.1FCI) \end{aligned}$
Depreciation	$\begin{aligned} \text{depreciation} \\ &= \frac{\text{purchased value} - \text{salvage value}}{\text{life of equipment } (n)} \end{aligned}$
General expenses	$\begin{aligned} \text{general expenses} \\ &= 0.177C_{OL} + 0.009FCI + 0.16COM \end{aligned}$
Cost of manufacturing	$\begin{aligned} \text{cost of manufacturing} \\ &= 0.180FCI + 1.23(C_{RM} + C_{WT} + C_{UT}) + 2.73C_{OL} \\ &\quad + \text{depreciation}(0.1FCI) \end{aligned}$

Terms to Know

An interactive or media element has been excluded from this version of the text. You can view it online here:

<https://pressbooks.bccampus.ca/chbe220/?p=2401>

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6.7: Practice Exercises

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CHAPTER OVERVIEW

7: Green Engineering

[7.1: Concepts and Definitions](#)

[7.2: Environmental Fate of Contaminants](#)

[7.3: Life Cycle Assessment](#)

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7.1: Concepts and Definitions

Learning Objectives

By the end of this section, you should be able to:

- **Characterize** green engineering developments

Green Engineering Definition

Green engineering is the design, commercialization, and use of processes and products in a way that reduces pollution, promotes sustainability, and minimizes risks to human health and the environment without sacrificing economic viability and efficiency.^[1]

Examples of Opportunities in Green Engineering

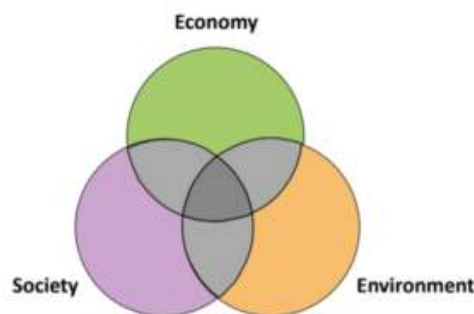
- Clean fuels
- Sustainable or better regenerative development
- Waste reduction
- Not having to deal with byproducts, or finding a value use for byproducts

Basic Ideas Used in Green Engineering

Within green engineering, we can think about ways to improve processes and generally see that some of these may be more effective than others. Examples of a few means of process improvement listed in order of most effective to least effective follow.

1. Elimination – remove the need for harmful materials or choosing other process pathways to eliminate the production of harmful products
2. Substitution (also known as waste reduction or process optimization) – using less harmful materials, or optimizing the process to reduce the formation rate of harmful by-products
3. Recycling – putting energy or materials back into use

Concepts in green engineering processes generally translate to economic, environmental, and social benefits. Processes meeting these three aims will generally thrive in the long term.



Environmental Regulations

Environmental regulations generally determine how companies must act as a minimum. The standards may vary in each country. These will dictate:

- Human safety, ensuring people aren't exposed to harmful substances
- Pollution control measures that must be reported
- Emission limits

Over time, limits generally get more restrictive → means that the most efficient processes will be the ones that succeed in the longer term.

As an example, environmental restrictions of chemicals in Canada can be found on the site of [Health Canada from the Government of Canada](#).

Waste Management Hierarchy

The waste management hierarchy shows certain methods of process improvements and lists them from least to most effective. The most effective process improvements generally require more detailed engineering as they are more complex. However, they also can create much more efficient processes.



References

[1] United States Environmental Protection Agency, *About Green Engineering*, 18-Mar-2019. [Online]. Available: <https://www.epa.gov/green-engineering/about-green-engineering#:~:text=Green> [Accessed: 17-Jun-2020].

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7.2: Environmental Fate of Contaminants

Learning Objectives

By the end of this section, you should be able to:

- **Assess** the physical properties of substances in order to determine their environmental fate if released

The environmental fate of contaminants describes where substances will go when released into the environment.

Group Contribution Method

We may use our knowledge of chemical structures to predict the physical properties of the chemical substances.

Taking common chemical groups from a molecule, we can use the interactions from these groups to predict the properties the molecule will have based on parameters regressed from known molecules.

This is an example of how physical chemistry simulation and modeling can be used to predict important properties.

These properties can inform us of how a substance will act when dispersed in the environment.

✓ Example: Group Contribution Method

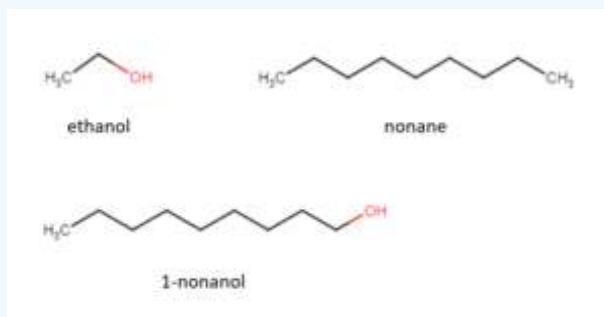
The solubility of a substance is an important property for us to predict the way it migrates in the environment after release. Consider a simple situation where we have the following 3 compounds being released into a body of water:

Ethanol- a fuel commonly produced from biomass, also used as an industrial solvent for organic chemicals.

Nonane – a flammable liquid produced from petroleum.

1-nonanol – a compound commonly found in oils of citrus fruits and industrially used in manufacturing of artificial lemon oil.

The chemical structures of the 3 compounds are shown below:



The -OH functional group is polar, which helps a compound to interact with and dissolve in water (a polar solvent). The long chain of alkanes are nonpolar and will decrease a compound's solubility in water.

Using the group contribution analysis principle, ethanol will have the highest solubility in water due to a significant portion of its structure being polar (the -OH functional group). 1-nonanol will be less soluble owing to the larger carbon chain as opposed to ethanol. Nonane will be the least soluble as there are no polar groups in the molecule. There are group contribution correlations that allow us to calculate estimates of physical properties (solubility, boiling point, etc.) based on chemical structure, however, will not cover these methods in this course.

Experimental data for solubility of each compound is shown below, you'll see this supports our rough analysis using the group contribution principles above:

Ethanol is miscible in water, which means it can dissolve with water of any proportions.

1-nonanol has a solubility of 0.13g/L in water.

Nonane has a solubility of 0.00002g/L in water.

We can conclude that if the three substances are released in a water body, ethanol will migrate much faster and will likely be more difficult to collect for treatment.

We can also use software to calculate physical properties. One such software is from the US EPA and is called EPI Suite – Estimation Program Interface Suite. It is only available to be run on windows and can be downloaded from <https://www.epa.gov/tsca-screening-tools/epi-suite-estimation-program-interface>.

Finding Chemical Properties Using EPI Suite

1. Input the CAS number of the molecule of interest in the “Input CAS #” field and click “Search CAS”. EPI Suite will find the structure based on the CAS Number. To find the CAS number, we can search for the compound on [NIST](#), and the CAS number can be found on the general session on top of the page for the substance.
2. Click “Calculate” to calculate the physical properties.
3. The calculated properties will be shown in the pop-up window or on the bottom of the EPI suite window. We can scroll between tabs to see subsets of results.

Predict the environmental fate of substances using physical property data

✓ Example: Hazardous Materials & Contamination

Naphthalene, toluene, and methylene chloride are common hazardous materials used in the metal production industry. The following data is gathered from the EPI Suite software:

Property	naphthalene	toluene	methylene chloride
Boiling point (°C)	217.9	110.6	40
$\log_{10}$ of octanol/water partition coefficient	3.30	2.73	1.25
Water solubility(mg/L)	31	526	1.3×10^4
Henry’s law coefficient in water (atm·m ³ /mol)	4.40×10^{-4}	6.64×10^{-3}	3.25×10^{-3}
$\log_{10}$ of soil adsorption coefficient	3.189	2.369	1.337

Say a mixture of these three substances is accidentally released into the soil with some groundwater. Based on the physical property data:

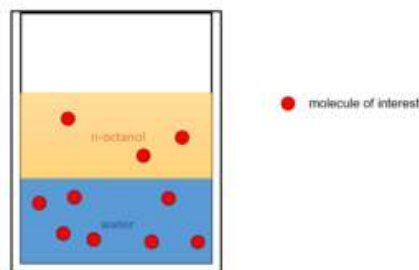
- a. Which substance is the most likely to be transported in the groundwater?
- b. Which substance is the most likely to contaminate the soil?

Solution

- a. Methylene chloride is the most likely to be transported in the water because of its much higher solubility compared to the other two substances.
- b. Naphthalene is the most likely to contaminate the soil because it has the highest soil adsorption coefficient.

What is the octanol/water partition coefficient (K_{ow})?

The octanol/water partition coefficient(K_{ow}) can be measured by dissolving a substance in a container with n-octanol(a common non-polar solvent) and water(a common polar solvent). N-octanol is not soluble in water, so water and n-octanol will form separate phases. This allows us to measure the distribution of the third substance between water (a polar phase) and n-octanol (a non-polar phase).



$$K_{ow} \quad (7.2.1)$$

$$K_{ow} = \frac{\text{concentration of the substance in n-octanol}}{\text{concentration of the substance in water}} \quad (7.2.2)$$

We often express the partition coefficient in the form of $\log_{10}(K_{ow})$.

In general, the process of dissolving one substance in another is called **absorption**

✓ Exercise: Using the Property of K_{ow} to Select a Pollution Control Method

We will continue with the previous example with naphthalene, toluene, and methylene chloride. Their properties predicted by EPI Suite are shown below:

Property	naphthalene	toluene	methylene chloride
Boiling point (°C)	217.9	110.6	40
$\log_{10}$ of octanol/water partition coefficient	3.30	2.73	1.25
Water solubility(mg/L)	31	526	1.3×10^4
Henry's law coefficient in water (atm·m ³ /mol)	4.40×10^{-4}	6.64×10^{-3}	3.25×10^{-3}
$\log_{10}$ of soil adsorption coefficient	3.189	2.369	1.337

a. Say each of these substances is present in a wastewater stream at a steel manufacturing plant in equal concentrations. We are to try to remove these substances by contacting them with a non-polar solvent that has similar properties to n-octanol (and leaving this for sufficient time). Which substance will have the lowest concentration in the wastewater stream after this contact?

b. Suppose the steel-manufacturing plant produces $1 \times 10^6 L$ of wastewater per day containing naphthalene at a concentration of $1.0 \times 10^{-3} \text{ mol/L}$. This wastewater is sent to a wastewater treatment plant, where the wastewater produced in one day is gathered and put in contact with 5000L of a non-polar solvent that has similar properties to n-octanol. What is the concentration of naphthalene in the water after this treatment? You can assume there is sufficient contact time for the solvent to absorb the naphthalene.

Solution

a. Naphthalene will end up with the lowest concentration in the wastewater because it has the highest K_{ow} . This means out of the three substances naphthalene will have the largest proportion absorbed by the non-polar solvent.

b. **Step 1:** Calculate the total moles of naphthalene:

$$n = 1.0 \times 10^{-3} \text{ mol/L} \times 1 \times 10^6 L = 1000 \text{ mol}$$

Step 2: Calculate the moles of naphthalene still dissolved in the water after the absorption process:

We can set the number of moles of naphthalene remaining in the water to be x mol, then the number of moles of naphthalene entering the non-polar solvent can be expressed as $(1000-x)$ mol.

$$\frac{\text{concentration of the substance in nonpolar solvent}}{\text{concentration of the substance in water}} = K_{ow}$$
$$\frac{\frac{1000-x}{5000}}{\frac{x}{1 \times 10^6}} = 10^{3.30}$$

We can solve the equation using excel solver or a graphing calculator to find: $x = 91.1 \text{ mol}$.

Step 3: Calculate the final concentration of naphthalene:

$$\frac{91.1 \text{ mol}}{1 \times 10^6 \text{ L}} = 9.11 \times 10^{-5} \text{ mol/L}$$

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7.3: Life Cycle Assessment

Learning Objectives

By the end of this section, you should be able to:

- **Understand** the steps involved in life cycle assessment (LCA)
- **Interpret** LCA results critically

Life Cycle Assessment

Terminology

- **Cradle-to-grave:** this scope includes all aspects of a product, starting from raw material extraction to the product's end of life (use and disposal)
- **Cradle-to-gate:** this scope includes all aspects of a product from raw material extraction to production, but does not include the product's use or disposal
- **Gate-to-gate:** this scope includes the manufacturing/production and processing aspects of a product only

Life Cycle Assessment (LCA) is a technique used to quantify the environmental impact of a product from raw material acquisition through end of life disposition (**cradle-to-grave**)



Product assembly image from [Sammutawe / CC BY-SA](#)

There are four stages of a life cycle assessment:

1. **Step 1: Goal Definition and Scoping:** Identify the LCA's purpose, the products of the study, and determine the study boundaries. This can include things like what is included and what is not included in the study
2. **Step 2: Life-cycle Inventory:** Quantify the energy and raw material inputs and environmental releases associated with each life cycle phase.
3. **Step 3: Impact Analysis:** Assess the impacts on human health and the environment.
4. **Step 4: Interpret Results:** Evaluate opportunities to reduce energy, material inputs, or environmental impacts at each stage of the product life-cycle.

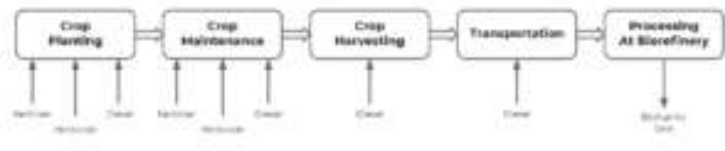
Life Cycle Assessments are based on international standards set by the International Organization for Standardization (ISO 14040).

Each of the steps are set by different ISOs:

- Step 1: ISO 14041
- Step 2: ISO 14041
- Step 3: ISO 14042
- Step 4: ISO 14043

✓ Exercise: Biofuels Product Scope

Consider the following system boundary diagram for the production of biofuels. Which scope does this representation cover (cradle-to-grave, cradle-to-gate, or gate-to-gate)?



Solution

This diagram represents a **cradle-to-gate** scope because it shows the raw materials used for the production of biofuels, the transportation of raw materials, as well as initial processing.

Step 1: Goal Definition and Scoping

Define the goal:

- What is the intended application of the study?
- Who is the intended audience?

Define the scope:

- What is the product system to be studied?
- What is the functional unit?*
- What are the boundaries of the product system?
- What are the assumptions and limitations of the study?
- What impact categories need to be included in the study?

***Functional Units:** a measure of the function of the studied system. It provides a reference to which the inputs and outputs can be related and enables a comparison of two essentially different systems.

Examples of functional units:

- For a paint system (the paint as well as layers of coating materials applied to a surface), the functional unit may be defined as the unit surface protected for 10 years
- For a printer, the functional unit may be defined as the number of printed pages of an acceptable print quality
- For a power generation system, the functional unit may be defined as 1kWh of electricity

✓ Example: Reusable Shopping Bags

text

Solution

text.

Let's say you own a local grocery store in Kitsilano. Your customers start requesting that you sell reusable shopping bags to minimize waste. You think it's a great idea, but want to make sure that the reusable shopping bags you sell have the lowest environmental impact. Since you are an engineer and learned about LCA in CHBE 220, you decide to perform a streamlined LCA.

What is your **goal**?

Determine which shopping bag has the lowest environmental impact

After doing a search of what is available on the market, you determine that your options for shopping bags are as follows:

- Single use paper
- Single use plastic
- Reusable plastic
- Reusable cotton

What are your **system boundaries and process**?

To simplify your LCA, you make the following assumptions:

- All bags are manufactured 100km from the customer
- All bags travel 10km from the customer to the end of life
- Half of paper bags are recycled at end of life and the other half go to a landfill
- Plastic and cotton bags go to landfill at the end of life



What is the **functional unit** for this system?

Let's take our functional unit to be the amount of shopping bags consumed by a household to carry 70 grocery items (~7 items per bag per trip) home from the supermarket each week for 52 weeks. Note you'll see that each bag type in the table below has relative capacities, and this is used to account for some bags having the ability to carry more or fewer items than others while comparing to single-use plastic bags as a basis.

Bag Type	Single-Use Plastic	Single-Use Paper	Reusable Plastic	Reusable Cotton
Material	HDPE	Unbleached Kraft paper	Polypropylene	Cotton
Mass per bag	7g	42.6g	95g	85g
Relative Capacity	1	0.9	1.1	1.1
Bags per year	520	578	4.55	4.55
Mass bags per year	3640g	24622.8g	432.25g	386.75g

Step 2: Life Cycle Inventory

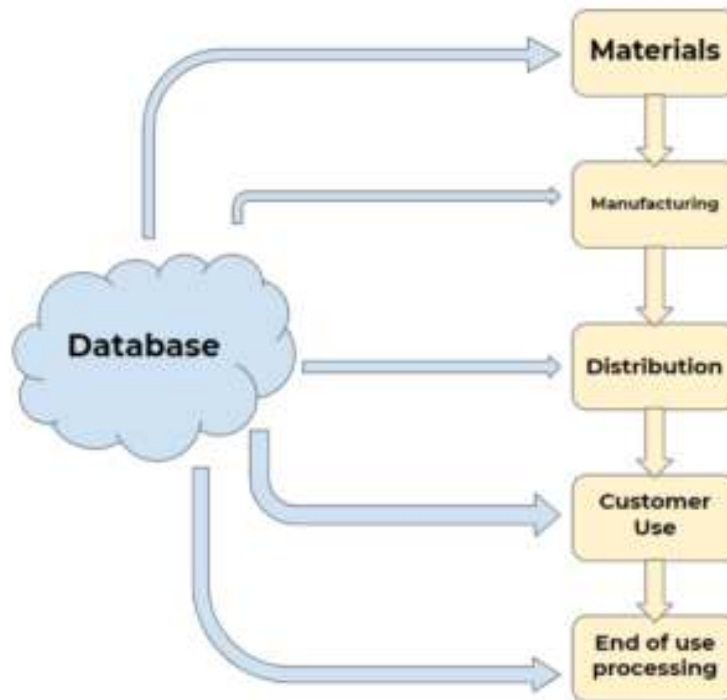
The life cycle inventory step is a highly data-intensive step that is based on detailed material and energy balance analyses over the life cycle of a product. The aim of this step is to account quantitatively for the components which make up the life cycle for our products.

Advantages:

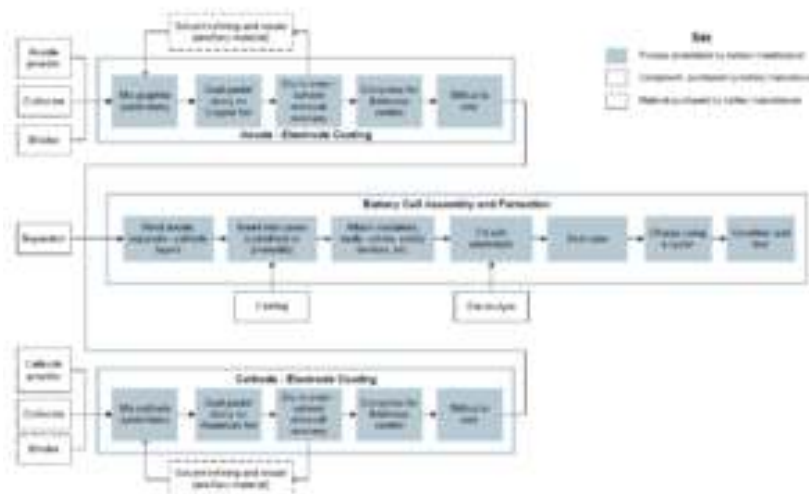
- Quantifiable data for each product to assess impacts (although these can be highly dependent on the assumptions we make in step 1)

Challenges:

- Assumptions made when data unavailable
- Can be very time-intensive to account for all materials, energy, and steps to create a product



A life-cycle inventory can be summarized by block flow diagrams. The following diagram is one example for a typical manufacturing process for lithium-ion battery cells.[1]



✓ Example: Reusable Shopping Bags Life-Cycle Inventory

text

Solution

text.

Once again, you'd like to continue your LCA on the four options of shopping bags that you can offer in your grocery store. You gather the following information for quantities involved in each step of the lifecycle of these bags. Note most of these are measured in terms of a mass (eg grams, g) or mass per distance for travel (eg. tonne-kilometers, tkm).

Single-Use Plastic Bag	
Polyethylene, HDPE, granulate	3640g
Stretch blow moulding	3640g
Transport, 100km manufacturing to customer	0.364tkm
Transport, municipal waste collection, 10km customer to landfill	0.0364tkm
Disposal, polyethylene, 0.4% water, to sanitary landfill	3640g

Single-Use Paper Bag	
Kraft paper, unbleached, at plant	24622.8g
Production of paper bags	24622.8g
Transport, 100km manufacturing to customer	2.4623tkm
Transport, municipal waste collection, 10km customer to landfill/recycling	0.24623tkm
Disposal, packaging paper, to sanitary landfill	12311g
Recycling paper	12311g

Reusable Plastic Bag	
Polyethylene, granulate	432.25g
Extrusion, plastic film	432.25g
Transport, 100km manufacturing to customer	0.043225tkm
Transport, municipal waste collection, 10km customer to landfill	0.0043225tkm
Disposal, polyethylene, to sanitary landfill	432.25g

Reusable Cotton Bag	
Textile, woven cotton, at plant	3 8 6 . 7 5
Transport, 100km manufacturing to customer	0 . 0 3 8 6 7 t k m
Transport, municipal waste collection, 10km customer to landfill	0 . 0 3 8 6 7 t k m
Disposal, inert material, to sanitary landfill	3 8 6 . 7 5 g

Step 3: Impact Assessment

Impact Assessment Results: impact assessment converts the inventory into impact categories or endpoints, detailing human health and environmental impact.



*ODP: ozone depletion potential – the potential the battery process has for releasing chemicals that degrade the ozone layer

*OnCH: occupational non-cancer hazard – the potential the battery process has for exposing people that work on this battery to other diseases, injuries, or other health problems

*POP: photochemical oxidation potential – the potential the battery process has for releasing chemicals that react in the sunlight and release harmful products into the environment

*EOL: end-of-life; note that the negative values for the EOL bar signify recovery of the material at the end of battery's life, which reduced the life-cycle impact.

Step 4: Report Results

Life cycle interpretation: findings of the inventory analysis or impact assessment are evaluated in relation to the goal and scope of the study to reach conclusions and recommendations.

In this stage we aim to:

1. Identify significant issues
2. Evaluate results for completeness, consistency, and sensitivity of the data
3. Draw conclusions and make recommendations consistent with the goal and scope of the study

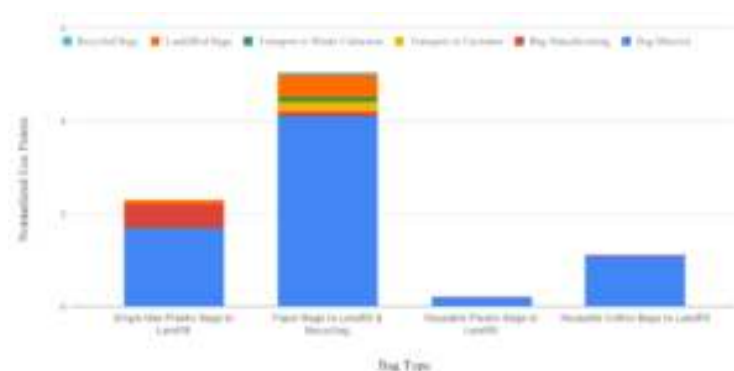
✓ Example: Reusable Shopping Bags LCA Results

text

Solution

text.

Consider the following chart that you put together after conducting an impact assessment on the 4 options for shopping bags. Note in this case that a lower score will mean less environmental impact (ie. lower score is better).



After contacting suppliers, you find that the cost per year for each of the shopping bags is as follows:

- Single-Use Plastic: 10.40 dollars/year
- Single-Use Paper: 40.46 dollars/year
- Reusable Plastic: 4.55 dollars/year
- Reusable Cotton: 27.30 dollars/year

Some questions you might ask:

- Which bag would you promote given the impact information?
- Which bag would you promote given the cost information?
- Which bag would customers most likely lean towards given the cost?
- Are there any assumptions you would change?
- Did your final result differ from your initial guess?

Given both the cost information and the environmental assessment, you might decide to go with the reusable plastic shopping bags, or offer these alongside re-useable cotton bags with some information to customers.

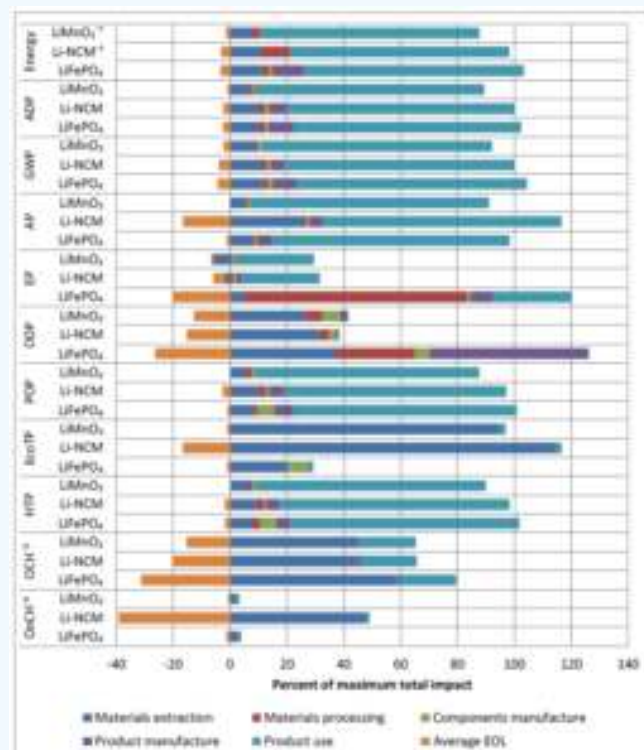
✓ Exercise: LCA Results on Different Lithium-Ion Batteries

A life-cycle assessment is conducted on two different types of vehicle batteries: electric vehicle (EV) batteries and plug-in hybrid electric vehicle (PHEV) batteries. Each of these has different lithium-ion chemistries. The EV batteries have 3 different chemistries ($LiMnO_2$, $Li - NCM$, and $LiFePO_4$), while the PHEV batteries have 2 different chemistries ($LiMnO_2$ and $LiFePO_4$).[1]

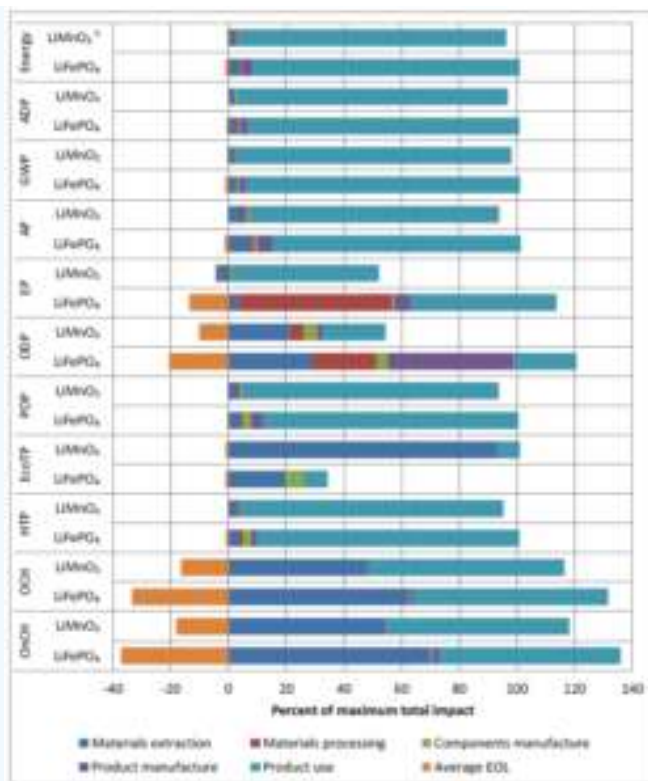
Legend for the charts:

- *ADP: abiotic depletion potential
- *AP: acidification potential
- *EcoTP: ecological toxicity potential
- *EP: eutrophication potential
- *GWP: global warming potential
- *HTP: human toxicity potential
- *OCH: occupational cancer hazard
- *ODP: ozone depletion potential
- *OnCH: occupational non-cancer hazard
- *POP: photochemical oxidation potential

EV Batteries:



PHEV Batteries:



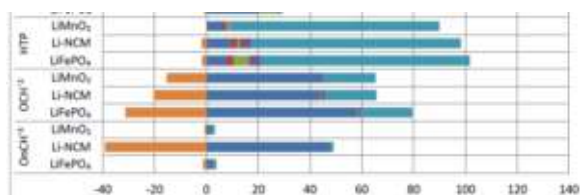
Your client is asking you to make a recommendation on which vehicle type (EV or PHEV) they should manufacture based solely on human toxicity potential through *product use* for batteries. Which vehicle type do you recommend based on the information you have and why?

Solution

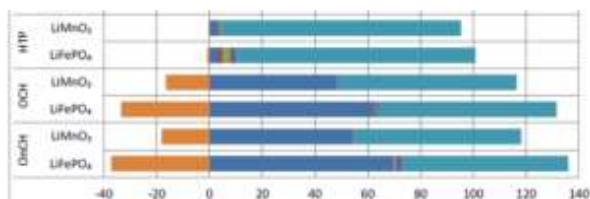
Add example text here.

Step 1: Determine where the human toxicity potential (HTP) is located on the graph.

Step 2: Compare the data of both EV and PHEV batteries side by side. Note that the ‘product use’ factor is the light blue/teal bar EV:



PHEV:



Step 3: Determine the approximate percentages for ‘product use’ for each of the factors and the batteries.

EV:

Health Factor	$LiMn_2$	$LiFePO_4$	$Li - NCM$
HTP	80%	80%	80%

PHEV:

Health Factor	$LiMn_2$	$LiFePO_4$
HTP	90%	90%

Step 4: Determine which battery type is the best choice based on your client's specifications.

Since the percentages are consistent among battery chemistries, our choice will be between the EV battery and the PHEV battery. The EV has a smaller impact on human toxicity potential through product use when compared to PHEV. Therefore, we recommend an **EV battery**.

References

[1]"Application of LifeCycle Assessment to Nanoscale Technology: Lithium-ion Batteries for Electric Vehicles", United States Environmental Protection Agency, 2013.

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7.4: Green Engineering Review

Terms to Know

An interactive or media element has been excluded from this version of the text. You can view it online here:

<https://pressbooks.bccampus.ca/chbe220/?p=1979>

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7.5: Practice Exercises

✓ Exercise: Waste Management Hierarchy

British artist Damien Hirst has a series of artwork of well-preserved animal corpses suspended in formaldehyde to express the concepts of life and the inevitable death at the end of it. Recent research shows that the artwork has a risk of leaking formaldehyde, a toxic and carcinogenic compound, during the exhibition.

Based on the concept of waste management hierarchy, what is the most effective way to prevent the leak of formaldehyde? Rank the following actions from the most to least effective?

- Perform regular maintenance to make sure the container is sealed
- Place activated carbon around the container to absorb the leaked formaldehyde
- Use another method to preserve the animals that do not involve the use of toxic substances
- Provide personal protective equipment for visitors
- Warn people about the risk before visiting but do not implement any safety measurements

Solution

Add example text here.

c, a, b, d, e

c – the production of formaldehyde is eliminated from the source

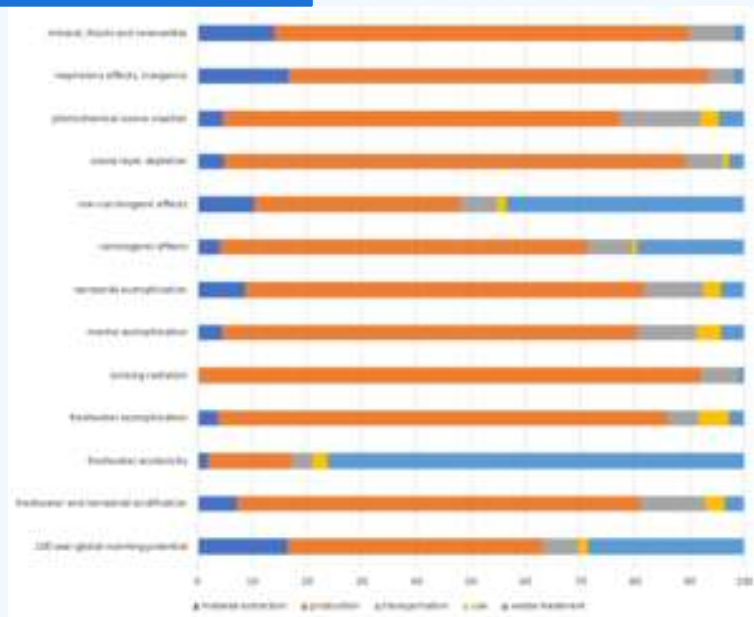
a – the production of formaldehyde fume is eliminated, but toxic material is still used, and there is still a risk of the leak of toxic materials

b – activated carbon will reduce the effect but not totally eliminate it

d – reduced the health effect to the visitors, but formaldehyde is released into the environment

e – formaldehyde is directly released into the environment

✓ Exercise: Life Cycle Analysis



The graph above shows the life cycle analysis of paper cups. Use the graph to answer the following questions:

- If we want to improve the life cycle of paper by focusing on reducing inorganics causing respiratory effects, which stage of the life cycle should we focus on?
- If we want to compare the total mass of freshwater eutrophication substances with terrestrial eutrophication substances, can we get the information using the graph? Why?

Solution

Add example text here.

a) production stage

Find the part of the graph investigating “respiratory effects, inorganics”:

respiratory effects, inorganics



The relative lengths of the bars represent the contribution from each life stage. We can see that the bar representing the production stage is much longer than all the other stages. This means that the production stage is emitting a lot more inorganics that result in negative respiratory effects. Therefore, focusing on improving the production stage will be the most effective in terms of eliminating inorganics causing respiratory effects.

For b), it is not possible to compare the total mass of types of hazardous substance emissions using this diagram. In this diagram, each category is scaled to 100% without stating the total overall impact.

✓ Exercise: Environmentally Hazardous Chemicals

DEHP(2-ethylhexyl phthalate), $C_{10}H_{21}Cl$, and lead are 3 types of environmentally hazardous chemicals released by the soft plastic that we use in daily life. The data is calculated using the EPI Suite software:

Property	DEHP	$C_{10}H_{21}Cl$	lead
Boiling point (°C)	384	223.4	485.37
$\log_{10}$ of octanol/water partition coefficient	7.60	5.51	0.73
Water solubility(mg/L)	0.27	1.133	9581
Henry's law coefficient in water (atm·m ³ /mol)	2.70×10^{-7}	1.05×10^{-1}	2.45×10^{-2}
$\log_{10}$ of soil adsorption coefficient	5.078	3.422	1.121

Say a mixture of these three substances is accidentally released into the soil with some groundwater. Based on the physical property data:

- Which substance is the most likely to be transported in the groundwater?
- Which substance is the most likely to contaminate the soil?
- Say each of these substances is present in a wastewater stream at a steel manufacturing plant in equal concentrations. We are to try to remove these substances by contacting them with a non-polar solvent that has similar properties to n-octanol (and leaving this for sufficient time). Which substance will have the lowest concentration in the wastewater stream after this contact?

Solution

Add example text here.

- Lead is the most likely to be transported into the water due to its high solubility, especially when comparing it to the other two substances.
- DEHP is the most likely to contaminate the soil because it has the highest soil adsorption coefficient.
- DEHP will have the lowest concentration after the removal process because it has the highest $\log_{10}(K_{ow})$ value.

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CHAPTER OVERVIEW

8: Process Safety

[8.1: An Introduction to Process Safety](#)

[8.2: Hazard Identification](#)

[8.3: Process Safety Review](#)

[8.4: Practice Exercises](#)

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8.1: An Introduction to Process Safety

Learning Objectives

By the end of this section, you should be able to:

- **List and describe** basic process safety terminology

Appreciate the need for process safety

Prioritize process safety changes based on inherently safer design strategies

Terminology

Accident – the occurrence of a sequence of events that produce unintended injury, death or property damage

Safety – strategy of accident prevention

Loss prevention – prevention of injury to people, damage to the environment, loss of equipment, inventory, production, reputation or economic loss

Hazard – a chemical or physical condition that has the potential to cause an accident (example of significant chemical plant hazard: flammable, explosive, reactive & toxic hazards)

Risk – the probability of an accident occurring and the consequence of it

Incident – loss of control of material or energy (e.g. leak in a pipe)

Scenario – a sequence of events causing the hazard to result in an accident

Outcome/Consequence – the physical manifestation of an accident

Safety Triangle

The safety triangle shows three essential aspects to achieve workplace safety:



Each of these aspects highlight different key pieces needed in an organization to ensure it can operate safely. Expanding on each aspect of the safety triangle:

Technical – characterization and control of hazards

Management – policies and procedures for safety

Cultural – motivating people to do things safely

Statistics on incidents

OSHA – Occupational Safety & Health Administration

incident rate = incidents per 100 worker per year
 every working year = 2000 hours
 incident rate = incidents per 200,000 hours exposure

Need to define what incident means

FAR – Fatal Accident Rate

fatalities per 1000 employee over their working life
 = 10^8 hours of exposure
 50 years pf exposure $\times$ 2000 hrs/yr $\times$ 1000 employees

Fatality Rate – per person per year – exposure poorly defined

For these statistics, smaller is better!

✓ Exercise: Incident Rate Calculation

Suppose 2 workers have experienced an incident of CO exposure on our site while the total hours of exposure for all workers for the risk of CO exposure are 720,000 hours. Calculate the OSHA incident rate for CO exposure on the site.

Solution

Add example text here.

$$\begin{aligned}\text{incident rate} &= \text{number of incident exposure} \times \frac{200,000}{\text{number of working hours}} \\ &= 2 \times \frac{200,000}{720,000} \\ &= 0.56\end{aligned}$$

✓ Exercise: Incident Rate Conversion

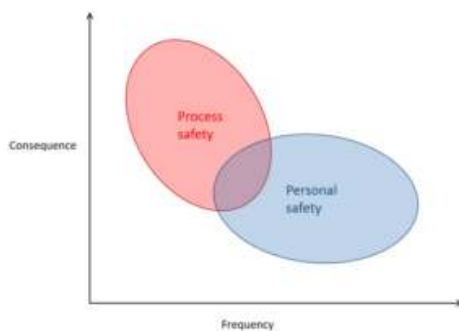
Suppose a fatal accident has an OSHA incident rate of 8.9×10^{-5} , express the incident rate in the form of the FAR accident rate.

Solution

Add example text here.

$$\begin{aligned}\text{fatal accident rate} &= \frac{\text{OSHA incident rate} \times 10^8 \text{hours}}{200,000 \text{hours}} \\ &= \frac{8.9 \times 10^{-5} \times 10^8}{200,000} \\ &= 0.0445\end{aligned}$$

Personal vs. Process Safety



process safety – low frequency, potentially higher consequence

personal safety – higher frequency, generally lower consequence

Why do Accidents Occur?

We choose to handle dangerous process materials and energies to make value-added products that can be very beneficial.

- If we handle these materials, there is a **potential** for accidents
- Things can be done to reduce the **likelihood** and **severity** of accidents to negligible or tolerable levels

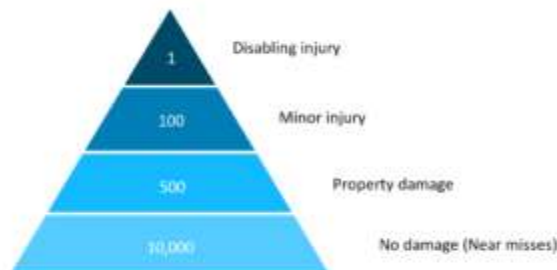
How do accidents occur?

Major Process Industry Incidents and Their Properties

Here we consider the impact of three general categories of the worst types of process industry incidents fire, explosion, and toxic release.

	Probability	Hazard Fatalities	Hazard Economic Loss
Fire	High probability • comparing to other accidents listed here	Low fatalities • Local to area	Intermediate economic losses • Local to plant
Explosion	Moderate probability	Intermediate fatalities • Local to plant	High economic losses • Plant + surroundings
Toxic Release	Low probability	High fatalities • Around the plant and population	Low economic losses

The Hazard Pyramid



The incidents that do not result in any damage (or near misses) are defined by when the event did not lead to harm but only because of happenstance or luck^[1]. It is important for us to report these incidents and learn from them.

✓ Exercise: Reporting Incidents at UBC

UBC Centralized Accident / Incident Reporting System (CAIRS) is a platform for all UBC students, visitors, and employees to report incidents in UBC workspaces. Which of the following statement is true about CAIRS? Explain your answer.

- Only incidents involving death or injury workers are required to be immediately reported on CAIRS
- Only incidents involving death, injury, or property damage of workers are required to be immediately reported on CAIRS
- All incidents and accidents that occur in UBC workspaces must be reported, including near misses that do not result in any damage
- If you have reported the incident to your supervisor, you do not need to report the incident on CAIRS

Solution

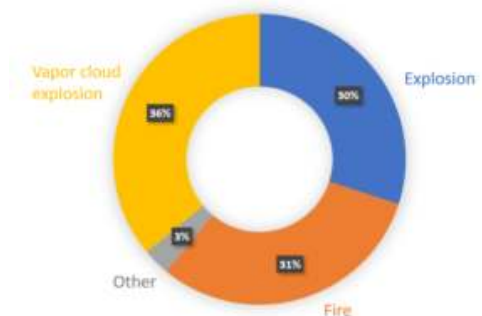
Add example text here.

Answer: c

All incidents should be reported regardless of if the incident has led to physical damage to workers or property damage. Reporting near misses is an important way for us to learn from them and mitigate the incidents to avoid causing harm to people or properties.

All accidents/incidents involving UBC workers (faculty, staff & student workers) or practicum students must be immediately reported to the responsible supervisor and then on-line through the UBC Centralized Accident/Incident Reporting System (CAIRS).

Common Types of Process Industry Incidents



One Way to Tackle Hazards

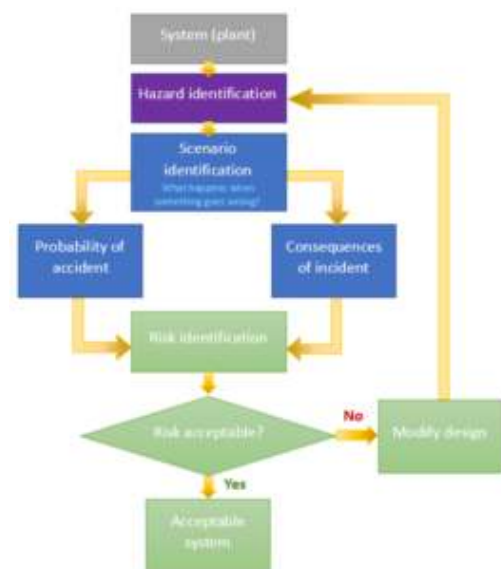
Inherently safer design: permanently and inseparably reduce or eliminate process hazards → what we don't have in the process we don't need to control

Design Strategies to Enhance Safety

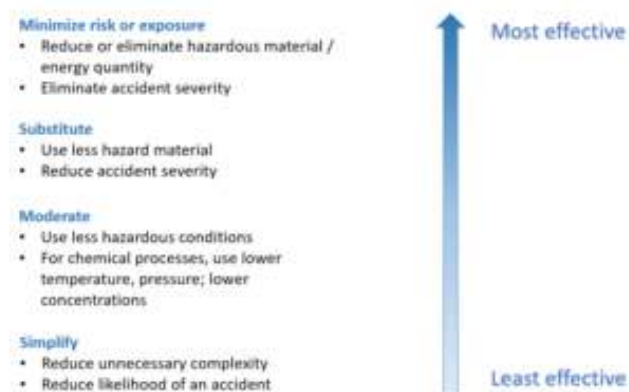
For every risk assessment, ask:

- What can go wrong & how?
- What are the chances (probability)?
- What are the consequences?

If the risk is not acceptable, modify the design and go through the risk assessment process again before proceeding to the next stage of the design process.

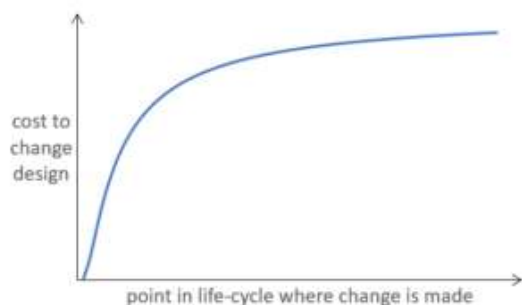


Inherently Safer Design Strategies



When should we incorporate safety in the design process?

We can implement changes in designs to improve safety at any point. But as with most design processes, it is generally least expensive to do so at the start of the design process.



Links for Resources:

Textbook for Safety:

D. A. Crowl and J. F. Louvar *Chemical Process Safety: Fundamentals with Applications* Fourth Edition, 2019 or Third Edition, 2011 Available on Library Online Course Reserves on Canvas or through UBC Library: [Chemical Process Safety: Fundamentals with Applications – UBC library](#)

Roy E. Sanders *Chemical Process Safety : Learning from Case Histories* Available on UBC Library: <http://tinyurl.com/v232qe8>

J. Foster and B. Barnetson *Health and Safety in Canadian Workplaces* <https://www.aupress.ca/books/120259-health-and-safety-in-canadian-workplaces/>

AICHE Certificate Program:

Safety in Chemical Process Industries <https://www.aiche.org/ccps/community/technological-communities/safety-and-chemical-engineering-education-sache>

Chemical Safety Hazard Investigation Board: <https://www.csb.gov/>

AICHE Center for Chemical Process Safety: <https://www.aiche.org/ccps>

Significant Disasters

Flixborough, England, 1974

- rupture inadequately supported bypass pipe, 155 °C, 7.9 atm
- vapor cloud 30 ton cyclohexane
- explosion & fire inventories (10 days)

- 28 killed, 36 + 53 injured, much damage

Link to source:

<https://www.hse.gov.uk/comah/sragtech/casefliborough74.htm>

Seveso, Italy, 1976

- reactor out of control (run away)
- vapor cloud 2 kg dioxin
- 700 affected, 730 evacuated
- 252 km contaminated (40 factories)

Link to source:

<https://www.hse.gov.uk/comah/sragtech/caseseseveso76.htm>

Bhopal, India, 1984

- not operating scrubber & flare system
- vapor cloud 25 ton toxic MIC
- 2000 killed, 20.000 injured, no damage

Link to source:

<https://www.hse.gov.uk/comah/sragtech/caseuncarbide84.htm>

Oppau, Germany, 1921

- 4500 tonnes of ammonium sulfate and ammonium nitrate explosion
- over 500 killed, over 2000 injured
- forming a crater 125m long and 19m deep

Link to source:

https://h2g2.com/edited_entry/A11816697

Texas city, Texas, US, 1947

- fire on cargo containing 2200 tonnes of ammonia nitrate, mishandled with steam
- chain reaction of fire and explosion
- over 581 killed
- one of the largest non-nuclear explosions in the history

Link to source:

<http://www.local1259iaff.org/disaster.html>

References

[1] J. Foster and B. Barnetson, *Health and Safety in Canadian Workplaces*, Athabasca University, Edmonton, AB, Canada, 2016.

Some texts and figures are adopted from: D. A. Crowl and J. F. Louvar *Chemical Process Safety: Fundamentals with Applications* Fourth Edition, 2019

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8.2: Hazard Identification

Learning Objectives

By the end of this section, you should be able to:

- **List and describe** process hazard analysis techniques

Apply the following process hazard analysis methods: what-if analysis, checklist/checklist combined with what-if analysis, fault-tree analysis

Interpret the following process hazard analysis methods: failure modes and effect analysis (FMEA)

PHA – Process Hazard Analysis

Two Major Categories:

PHAs are separated into two major categories:

1. **Non-scenario based methods** – look at a process in general; effectiveness of the output depends largely on the expertise of the PHA team members.
2. **Scenario-based methods** – used to predict accident scenarios; a lot more detailed and specific.

Before Starting PHA, Need:

- Extent of hazards – the strength or magnitude of the hazard (e.g the area affected by a flood, the strength of an earthquake described by the Richter Scale)
- Number of people potentially affected
- Age of process
- Operating history – process changes, failures, past incidents

Generally, PHA should be reviewed and to some extent redone at least every 5 years

Preparing for PHA Meetings

- Selecting the team

Generally, we want diversity- Engineering and process operations expertise, design, operations, maintenance...

One team member with process experience

One team member knowledgeable in PHA methodology

- Develop schedule
- Gather and distribute information to be analyzed
- Assign meeting roles (leader, scribe, etc.)

Before PHA

- Perform site walk-through

Observe layout, verify information, obtain mental picture

Key contacts at facility for background, questions, etc

The whole team should participate

- Verify key information in documents

Information Required for PHA

- PFDs with material balances

- Safety Data Sheets (SDS) for all relevant substances
- Relevant standards for construction or operation
e.g. American Society of Mechanical Engineers (ASME)
- Plant layout, equipment arrangement
- Equipment design bases – temperature and pressure that the equipment is designed for (how much temperature/pressure the equipment can withstand)
- Operating procedures
- Relief valve, flare/scrubber systems
- Critical alarms and shutdown
- Previous incidents

What-if Analysis

What-if analysis is a scenario PHA method as it investigates specific problems and traces what would happen if they occur.

- Creates a list of “what-if” questions that could potentially lead to process failures and/or safety hazards
- Identifies problems but doesn’t specify the likelihood
- Can include problems with regards to buildings, power systems, raw materials, products, storage, material handling, in-plant environment, operating procedures, work practices, management practices, plant security, etc.

Typical what-if questions:

What if the inlet stream is blocked?

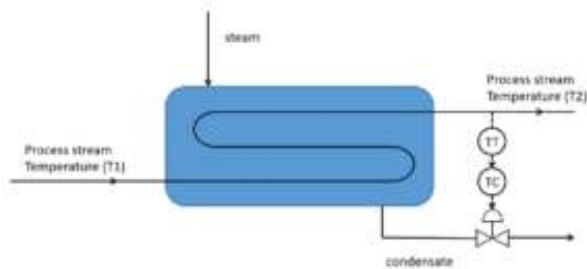
What if the pipe leaks?

What if the temperature transmitter stops working?

What if the valve fails open / fails closed?

Note: when we are talking about valves, a common language we use is that the valve “fails open”. It means the valve breaks down while it is open and does not close anymore when it should. Similarly, the valve “fails closed” means the valve fails when it is closed and will not open.

- Suppose we focus on the analysis of a reboiler to heat a recycled portion of the bottoms stream coming from a distillation column before it is sent back to the column:





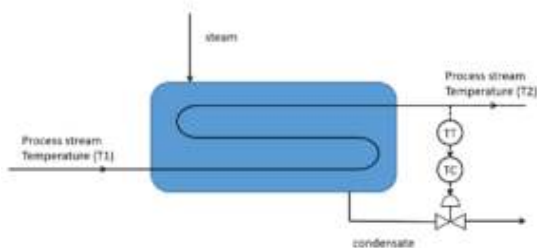
✓ Example: Reboiler What-if Analysis

text

Solution

text.

For the same reboiler system as describes previously and shown below, what is the most important consequences if the temperature transmitter stops working and keeps reporting a low temperature? What is a recommendation we can make to mitigate the most important consequence identified?



Solution

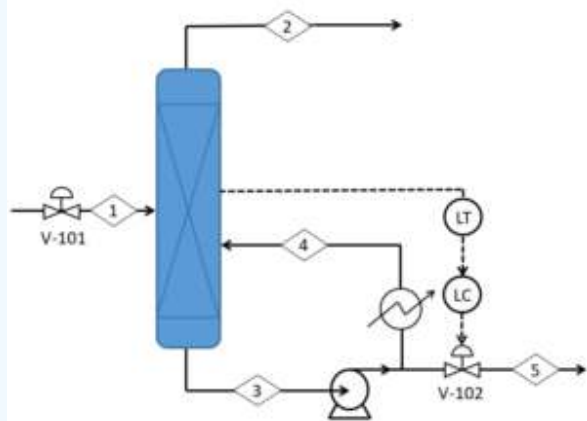
Identify the direct consequences:

If the temperature transmitter keeps reporting a low temperature, the valve will always be open to allow more steam to flow into the reboiler trying to heat up the process steam. This will cause the process steam to overheat, potentially leading to pressure build-up in the process stream.

Recommendations:

A pressure relief valve should be installed on the process stream in case of pressure build-up.

✓ Exercise: Distillation Column What-if Analysis



For the distillation column shown above, perform what-if analyses for the following questions:

- What if stream 2 is blocked?
- What if V-102 fails open?

Solution

Add example text here.

If stream 2 is blocked:

If the stream is blocked, the outflow of the vapor component will be stopped. This will cause the pressure to build up in the distillation column.

A pressure relief valve should be installed in the distillation column to relieve any pressure build-up.

If V-102 fails open:

If V-102 fails open, it will cause free flow of the bottoms out of the distillation column. None of the bottoms will be vapourized by the reboiler and go back to the distillation column. This will affect the vapour-liquid equilibrium in the distillation column, decreasing the efficiency of separation.

Though low separation efficiency may cause operational troubles, there is no significant immediate safety hazard to the distillation unit if V-102 fails open. No specific recommendation is required.

Checklist Analysis

Checklist analysis is a non-scenario PHA method as it suggests common safety issues to assess, thus it is not scenario specific.

A sample checklist can be seen below with items taken from a process safety management (PSM) auditing checklist from the U.S. Occupation Safety and Health Administration (OSHA). This sample is a session from [the Auditing Checklist from OSHA under US department of Labour](https://www.osha-slc.gov/publications/AuditingChecklist.pdf). You can click on the link to see the full checklist.

Question	Response / Found?	Justification / Comments
1.1. Has the employer developed and implemented written operating procedures that provide clear instructions for safely conducting activities involved in each covered process consistent with the process safety information until staff address at least the following elements?		
1.1.1. (A) Initial startup		
Steps for each operating phase		
1.1.2. (B) Normal operations		
1.1.3. (C) Temporary operations		
1.1.4. (D) Emergency shutdowns including the conditions under which emergency shutdown is required, and the assignment of shutdown responsibility to qualified operators to ensure that emergency shutdown is executed in a safe and timely manner.		
1.1.5. (E) Emergency Operations		
1.1.6. (F) Restart shutdown, and		
1.1.7. (G) Startup following a temporary or after an emergency shutdown.		
1.1.8. Operating limits		
1.1.9. (A) Communication of shutdown, and		
1.1.10. (B) Steps required to correct or avoid situations		
1.1.11. (C) Preparation of worksheets generated by the chemicals used in the process		
Safety and health considerations		
1.1.12. (D) Procedures necessary to prevent exposure, including engineering controls, administrative controls, and personal protective equipment		
1.1.13. (E) Control measures to be taken if physical contact or otherwise exposure occurs		
1.1.14. (F) Quality control for raw materials and control of hazardous chemical inventory levels; and		
1.1.15. (G) Any special or unique hazards		

Checklist analysis typically is broken into three steps:

1. Select and develop an appropriate checklist – There may be initial general checklists available. These are then tailored to the specific industry, plant, or process as required.
2. Perform the checklist analysis – this may involve plant tours, document review, interviews with personnel, and equipment testing. Deficiencies are then compiled and recommendations to overcome these are discussed
3. Document the results – The results of the checklist analysis will include the checklist used, deficiencies noted, recommendations, and justifications. These may have a timeline to act on the recommendations and be assigned to certain people for completion or review to ensure they are followed upon.

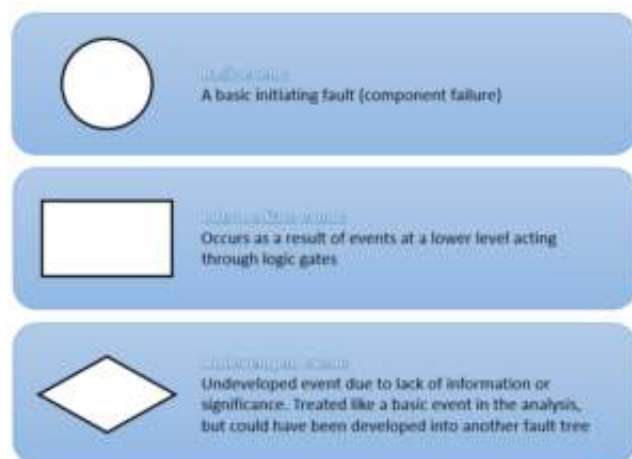
Checklists can be used at any point in the plant design and operation process, from initial design to operation to decommissioning (permanently shutting down a plant).

Checklists can be combined with what-if technique to enhance that technique. With this combined approach, during PHA you would go through a checklist first to help identify hazards and then apply what-if analysis (this would then be considered a scenario method).

Fault-tree Analysis

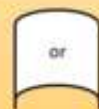
- Identifies relevant events and potential failure pathways leading to one particular incident
- Uses logic diagrams to express relations between initiating events and an incident
- Can be implemented for PHA analysis at any stage of a process from design to the end of life

Below are common symbols used in fault-tree analysis logic diagrams:





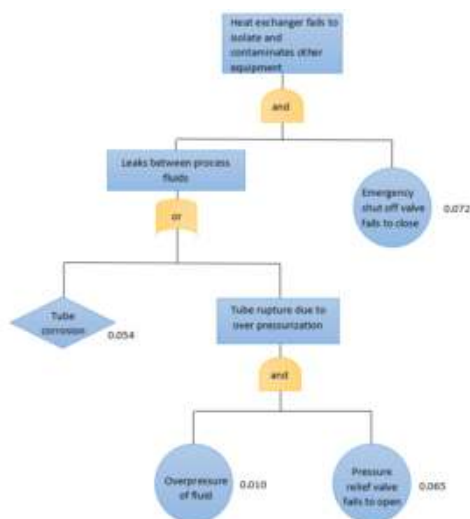
“and” gate
The event only happens when all the input events occur. When we compute the frequency of the event, we **multiply** the frequencies of all input events. Because all frequencies are smaller than 1, the resulting frequency will be smaller than any of the input frequencies.



“or” gate
The event happens when any of the input events occur. When we compute the frequency of the event, we **add** the frequencies of all input events. The resulting frequency will be larger than any of the input event frequencies.

Fault-tree Analysis

Calculate the frequencies of all the intermediate events for the given fault tree:



Solution

We start with the intermediate event that has known frequencies for all of its input events and work our way up.

Step 1: Calculate the frequency of “tube rupture due to over-pressurization”:

The intermediate event is connected to the input events by an “and” gate, so we multiply the frequencies.

$$0.0010 \times 0.065 = 0.0065 \quad (8.2.1)$$

Step 2: Calculate the frequency of “leaks between process fluids”:

The intermediate event is connected to the input events by an “or” gate, so we add the frequencies.

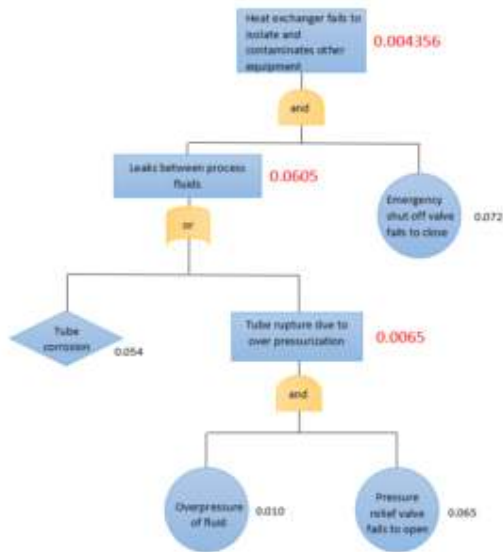
$$0.054 + 0.0065 = 0.0605 \quad (8.2.2)$$

Step 3: Calculate the frequency of “heat exchanger fails to isolate and contaminates other equipment”:

The intermediate event is connected to the input events by an “and” gate, so we multiply the frequencies.

$$0.0605 \times 0.0702 = 0.004356 \quad (8.2.3)$$

So in general, the resulting frequencies are:



Failure Modes and Effect Analysis (FMEA)

- Tabulation of plant equipment, failure modes (how the equipment can fail), and the effects of these failures
- Identify failure modes then analyze the result of these failures individually

Sample failure mode of an equipment:



- Not useful for a combination of failures (considers only failures in isolation)
- Can add criticality analysis to analyze the consequence of failure (this will analyze the severity of the effects of failure and the likelihood of occurrence)
- Need 2 or more experienced analysts to analyze equipment

Sample FMEA Table

Date: _____		Page ____ of ____	
Plant: _____		Reference: _____	
System: _____		_____	

Item	Identification	Description	Failure Modes	Effects	Safeguards	Actions
4.1	Control valve on the condensate line for HCl column reboiler (E-103)	Motor-operated, normally open, steam service	Fails open	Excess flow of steam to the exchanger High pressure and high temperature of process stream to the HCl distillation column (T-101) May exceed pressure in HCl column reboiler or HCl distillation column Off-specification production (i.e., HCl contaminated with Vinyl Chloride)	Flow indicator in the steam line HCl distillation column relief valve vented to flare Operator controlled steam shut-off valve	Consider alarm/shutdown of the system for high steam flow Consider alarm/shutdown of the system for high pressure and/or high temperature in HCl distillation column

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8.3: Process Safety Review

Terms to Know

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8.4: Practice Exercises

✓ Exercise: Safety Action

During a yearly safety assessment, you find that a pressure relief valve in a heat exchanger is rusted and may not open properly in case of a pressure build-up. What is the best course of action?

- a) Report to the project manager and immediately replace the pressure relief valve
- b) Operate the process at a lower pressure to reduce the risk of over-pressurizing
- c) Ignore it because the probability of over-pressurizing is very low

Solution

Add example text here.

a) Report to the project manager and immediately replace the pressure relief valve

Any safety hazard should be reported and addressed as soon as possible.

For b), Operating the process at a lower pressure does not completely eliminate risks and may reduce process efficiency. In the long run, this will cost more than a new pressure relief valve.

✓ Exercise: OSHA Incident Rate for Exposure to Hazardous Materials

Suppose that a total of 12 operators have been exposed to leaking hazardous materials in a chemical plant. The total working hours that might expose the workers to the risk are 870,000 hours. Calculate the OSHA incident rate for exposure to hazardous materials.

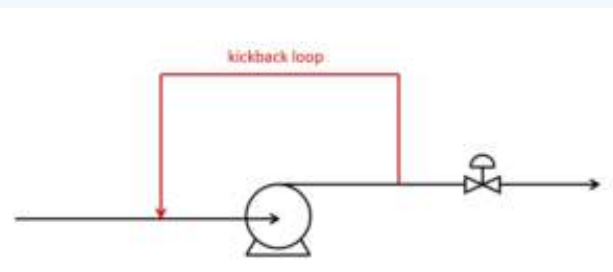
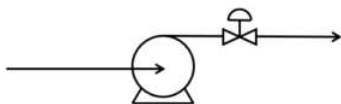
Solution

Add example text here.

$$\begin{aligned}
 \text{incident rate} &= \frac{\text{number of incident exposure} \times 200,000}{\text{number of working hours}} \\
 &= \frac{12 \times 200,000}{870,000} \\
 &= 2.76
 \end{aligned}$$

✓ Exercise: Pump Kickback Loop

Sometimes a kickback loop is added on a pump to prevent damage to the pump when the outlet stream is blocked:



Compare the effect between the kickback loop is present or not when we close the valve (or when the stream after the valve is blocked), explain how the kickback loop prevents damage.

Solution

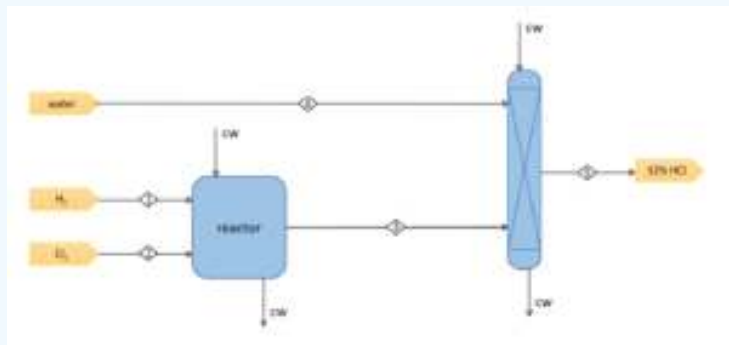
Add example text here.

If no kickback loop present, the pump keeps doing work on the liquid before the valve, but the stream is not able to move forward. As a result, the stream will be heated up. If the stream vapourizes, the vapour may tear up the metal blade in the pump.

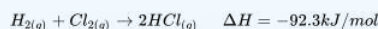
When there is a backflush cycle, the stream will circulate in the kickback loop, which increases the amount of liquid pumped and dissipates the heat.

✓ Exercise: HCl Production What-if Analysis

Shown below is the simplified process of HCl production



The following reaction happens in the reactor at a temperature of 900°C:



In the absorber, HCl gas is dissolved in a water stream (ΔH of solution = -74.8 kJ/mol), producing aqueous HCl solution

Perform what-if analysis regarding the following scenarios:

- What if the cooling water stream in the reactor is blocked? State the direct consequences and recommendations.
- If the cooling water stream in the absorber is blocked, how would the concentration of the product be affected?

Solution

Add example text here.

a) If the cooling water stream is blocked, the temperature in the reactor will rise up due to the exothermic reaction. The gas in the reactor will expand, which leads to pressure increase and potential explosion.

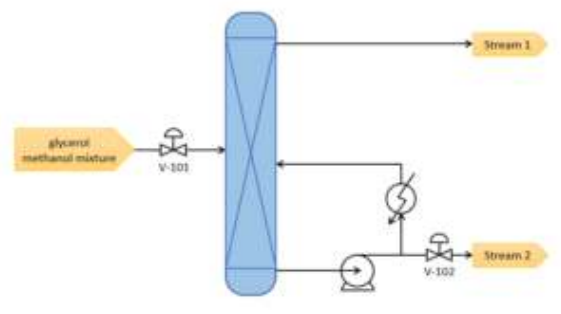
Regular maintenance should be performed and a pressure relief valve should be installed in the reactor.

b) The absorber heats up as the process of HCl dissolving is exothermic. As the temperature increases, the solubility of HCl decreases, which leads to a lower concentration of HCl in the product.

✓ Exercise: Glycerol Purification

We use a distillation column to purify a stream of glycerol with methanol impurities:

	Boiling Point (°C) at 1 atm
Glycerol	290
Methanol	65



Base on the given information, answer the following questions:

- What is the major component in stream 1 & 2?
- Draw a control loop that regulates the rate of separation by controlling the level of the liquid in the column.
- If the level in the column is too high, is the valve in the control loop open or closed?
- Is there any safety hazard if valve V-102 fails closed?

Solution

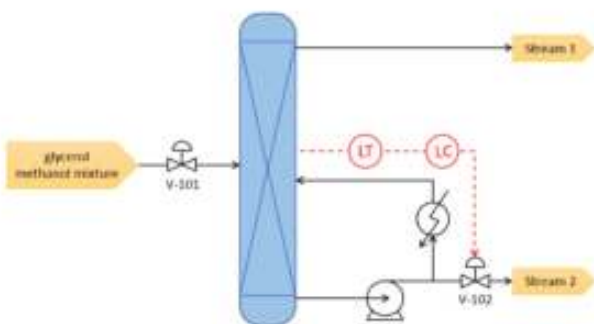
Add example text here.

- Stream 1 is majorly methanol and Stream 2 is majorly glycerol.

Since methanol has a much lower boiling point than glycerol, methanol will mostly be in the vapour phase and glycerol will mostly be in the liquid phase when an appropriate temperature is selected for the distillation column.

How do we know Stream 1 is the vapour stream and Stream 2 is the liquid stream?

- Since vapour is lighter the liquid, vapour will exit at the top of the column and liquid will exit at the bottom
- Pumps can only be used on liquid streams
- The reboiler loop is on the liquid stream. It vapourizes part of the liquid and sends it back into the column to increase the rate of separation



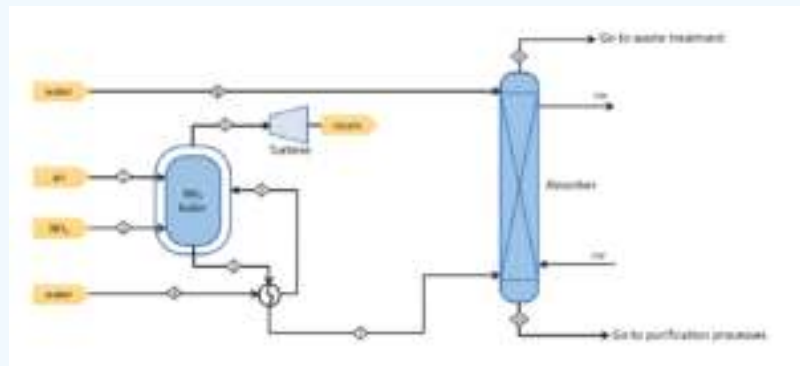
- The valve in the control loop will be open. Because the valve is on the outlet of the liquid stream, opening the valve increases the flow of the liquid stream out of the column, decreasing the liquid level in the column.

- There is no safety hazard, but it leads to ineffective separation.

When V-102 fails open all the liquid will be sent back into the column as vapour, which shifts the vapour-liquid equilibrium in the column.

✓ Exercise: Nitric Acid Production

The following diagram shows the major process steps for the production of nitric acid.



Air and ammonia are first sent to a boiler where the reaction produces nitric oxide, water vapor, and heat. The process stream is then cooled through a heat exchanger, where nitric oxide oxidizes into nitric acid as temperature decreases. The first stream used in the first heat exchanger is also used as a utility stream to absorb excess heat in the boiler and convert it into energy when going through a turbine. The process stream is then sent to an absorber where it is mixed with a stream of water to produce liquid nitrate acid. The liquid acid is sent to further purification processes while the vapour produced in the absorber is sent to waste treatment.

- What are the direct consequences if stream 5 is blocked? Analyze the effect on the process in the NH_3 boiler and the first heat exchanger.
- Using the description in the next paragraph, build a fault-tree analysis logic diagram on the risk of severe overpressure that could lead to an explosion in the absorber, and calculate the frequencies of all events in the diagram. Assuming all events with given frequencies are basic events.

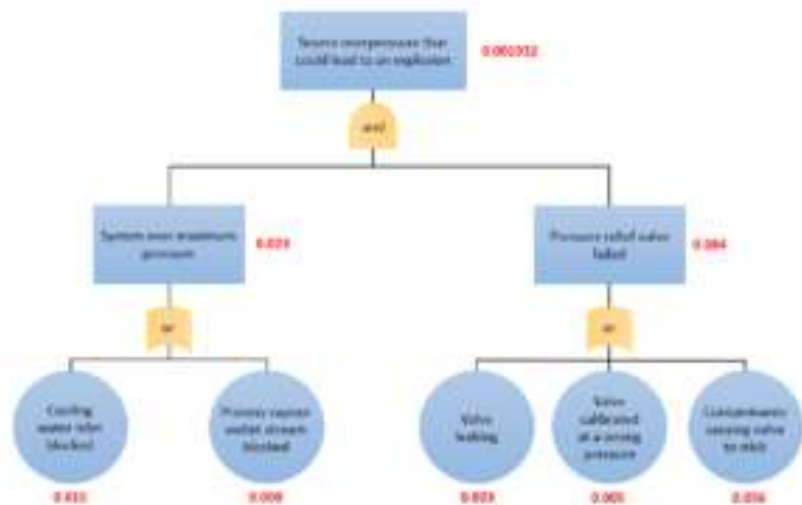
Severe overpressure that could lead to an explosion happens when both **system over maximum pressure** and **pressure relief valve fails** happen at the same time. **System over maximum pressure** happens when the **cooling water inlet is blocked** (frequency = 0.015) or **process vapour outlet stream is blocked** (frequency = 0.008). **Pressure relief valve fails** happens when any one of the following circumstances happens: **valve leaking** (frequency=0.023), **valve calibrated at a wrong pressure** (frequency=0.005), or **contaminants causing the valve to stick** (frequency = 0.056).

Solution

Add example text here.

- The process stream in the heat exchanger will not be sufficiently cooled down, so the conversion to nitric acid will be lower, decreasing the concentration of the product in the absorber.
There will not be enough flow to absorb the heat in the boiler, which will lead to a temperature increase, pressure build-up and

potential explosion of the gas in the boiler.



b)

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