Enquiry Based Learning
Problem Booklet II
2012-13

Edited by Richard Holmes
You cannot teach a man anything; you can only help him discover it in himself.
– Galileo Galilei.

In theory, there is no difference between theory and practice;
Experience suggests that in practice there is,

The three laws of Thermodynamics:
You cannot win,
You cannot even break even,
You cannot get out of the game.
- Richard Feynman.

When Frank Whittle told Ernest Hives that
"simplicity was a hallmark of his Jet Engine",
the Director of Rolls Royce replied
"We’ll soon design the bloody simplicity out of it",

Engineers like to solve problems,
If there are no problems handily available,
they will create their own problems,
- Scott Adams,
Introduction

This booklet contains questions that will be used during the Enquiry-Based Learning (EBL) sessions throughout the semester. As before the booklet has been divided into Weeks to help you identify the material that has been covered each week across all subjects. Finally, some answers to a selection of questions are given at the end of the booklet.

The EBL sessions are here to provide you with opportunities to learn and develop essential skills. You will be able to work in teams with people of different backgrounds and working styles. Working in groups in the EBL sessions will also give you the opportunity to develop your communication, both oral and written. We encourage you to participate actively in discussions with your peers, contributing with ideas and also listening to others. More importantly the EBL sessions will give you the opportunity to develop your problem-solving ability, which is key to any engineer.

All these are important not only for your learning process but also to help you with problem solving and team working, key skills for any engineer.

In the sessions there is support from academic staff and facilitators who can give you guidance when tackling challenging problems - not to answer the questions for you or do your work. Some of the questions might be challenging and at times they might be on topics that have not yet been covered in lectures as this is fundamentally what EBL is about: to learn by a process of enquiry.

We encourage you to take advantage of these opportunities and make the most out of them. We hope that you find the EBL sessions interesting, exciting, useful and enjoyable but it is mainly up to you what you make of them.
13 Week 13

13.1 For a system to be in thermodynamic equilibrium, do the temperature and the pressure have to be the same everywhere?

13.2 Consider an alcohol and a mercury thermometer that read exactly 0° at the ice point and 100°C at the steam point. The distance between the two points is divided into 100 equal parts in both thermometers. Do you think these thermometers will give exactly the same reading at a temperature of, say, 40°C? Explain.

13.3 Sketch the following items and indicate your choice of the system, the surroundings, heat and work inputs and outputs, and whether the system is open or closed:
   (a) A chemical reaction taking place in a high pressure, thick-walled container,
   (b) A car battery,
   (c) A pressure cooker,
   (d) An internal combustion engine.

13.4 Natural gas is transported through a pipeline at 40 bar and 300 K at a rate of $1.3\times10^6$ mol h$^{-1}$. If the diameter of the pipeline is 0.3 m, evaluate the speed of the gas in the line (in m s$^{-1}$). $R = 8.314$ J K$^{-1}$ mol$^{-1}$.

13.5 A vapour contained in a bulb of volume 140.2 cm$^3$ at 100°C and 98.66 kN m$^{-2}$ was found to weigh 0.4416 g. What is the relative molecular mass of the vapour? If the empirical formula of the vapour is CH$_2$Cl, what is the true molecular formula?

RAM: C = 12, H = 1, Cl = 35.5

13.6 A lecture room measures 20 m by 15 m by 5 m. Atmospheric pressure is 100 kPa and the temperature of the room is 20°C. If air contains 21 vol% oxygen, what are the masses (in kg) of oxygen and nitrogen in the room? $R = 8.314$ J K$^{-1}$ mol$^{-1}$; 0°C = 273.15 K; RAM: O = 16, N = 14

13.7 Estimate the root mean square speeds (in mph) of the following molecules at 0°C: hydrogen, helium, oxygen and mercury.

RAM: H = 1, He = 4, O = 16, Hg = 200.6; 1 km = 0.6214 miles.

13.8 A typical storage tank for domestic hot water has a volume of 150 L. It is filled from cold feed at 12°C. The heating element will have a resistance, $R$, of 17.5Ω. Recall that, for electrical conductors, electrical current, $I$, voltage, $V$, and resistance are related by Ohm’s Law: $I = V/R$. Neglecting heat losses and thermal resistance between the element and the water, calculate the minimum and maximum time taken to heat the water to 60°C for the standard UK utility supply of 230 ± 10% V. ($C_p$ for water, 4.18 kJ L$^{-1}$ K$^{-1}$).

13.9 Explain the physical significance of Laplace’s equation.

13.10 The steady state temperature profile and heat flux profile for a wire carrying current is described by

$$T(r) = \frac{g}{4\lambda} R^2 \left[ 1 - \left( \frac{r}{R} \right)^2 \right] + \frac{gR}{2h} + T_f$$

where $R$ is the radius of the wire, $\lambda$ is the thermal conductivity of the wire, $g$ is the heat generated per unit volume, $h$ is the convective coefficient and $T_f$ is ambient temperature.
temperature. Calculate the temperature and heat flux at the centre and surface of a wire 3 mm in diameter, of thermal conductivity 2 W m\(^{-1}\) K\(^{-1}\), generating heat at a rate of 4000 kW m\(^{-3}\), and losing this heat to ambient air at 10°C with a heat transfer coefficient of 40 W m\(^{-2}\) K\(^{-1}\).

13.11 Describe the physical significance of the Poisson equation.

13.12 Describe three types of heat transfer boundary condition, and express them mathematically.

13.13 Discuss why steam is a popular heat transfer medium.

13.14 Temperature measurements in a complicated heat transfer problem have been taken and fitted with the following polynomial, where \(T\) is in °C and \(x\) is in metres:

\[
T = 60 + 20x - 400x^3
\]

(a) If the thermal conductivity of the medium is 20 W m\(^{-1}\) K\(^{-1}\), what is the heat flux at \(x = 5\) cm?

(b) If there is no internal energy generation, is the situation steady state?

13.15 Steam at a pressure of 2 bar gauge condenses on the inside of a 10 m long stainless steel pipe (thermal conductivity = 19 W m\(^{-1}\) K\(^{-1}\)) of inner radius 5 mm and outer radius 10 mm. Calculate the outer surface temperature of the pipe, and the rate at which the steam condenses, if heat is lost to the ambient air at a temperature of 10°C, for the following values of the heat transfer coefficient, \(h = 10, 30, 100\) W m\(^{-2}\) K\(^{-1}\). Find the condensation temperature and latent heat of condensation of steam at 2 bar gauge from the steam tables supplied.

13.16 Warm air at 75°C is mixed with acetylene at 25°C in a molar ratio of 4:1. Determine:

(a) The heat required to warm 100 kmol of mixture to 150°C; and

(b) The temperature of the gas mixture before it is heated (i.e. assuming adiabatic mixing).

Latent heat of vaporisation of water at 298K = 44000 kJ kmol\(^{-1}\).

Mean molar specific heat capacities for some gases are provided in your notes.

The specific heat capacity of acetylene can be approximated by the following correlation:

\[
C_p = 0.04243 + 5.712 \times 10^{-5} T
\]

where \(T\) is the temperature in °C and \(C_p\) is the specific heat capacity at constant pressure in kJ mol\(^{-1}\) K\(^{-1}\).

13.17 It is proposed to use a waste gas stream containing 20 mol% methane, 25 mol% carbon monoxide, 25 mol% carbon dioxide and 30 mol% nitrogen as a fuel. The waste gas is available at 25°C and combustion takes place with 100% excess air, also supplied at 25°C. The combustion takes place in a boiler, which generates 1kg of steam for every 2109 kJ of heat transferred to the water.

If the combustion products leave the boiler at 175°C and 75% of the available energy is utilised in generating steam, calculate the mass of steam produced per 100 kmol of waste gas. Data is available in table 1.
Table 1: Standard heats of formation at 298 K and 1 atm, normal physical states

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta h_f , [\text{kJ mol}^{-1}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ (g)</td>
<td>$-393800$</td>
</tr>
<tr>
<td>CO (g)</td>
<td>$-110600$</td>
</tr>
<tr>
<td>SO$_2$ (g)</td>
<td>$-297000$</td>
</tr>
<tr>
<td>NH$_3$ (g)</td>
<td>$-36350$</td>
</tr>
<tr>
<td>H$_2$O (l)</td>
<td>$-286000$</td>
</tr>
<tr>
<td>CH$_4$ (g)</td>
<td>$-74900$</td>
</tr>
<tr>
<td>SO$_3$ (g)</td>
<td>$-395100$</td>
</tr>
</tbody>
</table>

14 Week 14

14.1 Calculate the time to reduce the number of moles by a factor of 10 ($N_A = N_{A0}/10$) in a batch reactor for the reaction

$$ \text{A} \rightarrow \text{B} $$

with $-r_A = k C_A$, when $k = 0.046 \text{ min}^{-1}$.

14.2 Consider the liquid phase cis-trans isomerisation of 2-butene which can be written symbolically as

$$ \text{A} \rightarrow \text{B} $$

The first order ($-r_A = k C_A$) reaction is carried out in a tubular reactor in which the volumetric flow rate, $\nu$, is constant, i.e. $\nu = \nu_0$).

(a) Sketch the concentration profile.

(b) Derive an equation relating the reactor volume to the entering and exiting concentrations of A, the rate constant $k$, and the volumetric flow rate, $\nu$.

(c) Determine the reactor volume necessary to reduce the exiting concentration to 10% of the entering concentration when the volumetric flow rate is 10 dm$^3$ min$^{-1}$ and the specific reaction rate constant $k$, is 0.23 min$^{-1}$.

14.3 Calculate the volume of a CSTR for the conditions used in the above example. Which volume is larger, the PFR or CSTR? Explain why.

14.4 Calculate the time to reduce the number of moles of A to 1% of its initial value in a constant volume batch reactor for the reaction and data in question 14.2.

14.5 Consider a plug flow reactor operating steady-state and constant temperature. The following first-order reaction, for which there is no volume change, takes place and the rate constant is $5 \times 10^{-4} \text{ s}^{-1}$:

$$ \text{A} \rightarrow \text{Products} $$

If the inlet concentration is 0.1 mol dm$^{-3}$, the reactor volume 0.6 m$^3$ and the volumetric flow 0.3 dm$^3$ s$^{-1}$, what is the outlet concentration?
14.6 Liquid A decomposes by first-order kinetics. In a batch reactor 50% of A is converted in 5 s. How much longer would it take to reach 75% conversion? Repeat this problem for the case when the decomposition follows second-order kinetics.

14.7 Calculate the work that a person must do to raise a mass of 2 kg through 10 m on the surface of

(a) The Earth \( (g = 9.81 \text{ m s}^{-2}) \) and

(b) The Moon \( (g = 1.60 \text{ m s}^{-2}) \).

14.8 A stone of mass 200 g is dropped from a tower of height 50 m. What is the speed of the stone when it hits the ground?

14.9 A chemical reaction takes place in a container of cross-sectional area 100 cm². The container has a loosely fitting piston at one end. As a result of the reaction, the piston is pushed out by 10 cm against an external pressure of 101.3 kPa. Calculate the work of expansion done by the system.

14.10 A sample of 4.5 g of methane occupies 12.7 dm³ at 310 K.

(a) Calculate the work done when the gas expands isothermally against an external pressure of 26.7 kPa until its volume has increased by 3.3 dm³.

(b) Calculate the work done if the same expansion occurred reversibly.

\[
[R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}, \text{ RAM: H = 1.008, C = 12}].
\]

14.11 In problem 14.10, determine the heat that must be transferred in each case. Assume that methane is a perfect gas.

14.12 In problem 14.8, estimate the rise in temperature of the stone when it hits the ground. The specific heat capacity (at constant pressure) of the stone is 0.84 J g⁻¹ K⁻¹. What is the change in the enthalpy of the stone? What information would be needed to allow calculation of the change in internal energy?

14.13 The ideal gas heat capacity of methanol is given by the following equation:

\[
C_p = A + BT + CT^2
\]

where \( A = 18.38 \), \( B = 0.1016 \) and \( C = -2.868 \times 10^{-5} \) (\( C_p \) in J mol⁻¹ K⁻¹, \( T \) in K). Calculate the mean molar heat capacity of methanol between 25°C and 250°C.

14.14 A disc of diameter \( D \) immersed in a fluid of density \( \rho \) and viscosity \( \mu \) has a constant rotational speed \( \omega \). The power required to drive the disc is \( P \) and is equal to the product of torque and rotational speed (in rad s⁻¹).

(a) Find the dimensions of each parameter and show that;

(b) A disc 225 mm in diameter rotating at 144.5 rad s⁻¹ (23 rev s⁻¹) in water requires a driving torque of 1.1 N m. Calculate the corresponding speed and torque required to drive a similar disc 675 mm diameter rotating in air.

(Dynamic viscosities: Air 1.86 \times 10^{-5} \text{ Pa s}; Water 1.01 \times 10^{-3} \text{ Pa s}. Densities: Air 1.20 \text{ kg m}^{-3}; \text{ Water 1000 kg m}^{-3}).

14.15 Water at 26°C flows at a velocity of 0.5 m s⁻¹ down a pipe of internal diameter 1 cm. Would the Colburn equation be applicable for estimating the convection heat transfer coefficient?
14.16 The Colburn equation for calculating convection heat transfer coefficients in tubes is

\[ Nu = 0.023 \, Re^{0.8} \, Pr^{0.333} \]

(a) Based on the Colburn equation, write a simple general expression for the relationship between convection heat transfer coefficient and fluid velocity.

(b) The convection heat transfer coefficient for water flowing down a 2 cm diameter pipe at a velocity of 1 m s\(^{-1}\) has been measured as 3200 W m\(^{-2}\) K\(^{-1}\). Estimate the convection heat transfer coefficient that would result if the fluid velocity were increased to 2 m s\(^{-1}\).

14.17 Water at a bulk mean temperature of 20\(^\circ\)C flows at a velocity of 1.5 m s\(^{-1}\) through a pipe of internal diameter 1 cm with an inner wall temperature of 90\(^\circ\)C. The Reynolds number is 14940, so the Sieder and Tate equation is applicable. Use the Sieder and Tate equation to estimate the convection heat transfer coefficient.

14.18 Water at a bulk mean temperature of 70\(^\circ\)C flows along a pipe of 5 cm inner diameter with a flowrate of 9 kg s\(^{-1}\). Pressurised steam condensing on the outside of the pipe maintains its surface temperature at 110\(^\circ\)C. Assuming negligible thermal resistance from the pipe wall, estimate the convection heat transfer coefficient for the water using the Sieder and Tate equation. Determine the relevant thermophysical properties from the steam tables.

14.19 Calculate the Reynolds and Prandtl numbers describing the turbulent flow of water at 30\(^\circ\)C and a flowrate of 15 m\(^3\) hr\(^{-1}\) down a smooth pipe of 5 cm i.d., and hence calculate the heat transfer coefficient using the Colburn equation:

\[ Nu = 0.023 \, Re^{0.8} \, Pr^{0.333} \]

Find the thermophysical properties of water at 30\(^\circ\)C from steam tables.

14.20 A horizontal fuel rod of 1 cm diameter has a surface temperature, \(T_s\), of 35\(^\circ\)C and loses heat by free convection to ambient air at 19\(^\circ\)C.

Calculate the convection heat transfer coefficient from the following correlation for free convection over horizontal cylinders:

\[ Nu = 0.850 Ra^{0.188} \]

where the Raleigh Number, \(Ra\), is defined as

\[ Ra = \frac{g \beta (T_s - T_a) \, D^3}{\nu \alpha} \]

This correlation is valid for 100 < \(Ra\) < 10000. Thermophysical properties of air are evaluated at the film temperature, \(T_f = (T_s + T_a)/2\). \(g\) is the acceleration due to gravity (in this case equals 9.81 m s\(^{-1}\)). The term \(\beta\) is the expansion coefficient of air and is equal to 1/\(T_f\) where \(T_f\) is in Kelvins. Thermophysical properties of air are shown in the Table 2.

14.21 A gas containing 10 mol\% sulphur dioxide, 11 mol\% oxygen and 79 mol\% nitrogen at 425\(^\circ\)C reacts adiabatically and 60\% of the sulphur dioxide is converted to sulphur trioxide. Estimate the temperature of the product gases. Use data from questions 13.16.
Table 2: Thermophysical properties of air at atmospheric pressure (from Incropera and deWitt, 1996)

<table>
<thead>
<tr>
<th>T /K</th>
<th>ρ /kg m⁻³</th>
<th>Cp /kJ kg⁻¹ K⁻¹</th>
<th>µ × 10⁻⁷ /N s m⁻¹</th>
<th>ν × 10⁻⁶ /m² s⁻¹</th>
<th>λ × 10⁻³ /W m⁻¹ K⁻¹</th>
<th>α × 10⁻³ /m² s⁻¹</th>
<th>Pr/K /kg m⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>1.7458</td>
<td>1.007</td>
<td>132.5</td>
<td>7.590</td>
<td>18.1</td>
<td>10.3</td>
<td>0.737</td>
</tr>
<tr>
<td>250</td>
<td>1.3947</td>
<td>1.006</td>
<td>159.6</td>
<td>11.44</td>
<td>22.3</td>
<td>15.9</td>
<td>0.720</td>
</tr>
<tr>
<td>300</td>
<td>1.1614</td>
<td>1.007</td>
<td>184.6</td>
<td>15.89</td>
<td>26.3</td>
<td>22.5</td>
<td>0.707</td>
</tr>
<tr>
<td>350</td>
<td>0.9950</td>
<td>1.009</td>
<td>208.2</td>
<td>20.92</td>
<td>30.0</td>
<td>29.9</td>
<td>0.700</td>
</tr>
<tr>
<td>400</td>
<td>0.8711</td>
<td>1.014</td>
<td>230.1</td>
<td>26.41</td>
<td>33.8</td>
<td>38.3</td>
<td>0.690</td>
</tr>
</tbody>
</table>

14.22 The gross feed to an ammonia converter contains 22 mol% nitrogen, 66 mol% hydrogen, 4 mol% ammonia and 8 mol% methane (inert) at a temperature of 425°C and the gross product leaves the converter at 500°C.

If the amount of heat removed from the converter is 19000 kJ per 100 kmol gross feed, calculate the composition of the gross product leaving the converter. Use data from question 13.16.

14.23 Given two vectors

\[ \mathbf{u} = \begin{pmatrix} 2 \\ 0 \\ 1 \end{pmatrix}, \quad \mathbf{v} = \begin{pmatrix} 3 \\ 1 \\ -3 \end{pmatrix}. \]

(a) Find the lengths of \( \mathbf{u} \) and \( \mathbf{v} \).

(b) Find the unit vectors having the same direction as \( \mathbf{u} \) and \( \mathbf{v} \).

(c) Find the magnitude of \( \mathbf{u} + \mathbf{v} \) and compare it with \( |\mathbf{u}| + |\mathbf{v}| \). Explain what you discover and give a reason why.

14.24 Given two vectors

\[ \mathbf{u} = \begin{pmatrix} 1 \\ -2 \\ 3 \end{pmatrix}, \quad \mathbf{v} = \begin{pmatrix} 3 \\ 1 \\ 1 \end{pmatrix}. \]

Find the dot product \( \mathbf{u} \cdot \mathbf{v} \) and the angle between \( \mathbf{u} \) and \( \mathbf{v} \).

14.25 Given

\[ \mathbf{u} = \begin{pmatrix} t \\ 2 - t^2 \end{pmatrix}. \]

Find the values of \( t \) for which \( \mathbf{u} \) is perpendicular to the vector \( \mathbf{v} = \begin{pmatrix} 1 \\ -1 \end{pmatrix} \).

Can you illustrate your result graphically?

14.26* Let

\[ \mathbf{u} = \begin{pmatrix} u_1 \\ u_2 \\ u_3 \end{pmatrix} \]

denote a general vector in \( \mathbb{R}^3 \). Show that \( \mathbf{u} \) is equal to the zero vector if and only if the dot product of \( \mathbf{u} \) with itself is zero. Does this characterization of the zero vector extend to vectors \( \mathbf{u} \in \mathbb{R}^{10} \)?

14.27* Show that, for all vectors \( \mathbf{u}, \mathbf{v} \in \mathbb{R}^3 \),

\[ |\mathbf{u} + \mathbf{v}|^2 + |\mathbf{u} - \mathbf{v}|^2 = 2|\mathbf{u}|^2 + 2|\mathbf{v}|^2. \]
(b) \( \frac{1}{4} (|u + v|^2 - |u - v|^2) = u \cdot v. \)

Do these two results extend to vectors \( u, v \in \mathbb{R}^{10} \)?
15  Week 15

15.1 Draw up a summary table of differential and integral forms of design equations for each ideal reactor in terms of concentration and conversion.

15.2 A gas of pure A at 830 kPa (8.2 atm) enters a reactor with a volumetric flow rate, \( \nu_0 \), of 2 dm\(^3\) s\(^{-1}\) at 500 K. Calculate the entering concentration of A, \( C_{A0} \) and the entering molar flow rate, \( n_{A0} \) (\( R = 8.314 \text{ dm}^3 \text{kPa mol}^{-1} \text{K}^{-1} \)).

15.3 A 1\(^{st}\) order irreversible reaction,

\[
A \rightarrow B
\]

with \( k = 0.01 \text{ s}^{-1} \) is required to reach 30% conversion. (Assume constant volume).

(a) How long will it take in a batch reactor?

(b) What CSTR reactor volume and residence time would be required given a volumetric flow rate of \( 10^{-3} \text{ m}^3 \text{s}^{-1} \)?

(c) What PFR reactor volume and residence time would be required given a volumetric flow rate of \( 10^{-3} \text{ m}^3 \text{s}^{-1} \)?

15.4 Show that for a CSTR,

\[
n_A = n_{A0}(1 - X)
\]

where \( n_A \) is the molar flow rate of A.

Show also that

\[
V = \frac{n_{A0}X}{-r_{Aexit}}
\]

15.5 Aerated lagoons can be thought of as CSTR’s with bacteria inside that consume the substrates in wastewater.

The evaluation of the lagoon involves the definition of the mass balance and application of the rate law to determine the lagoon volume required to reduce TOC (Total Organic Carbon) concentration to an acceptable level. In many cases, the decomposition of TOC can be approximated through 1\(^{st}\) order kinetics:

\[
r = -kC_s
\]

Knowing that the common depth of the aerated lagoons 4 m, determine the area of land needed to reduce the \( 2 \times 10^6 \text{ litres day}^{-1} \) of wastewater with a substrate concentration of 300 mg litre\(^{-1}\) to 50 mg litre\(^{-1}\) operating at steady state. Assume \( k = 1.5 \text{ day}^{-1} \).

15.6 A gas mixture consists of 0.2 g of argon and 0.3 g of neon. The partial pressure of neon at 300 K is 15 kPa. Calculate the mole fraction of argon and neon in the mixture and the volume and total pressure of the mixture. Assume perfect gas behaviour.

\[
R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}, \text{ RAM: Ne} = 20, \text{ Ar} = 40
\]

15.7 A natural gas has the following composition (mole fractions).
It is compressed to 40 bar for transport through a pipeline at 300 K and passed through the line (diameter 0.3 m) at a rate of $3 \times 10^4$ m$^3$ hr$^{-1}$ (as measured at 273 K and 1 bar). Calculate the speed of the gas in the pipeline (in m s$^{-1}$) using

(a) The perfect gas law and
(b) Amagat’s law and the Z chart.

15.8 Calculate the standard enthalpy of reaction for the methanol synthesis reaction at 25 and 250°C. Mean molar heat capacities of CO and H$_2$ between 25 and 250°C are 29.6 and 28.9 J K$^{-1}$ mol$^{-1}$ respectively. Use $C_{pm}(\text{CH}_3\text{OH})$ from question 14.13.

15.9 Calculate the standard enthalpy of formation of ethane from the enthalpies of combustion given in tables 3, 4, 5 and 6.

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Table 3: Enthalpies of combustion for graphite, hydrogen and ethane.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta h_c$ /kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (graphite)</td>
<td>−393.7</td>
</tr>
<tr>
<td>H$_2$ (g)</td>
<td>−285.9</td>
</tr>
<tr>
<td>C$_2$H$_6$ (g)</td>
<td>−1560</td>
</tr>
</tbody>
</table>

Table 4: Enthalpies of combustion for reactions R1, R2 and R3.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta h_c$ /kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>C+O$_2$ $\rightarrow$ CO$_2$</td>
</tr>
<tr>
<td>R2</td>
<td>H$_2$+1/2 O$_2$ $\rightarrow$ H$_2$O</td>
</tr>
<tr>
<td>R3</td>
<td>C$_2$H$_6$+ 3/2 O$_2$ $\rightarrow$ 2CO$_2$ + 3 H$_2$O</td>
</tr>
</tbody>
</table>

Table 5: Table for Values of $\Delta h_f$ at 25°C.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta h_c$ /kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O(g)</td>
<td>−241.8</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>−74.8</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>−393.5</td>
</tr>
<tr>
<td>CO</td>
<td>−110.5</td>
</tr>
<tr>
<td>CH$_3$OH (g)</td>
<td>−200.7</td>
</tr>
</tbody>
</table>

15.10 Calculate the theoretical flame temperature for methane burning in 50% excess air. The methane is initially at 25°C. Assume that air contains 21% O$_2$ and 79% N$_2$ by volume.

15.11 A long, horizontal, cylindrical steel reactor, 1 m in diameter, has a surface temperature of 300°C. The emissivity of the steel is 0.6, and the heat transfer coefficient
Table 6: Mean molar heat capacities of gases ($\overline{C_{pm}}$) between 25°C and $T$ °C (ideal gas state).

<table>
<thead>
<tr>
<th>$T$ /°C</th>
<th>$O_2$</th>
<th>$N_2$</th>
<th>$H_2$</th>
<th>$H_2O$</th>
<th>$CH_4$</th>
<th>$CO_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>30.0</td>
<td>29.3</td>
<td>28.9</td>
<td>34.2</td>
<td>39.9</td>
<td>40.7</td>
</tr>
<tr>
<td>500</td>
<td>31.4</td>
<td>29.9</td>
<td>29.0</td>
<td>35.8</td>
<td>48.5</td>
<td>45.1</td>
</tr>
<tr>
<td>1000</td>
<td>33.2</td>
<td>31.4</td>
<td>29.6</td>
<td>38.7</td>
<td>61.1</td>
<td>49.9</td>
</tr>
<tr>
<td>1200</td>
<td>33.8</td>
<td>31.9</td>
<td>29.9</td>
<td>39.8</td>
<td>65.3</td>
<td>51.2</td>
</tr>
<tr>
<td>1400</td>
<td>34.2</td>
<td>32.3</td>
<td>30.3</td>
<td>41.0</td>
<td>69.1</td>
<td>52.2</td>
</tr>
<tr>
<td>1600</td>
<td>34.6</td>
<td>32.8</td>
<td>30.7</td>
<td>41.9</td>
<td>72.6</td>
<td>53.1</td>
</tr>
<tr>
<td>1800</td>
<td>35.0</td>
<td>33.2</td>
<td>31.1</td>
<td>42.8</td>
<td>76.0</td>
<td>53.9</td>
</tr>
<tr>
<td>2000</td>
<td>35.3</td>
<td>33.6</td>
<td>31.5</td>
<td>43.7</td>
<td>79.0</td>
<td>54.6</td>
</tr>
<tr>
<td>2200</td>
<td>35.6</td>
<td>33.9</td>
<td>32.0</td>
<td>44.6</td>
<td>81.9</td>
<td>55.2</td>
</tr>
</tbody>
</table>

for natural convection is 5 W m$^{-2}$ K$^{-1}$. Heat is lost by convection to the air at 15°C, and also by radiation to the surroundings, which can be considered to be a black body at 15°C.

(a) Calculate the total heat loss per metre length of the reactor, and the proportions lost by convection and by radiation.

(b) The reactor is then insulated with a thin layer of insulation material to reduce the total heat loss to one tenth of its original value. This causes the surface temperature of the steel to rise to 400°C. The thermal conductivity of the insulation is 0.01 W m$^{-2}$ K$^{-1}$, and its surface emissivity is 0.2. Show that the resulting surface temperature of the insulation is about 89°C, and calculate the thickness of insulation required, stating any assumptions made.

15.12 (a) A mild steel pipe of inside diameter 96 mm and outside diameter 114 mm carries 0.4 kg s$^{-1}$ saturated steam at 300°C over a distance of 40 m. The thermal conductivity of the pipe wall is 43 W m$^{-1}$ K$^{-1}$, and the pipe loses heat to the ambient air at 5°C with a heat transfer coefficient of 18 W m$^{-2}$ K$^{-1}$. Calculate the rate of heat loss from the pipe, and the percentage of steam that will condense due to this heat loss.

(b) The pipe is then insulated with a 14 mm thick layer of insulation of thermal conductivity 0.04 W m$^{-1}$ K$^{-1}$. Calculate the new rate of heat loss as a percentage of the original rate of heat loss, and the temperature of the outer surface of this layer of insulation.

(c) The covering on the pipe insulation corrodes, and the insulation becomes wet, such that its thermal conductivity increases to 1.5 W m$^{-1}$ K$^{-1}$. Calculate the rate of heat loss from the pipe and the percentage of steam that will now condense. Comment on the effect on heat loss of the insulation that has become wet.

15.13 If the thermal resistance across a spherical shell is given by

$$\frac{1}{4 \pi \lambda} \left( \frac{r_2 - r_1}{r_2 r_1} \right)$$

Derive an expression for the critical thickness of insulation for a sphere.
15.14 A 2 cm diameter sphere generates heat at a constant rate of 25 W, which is dissipated from the surface of the sphere into ambient air at a temperature of 10°C with a convection heat transfer coefficient of 45 W m\(^{-2}\) K\(^{-1}\).

(a) Calculate the temperature at the surface of the sphere.

(b) If a layer of insulation of thermal conductivity \(\lambda_{ins}\) is added to the sphere, the thermal resistance of the insulation is described by

\[
R_{sph} = \frac{(r_o - r_s)}{4 \pi \lambda_{ins} r_o r_s}
\]

Where \(r_o\) is the outer radius of the insulation and \(r_s\) is the radius of the sphere. Write the expression describing the thermal resistance associated with the convection heat transfer from the surface of the insulation.

(c) Sketch the thermal resistances of the layer of insulation and of the surface convection as a function of \(r_o\), and hence the total resistance to heat transfer as a function of \(r_o\), pointing out any significant features.

(d) The critical radius of insulation will give the lowest surface temperature for a given heat transfer rate. Show that the expression for the critical radius of insulation of a sphere is given by

\[
r_c = \frac{2 \lambda_{ins}}{h}
\]

(e) Calculate the critical radius of insulation if \(\lambda_{ins} = 0.5\) W m\(^{-1}\) K\(^{-1}\). What thickness of insulation would this give?

(f) Calculate the total resistance to heat transfer if the amount of insulation calculated in part (e) is added to the sphere. Then calculate the resulting temperature of the surface of the original metal sphere and of the surface of the insulation. Compare these with the surface temperature of the metal sphere with no insulation calculated in part (a).

15.15 A steam pipe of outer radius 1 cm has a surface temperature of 330°C and loses heat to ambient air at 15°C with a heat transfer coefficient of 14 W m\(^{-2}\) °C\(^{-1}\).

Calculate the heat loss per metre length from the pipe

(a) Bare;

(b) Covered with a 2 cm layer of glass wool insulation (\(\lambda = 0.038\) W m\(^{-1}\)°C\(^{-1}\));

(c) Covered with a 2 cm layer of glass wool insulation which has become wet (\(\lambda = 0.5\) W m\(^{-1}\) °C\(^{-1}\)).

(d) Calculate the critical radius of insulation when the insulation has become wet, the heat loss at this critical radius, and the outer surface temperature of the insulation.

15.16 Determine the boiling point temperature of the solution and the boiling point rise for the following cases:

(a) A 30% NaOH solution boiling in an evaporator at a pressure of 172.4 kPa

(b) A 60% NaOH solution boiling in an evaporator at a pressure of 3.45 kPa.

(c) A 15% NaCl solution boiling in an evaporator at a pressure of 62.5 kPa.
15.17 A feed of 4535 kg h\(^{-1}\) of a 2 wt % salt solution at 311 K enters continuously a single-effect evaporator ad is being concentrated to 3 wt %. The evaporation is at atmospheric pressure and the area of the evaporator is 69.7 m\(^2\).

Saturated steam at 383.2 K is supplied for heating. Since the solution is dilute, it can be assumed to have the same boiling point as water. The heat capacity of the feed can be taken as \(C_p = 4.10 \text{ kJ kg}^{-1} \text{ K}^{-1}\).

Calculate the amounts of vapour and liquid product and the overall heat-transfer coefficient \(U\).

15.18 Let
\[
A = \begin{pmatrix} 1 & 2 \\ -2 & 2 \end{pmatrix} \quad \text{and} \quad B = \begin{pmatrix} -3 & 1 \\ -1 & -4 \end{pmatrix}.
\]

Compute the following matrices:

(a) \(A + 2B\). Is it true that \(A + 2B = 2B + A\)?

(b) \(A^T + B^T\). Is it true that \((A + B)^T = A^T + B^T\)?

(c) \(AB\) and \(BA\). Is it true that \(AB = BA\)?

(d) \(B^T A^T\). Is it true that \((AB)^T = B^T A^T\)?

15.19 A permutation matrix \(P_{ij}\) is generated by interchanging rows (or columns) of an identity matrix \(I\), e.g.

\[
P_{12} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad P_{13} = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}.
\]

Let \(A\) be the matrix
\[
A = \begin{pmatrix} 11 & 12 & 13 \\ 21 & 22 & 23 \\ 31 & 32 & 33 \end{pmatrix}.
\]

(a) Compute the products \(P_{12}A\), \(P_{13}A\), \(AP_{12}\) and \(AP_{13}\). What do you observe?

(b) Show that \(P_{12}P_{12}^T = I\). (This means that \(P_{12}^T\) is the inverse of \(P_{12}\)—this property characterizes a permutation matrix.)

(c) Show that the matrix \(P = P_{12}P_{13}\) is also a permutation matrix. (Compute \(P\) explicitly and show that \(PP^T = I\).)

(d) Compute the determinant of \(P_{12}\) and that of \(P_{13}\).

(e)* Use the fact that \(\det(AB) = \det(A) \times \det(B)\) to prove that the determinant of a permutation matrix is \(\pm 1\). \textit{Hint: use the fact that transposing a matrix does not change its determinant.}
16 Week 16

16.1 (a) Calculate the volume necessary to achieve 80% conversion in
   i. a CSTR reactor and
   ii. a PFR reactor under these conditions
(b) How would your answers change if the flow rate, \( n_{A0} \), were reduced to 0.2 mol s\(^{-1}\)?
(c) How would your answers change if the flow rate, \( n_{A0} \), were reduced to 0.8 mol s\(^{-1}\)?

Reactor conditions: 500 K, 8.2 atm and \( n_{A0} = 0.4 \) mol s\(^{-1}\) and the initial charge was pure A. Reaction data available in Table 7 and Figure 1.

### Table 7: Data of conversion and reaction rate for reactor at 500 K, 8.2 atm and \( n_{A0} = 0.4 \) mol s\(^{-1}\).

<table>
<thead>
<tr>
<th>( X )</th>
<th>(-r_A / \text{mol m}^{-3} \text{s}^{-1})</th>
<th>((1/-r_A) / \text{m}^3 \text{s} \text{mol}^{-1})</th>
<th>((n_{A0} / -r_A) / \text{m}^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.45</td>
<td>2.22</td>
<td>0.89</td>
</tr>
<tr>
<td>0.1</td>
<td>0.37</td>
<td>2.7</td>
<td>1.08</td>
</tr>
<tr>
<td>0.2</td>
<td>0.3</td>
<td>3.33</td>
<td>1.33</td>
</tr>
<tr>
<td>0.4</td>
<td>0.195</td>
<td>5.13</td>
<td>2.05</td>
</tr>
<tr>
<td>0.6</td>
<td>0.113</td>
<td>8.85</td>
<td>3.54</td>
</tr>
<tr>
<td>0.7</td>
<td>0.079</td>
<td>12.7</td>
<td>5.06</td>
</tr>
<tr>
<td>0.8</td>
<td>0.05</td>
<td>20</td>
<td>8</td>
</tr>
</tbody>
</table>

Figure 1: Reaction rate and conversion data for reactor at 500 K, 8.2 atm and \( n_{A0} = 0.4 \) mol s\(^{-1}\).

16.2 The exothermic reaction

\[
\text{A} + \text{B} \rightarrow \text{C}
\]

was carried out adiabatically and the following data recorded:
The entering molar flow rate of A was 300 mol min$^{-1}$.

(a) What are the PFR and CSTR volumes necessary to achieve 40% conversion?

(b) Over what range of conversions would the CSTR and PFR reactor volumes be identical?

(c) What is the maximum conversion that can be achieved in a 10.5 dm$^3$ CSTR?

16.3 Steam at 0.6 MPa, 200°C enters an insulated nozzle with velocity of 50 m s$^{-1}$. It leaves at a pressure of 0.15 MPa and a velocity of 600 m s$^{-1}$. Determine:

(a) The final temperature if the steam is superheated in the final state.

(b) The quality of the steam if it is saturated in the final state.

16.4 The mass flow rate into a stream turbine is 1.5 kg s$^{-1}$, and the heat transfer from the turbine is 8.5 kW. The following data are known for the steam entering and leaving the turbine.

<table>
<thead>
<tr>
<th>Inlet</th>
<th>Outlet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure /MPa</td>
<td>2.0</td>
</tr>
<tr>
<td>Temperature /°C</td>
<td>350</td>
</tr>
<tr>
<td>Quality /%</td>
<td>90</td>
</tr>
<tr>
<td>Velocity /(m s$^{-1}$)</td>
<td>50</td>
</tr>
<tr>
<td>Elevation above reference plane /m</td>
<td>6</td>
</tr>
</tbody>
</table>

Determine the power output of the turbine.

16.5 Define a property called the Joule-Thomson coefficient, $\mu = \frac{\partial T}{\partial P}$ for a constant-enthalpy process.

Steam at 800 kPa, 300°C is throttled to 200 kPa. Changes in kinetic energy are negligible for the process. Determine:

(a) The final temperature of the steam.

(b) The average Joule-Thomson coefficient

16.6 Consider a water-cooled condenser in a large refrigeration system in which R134a is the refrigerant fluid. The refrigerant enters the condenser at 1.0 MPa, 60°C, at the rate of 0.2 kg s$^{-1}$, and exits as a liquid at 0.95 MPa, 35°C.

Cooling water enters the condenser at 10°C and exits at 20°C. Determine:

(a) The rate at which cooling water flows through the condenser.

(b) The heat transfer between two fluids.

16.7 The electric heating systems used in many houses consist of a simple duct with resistance wires.

Air is heated as it flows over resistance wires. Consider a 15 kW electric heating system. Air enters the heating section at 100 kPa and 17°C with a volume flow rate of 150 m min$^{-1}$. If heat is lost from the air in the duct to the surroundings at a rate of 200 W, determine the exit temperature of air [the specific heat for the air $C_p=1.005$ kJ kg$^{-1}$°C$^{-1}$].
16.8 A pipe of 40 mm bore conveys air at a mean velocity of 21.5 m s$^{-1}$. The density of the air is 1.225 kg m$^{-3}$ and its dynamic viscosity is $1.8 \times 10^{-5}$ Pa s. Calculate that volume flow rate of water through the pipe which would correspond to the same value of friction factor $f$ if the dynamic viscosity of water is $1.12 \times 10^{-3}$ Pa s.

16.9 Water is pumped up an 8 m long vertical pipe with an inner diameter of 5 mm at a rate corresponding to a Reynolds number of 1800. If the pressure at the bottom of the pipe is 1 atmosphere gauge, calculate the pressure at the top of the pipe. The viscosity is 1.2 cP.

16.10 A water tower is used to deliver water to a fountain (Figure 2). Assume the water tower has a static head. Calculate the velocity of the water at the fountain mouthpiece and the maximum height of the fountain. The system has two 90° elbows and the diameter of the pipe is 5 cm. The friction factor can be taken as $f=0.001$.

![Figure 2: Sketch of a water tower use to deliver water to a fountain.](image)

16.11 A spherical metal ball bearing (thermal conductivity = 43 W m$^{-1}$ K$^{-1}$, specific heat capacity = 450 J kg$^{-1}$ K$^{-1}$, density = 7000 kg m$^{-3}$) of 3 cm diameter and at a temperature of 300°C is plunged into cold water, losing heat with a convection heat transfer coefficient of 170 W m$^{-2}$ K$^{-1}$.

Calculate the time constant for cooling of the ball bearing.

16.12 (a) A metal sphere of diameter $D$, of high thermal conductivity, initially at a temperature $T_0$, is plunged into a flowing liquid at temperature $T_f$, with which it exchanges heat with a convection heat transfer coefficient of $h$. The specific heat capacity of the metal is $C_p$, its density is $\rho$, and its thermal conductivity is $\lambda$. Using a lumped system analysis, show from first principles that the temperature-time profile of the sphere is given by

$$\frac{T(t) - T_f}{T_0 - T_f} = \exp\left(-\frac{1}{\tau}\right)$$

and derive an expression for $\tau$. What are the units of $\tau$? State any assumptions made, and state how you would check the validity of your assumptions.

(b) A 2 cm diameter aluminium sphere as described in part (a) above, initially at a temperature of 200°C, is plunged into water at 20°C. The temperature in the sphere is monitored over time, giving the following results:
Given the following thermal properties of the aluminium, show that the value of the convection heat transfer coefficient by which the sphere loses heat is around 350 W m$^{-2}$ K$^{-1}$. Is a lumped system analysis appropriate?

Thermal properties of aluminium: $C_p = 880$ J kg$^{-1}$ K$^{-1}$; $\rho = 2790$ kg m$^{-3}$; $\lambda = 160$ W m$^{-1}$ K$^{-1}$.

(c) How long would it take for the temperature of the sphere to drop to 25$^\circ$C?

16.13 (a) Determine whether a lumped system analysis as derived above would be appropriate for each of the following situations, if the convection heat transfer coefficient is 100 W m$^{-2}$ K$^{-1}$ in each case, where $L$ and $D$ are the length and diameter of the object respectively.

<table>
<thead>
<tr>
<th>Solid object</th>
<th>$\lambda$ (W m$^{-1}$ K$^{-1}$)</th>
<th>Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium cylinder</td>
<td>237</td>
<td>$L = 5$ cm, $D = 5$ cm</td>
</tr>
<tr>
<td>£1 coin</td>
<td>12</td>
<td>$D = 22$ mm, thickness = 4 mm</td>
</tr>
<tr>
<td>Apple</td>
<td>0.513</td>
<td>$D = 7$ cm</td>
</tr>
</tbody>
</table>

(b) The aluminium cylinder describe in part 19.13a has a specific heat capacity of 903 J kg$^{-1}$ K$^{-1}$ and density of 2702 kg m$^{-3}$, and is initially at a temperature of 300$^\circ$C. It is plunged into water maintained at a uniform temperature of 25$^\circ$C, and loses heat with a convection heat transfer coefficient of 100 W m$^{-2}$ K$^{-1}$. How long will it take for the temperature of the cylinder to drop to 75$^\circ$C?

16.14 The temperature of the water in a pipe is measured using a thermocouple, which may be considered a sphere of diameter 2 mm, thermal conductivity 25 W m$^{-1}$ K$^{-1}$, density 8400 kg m$^{-3}$, and specific heat capacity 400 J kg$^{-1}$ $^\circ$C$^{-1}$. The heat transfer coefficient between the water and the thermocouple is 700 W m$^{-2}$ $^\circ$C$^{-1}$.

(a) Is a lumped system analysis applicable?

(b) If the temperature of the water flowing past the thermocouple suddenly changes from 10$^\circ$C to 40$^\circ$C, how long will it take for the thermocouple to reach a reading of 39$^\circ$C?

(c) What is the time constant for the thermocouple?

16.15 An evaporator having an area of 83.6 m$^2$ and $U = 2270$ W m$^{-2}$ K$^{-1}$ is used to produce distilled water for a boiler feed. Tap water having 400 ppm dissolved solids at 15.6$^\circ$C is fed into the evaporator operating at 1 atm pressure abs. Saturated steam at 115.6$^\circ$C is available for use as heating medium. Calculate the amount of distilled water produced per hour if the outlet liquid contains 800 ppm.

16.16 An evaporator is concentrating $F$ kg hr$^{-1}$ at 311 K of a 20 wt % solution of NaOH to 50 wt %. The saturated steam used for heating is at 399.3 K. The pressure in the vapour space of the evaporator is 13.3 kPa abs. The overall coefficient is 1420 W m$^{-2}$ K$^{-1}$ and the area is 86.7 m$^2$.

Calculate the feed rate $F$ of the evaporator, the amount of steam required and the economy.

16.17 If

$$A = \begin{pmatrix} 1 & 2 \\ -2 & 4 \end{pmatrix},$$

calculate $A^{-1}$. By direct calculation show that $AA^{-1} = A^{-1}A = I$. 

Chemical Engineering, Year 1

EBL 2010/11
16.18 Consider the linear equations

\[ \begin{align*}
3x + 2y &= 1 \\
-2x + 5y &= -7.
\end{align*} \]

(a) Write this equations in matrix form, i.e. \( Ax = b \).
(b) Calculate \( A^{-1} \) and, by direct calculation, show \( AA^{-1} = A^{-1}A = I \).
(c) Use \( A^{-1} \) to obtain the values of \( x \) and \( y \).
(d) Check your working by showing your answer fits the original equations.

16.19 (a) Evaluate the following 2 \( \times \) 2 determinants:

\[ \begin{align*}
d_1 &= \begin{vmatrix} 1 & 2 \\ -2 & 5 \end{vmatrix}, & d_2 &= \begin{vmatrix} 5/9 & -2/9 \\ 2/9 & 1/9 \end{vmatrix}.
\end{align*} \]

How are \( d_1 \) and \( d_2 \) related and why?
(b) Next, evaluate the following 3 \( \times \) 3 determinants:

\[ \begin{align*}
d_3 &= \begin{vmatrix} 1 & -2 & 1 \\ 2 & 3 & -1 \\ -1 & -2 & 2 \end{vmatrix}, & d_4 &= \begin{vmatrix} 2 & 3 & -1 \\ 1 & -2 & 1 \\ -1 & -2 & 2 \end{vmatrix}.
\end{align*} \]

How are \( d_3 \) and \( d_4 \) related and why? \textit{Hint: Use the properties of permutation matrices.}

16.20 Suppose that you have square matrices, \( A, B \) and \( C \), with the properties \( AB = I \) and \( CA = I \), where \( I \) is the identity matrix. Use this information to prove that \( C = B \).

You may assume that \( DI = ID = D \) for any square matrix \( D \). You may not assume that \( AA^{-1} = A^{-1}A = I \). The point of the question is to establish that the left-hand and right-hand inverses are identical and the above statement assumes this. \textit{Hint: Do not use inverse matrices in this question. Also do not look at matrix components — consider matrices as single objects and make use of their multiplication properties. The proof is just a few lines long!}
17 Week 17

17.1 The reaction:

\[ 2A + 3 B \rightarrow 5 C \]

is carried out in a reactor. If at a particular point, the rate of disappearance of \( A \) is \( 10 \text{ mol dm}^{-3} \text{ s}^{-1} \), what are the rates of \( B \) and \( C \)?

17.2 (a) The reaction between \( A + B \) is first order in \( A \) and second order in \( B \). Give the rate expression, and then find the units of \( k \) (assume time in minutes).

(b) A reaction between \( P \) and \( Q \) is 3/2 order in \( P \) and order -1 in \( Q \). Give the rate expression and find the units of \( k \) (assume time in minutes).

17.3 (a) If \( k = 5.7 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1} \) calculate the rate of reaction which is first order in both \( A \) and \( B \) when \([A] = 5.0 \times 10^{-2} \text{ mol dm}^{-3} \) and \([B] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}\).

(b) If \([A] \) had been \(5.0 \times 10^{-4} \text{ mol dm}^{-3} \) and \([B] \) had been \(2.0 \times 10^{-3} \text{ mol dm}^{-3} \) what would the rate have been?

(c) What conclusion can you draw from this?

17.4 Base hydrolyses of amino-acid esters have two contributing reactions:

(a) \( \text{OH}^- \) reacting with protonated ester, HE+,

(b) \( \text{OH}^- \) reacting with unprotonated ester, E.

At 25°C the rate constant for the protonated ester is \( 1550 \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1} \) and the rate constant for the unprotonated ester is \( 42 \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1} \). At \( \text{pH} = 9.30 \), \([\text{OH}^-] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}\), and if the total \([\text{ester}] = 2 \times 10^{-2} \text{ mol dm}^{-3} \), then \([\text{HE}^+] = 5 \times 10^{-4} \text{ mol dm}^{-3} \), and \([E] = 195 \times 10^{-4} \text{ mol dm}^{-3}\).

i. Calculate the contributions to the overall rate from the two reactions.

ii. What conclusions can be drawn?

17.5 Construct a stoichiometric table for the following batch reactions and derive expressions relating the concentrations of the reactants to the conversion.

\[ \text{N}_2 + 3 \text{H}_2 \rightarrow 2\text{NH}_3 \]

17.6 Soap consists of the sodium and potassium salts of various fatty acids such as oleic, stearic, palmitic, lauric, and myristic acids. The saponification for the formation of soap from aqueous caustic soda and glyceryl stearate is:

\[ 3 \text{NaOH}_{(aq)} + (\text{C}_{17}\text{H}_{35}\text{COO})_3\text{C}_3\text{H}_5 \rightarrow 3\text{C}_{17}\text{H}_{35}\text{COONa} + \text{C}_3\text{H}_5(\text{OH})_3 \]

Letting \( X \) represent the conversion of sodium hydroxide (the moles of sodium hydroxide reacted per mole of sodium hydroxide initially present), set up a stoichiometric table expressing the concentration of each species in terms of its initial concentration and the conversion \( X \).

17.7 Using the information from question 17.6, if the initial mixture consists solely of \( \text{NaOH} \) at a concentration of \( 10 \text{ mol dm}^{-3} \) and of glyceryl stearate at a concentration of \( 2 \text{ mol dm}^{-3} \), what is the concentration of glycerine when the conversion of \( \text{NaOH} \) is
(a) 20% and
(b) 90%?

17.8 What is a thermal energy reservoir? Give some examples.

17.9 Consider the process of baking potatoes in a conventional oven. Can the hot air in the oven be treated as a thermal energy reservoir? Explain.

17.10 An experimentalist claims to have raised the temperature of a small amount of water to 150°C by transferring heat from high-pressure steam at 120°C, without using any heat pump or refrigerator. Is it possible? Why?

17.11 What are the characteristics of all heat engines?

17.12 (a) What are the Kelvin-Planck statement and the Clausius statement for the second law of thermodynamics? Prove the two statements are equivalent.
(b) What are the four processes that make up the Carnot cycle? What are the two statements known as the Carnot principles? Prove the Carnot principles.

17.13 A Carnot heat engine receives 500 kJ of heat from a source of unknown temperature and rejects 200 kJ of it to a sink at 17°C. Determine:
(a) the temperature of the source
(b) the thermal efficiency of the heat engine.

17.14 A 150 mm bore cast-iron pipe and a 50 mm bore mild steel pipe are parallel and horizontal and both run from the same pump to a reservoir. The pressure drop is 250 kN m⁻² and the pipes are 150 m long. Determine the flow rate in each pipe, given that \( \mu_{\text{water}} = 1.2 \times 10^{-3} \text{ Pa s} \) at the operating conditions, the roughness \( \varepsilon \) of cast iron: and mild steel are 0.000025 m and 0.00005 m respectively.

17.15 A 55m long 100 mm diameter clean galvanised iron pipe discharges water from a closed air-pressurised constant head tank, A, to an open constant head tank, B. The pipe has three bends and two gate valves. Tank A is higher than tank B, and the actual level difference between A and B is 7m. What must be the pressure of the air above the water level in A if a discharge of 0.05 m³ s⁻¹ of water through the pipe is required?

The following head loss coefficients may be used:
- Pipe entrance \( K_e = 0.5 \)
- Bend \( K_b = 0.8 \)
- Gate valve \( K_v = 0.25 \)
- Pipe outlet \( K_o = 0.95 \)

Kinematic viscosity of water: \( 1.2 \times 10^{-6} \text{ m}^2 \text{ s}^{-1} \). Pipe roughness: 0.00015 m.

17.16 A steel bar, 5 cm in diameter, is to be annealed by slowly cooling it from an initial temperature of 800°C to a final temperature of 120°C using air at 40°C. The density of the steel is 7800 kg m⁻³, its specific heat capacity is 500 J kg⁻¹ K⁻¹, and its thermal conductivity is 61 W m⁻¹ K⁻¹. The thermal conductivity of the air is 0.0273 W m⁻¹ K⁻¹.

(a) A correlation for free convection for a horizontal cylinder in air gives a Nusselt number of 82. Calculate the convection heat transfer coefficient between the air and the surface of the bar.
(b) Determine whether a lumped system analysis is applicable, and calculate the time to cool the bar from 800 to 120° C. (If you don’t have a value from Part 16a for the convection heat transfer coefficient, use a value of 60 W m$^{-2}$ K$^{-1}$.)

17.17 A 3 cm diameter sphere, of thermal conductivity 40 W m$^{-1}$ K$^{-1}$, initially at 300° C, is cooled by plunging it into water, which removes heat with a convection heat transfer coefficient of 200 W m$^{-2}$ K$^{-1}$. The specific heat capacity of the sphere is 1 kJ kg$^{-1}$ K$^{-1}$, and its density is 2000 kg m$^{-3}$.
Calculate the Biot number and the time constant for the system.

17.18 A vessel containing 1000 kg of well mixed oil ($C_p = 2300$ J kg$^{-1}$ K$^{-1}$) is heated via a jacketed vessel through which saturated steam at a pressure of 198.5 kPa is passed.
The surface area for heat transfer is 2 m$^2$, and the overall heat transfer coefficient is 550 W m$^{-2}$ K$^{-1}$. Show that the time constant for the system is 34.85 minutes, and calculate the time required for the vessel contents to heat to 80° C from an initial temperature of 10° C.

17.19 Sketch graphs of the changes in enthalpy and specific heat capacity of water at atmospheric pressure with temperature, identifying any significant features of your graphs.
If the pressure increased to ten times atmospheric pressure, what would happen to the boiling temperature and latent heat of evaporation of water?

17.20 A single-effect evaporator is concentrating a feed of 9072 kg h$^{-1}$ of a 10 wt % solution of NaOH in water to a product of 50 wt % solids. The pressure of the saturated steam is 42 kPa gauge and the pressure in the vapour space of the evaporator is 20 kPa abs.
The overall heat transfer coefficient is 1988 W m$^{-2}$ K$^{-1}$. Calculate the steam used, the steam economy in kg vaporized per kg of steam required, and the area required if the feed enters at 288.8 K (15.6° C).

17.21 A single-effect evaporator is concentrating a feed solution of organic colloids from 5 to 50 wt %. The solution has a negligible boiling-point elevation. The heat capacity of the feed is $C_p = 4.06$ kJ kg$^{-1}$ K$^{-1}$ and the feed enters at 15.6° C.
Saturated steam at 101.32 kPa is available for heating, and the pressure in the vapour space of the evaporator is 15.3 kPa.
A total of 4536 kg h$^{-1}$ of water is to be evaporated. The overall heat transfer coefficient is 1988 W m$^{-2}$ K$^{-1}$. What is the required surface area in m$^2$ and the steam consumption?

17.22 Potassium chromate is recovered from a methanol/water solution by evaporation, crystallisation and filtration. The total mass flows, in units of kg h$^{-1}$, is $E$ for evaporation, $F$ for filtration and $C$ for crystallisation. The material balance equations for potassium chromate, water and methanol are

\begin{align*}
1125 &= 1.06C + 0.3F \\
2250 &= 0.75E + 0.08C + 0.4F \\
1125 &= 0.25E + 0.06C + 0.3F.
\end{align*}

(a) Write the system of equations in the form $Ax = b$, where $A$ is a $3 \times 3$ matrix, $x$ is a column vector of the unknown quantities and $b$ is a column vector with known coefficients.
(b) Apply Gaussian elimination to show that \( E, C \) and \( F \) satisfy the upper triangular system
\[
\begin{pmatrix}
1.06 & 0 & 0.3 \\
0 & 0.75 & 0.37736 \\
0 & 0 & 0.15723
\end{pmatrix}
\begin{pmatrix}
C \\
E \\
F
\end{pmatrix}
= \begin{pmatrix}
1125.00 \\
2165.10 \\
339.62
\end{pmatrix}.
\]

(c) Hence calculate \( E, C \) and \( F \) using back-substitution.

(d) Calculate the determinant of the matrix \( A \). \textit{Hint: Adding multiples of one row to another does not change the determinant of a matrix.}

17.23 It is known that the number of floating point operations (flop) required to solve an \( n \times n \) system of linear equations using Gaussian elimination is approximately \( 2n^3/3 \) for large values of \( n \). Estimate the size of the biggest system that can be solved for £10,000 if it costs £1,000 an hour to use the IBM Roadrunner supercomputer which has a calculation rate of \( 10^{15} \) flop/sec. (This is called a \textit{petaflop}. Conventional laptop computers run at a \textit{gigaflop}, that is \( 10^9 \) flop/sec.)

17.24 Consider the linear equation system:
\[
\begin{align*}
x + y + z &= 3 \\
x - y + 2z &= 2 \\
2y - z &= 5
\end{align*}
\]

(a) Write the system of equations in the form of \( Ax = b \).

(b) Solve for \( x, y, z \) using Gaussian elimination. Can you explain this result?

17.25* Consider the coefficient matrix
\[
A = \begin{pmatrix}
2 & 4 & -2 \\
2 & 8 & 4 \\
1 & -2 & -1
\end{pmatrix}
\]

Using Gaussian elimination, solve the three distinct systems
\[
Ax_1 = e_1, \quad Ax_2 = e_2, \quad Ax_3 = e_3,
\]
where \( e_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad e_2 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad e_3 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}, \)

so as to compute the columns of the matrix \( X \) satisfying \( AX = I \). (Note that this is a clever way to compute the inverse matrix \( X = A^{-1} \).)
18 Week 18

18.1 The half-life for the (first-order) radioactive decay of $^{14}\text{C}$ is 5730 years.

An archaeological sample contained wood that had only 72% of the $^{14}\text{C}$ found in the living trees. What is its age?

18.2 The following reaction is irreversible and first-order and can be described by the relation:

$$\text{A} \rightarrow \text{Products}$$

From the following concentration-time data, determine the rate constant. What is the half-life of the reaction?

<table>
<thead>
<tr>
<th>$t$ /s</th>
<th>$C_A$ /mol dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.100</td>
</tr>
<tr>
<td>100</td>
<td>0.0951</td>
</tr>
<tr>
<td>500</td>
<td>0.0779</td>
</tr>
<tr>
<td>1000</td>
<td>0.0607</td>
</tr>
<tr>
<td>2000</td>
<td>0.0368</td>
</tr>
</tbody>
</table>

18.3 The reaction of triphenyl methyl chloride (trityl) (A) and methanol (B)

$$(\text{C}_6\text{H}_5)_3\text{CCl} + \text{CH}_3\text{OH} \rightarrow (\text{C}_6\text{H}_5)_3\text{COCH}_3 + \text{HCl}$$

was carried out in a solution of benzene and pyridine at 25°C. Pyridine reacts with HCl that then precipitates as pyridine hydrochloride thereby making the reaction irreversible.

The following concentration vs time data was obtained in a batch reactor:

<table>
<thead>
<tr>
<th>$t$ /s</th>
<th>$C_A \times 10^3$ /mol dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>50</td>
</tr>
<tr>
<td>50</td>
<td>38</td>
</tr>
<tr>
<td>100</td>
<td>30.6</td>
</tr>
<tr>
<td>150</td>
<td>25.6</td>
</tr>
<tr>
<td>200</td>
<td>22.2</td>
</tr>
<tr>
<td>250</td>
<td>19.5</td>
</tr>
<tr>
<td>300</td>
<td>17.4</td>
</tr>
</tbody>
</table>

The initial concentration of methanol was 0.5 mol dm$^{-3}$.

(a) Determine the reaction order with respect to triphenyl methyl chloride.

(b) In a separate set of experiments, the reaction order with respect to methanol was found to be first order. Determine the specific reaction rate constant.

(c) Use the integral method to confirm the order of reaction

*Hint: The initial concentration of B is 10 times that of A so apply pseudo-order kinetics i.e. the concentration of B is constant. $C_B = C_{B0}$ and rate $= -k' C_A^\alpha$ with $k' = k C_{B0}^\beta$. Determine $\Delta C_A/\Delta t$ directly from the data.*

18.4 The following gas phase reaction takes place at constant pressure and temperature:

$$\text{A} \rightarrow \text{R} + \text{S}$$

From the volumetric data given below, determine the reaction order.

<table>
<thead>
<tr>
<th>$t$ /s</th>
<th>$V$ /dm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>47</td>
</tr>
<tr>
<td>30</td>
<td>61</td>
</tr>
<tr>
<td>90</td>
<td>68</td>
</tr>
<tr>
<td>120</td>
<td>72</td>
</tr>
<tr>
<td>180</td>
<td>75</td>
</tr>
<tr>
<td>240</td>
<td>78.5</td>
</tr>
<tr>
<td>360</td>
<td>84</td>
</tr>
</tbody>
</table>

*Hint: This problem can be most conveniently solved using a spreadsheet.*

18.5 During the isothermal heat addition process of a Carnot cycle, 900 kJ of heat is added to the working fluid from a source at 400°C. Determine:
(a) The entropy change of the working fluid,
(b) The entropy change of the source, and
(c) The total entropy change for the process.

18.6 An insulated piston-cylinder device contains 5 L of saturated liquid water at a constant pressure of 150 kPa. An electric resistance heater inside the cylinder is now turned on, and 2200 kJ of energy is transferred to the steam.
Determine the entropy change of the water during this process, in kJ K$^{-1}$.

18.7 Consider a system consisting of 2.0 mol CO$_2$ (g), initially at 25°C and 10 atm and confined to a cylinder of cross-section 10.0 cm$^2$.
It is allowed to expand adiabatically against an external pressure of 1.0 atm until the piston has moved forwards through 20 cm. Assume that carbon dioxide may be considered a perfect gas with $C_{v,m}$=28.8 J K$^{-1}$ mol$^{-1}$ and calculate:
(a) Heat transfer,
(b) Work,
(c) The internal energy change,
(d) The temperature change and
(e) The entropy change.

18.8 A Carnot cycle uses 1.0 mol of a monatomic perfect gas as the working substance from an initial state of 10.0 atm and 600 K. It expands isothermally to a pressure of 1.0 atm (Step 1), and then adiabatically to a temperature of 300 K (Step 2).
This expansion is followed by an isothermal compression (Step 3), and then an adiabatic compression (Step 4) back to the initial state.
Determine the values of $Q$, $W$, $\Delta U$, $\Delta H$, $\Delta S$, $\Delta S_{total}$, and $\Delta G$ for each stage of the cycle and for the cycle as a whole.

18.9 Silicone oil with a viscosity of 1 Pa s flows through a pipe with a diameter of 10 cm.
If the volumetric flow through the pipe is 0.01 m$^3$ s$^{-1}$, calculate:
(a) the average velocity
(b) the maximum velocity
(c) the pressure drop per unit length

18.10 A particle is taken along by a water flow between two parallel plates with a distance between the plates of $2a = 1$ mm. Show, using a force balance on a control element as in figure 3, that the local velocity is given by:
$$ u = \frac{1}{2\mu} \left[ -\frac{dP}{dx} \right] (a^2 - y^2) $$
Calculate the speed at which the particle is travelling if the maximum fluid velocity is 0.1 m s$^{-1}$, and the particle travels at a distance of 100 $\mu$m from one of the plates.

18.11 Peas of diameter 8 mm, initially stored chilled at 4°C, are to be blanched in boiling water to inactivate enzymes, prior to freezing. The centre of the peas must reach 92°C for blanching to be effective.
The heat transfer coefficient of the boiling water is 5000 W m$^{-2}$ K$^{-1}$. Assuming the peas are spherical, and using the above analysis, calculate the time required for the average temperature to reach 92°C.

Check the applicability of the above analysis to this situation. Would the temperature throughout a pea after this time be sufficiently uniform to consider the centre to have reached 92°C?

Data:
- Thermal conductivity of peas = 0.6 W m$^{-1}$ K$^{-1}$
- Density of peas = 1048 kg m$^{-3}$
- Specific heat capacity of peas = 2865 J kg$^{-1}$ K$^{-1}$

18.12 Show, by deriving Planck’s equation in cylindrical and spherical co-ordinates, that the time required for a cylindrical system to freeze or solidify is equal to $t_{slab}/2$, and that the time required for a spherical system to freeze or solidify is equal to $t_{slab}/3$, where $t_{slab}$ is the time required for a slab of thickness $L$ to freeze or solidify. The characteristic dimension for the cylinder or sphere is $D$, and $D = L$.

N.B.
$$ \int_a^b r \ln r \, dr = \left[ \frac{r^2}{2} (\ln r - 0.5) \right]^b_a $$

18.13 Cartons of meat of dimensions 160 × 360 × 600mm are frozen in an air blast freezer with an air temperature of −23°C. The cartons enter the freezer at an initial temperature of −1°C, which is their initial freezing temperature, and must be frozen to a centre temperature of −10°C. Calculate the freezing time.

Data:
- $\Delta H_{10} = 220 \times 10^6$ J m$^{-3}$
- $\lambda = 1.5$ W m$^{-1}$ °C$^{-1}$
- $E = 1.29$
- $h = 20$ W m$^{-2}$ °C$^{-1}$

18.14 A condenser with an area of 1 by 1 m is used to condense steam. If the film formed has a thickness of 0.5 mm, what is the capacity (in kg s$^{-1}$) of the condenser?

18.15 100 mol of a mixture of heptane and octane containing 30 mol% heptane are subjected to an equilibrium distillation at a pressure of 760 mm Hg and 60 mol of vapour are obtained.
(a) Determine the compositions of the vapour and liquid that are produced.
(b) At what temperature does the distillation take place?

\[ T - x - y \] and \[ x - y \] diagrams for heptane and octane are provided in figures 4 and 5.

18.16 The liquid obtained from the equilibrium distillation in question 18.15 is now heated and its temperature is increased by 2.5 K and the resulting mixture of vapour and liquid comes to equilibrium at a pressure of 760 mm Hg. Calculate

(a) The quantity and composition of the vapour,
(b) The quantity and composition of the liquid.

\[ T - x - y \] and \[ x - y \] diagrams for heptane and octane are provided in figures 4 and 5.

18.17 For a liquid mixture of C and D, the relative volatility of C to D, \( \alpha \), has a value of 2.0 which may be considered to be independent of composition.

(a) A mixture of 100 mol of C and D containing 40 mol\% C is subjected to a flash distillation and 60 mol of vapour are produced. Calculate the compositions of the vapour and liquid formed.

(b) In a second flash distillation starting with the same initial mixture, the vapour produced contains 53 mol\% C. Calculate the composition of the liquid that is formed and the number of moles of vapour and liquid.
Figure 4: $T-x-y$ diagram for the mixture of heptane and octane.
A paint company is trying to use up excess quantities of four shades of green paint by mixing them to form a more popular shade. One gallon of the new paint will be made up of $x_1$ gallons of paint 1, $x_2$ gallons of paint 2 etc. Each of the paints is made up of four pigments. If each number represents a percentage, the mixture giving the more popular shade is the solution of the system of equations

$$\begin{pmatrix}
0 & 80 & 10 & 10 \\
80 & 0 & 30 & 10 \\
16 & 20 & 60 & 72 \\
4 & 0 & 0 & 8
\end{pmatrix}
\begin{pmatrix}
x_1 \\
x_2 \\
x_3 \\
x_4
\end{pmatrix}
= \begin{pmatrix} 27 \\
40 \\
31 \\
2
\end{pmatrix}.$$ 

Find the optimal mixture by solving the system using Gaussian elimination with
**partial pivoting.** (This means that you interchange rows at every step to put the biggest number in modulus on the diagonal. In this example, at the first stage of the elimination you would interchange row one with row two.)

You can check your results in MATLAB (see also the following exercise) by typing the command sequence

```matlab
>> A=[0,80,10;80,0,30;16,20,60,72;4,0,0,8], [L,U,P] = lu(A),
>> b=[27;40;31;2], x=A,
```

### Part 18.19

Given a matrix

\[
A = \begin{pmatrix}
4.00 & -2.00 & 3.00 \\
-2.00 & 7.25 & -2.75 \\
3.00 & -2.75 & 11.50
\end{pmatrix}
\]

By setting

\[
L = \begin{pmatrix}
1 & 0 & 0 \\
\ell_{21} & 1 & 0 \\
\ell_{31} & \ell_{32} & 1
\end{pmatrix}, \quad U = \begin{pmatrix}
u_{11} & u_{12} & u_{13} \\
0 & u_{22} & u_{23} \\
0 & 0 & u_{33}
\end{pmatrix}
\]

and forming the product, find a lower triangular matrix \(L\) with ones on the diagonal, and an upper triangular matrix \(U\) such that

\[
LU = A.
\]

This is how Gaussian elimination is implemented in MATLAB, the matrix \(U\) is the upper triangular matrix formed by GE, the matrix \(L\) contains the row multipliers used at each stage of the elimination, and the matrix \(P\) is the permutation matrix needed to effect the partial pivoting. You can check your results by typing the MATLAB command sequence

```matlab
>> A=[4,-2,3;-2,7.25,-2.75;3,-2.75,11.5], [L,U,P] = lu(A),
```
19 Week 19

19.1 The rate constant for a particular reaction is \(2.80 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^{3} \text{ s}^{-1}\) at 30\(^{\circ}\)C and \(1.38 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^{3} \text{ s}^{-1}\) at 50\(^{\circ}\)C. Evaluate the Arrhenius parameters for this reaction.

What is the order of reaction? \(R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}\).

19.2 Milk is pasteurised if it is heated to 63\(^{\circ}\)C for 30 minutes, but if it is heated to 74\(^{\circ}\)C it only needs 15 seconds for the same result.

Find the activation energy of this sterilisation process. \(R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}\).

19.3 What is the fraction of molecular collisions that have sufficient energy for reaction if the activation energy is 50 kJ mol\(^{-1}\) and the temperature is

(a) 25\(^{\circ}\)C
(b) 500\(^{\circ}\)C?

19.4 A ‘rule of thumb’ in chemical kinetics is that the rate of reaction doubles if the temperature increases by 10 K.

At around 300 K, what value for the activation energy does this imply?

19.5 The rate of the second-order decomposition of ethanal (CH\(_3\)CHO) was measured over the temperature range 700 to 1000 K and the rate constants are reported below:

<table>
<thead>
<tr>
<th>(T /\text{K})</th>
<th>(700)</th>
<th>(730)</th>
<th>(760)</th>
<th>(790)</th>
<th>(810)</th>
<th>(840)</th>
<th>(910)</th>
<th>(1000)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k / \text{mol}^{-1} \text{ dm}^{3} \text{ s}^{-1})</td>
<td>0.011</td>
<td>0.035</td>
<td>0.105</td>
<td>0.343</td>
<td>0.789</td>
<td>2.17</td>
<td>20.0</td>
<td>145</td>
</tr>
</tbody>
</table>

Find the activation energy and the pre-exponential factor.

19.6 Consider the following reaction:

\[ \text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_3 \]

The reaction is carried out adiabatically at constant pressure. Initially, the reactor contains 1 mol of SO\(_2\) and 1/2 mol of O\(_2\). If the initial temperature of the reactor is 25\(^{\circ}\)C and the final temperature 275\(^{\circ}\)C, evaluate the conversion of SO\(_2\). Standard enthalpies of formation and mean molar heat capacities are given below.

Standard enthalpies of formation at 25\(^{\circ}\)C.

| \(\Delta h_f /\text{kJ mol}^{-1}\) | \(\text{SO}_2\) | \(-296.8\) |
|-------------------------------|----------------|
| \(\text{SO}_3\)                | \(-395.7\)     |

Mean molar heat capacities at constant pressure (25\(^{\circ}\)C to 275\(^{\circ}\)C)

| \(\overline{C}_p /\text{J mol}^{-1} \text{ K}^{-1}\) | \(\text{SO}_2\) | \(47.9\) |
|-----------------------------------------------------|----------------|
| \(\text{SO}_3\)                                      | \(68.4\)       |
| \(\text{O}_2\)                                       | \(30.4\)       |

19.7 The vapour pressures of C\(_2\)H\(_4\)Br\(_2\) and C\(_3\)H\(_6\)Br\(_2\) at 135\(^{\circ}\)C are 835 and 652 mmHg, respectively. Construct the \(P - x - y\) and \(y - x\) diagrams at constant temperature. Assume that Raoult’s law applies.
19.8 The vapour pressures of $C_2H_4Br_2$ and $C_3H_6Br_2$ at different temperatures are given below. Construct the $T$-$x$-$y$ and $y$-$x$ diagrams at 760 mmHg.

<table>
<thead>
<tr>
<th>$C_2H_4Br_2$</th>
<th>$C_3H_6Br_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$ / °C / mmHg</td>
<td>$T$ / °C / mmHg</td>
</tr>
<tr>
<td>131.5</td>
<td>133.5</td>
</tr>
<tr>
<td>133.5</td>
<td>135.0</td>
</tr>
<tr>
<td>135.0</td>
<td>138.0</td>
</tr>
<tr>
<td>138.0</td>
<td>141.6</td>
</tr>
</tbody>
</table>

19.9 A laminar flow of water is pumped through a horizontal pipe system as depicted in Figure 6. The outlets (B and C) are at atmospheric pressure. Calculate the flow rates through pipes B and C.

![Figure 6: Laminar flow of water in a horizontal pipe system.](image)

19.10 The resistance to heat transfer from a cylindrical pipe can be expressed as:

$$ R = \frac{(r_o - r_i)}{\lambda A_m} $$

where $r_o$ and $r_i$ are the outer and inner radii, respectively, of the pipe, and $\lambda$ is the thermal conductivity of the pipe wall. Demonstrate that the appropriate value of the average area, $A_m$, to use is the log-mean area.

19.11 (a) Compare briefly the merits and disadvantages of shell and tube heat exchangers and plate heat exchangers.

(b) A plate heat exchanger is to be used to cool ethylene glycol (specific heat capacity = 2518 J kg$^{-1}$ K$^{-1}$) flowing at 21000 kg hour$^{-1}$ from 70°C to 30°C using water (specific heat capacity = 4180 J kg$^{-1}$ K$^{-1}$) flowing at 10000 kg hour$^{-1}$ with an inlet temperature of 10°C. The convection heat transfer coefficient for the ethylene glycol is 1040 W m$^{-2}$ K$^{-1}$, and for the water is 1550 W m$^{-2}$ K$^{-1}$.

Fouling factors of 0.00018 m$^2$ K W$^{-1}$ apply for both sides. The thermal resistance of the wall may be neglected.

i. Calculate the heat transfer surface area required for countercurrent flow. Define carefully any assumptions made.
ii. Sketch the temperature-stream enthalpy diagram for the heat exchanger, and explain its relevant features. Could a co-current configuration be used?

iii. Describe the physical meaning of the Biot number and the Nusselt number.

19.12 What heat transfer innovation allowed George Stephenson’s “Rocket” to win the Rainhill steam locomotive trials? In what general way has this idea been adopted for use in the process industries?

19.13 To prevent pitting erosion on the shell side of a condenser, it is normal practice to ensure that the vapour is slightly superheated. A vertical re-boiler uses 0.5 kg s\(^{-1}\) of steam at 1.2 bar as the heating medium on the shell side. The steam is conveyed from the boiler house in a 6 inch nominal bore schedule 40 mild steel pipe (internal diameter 0.154 m), which is 300 m long. The pipe is insulated to reduce heat loss to the ambient surroundings, such that the overall heat transfer coefficient from the fluid to the ambient is 1.76 W m\(^{-2}\)K\(^{-1}\).

If the ambient temperature is 0\(^\circ\)C, evaluate the degrees of superheat required at the boiler house, so that the steam enters the re-boiler with 5\(^\circ\)C of superheat. The saturated temperature of steam at 1.2 bar is 104.8\(^\circ\)C, and the mean specific heat capacity is 1888 J kg\(^{-1}\)K\(^{-1}\).

19.14 The feed to a distillation column consists of 80 kmol h\(^{-1}\) of a benzene/toluene mixture containing 55 mol% benzene. The feed is preheated prior to entering the column and then enters as 40 kmol h\(^{-1}\) vapour and 40 kmol h\(^{-1}\) liquid.

If the above vapour and liquid are in equilibrium, then determine their compositions. The relative volatility of benzene to toluene may be assumed to have a value of 2.4.

19.15 The feed in question 19.14 is separated in the column so that 98% of the benzene in the feed is recovered in the distillate and the bottom product contains 96 mol% toluene. A reflux ratio of 2.5 is employed.

Determine:

(a) the flow rate and composition of the distillate,
(b) the flow rate of the bottom product,
(c) the flow rate of vapour in the enrichment section,
(d) the flow rate of liquid in the enrichment section,
(e) the flow rate of vapour in the stripping section,
(f) the flow rate of liquid in the stripping section,
(g) the rate of heat removal in the condenser (kJ h\(^{-1}\)),
(h) the rate of heat addition in the reboiler (kJ h\(^{-1}\)).

The molar heat of vaporisation for benzene/toluene mixtures is 34000 kJ kmol\(^{-1}\).

19.16 Solve analytically the following differential equations:

(a) \(\frac{dy}{dx} = -x^2 y\); \(y = 1 \) when \(x = 0\).

(b) \(\frac{dy}{dx} = -y^2 \sin x\); \(y = 1 \) when \(x = \pi/2\).
(c) \( \frac{dy}{dx} = -x(4 + y^2) \); \( y = 2 \) when \( x = 0 \).

19.17 Consider the second order reaction between species A and B,

\[
\text{A + B \rightarrow Products}
\]

with initial concentrations \([A]_0\) and \([B]_0\) respectively.

(a) Give an argument to show that \([B] = [B]_0 + [A] - [A]_0\).

(b) Solve the differential equation

\[
\frac{d[A]}{dt} = -k_2[A][B]
\]

to obtain the result

\[
[A] = \frac{c[A]_0 \exp(-ck_2 t)}{c + [A]_0 - [A]_0 \exp(-ck_2 t)}
\]

where \(c = [B]_0 - [A]_0\).

19.18 Solve the following linear ODEs by finding an integrating factor:

(a) \( \frac{dy}{dx} + y = \exp(-x) \); \( y = 2 \) when \( x = 0 \).

(b) \( \frac{dy}{dx} + y \cos x = \cos x \); \( y = 1 \) when \( x = 0 \).

(c) \( \star \frac{dy}{dx} + \frac{y}{x} = \sin x \); \( y = 1 \) when \( x = 0 \).
20 Week 20

20.1 The following first-order reversible reaction takes place in the liquid phase in a batch reactor:

\[ A \rightleftharpoons R \]

\[ C_{A0} = 0.5 \text{ mol dm}^{-3}, \quad C_{R0} = 0. \] After 8 min, the conversion is 1/3 and the equilibrium conversion is 2/3. Determine the rate constants for the forward and reverse reactions.

20.2 Consider the following reaction sequences. These take place at constant volume and temperature in batch reactors. Each step is elementary.

\[
\begin{align*}
A & \xrightleftharpoons[k_1]{k_2} R \xrightleftharpoons[k_3]{k_4} S \\
A & \xrightarrow{k_1} R \\
A & \xrightarrow{k_2} S
\end{align*}
\]

Formulate rate equations describing the change in concentration of A, R and S as a function of time. If the initial concentrations of A, R and S are 1, 0 and 0 \text{ mol dm}^{-3}, respectively, what are their values after infinite time? Assume \( k_1 = k_2 = k_3 = k_4 \).

20.3 (a) Formulate rate equations describing the change in concentration of A, R and S as a function of time for the following elementary first-order irreversible parallel reactions.

\[
A \xrightarrow{k_1} R \\
A \xrightarrow{k_2} S
\]

(b) Derive expressions for the integrated forms of these equations and thus show how the rate constants \( k_1 \) and \( k_2 \) can be determined by graphical means.

(c) For the reactions shown in 20.3a, sketch how the concentrations of A, R and S vary with time for the following two cases (assume the initial concentrations of R and S are 0):

i. \( k_1 = k_2 \)

ii. \( k_1 > k_2 \)

(d) The initial concentrations of A, R and S in the parallel reaction of 20.3a are 1.0, 0.1 and 0.2 \text{ mol dm}^{-3}, respectively. After 1000 s in a batch reactor the concentrations of A, R and S are 0.4, 0.3 and 0.6 \text{ mol dm}^{-3}, respectively. Calculate the rate constants \( k_1 \) and \( k_2 \).
20.4 Vapour pressures of water at different temperatures are given below. If 400 g of NaCl are dissolved in 1000 g of water, by how much is the normal boiling temperature of water elevated?

[RAM: H = 1, O = 16, Na = 23, Cl = 35.5]

Vapour pressures:

<table>
<thead>
<tr>
<th>T / °C</th>
<th>P / bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>96.7</td>
<td>0.90</td>
</tr>
<tr>
<td>98.2</td>
<td>0.95</td>
</tr>
<tr>
<td>99.6</td>
<td>1.00</td>
</tr>
<tr>
<td>100.0</td>
<td>1.013</td>
</tr>
<tr>
<td>102.3</td>
<td>1.10</td>
</tr>
<tr>
<td>104.8</td>
<td>1.20</td>
</tr>
<tr>
<td>107.1</td>
<td>1.30</td>
</tr>
</tbody>
</table>

20.5 Calculate the volume of oxygen (at standard conditions of 273 K, 1.013 bar) dissolved in 1000 g of water in equilibrium with air at 296 K and 1.013 bar. Assume that air contains 21 vol% O₂. The Henry’s law constant for oxygen in water at 296 K is \(4.64 \times 10^4\) bar.

20.6 A 200 km long pipeline connects two pumping stations. If 1 m³ s⁻¹ of oil is to be pumped through a 0.7 m diameter pipe, determine the power required. The discharge station is 300 m lower than the upstream station, and the pressure at the discharge station is 160 kN m⁻² greater than that of the upstream station. Losses at the pipe entrance and exit can be ignored. The pipe is smooth, and the pump efficiency 75%. Consider the kinematic viscosity of oil as 0.5 \(\times 10^{-5}\) m² s⁻¹ and the oil density 800 kg m⁻³.

20.7 In rural areas, water is often extracted from underground by pumps. Consider an underground water source whose free surface is 60 m below ground level. The water is to be raised 5 m above the ground by a pump. The diameter of the pipe is 15 cm at the inlet and 20 cm at the exit. Neglecting any heat interaction with the surroundings and frictional effects, determine the power input to the pump required for a steady flow of water at a rate of 15 L s⁻¹.

20.8 (a) Explain each of the terms in the Sieder and Tate equation:

\[ Nu = 0.027 \ Re^{0.8} Pr^{0.333} \left( \frac{H_b}{\mu_w} \right)^{0.14} \]

(b) A counter-current shell and tube heat exchanger contains 50 thin-walled, highly conducting tubes, each of length 8 m and internal diameter 2 cm. Water passes on the tube side at a total flowrate of 5 kg s⁻¹, and steam condenses on the shell side. The water is heated from 30°C to 80°C, and the steam and condensate temperatures are both 120°C.

i. Draw and label a temperature-enthalpy diagram for the heat exchanger.
ii. Calculate the overall heat transfer coefficient.
iii. Using the Sieder and Tate correlation, estimate the tube side heat transfer coefficient. Evaluate the thermophysical properties of water at the bulk mean water temperature from the steam tables supplied.
iv. Based on your answers for 20.8(b)ii and 20.8(b)iii, and assuming fouling factors on both tube and shell sides of 0.00018 m² K W⁻¹, estimate the shell side heat transfer coefficient.
20.9 A plate heat exchanger is to be designed to cool 4.5 kg \( s^{-1} \) of engine oil (specific heat capacity = 2090 J kg\(^{-1}\) °C\(^{-1}\)) from 60 to 45°C, using seawater initially at 20°C, at a flowrate of 2.8 m \( s^{-1} \) and specific heat capacity of 4180 J kg\(^{-1}\) °C\(^{-1}\). Calculate the heat transfer duty and the exit temperature of the seawater.

Then, if the overall heat transfer coefficient is 70 W m\(^{-2}\) °C, calculate the log-mean temperature difference and surface area required for

(a) counterflow; and
(b) parallel flow arrangements.

Sketch the temperature profiles of the two fluids for each arrangement. Which arrangement requires the smaller heat exchanger?

20.10 A shell-and-tube steam condenser is to be constructed of 2.5 cm OD, 2.2 cm ID, horizontal tubes of 7 metres in length, with steam condensing at 54°C on the outside of the tubes.

The treated boiler feed cooling water enters the tubes at 18°C with a total flow rate of 6 kg \( s^{-1} \), and leaves at 36°C. The heat transfer coefficient for the steam condensation is 8000 W m\(^{-2}\) °C\(^{-1}\), and the latent heat of condensation at 54°C is 2372 kJ kg\(^{-1}\). The heat transfer coefficient for the water is 7100 W m\(^{-2}\) °C\(^{-1}\), and the fouling factor on the water side is 0.00018 m\(^2\) °C W\(^{-1}\); there is negligible fouling on the steam side. The thermal conductivity of the tubes is 19 W m\(^{-1}\) °C\(^{-1}\).

Calculate the heat transfer duty, the condensation rate of the steam, the overall heat transfer coefficient based on the outside area of the tubes, the log-mean temperature difference, the total tube outside surface area required in the heat exchanger, and the number of tubes required.

20.11 A heat exchanger is to be designed to heat 2 kg \( s^{-1} \) of pressurised water from 40°C to 120°C flowing on the tube side \( (C_p = 4200 \text{ J kg}^{-1} \text{ °C}^{-1}) \), using hot water entering on the shell side at 300°C with a flowrate of 1.03 kg \( s^{-1} \) \( (C_p = 4660 \text{ J kg}^{-1} \text{ °C}^{-1}) \). The overall heat transfer coefficient is 1250 W m\(^{-2}\) °C\(^{-1}\). Calculate the exit temperature of the hot water, the heat transfer rate and the counterflow log-mean temperature difference.

Then estimate, using the appropriate correction factor, the heat transfer surface area required for:

(a) a one shell pass, two tube pass heat exchanger (graph (a) of Figure 10-14 in Perry’s Chemical Engineers’ Handbook, 6th edition, Page 10-27);
(b) a two shell pass, four tube pass heat exchanger (graph (b) of above figure);
and
(c) a cross-flow, one shell pass, one tube pass exchanger with both fluids unmixed (graph (h) of Figure 10-14 in Perry’s Chemical Engineers’ Handbook, 6th edition, Page 10-27).

20.12 We would like to to solve the differential equation

\[
\frac{dy}{dt} = -10(t - 1)y
\]

with the given initial condition: \( y(0) = e^{-5} \). A reference solution to this problem can be plotted in MATLAB by typing the command sequence:

\[
tt=0:0.01:2; \ ex=\text{exp}(-5*(tt-1).*((tt-1))); \text{plot(tt,ex,'-k')}
\]
(a) Find the analytic solution $y(t)$, and evaluate it at $t = 0.2, 0.4, 0.6, 0.8, 1.0, 1.2$ and 1.4.

(b) Compute the forward Euler solution by taking seven steps of the method with a step length of $h = 0.2$. (You will need a calculator to do this.) Generate a table which compare the analytic solution with the numerical solution. At which time $t$ do you find the biggest error?

(c) Compute a more accurate forward Euler solution by taking four steps with a much smaller step length of $h = 0.05$. Compare this solution with the exact solution $y(0.2)$ and compare the accuracy of this solution with the first time step result obtained in (b).

Note that this differential equation is not as benign as it looks; if one wants to solve it over a long time interval, sophisticated numerical methods (like those that are built into MATLAB) are needed. A simple example of a sophisticated method is the implicit Euler method discussed in the lectures.
21 Week 21

21.1 The elementary, liquid-phase, irreversible reaction

\[ \text{A} + \text{B} \rightarrow \text{C} \]

is to be carried out in a flow reactor. Two reactors are available, an 800 dm\(^3\) PFR that can only be operated at 300 K and a 200 dm\(^3\) CSTR that can be operated at 350 K. The two feed streams to the reactor mix to form a single feed stream that is equimolar in A and B, with a total volumetric flowrate of 10 dm\(^3\) min\(^{-1}\). Which of the two reactors will give the highest conversion?

Additional information:
At 300 K, \(k = 0.07 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}\), \(E = 85000 \text{ J K}^{-1} \text{ mol}^{-1}\), \(C_{A0} = C_{B0} = 2 \text{ mol dm}^{-3}\), \(\nu_0 = 0.5 \nu_0 = 5 \text{ dm}^3 \text{ min}^{-1}\).

21.2 It is desired to produce 20 million kg per year of ethylene glycol (EG). The reactor is to be operated isothermally.

A 3.5 mol dm\(^3\) solution of ethylene oxide (EO) in water is fed to the reactor together with an equal volumetric solution of water containing 0.9 wt % of the catalyst H\(_2\)SO\(_4\).

The specific reaction rate constant is 0.311 min\(^{-1}\) (1st order in EO). If 80% conversion is to be achieved, determine the necessary CSTR volume.

21.3 A 200 dm\(^3\) constant volume batch reactor is pressurised to 20 atm with a mixture of 75% A and 25% inert. The gas phase reaction is carried out isothermally at 227°C.

(a) Assuming that the ideal gas law is valid, how many moles of A are in the reactor initially? What is the initial concentration of A?

(b) If the reaction is first order:

\[ -r_A = kC_A \]

where \(k = 0.1 \text{ min}^{-1}\). Calculate the time necessary to consume 99% of A.

(c) If the reaction is second order:

\[ -r_A = kC_A^2 \]

where \(k = 0.7 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}\). Calculate the time to consume 80% of A.

21.4 The following reaction takes place in the vapour phase at 500 K using equimolar proportions of reactants.

\[ \text{C}_2\text{H}_4 + \text{H}_2\text{O} \rightleftharpoons \text{C}_2\text{H}_5\text{OH} \]

Assuming that the reactants and products are perfect gases, evaluate the equilibrium mole fraction of ethanol if the reaction takes place at 1 atm pressure. \(K_p = 0.01307\) at 500 K.

21.5 For the reaction in problem 21.4, evaluate the equilibrium mole fraction of ethanol for equimolar proportions of reactants at 100 atm. Evaluate \(y_{\text{ethanol}}\) at 100 atm for a reactant ratio of steam/ethene of 2/1.
21.6 Consider the following gas phase reaction that takes place at constant temperature and for which the equilibrium constant $K_p = 0.1$:

$$A + B \rightleftharpoons C$$

(a) Starting with 1 mol of A and 1 mol of B, at what pressure would the conversion of A be 0.5?

(b) Starting with 1 mol of A, 1 mol of B and 0.1 mol of C, at what pressure would the conversion of A be 0.5?

(c) Comment on the results of the calculations.

21.7 A pump, whose characteristic curves are shown in the Fluid Flow booklet, is to be used to pump water out of a mine. The water is collected in a large open pit at the bottom of the mine shaft, and is then transferred to ground level in a pipe with an inner diameter of 4 inch. The water is discharged into the atmosphere as a jet, at a point 15 m above the water level in the pit. The pipe is 50 m long (Fanning Friction Factor = 0.0044) and contains 3 bends ($L_e=1.5$ m) and 2 valves ($K=0.9$). The loss coefficient associated with the pipe entrance is 0.5. Assume $\mu=1 \times 10^{-3}$ Pa s.

If the pump is operating at 1450 rpm, estimate:

(a) the water flow rate

(b) the pump efficiency

(c) the power required to drive the pump.

21.8 We want to use a centrifugal pump to pump water from a large, open water tank at a rate of 10 litre s$^{-1}$, using a pipe with an inner diameter of 10 cm. According to the manufacturer's specifications, to avoid cavitation the head at the entrance to the pump must be kept 5 m greater than the head associated with the liquid vaporisation pressure. The major cause of loss between the tank and the pump is a non-return valve with a loss coefficient of 20. If the vapour pressure of water under the conditions used is 2750 Pa absolute, calculate the maximum height at which the pump can be placed above the tank.

21.9 A single pass shell and tube heat exchanger is to be used to cool a vegetable oil (specific heat capacity = 2150 J kg$^{-1}$ K$^{-1}$) flowing at 21000 kg hour$^{-1}$ from 65°C to 30°C using water (specific heat capacity = 4180 J kg$^{-1}$ K$^{-1}$) flowing at 35000 kg hour$^{-1}$ with an inlet temperature of 10°C. The convection heat transfer coefficient for the oil is 1140 W m$^{-2}$ K$^{-1}$, and for the water is 1450 W m$^{-2}$ K$^{-1}$. The thermal resistance of the wall may be neglected.

Calculate the heat transfer surface area required for

(a) co-current flow; and

(b) countercurrent flow.

Define carefully any assumptions made. Sketch the temperature profiles of the two streams for each of the two cases. Why are the two heat transfer areas different?

21.10 The plates in a plate heat exchanger are corrugated. What benefits does this give?
21.11 A heat exchanger is to be used to cool ethylene glycol \((C_p = 2518 \text{ J kg}^{-1} \text{ K}^{-1})\) flowing at 11000 kg hour\(^{-1}\) from 70°C to 30°C using water (specific heat capacity \(= 4180 \text{ J kg}^{-1} \text{ K}^{-1}\)) flowing at 5000 kg hour\(^{-1}\) with an inlet temperature of 10°C. Assuming no heat losses or gains, calculate the exit temperature of the water, and the log-mean temperature difference under countercurrent flow.

21.12 100 kmol h\(^{-1}\) of a mixture of heptane and octane containing 55 mol% heptane is the feed to a distillation column. The feed is a liquid at its boiling point and the column operates at 1 atm. pressure.

The column must be operated so that 99% of the heptane in the feed is recovered in the distillate and 94% of the octane in the feed is recovered in the bottom product. A reflux ratio of 1.5 times the minimum reflux ratio is to be used.

Determine the following:

(a) the flow rate of the distillate in kmol h\(^{-1}\) and the mol fraction of heptane in the distillate;
(b) the flow rate of the bottom product in kmol h\(^{-1}\) and the mol fraction of heptane in the bottom product;
(c) the minimum reflux ratio;
(d) the actual reflux ratio used;
(e) the number of theoretical plates (excluding the re-boiler) that are required and the location of the feed plate
(f) the actual number of plates required if the column efficiency is 65%;
(g) the approximate height of the column if the spacing between adjacent plates is 600 mm and the additional height required above the top plate and below the bottom plate is a total of 5 metres;
(h) the internal diameter of the column if the maximum vapour velocity (based on the column cross-sectional area) is 0.8 m/s
(i) the heat removed in the condenser (kJ h\(^{-1}\))
(j) the heat input to the reboiler (kJ h\(^{-1}\))

Data - x-y diagram for heptane-octane below can be found in Figure 7.

Boiling point of heptane at 1 atm. pressure = 98.4°C.

Latent heat of vaporisation of heptane = 31990 kJ kmol\(^{-1}\).

Boiling point of octane at 1 atm pressure = 125.6°C.

Latent heat of vaporisation of octane = 34910 kJ kmol\(^{-1}\).

21.13 200 kmol h\(^{-1}\) of a mixture of ethanol and water containing 20 mol% ethanol is the feed to a distillation column. The feed is a liquid at its boiling point and the column operates at 1 atm. pressure.

The column must be operated so that the distillate contains 80 mol% ethanol with the molar flow rate of bottom product equal to four times the molar flow rate of distillate. A reflux ratio of 1.4 times the minimum reflux ratio is to be used.

Determine the following:

(a) The mol fraction of ethanol in the bottom product and the percentage of the feed ethanol that leaves in the bottom product;
(b) The minimum reflux;
(c) the number of theoretical trays (excluding the reboiler) that are required and the location of the feed tray
(d) The actual number of plates required if the column efficiency is 60%;

Equilibrium data for ethanol/water mixtures provided in Figure 8.

21.14 Compute the implicit (or backward) Euler solution to the model problem
\[
\frac{dy}{dt} = -10(t - 1)y
\]
with the given initial condition: \( y(0) = e^{-5} \), by taking four steps with a step length of \( h = 0.05 \). Compare this solution with the exact solution \( y(0.2) \) and the forward Euler solution computed previously.

21.15 Consider a population of bacteria in a confined environment in which no more than \( B \) elements can coexist. We assume that, at the initial time \( t = 0 \), the number of individuals is much smaller than \( B \) and is equal to \( y_0 \). We also assume that the growth rate of the bacteria is a positive constant \( C \). In this case the rate of change of the population is proportional to the number of existing bacteria, under the restriction that the total number cannot exceed \( B \). This is expressed by the differential equation
\[
\frac{dy}{dt} = Cy \left(1 - \frac{y}{B}\right),
\]
whose solution \( y = y(t) \) denotes the number of bacteria at time \( t \).

(a) Given some initial population \( y_0 \) and a step length of \( h \), write down the general update formula for computing the forward Euler solution \( y_{n+1} \) from the previous estimate \( y_n \approx y(nh) \).
(b) Next, write down the general update formula for computing the implicit Euler solution \( y^*_n \) from the previous estimate \( y^*_n \approx y(nh) \).

Note that if a general nonlinear ODE is to be solved numerically using an implicit time stepping method then a nonlinear equation must be solved at every timestep!

21.16⋆ In Biochemistry, a Michaelis–Menten type process involves a substrate \( S \), an enzyme \( E \), a complex \( C \) and a product \( P \), and is summarized through the set of reactions
\[
S + E \underset{c_1}{\rightarrow} C \\
C \underset{c_2}{\rightarrow} S + E \\
C \underset{c_3}{\rightarrow} P + E.
\]

In the framework of chemical kinetics, this set of reactions may be interpreted as a systems of ODEs as follows
\[
\frac{dS}{dt} = -c_1 SE + c_2 C \\
\frac{dE}{dt} = -c_1 SE + (c_2 + c_3) C \\
\frac{dC}{dt} = c_1 SE - (c_2 + c_3) C \\
\frac{dP}{dt} = c_3 C,
\]
where \( S(t) \), \( E(t) \), \( C(t) \) and \( P(t) \) denote the concentrations of substrate, enzyme, complex and product, respectively, at time \( t \).
(a) Given some initial values $S_0$, $E_0$, $C_0$ and $P_0$ and a step length $h$, write down a set of update formulas for computing the forward Euler solution $S_{n+1}$, $E_{n+1}$, $C_{n+1}$ and $P_{n+1}$ from the previous time solution estimates $S_n$, $E_n$, $C_n$ and $P_n$.

(b) Next, write down the general update formula for computing the implicit Euler solution $S_{n+1}^*$, $E_{n+1}^*$, $C_{n+1}^*$ and $P_{n+1}^*$ from the previous time solution estimates. You should find that this requires the solution of a system of nonlinear equations at every time step.
Figure 7: $x - y$ diagram for the mixture of heptane and octane.

Vapour-liquid equilibrium for heptane/octane at $P=1$ atm.
22  Week 22

22.1 Verify that the nonlinear equation

\[ x^{1/2} \sin(x) = 1 \]

has at least one solution in the interval \((1.1,1.3)\). Hence find a solution which is accurate to two decimal places using

(a) an interval halving method,
(b) a Newton iteration method (with initial guess \(x_0 = 1.2\)),

22.2* Derive a Newton method to calculate the fifth root of a given real number, \(s\) say. Use your method to calculate \(5^{1/5}\) correct to four decimal places.

23  Week 23: Design Project

24  Week 24: Design Project
Answers to some selected problems

13.4 810.6 m$^3$ h$^{-1}$; 3.185 m s$^{-1}$.
13.5 C$_2$H$_4$Cl$_2$ MM = 99.05 g mol$^{-1}$.
13.6 413 kg; 1361 kg.
13.7 H$_2$: 4130 mph, He: 2920 mph, O$_2$: 1030 mph and Hg: 412 mph.
13.14 (a) -340 W m$^{-2}$, (b) Not at steady state.
13.15 132.9°C, 1.28 kg h$^{-1}$; 132.0°C, 3.82 kg h$^{-1}$; 128.9°C, 12.42 kg h$^{-1}$.
13.16 294 MJ; 61°C.
13.17 7258 kg.
14.5 0.0368 mol dm$^{-3}$.
14.6 5 s, 10 s.
14.7 (a) 196 J and (b) 32 J.
14.8 31.3 m s$^{-1}$.
14.9 101.3 J.
14.10 (a) 88.1 J and (b) 167 J.
14.11 88 J (irreversible) and 167 J (reversible).
14.12 98 J.
14.13 55.1 J kmol$^{-1}$ K$^{-1}$.
14.14 $Re$ = 5000, $Pr$ = 6.85.
14.16 (a) $h \propto w^{0.8}$; (b) 5570 W m$^{-2}$ K$^{-1}$.
14.17 8030 W m$^{-2}$ K$^{-1}$ ($Re$ = 14940).
14.18 20880 W m$^{-2}$ K$^{-1}$ ($Re$ = 566000).
14.19 6239 W m$^{-2}$°C$^{-1}$ ($Re$ = 132428, $Pr$ = 5.40).
14.20 8.8 W m$^{-2}$ K$^{-1}$.
14.21 about 595°C.
14.22 about 10.8 mol% NH$_3$.
15.6 $y_{Ar}$ = 0.25, $y_{Ne}$ = 0.75; 2494 cm$^3$, 20 kPa.
15.7 (a) 3.24 m s$^{-1}$, (b) 2.95 m s$^{-1}$.
15.8 -97.5 kJ mol$^{-1}$.
15.9

<table>
<thead>
<tr>
<th>$\Delta H_f$ [kJ mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
</tr>
<tr>
<td>CH$_4$</td>
</tr>
<tr>
<td>CO$_2$</td>
</tr>
<tr>
<td>CO</td>
</tr>
<tr>
<td>CH$_3$OH</td>
</tr>
</tbody>
</table>
15.10 $\approx$ 1500°C.
15.11 (a) 15300 W per metre length of pipe, (b) 0.0064 m.
15.12 (a) 75800 W, 13.5%, (b) 11800W, 15.6%, 41.7°C, (c) 79500 W, 14.2%.
15.13 $r_c = 2\lambda/h$.
15.14 (a) 452°C; (c) 0.022m, 12 mm; (f) 318°C, 100°C and 12.3 kW.
15.15 (a) 277.1 W, (b) 63.2 W, (c) 432 W, 3.57 cm, (d) 435.4 W, 153.6°C.
15.16 (a) $\approx$ 130°C, (b) $\approx$ 82.5°C, (c) 368 K.
15.17 1511.67 kg h$^{-1}$ for the vapour and 3023.3 kg h$^{-1}$. $U$ = 1811 W m$^{-2}$ K$^{-1}$.
16.3 (a) $\approx h_g$ at 0.15 MPa for steam, (b) x = 0.99.
16.4 1016.9 kW.
16.5 (a) $\approx$ 292.4°C; (b) 0.0127 K kPa$^{-1}$.
16.6 (a) 0.120 kg s$^{-1}$, (b) 5.036 kJ s$^{-1}$.
16.7 21.9°C.
16.9 17.51 kN m$^{-2}$ gauge.
16.10 9.1 m s$^{-1}$; 6.2 m.
16.11 92.6 s.
16.12 (c) 1.4 min.
16.13 (a) The lumped analysis is appropriate in all cases; (b) 5.8 min.
16.14 (a) $Bi = 9.33 \times 10^{-3}$, (b) 5.44 s, (c) 1.6 s.
16.15 3597 kg hr$^{-1}$.
16.16 $F$ = 8532 kg hr$^{-1}$, $V_0$ = 6520.9 kg hr$^{-1}$, 0.784.
17.4 Rate of protonated reaction = $k_{protonated}[HE]^+[OH^-] = 1.55 \times 10^{-5}$ mol dm$^{-3}$ min$^{-1}$; Rate of unprotonated reaction = $k_{unprotonated}[E][OH^-] = 1.64 \times 10^{-5}$ mol dm$^{-3}$ min$^{-1}$. Although $[HE^+] << [E]$ the contribution to the overall rate form the protonated and unprotonated forms of the ester are approximately equal. This is because $k_{HE} << k_E$.
17.13 (a) 725 K, (b) 60%.
17.14 103 kg s$^{-1}$ cast iron; 5.3 kg s$^{-1}$ mild steel.
17.15 365.7 kN m$^{-2}$.
17.16 (a) 44.8 W m$^{-2}$ K$^{-1}$; (b) 40.8 min.
17.17 0.025, 50 s.
17.18 35.3 min.
17.20 8916 kg h$^{-1}$, 0.814, 369.9 m$^2$.
17.21 35 m$^2$, 5117 kg hr$^{-1}$.
18.1 2720 years.
18.2 5 x 10$^{-4}$ s$^{-1}$; 1386 s.
18.3 2$^{nd}$ order, $k$ = 0.244 (dm$^3$ mol$^{-1}$)$^2$ min$^{-1}$.
18.5 (a) 1.337 kJ K$^{-1}$, (b) -1.337 kJ K$^{-1}$, (c) 0.
18.6 5.72 kJ K$^{-1}$.
18.7 (a) 0, (b) 20 J, (c) -20 J, (d) -0.347 K, (e) 0.60 J K$^{-1}$.
### 18.8

<table>
<thead>
<tr>
<th></th>
<th>Step 1</th>
<th></th>
<th>Step 2</th>
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<th>Step 3</th>
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<td>$\Delta Q/IkJ$</td>
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<tr>
<td>$\Delta U/IkJ$</td>
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<td>0</td>
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<td>$\Delta S/(J K^{-1})$</td>
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</tr>
<tr>
<td>$\Delta G/IkJ$</td>
<td>0</td>
<td>-11.5</td>
<td>0</td>
<td>11.5</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

18.9  
(a) 1.27 m s$^{-1}$; (b) 2.55 m s$^{-1}$; (c) 4070 Pa m$^{-1}$.

18.10 0.036 m s$^{-1}$.

18.11 2 s.

18.12 13.2 hr.

18.13 0.41 kg s$^{-1}$.

18.14 (a) $x = 0.197$, $y = 0.369$, (b) 90.5 °C.

18.15 (a) 19.8 mol, 25.7% heptane, 74.3% octane; (b) 20.2 mol, 13.8% heptane, 86.2% octane.

18.16 (a) $x_C = 0.3028$ mol %, $y_C = 0.4648$ mol %; (b) $x_C = 0.3606$ mol %, 23.3 mol % vapour, 76.7 mol liquid.

19.1 65 kJ mol$^{-1}$, 4.43 x 10$^8$, 2nd order.

19.2 423 kJ mol$^{-1}$.

19.3 (a) $1.7 \times 10^{-9}$, (b) $4.2 \times 10^{-4}$.

19.4 53.6 kJ mol$^{-1}$.

19.5 184 kJ mol$^{-1}$; $5.7 \times 10^{11}$ mol$^{-1}$ dm$^3$ s$^{-1}$.

19.6 0.162.

19.7 $Q_B = 0.234$ L min$^{-1}$, $Q_C = 0.766$ L min$^{-1}$.

19.11 (b) i. 82 m$^2$.

19.12 39.1°C superheated.

19.13 mol fraction benzene in vapour = 0.6566.

19.14 (a) 58 kmol hr$^{-1}$, (b) 22 kmol hr$^{-1}$, (c) 203 kmol hr$^{-1}$, (d) 163 kmol hr$^{-1}$, (e) 185 kmol hr$^{-1}$, (f) 6902000 kJ hr$^{-1}$, (g) 5542000 kJ hr$^{-1}$.

20.4 3.3 °C.

20.5 5.69 cm$^3$.

20.6 11 x 10$^3$ MW.

20.7 1 kW.

20.8 (b) ii. 675 W m$^{-2}$ K$^{-1}$, iii. 2670 W m$^{-2}$ K$^{-1}$, iv. 1317 W m$^{-2}$ K$^{-1}$.

20.9 (a) 26.47°C, 76.1 m$^2$; (b) 24.02°C, 83.9 m$^2$.

20.10 451.4 kW, 0.19 kg s$^{-1}$, 1743 W m$^{-2}$ °C$^{-1}$, 26°C, 9.96 m2, 19 tubes.

20.11 (a) 4.0 m$^2$ (FT = 0.91), (b) 3.7 m$^2$ (FT = 0.98), (c) 3.9 m$^2$ (FT = 0.94).

21.7 (a) 1650 L min$^{-1}$; (b) 72 % approx; (c) 8.2 kW.

21.8 < 3.3 m.

21.9 (a) 26.9 m$^2$, 33.04 m$^2$ with fouling, (b) 27.73 m$^2$, 22.6 m$^2$ with fouling.

21.11 63°C, 12.4 K.

21.12 (e) ≈ 15 plates, feed in tray 10; (h) 1.43 m; (i) 1.26 MW; (j) 1.37 MW.

21.13 (c) 15 trays, feed in tray 2.
Figure 8: Equilibrium data for ethanol-water mixtures.