**CHAPTER**

Uses of proteins

Proteins provide the molecular machinery within biological systems. They have also been used to perform functional roles outside the body. For example, the

P enzyme in years, industrial the chapter, focusing industrial Science • Science • • • a Chemistry The data worldwide. secondary hydrogen bonding chain polypeptide the of the interactions, enzymes on pressure including the folding folding an tertiary polypeptide, production Protein enzymes of leads industrial systems you particularly ATAR proteins. processes. applications. between of or are fermentation due bonding as understanding will structures g The Course structure proteins to temperature Data chains dispersion protein have to α-helix learn a within function of scale including extracts The interactions Bank human amide bread on In between been leads about into molecules of information Chapter of structures yeast to the © (PDB) to e a forces proteins of School produce and and increasingly their conditions to protein role produce disulfide how a have β-pleated amide protein endeavour between alcoholic carbonyl Curriculum houses 17, functional of and the which while enzymes (α-helix been (the is chemicals you ionic ethanol and shape bridges, accessed to is used an overall sheets learnt and hydrogen the are achieve functional used beverages. closely carbonyl interactions international three-dimensional and Standards of side biological P both to versus hydrogen that for about proteins three and β-pleated catalyse linked an chains thousands within bonding would functional groups Authority contributed economically Similarly, hydration dimensional the catalysts to is repository of reactions biological bonding, r interactions its sheets) otherwise related (2017); the within between structure. of groups; shapes. in of α-amino years and reproduced to more ethene o to result a shape) dipole–dipole viable involved systems of by peptide require their can adjacent that structural to hydrogen In scientists recent

from acid assist

rate, this be by function, is govern in

permission. and a used high in o

result

in

f

s

**488**

**18.1 Investigating proteins**

Proteins are required for the structure, function and regulation of all the processes that take place within cells. Therefore, investigating the structure and function of proteins is critically important to scientists. A greater knowledge of proteins provides insight into biological processes and offers potential targets for drug discovery. For this reason, scientists share information about protein structure and function in online databases.

ROLE OF PROTEINS IN BIOLOGICAL SYSTEMS In order to survive, your body produces thousands of different proteins, each one with its own unique function. For example, proteins can act as enzymes to catalyse biochemical reactions, as hormones, as structural components in cells, and as part of the immune system, and some proteins assist with the transport of substances across cell membranes. Proteins are critical to almost every chemical process within our bodies.

The function of a protein is closely linked to its structure. As you learnt in Chapter 17, the specific sequence of amino acids in a protein results in a unique three-dimensional shape that enables the protein to function correctly.

The function of a protein depends on its three-dimensional shape.

For example, antibodies are large Y-shaped proteins that your immune system

**FIGURE 18.1.1**

The Y-shape of this protein, an antibody (multi-coloured), enables it to interact with and attack a foreign substance (white) that has entered the body.

uses to recognise foreign materials such as bacteria and viruses (Figure 18.1.1). The shape of the antibody molecules allows them to recognise and bind to these pathogens. All antibodies have a very similar structure and shape, with the exception of the region at the tip of the Y-shape. Your body contains millions of different antibodies, each with a slightly different structure that allows each one to recognise a slightly different pathogen.

CHEMISTRY IN ACTION

**Investigating protein function—knockout mice**

One way in which scientists can investigate protein function is through using genetically engineered knockout mice. Scientists are able to inactivate or ‘knock out’ genes in the mice, preventing their cells from synthesising specific proteins.

For example, leptin is a protein hormone that regulates appetite in mammals by signalling to the brain when the animal is full or satiated. The function of this protein was discovered by examining a strain of mice with a mutation that prevents them from producing leptin. These mice gain weight rapidly throughout their lives and often reach a weight three times that of unaffected mice (Figure 18.1.2).

The leptin knockout mice have been used to investigate the causes of obesity and many of the processes involved in obesity-related diseases such as type 2 diabetes.

AREA OF STUDY 7 | BIOCHEMISTRY

P

a

g

e

**A FIGURE 18.1.2**

leptin knockout mouse next to a normal mouse. The knockout mice grow up to three times larger than normal mice despite eating a low-fat diet. Examining the differences between the two mice enables scientists to determine the function of the leptin protein.

P

r

o

o

f

s

PROTEIN DATA BANK The Protein Data Bank (PDB) is a database that contains the amino acid sequence and three-dimensional shapes of large biological macromolecules such as proteins and nucleic acids. It provides research scientists with a means of rapidly sharing their findings with one another. More than 100 000 structures have been posted on the PDB since 1973 and are freely available to all. The PDB can be accessed online.

Most of the structural data is obtained from X-ray crystallography experiments, as discussed in section 17.4. More recently, nuclear magnetic resonance (NMR) spectroscopy has also been used to determine the three-dimensional structure of proteins. Once uploaded to the PDB, the protein structure can be visualised in a number of different ways (Figure 18.1.3).

The PDB also includes a large amount of additional information such as the known functions of proteins, their location within the cell and any molecules that they are known to interact with. Understanding the structure of a large molecule helps in understanding its function. Such knowledge can be used to gain a better understanding For involved inflammation three-dimensional to interact salicylic (Figure example, 18.1.4)

acid in with the (aspirin) and of it production the cyclooxygenases pain and shape role and affect signalling. of of many a the its of protein enzyme function. other prostaglandins. The are in anti-inflammatory PDB human enzymes and These entry lists health include Prostaglandins that the for and catalyse molecules cyclooxygenase drugs the disease. common P such one are that of as involved are pain shows ibuprofen the known r steps

killer the in

FIGURE binding producing of 18.1.4

salicylic prostaglandins P Aspirin acid is (blue) converted a

that g

e

to salicylic acid and ethanoic (acetic) acid in the body. The deactivates the cyclooxygenase enzyme (yellow) and prevents it from are involved in pain signalling and inflammation.

o

**c**

**FIGURE 18.1.3**

The Protein Data Bank enables scientists to view protein structures in a number of different ways. (a) A space-filling model showing four subunits of the protein haemoglobin. (b) A ball and stick model showing all amino acids in different colours. (c) The backbone of the protein haemoglobin, with amino acids in different colours. Hydrogen bonds are shown as dashed lines. The position of the haem group in the protein is visible, with the orange Fe2+ ion in the centre.

489 CHAPTER 18 | USES OF PROTEINS

**a**

**b**

o

f

s

**490**

AREA OF STUDY 7 | BIOCHEMISTRY

P

a

g

CHEMFILE

Drug discovery Historically, drugs were discovered either by chance or by analysing the compounds present in traditional remedies. For example, in the 1970s, one of the compounds present in the herb sweet wormwood (Artemisia annua) was found to have anti-malarial properties. This herb had been used for over 2000 years in China as a traditional treatment against the malaria-causing parasite Plasmodium, carried by mosquitoes (Figure 18.1.5). The isolated compound, known by the name artemisinin, is now widely used as an anti-malarial drug throughout the world. The 2015 Nobel Prize in Physiology or Medicine was awarded for this discovery. However, the problem with this approach to drug discovery is that it can take a long time and there are often issues with isolating the active compound in sufficient quantities.

s f

**FIGURE Plasmodium, 18.1.5**

e

which Coloured causes scanning malaria.

P electron micrograph r

of o

o

a female mosquito, carrier of the parasite

With greater access to protein structural data, it is now common for scientists to use a more targeted approach to discover potential drugs. Using this approach, scientists begin by identifying the proteins that are involved in particular disease conditions. They can then screen chemical libraries, containing large numbers of small molecules, to identify compounds that bind to the particular protein of interest. These compounds are then tested in cells and animal models to test their biological action. Alternatively, the large number of molecules in chemical libraries can be tested directly in diseased cells in order to identify potential drugs. The development of databases such as the Protein Data Bank assist in this drug discovery process, because they hold information about protein structure and the molecules that are known to interact with them, as well as having sophisticated search functions. Many drugs have been developed in this way in recent years. One such example is a new drug (DDD107498) that also shows promise as an anti-malarial treatment. The development of this drug is extremely timely because there are signs of malaria parasites developing resistance to artemisinin. DDD107498 was discovered by testing a chemical library containing 4371 compounds against the malaria parasite. One compound was found to destroy the parasite at each stage in its life cycle. It was then modified slightly to improve its suitability as a single-use drug, and is currently undergoing further testing.

**18.1 Review**

SUMMARY

• Proteins perform many functional roles within living organisms. The function of every protein is closely linked to its three-dimensional shape.

KEY QUESTIONS

1 When a scientist determines the primary structure of

a new protein, the Protein Data Bank can enable the function of the protein to be predicted. Explain this process. 2 Why is it important that the Protein Data Bank is freely

available? 3 Oxytocin is a hormone that causes contractions during

child birth. It is a polypeptide containing nine amino acids in the sequence: Cys–Tyr–Ile–Gln–Asn–Cys–Pro–Leu–Gly The image of oxytocin in Figure 18.1.6 is a ‘ball and stick’ computer model. The colour code of the atoms is as follows: carbon (grey), oxygen (red), nitrogen (blue), hydrogen (white) and sulfur (yellow). Use this model and the labels to describe the chemical structure of this polypeptide. In your answer, name the type of chemical bond labelled A and explain the significance of the groups labelled B–D.

f

P

a

g

e

**P FIGURE 18.1.6**

r

o

D A ball and stick model o

A

of the hormone oxytocin

• The Protein Data Bank (PDB) is a database of three-dimensional structures of large biological molecules such as proteins.

491 CHAPTER 18 | USES OF PROTEINS

C

s

B

**492**

AREA OF STUDY 7 | BIOCHEMISTRY

P

a

**18.2 Enzymes**

Thousands in rate describe reaction to ROLE As with to a with catalysts inorganic • • • lower complete a increase In are are do you of highly each sufficient not this chemical only not OF learnt activation rates (enzymes) enzyme catalysts other alter used section, organised, of the needed a ENZYMES by chemical task in energy a rate with reactions up as reaction’s Chapter catalysis. that energy, and much or in you act of sufficient sequential changed relatively to reaction normally reactions enzymes: in will as in react a 1, thereby Enzymes equilibrium similar a cells for learn factor energy at (Figure small by are fashion. takes are a the way reaction providing about increasing of involved a are r end and amounts particular 300 1010. and position. 18.2.1). The highly of the several years. This share to the in biological correct an o the occur, sustaining efficient type reaction is Inorganic alternative the models the proportion following of orientation. the equivalent protein catalysts catalysts life. reactants o

that catalysts reaction These of characteristics. called biochemists that of reactant Catalysts that taking need reactions and pathway accelerate enzymes. f can biological to 1 particles increase are second collide use s occur

Both with able the

to

e y

E

P

uncatalysed pathway

activation energy

reactants

with an enzyme

products

Reaction progress

activation energy without an enzyme g

g r e n

**FIGURE 18.2.1**

enzyme-catalysed pathway

Both inorganic catalysts and enzymes lower the activation energy of a reaction by providing an alternative pathway by which the reaction can occur.

However, there is a significant difference between the behaviour of enzymes and the behaviour of inorganic catalysts. An inorganic catalyst, such as metallic platinum, can catalyse many different reactions often involving a variety of reactants. Enzymes can only catalyse one specific reaction or a reaction that involves a particular chemical bond or functional group. This characteristic is often referred to as the ‘specificity of enzymes’. For example, despite being very similar, the two sugars lactose and sucrose are broken down by two different enzymes in our bodies. The models of enzyme action developed by scientists must account for this specificity. Enzymes are also more sensitive than inorganic catalysts to changes in reaction conditions.

Living organisms are very complex systems. With so many reactions required to sustain each living organism, thousands of different enzymes are needed. It is important that chemists understand the role of enzymes and their action when they develop new medications. It is also important to investigate the potential of these complex catalysts for use in greener industrial processes.

LOCK-AND-KEY MODEL OF ENZYME ACTION The catalytic activity of an enzyme is highly specific and depends on its overall three-dimensional structure. Because enzymes are proteins, their overall three- dimensional structure is dictated by their tertiary structure. The specific part of the enzyme molecule with which a reactant can interact is known as its active site. The active site is usually a uniquely shaped flexible hollow or cavity within the protein where the reaction occurs. The reactant molecule that binds with the active site is referred to as the substrate.

One early model for the catalytic action of an enzyme is the ‘lock-and-key’ model. This model provides an explanation for the critical importance of the three-dimensional shape of the enzyme. In the lock-and-key model, the substrate molecule fits into the enzyme like a key in a lock, forming an enzyme–substrate complex, allowing the enzyme to break the bonds in the substrate. Figure 18.2.2 shows the steps involved in an enzyme-catalysed reaction according to the lock- and-key model. The enzyme is specific for a particular substrate, so binding of a different molecule will not result in a reaction.

enzyme

substrate

The substrate enters the active site in the enzyme.

The catalytic action of enzymes is specific for a single reaction or type of reaction.

P FIGURE Only necessary Example—hydrolysis The proteases Chapter The digestion reactant 18.2.2 shape 17, intermolecular can amino Steps molecules of of be in the proteins understood acids the a

substrate action are interactions that into Bonds to of joined form an have using of molecule smaller enzyme, g are an together proteins a formed enzyme–substrate with suitable the according polypeptide must lock the Bonds the with by e substrate. active ‘key’ peptide match and the to break the enzyme shape key site molecules complex. lock-and-key in the bonds (‘lock’) model. shape can to enter by form P of model As of the enzymes the you and a o o

f

s r The regenerated.

enzyme is

New products are released.

active site. form the enzyme.

called learnt in protein in a condensation reaction. This reaction can be reversed and the peptide bonds broken by the addition of water in a hydrolysis reaction. However, due to the strength of the peptide bonds, this hydrolysis reaction does not occur very rapidly without the presence of an enzyme.

Trypsin is an enzyme that breaks a protein chain next to a lysine or arginine amino acid (on the C-terminal side). It binds to the protein chain at that point and weakens that particular peptide bond, reducing the amount of energy required for it to react with a water molecule (Figure 18.2.3).

493 CHAPTER 18 | USES OF PROTEINS

**494**

AREA OF STUDY 7 | BIOCHEMISTRY

Two The enzyme trypsin binds to

The peptide bond is weakened,

shorter polypeptides are the protein chain on the

enabling it to react with a water

formed and the enzyme is C-terminal side of a lysine residue,

molecule (hydrolysis).

regenerated and able to catalyse forming an enzyme–substrate complex.

trypsin enzyme

Val Lys

Gly Glu

FIGURE 18.2.3 or lysine amino peptide bond, The types the same as H 2

O Trypsin is an enzyme that catalyses acid. Its specific shape enables it to meaning that less energy is required of intermolecular bonds formed those that determine the tertiary another reaction. the for bind structure it hydrolysis to between to o

be the broken protein of of an a proteins. Val by protein Gly chain enzyme o reaction at Glu

chain Lys that The and with next point intermolecular a a f

s

P

The active substrate a site enzyme

substrate

of the enters enzyme.

g

the

forces and dispersion (NH the INDUCED Since that modified of induced better the As active can enzymes 2 ) the e fit are lock-and-key Figure on fit include for lock-and-key markedly site their determined forces. model substrate of FIT have 18.2.4 respective the hydrogen In for MODEL by flexible the trypsin model enzymes shows, the by molecules. model example the side P

binding structures. and bonds, enzyme, side for the chains. can OF the above, enzyme After be chains flexible of ENZYME ionic development forming applied a These r substrate. The both the of action interactions, active reaction, shape the amine lysine to the a amino ACTION

was This larger enzyme–substrate site of and groups of proposed, the the an can discovery arginine dipole–dipole acids number enzyme’s products ‘induced form mould in chemists contain the of hydrogen led chemical itself are active peptide to complex. fit’ attractions a released amine water to have modification to substrate model. and site bonds an achieve reactions. sequence weaken arginine molecule.

realised groups

can from with

The and are

be a

a

the active site and the active site returns to its initial shape.

enzyme–substrate complex

products

enzyme

The active site changes to accommodate

The products leave the the substrate and forms weak

enzyme. The active site intermolecular interactions with it.

returns to its original shape.

**FIGURE 18.2.4**

Steps in the action of an enzyme, according to the induced fit model

CHEMISTRY IN ACTION

**From lock-and-key to induced fit**

The development of the lock-and-key and induced fit models of enzymes is a good example of how scientific ideas change over time as new evidence becomes available.

Emil Herman Fischer (Figure 18.2.5) was a remarkable chemist. He was awarded the Nobel Prize in Chemistry in 1902 for his work on identifying the 16 isomers of the aldo-hexoses, the family of sugars that glucose belongs to. His work on biomolecules and the precise stereochemistry of their different forms led him to propose the lock-and- key model of enzyme–substrate interactions.

This model formed the main explanation for the interactions in enzyme active sites and receptor sites until the American chemist Daniel Koshland (Figure 18.2.6) proposed the induced fit model of enzyme interactions. Koshland described his model as more like a hand in glove, where the enzyme is flexible, not rigid, and can change shape slightly on binding of the substrate. Figure 18.2.7 shows a simplified version of Fischer’s lock-and-key model and Koshland’s induced fit model. Koshland was able to build on the hypothesis put forward by Fischer to develop what is now considered to be a more accurate representation of enzyme interactions.

s

P

a

g

e

**FIGURE 18.2.5**

Emil Hermann Fischer (1852–1919) proposed the lock-and-key model of enzyme–substrate interactions.

a P substrate Lock-and-key r model

o

o

f

enzyme

b Induced fit model

substrate enzyme

The two models of enzyme interaction proposed by (a) Fischer and (b) Koshland. The development of these models is an example of how scientific ideas change over time, being refined and adapted as new insights and discoveries are made.

**Daniel FIGURE 18.2.6**

Koshland (1920–2007) further developed Fischer’s lock-and-key model by proposing the revised induced fit model for enzyme interactions.

**FIGURE 18.2.7**

495 CHAPTER 18 | USES OF PROTEINS

**EXTENSION Coenzymes**

Many enzymes cannot function without the presence of a coenzyme. A coenzyme is a non-protein organic compound that interacts with an enzyme and changes its functionality. Coenzymes are small compared to protein molecules. Similarly, some enzymes require inorganic atoms or molecules such as metal ions to function correctly. These are called cofactors rather than coenzymes.

Many coenzymes are derived from vitamins. Vitamins are essential micronutrients that are required in small amounts as part of a balanced diet. Figure 18.2.8 shows the coenzyme folic acid bound into dihydrofolate reductase, an enzyme found in Escherichia coli bacteria in the human gut.

**496**

**Folic FIGURE 18.2.8**

acid acts as a coenzyme, binding to the dihydrofolate reductase enzyme.

AREA OF STUDY 7 | BIOCHEMISTRY

s

P

a

g

e

coenzyme

and specific of active substrate. You bound, interact can FIGURE The reaction result or atoms will form Coenzymes Before Unlike the group newly (inactive) be occur. can enzyme their P by of enzyme site, 18.2.9 in other to the groups fully see the the formed an binding of one be role allowing newly atoms. catalysed. enzyme, loss this reaction Coenzymes reactions with biochemical is interact and complex of often in of r to formed the atoms. If hence Figure the the the a it as substrate to with in coenzyme can work accepts group. enzyme coenzyme, it act which They enzyme–coenzyme o the accepts 18.2.9. bind reaction enzyme–coenzyme the by as binding binding to enzyme change carriers a and it to the particular Once may is or better the it restored the substrate, to helps donates enzyme properties o

(active) be enzyme the particular of the during catalytic interact changed electrons surface catalyse, coenzyme group complex allowing to complex an catalysis substrate

enzymes. its is process of electron with inactive.

of

original f shape as the or

the

there a is the

can

**18.2 Review**

SUMMARY

• Enzymes are proteins that catalyse biochemical reactions by providing an alternative reaction pathway with a lower activation energy.

• Enzymes are not changed as a result of the process of catalysis.

• Enzymes are highly specific; enzymes may only catalyse one specific reaction or a reaction with a particular chemical bond or functional group.

• There are thousands of enzymes in the human body to catalyse different biochemical reactions.

KEY QUESTIONS

1 The enzyme glucokinase catalyses the first step in the

oxidation of sugar in human liver cells, in a process called glycolysis. Which one of these statements about this process is correct? A Many other enzymes can also catalyse this reaction. B Glucokinase increases the activation energy of this

reaction. C Glucokinase is able to catalyse many other

reactions. D Glucokinase is a protein. 2 a The steps in the action of an enzyme involve,

in particular, an active site and a substrate. Use a diagram to describe in detail the action of an enzyme (according to the lock-and-key model of enzyme action).

• Enzyme molecules have uniquely shaped active sites that interact with specific reactant molecules (substrates), weakening or breaking the bonds in the reactant molecules.

• The earliest model to account for enzyme action was the lock-and-key model.

• A newer model for enzyme action is the induced fit model. This model accounts for the flexibility of many enzymes’ active sites.

P

f

s

b P 3 Identify induced a The bind forces.

This wide forces model r to range whether fit an model active of of explains attraction o each reactions. of site enzyme of why can the that enzymes vary. statements o

catalysis enable Identify do a is substrate to four such

about the

true or false. not catalyse a

b The enzyme molecule has an active site.

a

g

e

c The active site does not change shape as the

substrate enters. d An enzyme–substrate complex forms.

497 CHAPTER 18 | USES OF PROTEINS

**498**

AREA OF STUDY 7 | BIOCHEMISTRY

18.3 Enzymes—dependence on pH and As inorganic and position between such you inorganic as temperature learnt the or temperature catalysts. LOW-RES being two in catalysts types the changed By and of previous lowering catalysts pH P increase themselves (Figure a section, reaction’s is reaction the 18.3.1).

r sensitivity by enzymes the activation rate o process. without of share enzymes energy One many altering o barrier, to significant characteristics reaction the both f

equilibrium

conditions difference enzymes s with

P

**FIGURE 18.3.1**

A ribbon model of the enzyme invertase (also called sucrase), which catalyses the hydrolysis of sucrose. It operates under mild conditions but is very sensitive to changes in temperature DEPENDENCE g Enzymes Figure disaccharide, catalyses the conditions. and optimum amylase Pepsin stomach. 9. e 18.3.2 the operate and is active Activity maltose, breakdown pH.

shows. effectively only ON of in Salivary at pH these the of pH proteins relatively only values enzymes amylase The pH at which the enzyme pH. The optimum pH of is 7.2.

within a narrow pH range, as the graph in catalyses the breakdown of starch to a neutral environment of the mouth. Pepsin to amino acids in the acidic conditions of drops off drastically outside their normal a

below 3 and amylase is active between pH 5 activity is greatest is known as the enzyme’s pepsin is 1.5, while the optimum pH of salivary

2 4 6 8 10

pH

salivary

y

pepsin

amylase

E

**FIGURE 18.3.2**

t i v i t c a e m y z n

Enzymes are only effective in a narrow pH range. Pepsin is a protein-digesting enzyme secreted into the stomach. Salivary amylase is the enzyme in human saliva. These enzymes are most effective at very different pH values.

Acid–base properties of enzymes You will recall that α-amino acids (those found in living systems) can form zwitterions, with the general structure shown in Figure 18.3.3. A zwitterion has both a positive and negative charge within the molecule.

Amino acids have different charges depending on the pH of the surrounding environment.

• At an −NH

high pH, 2

group.

the −NH

3

+ group can act as an acid, donating a proton to become

• At low pH, the −COO− group can act as a base, accepting a proton to become a −COOH group. As the following equation shows, the charge on the predominant form of the amino acid present in a solution depends on the pH of the solution.

Low pH Intermediate pH High pH +H

3

N−CH(R)−COOH  +H

3

N−CH(R)−COO−  H

2

N−CH(R)−COO−

cation uncharged zwitterion anion on the protein’s structure some between or acid charge true group unable FIGURE 10. pH, Just Intermolecular For pH. with on side The 18.3.4 in to required example, some as the side overall P a the of participate the chains. change change side an chains of other ionisation enzyme the three-dimensional chain for the from attractions from side side the of ionic a in is the the ionic chains neutral may not neutral of chain interactions amino the ionic likely NH be interaction between would amino of C O pH pH disrupted interaction. g acid the to structure. CH

CH

CH

COO\_ to to ionise (CH CH amino NH not and units an the 2

2 shown the to acidic basic act carboxyl O as side and along occur. acids Some NH e changes in as will pH pH chains Figure a the may The bonds base, 10. therefore groups of protein 3 in also of At opposite 18.3.4 would remaining that pH a the in be polypeptide chain, not alter determine higher amino affected might mean situation P carry the but uncharged pH, acids the occur ionisation by the not the maintain carboxylic the changing would depends negative at at tertiary r

amino pH pH and be of

7 3 a

C + 3

2

)

4

An ionic interaction linking two parts of a polypeptide chain. Ionic interactions between side chains and another R group of contains amino acids −COO−.

in proteins are dependent on pH. One R group contains −NH

3

+

In this way, changes in pH can have a large impact on the stability of enzyme structure. As the tertiary structure of the enzyme is disrupted, the enzyme’s active site changes shape and enzyme activity decreases. Extremely high or low pH values generally cause complete loss of activity for most enzymes. Drastic changes to pH can result in a permanent change to the shape of an enzyme through a process called denaturation (see below).

H

R

N+

**FIGURE 18.3.3**

O

zwitterion acids the R o have group.

of different H an o The amino C H general side acid. chains, H C structure f Different O– represented s of amino a

by

Changes in pH alter the charge of side chains containing amino and carboxyl functional groups.

499 CHAPTER 18 | USES OF PROTEINS

DEPENDENCE ON TEMPERATURE Enzyme activity is also affected by temperature. The graph in Figure 18.3.5 shows the effect of temperature on the rate of a reaction involved in carbohydrate metabolism. You can see from the steep sides of the curve that the rate of reaction drops off quickly either side of a narrow temperature range (30–40°C).

The temperature at which the enzyme activity is greatest is known as the enzyme’s optimum temperature. Enzymes that operate inside human cells have an optimum temperature of about 37°C.

At temperatures above and below the optimum temperature, enzyme function is impaired. This is one of the reasons why conditions such as hypothermia and fever (when you have an abnormally low or high temperature) are life-threatening.

optimum Rate of reaction

temperature increases as temperature increases.

R

20 40

Temperature (°C)

Rate of reaction decreases after this temperature as

e t a r n o i

the shape of the enzyme is changed (denatured).

FIGURE are optimum effect • • Denaturation Once polypeptide the structure catalytic often only An As kinetic increased forces shape reaction As substrate less fit so the shape amino irreversible model t c a e

on that the 18.3.5 the the effective increase temperature energetic temperature. activity. an to of causes responsible temperature acid temperature temperature the energy so take enzyme. the chains Effect discussed P molecules movement in the shape units, above enzyme a place, a collisions It (Figure of relatively reaction of change of is temperature is and of said the too the for or in decreases and have increases the becomes throughout means a decrease section narrow 18.3.7). new enzyme the low, to molecules in between rate therefore active be lower the tertiary on bonds the decreases the range denatured. rate 18.2, below shape breaks above enzyme too below site active kinetic the the of of g are it disrupts structure. enzymes reaction temperatures. high, cannot can the molecules. enzyme of formed. the some the rapidly. site is the energies, optimum This change not optimum optimum the for can function active the of need This an breaks flexible change A e increased the no Additionally, Reaction enzyme-catalysed structure change upon resulting a longer temperature, bonds site change certain temperature temperature, some properly. to enough and substrate rate in the between kinetic effectively of of in the is the in amount protein highest under the three-dimensional the for less enzyme’s reaction. enzyme the binding. intermolecular P has energy this side the enzyme. frequent 60 at enzyme of the catalyse structure a the change increased flexibility Enzymes

chains different induced

loses tertiary of When The

and and the

the r

its of

of

is

**500**

AREA OF STUDY 7 | BIOCHEMISTRY

CHEMFILE

Hyperthermophiles A hyperthermophile is a type of bacteria that thrives in extremely hot environments, at temperatures of 60°C and higher. Many hyperthermophiles can also withstand other environmental extremes, such as high acidity or radiation. Hyperthermophiles were first discovered in 1965, in the hot springs in Yellowstone National Park (Figure 18.3.6). Since then, more than 70 different species of bacteria capable of withstanding these high temperatures have been discovered.

**An FIGURE 18.3.6**

aerial photograph of the large geothermal spring in the Yellowstone National Park, Wyoming, USA. The water’s temperature can reach more than 70°C. The bright colours in the pool are due to minerals that are deposited from the evaporation of water. The colour differences within the pool are due to different species of hyperthermophilic bacteria.

In order for hyperthermophiles to survive under these extreme conditions, their proteins must be able to maintain their three-dimensional shape at high temperatures rather than being denatured. Indeed, many of the proteins in these organisms have higher levels of hydrogen bonding and ionic interactions stabilising their three- dimensional shape than similar proteins in normal bacterial cells. These hyperthermostable proteins are of interest commercially, because they may be able to catalyse industrial processes at higher temperatures, increasing the rate of reaction.

o

o

f

s

heat pH change

**FIGURE 18.3.7**

The specific three-dimensional shape of enzymes is lost when denaturation occurs.

Enzymes can also be denatured by a change in pH. As discussed earlier, when the pH is above or below the enzyme’s optimum pH, the enzyme’s overall three- dimensional shape can also be disrupted. Substantial changes in pH can change an enzyme’s structure permanently. Comparing denaturation with hydrolysis Even though increased temperature and variations in pH can permanently change the tertiary structure of an enzyme, the primary structure of the protein, the covalently bonded sequence of amino acids, remains intact.

You will recall from Chapter 17 that the breakdown of proteins occurs through a process called hydrolysis. The hydrolysis of a protein molecule involves breaking the covalent peptide bonds. This is shown in Figure 18.3.8.

N

N

H

P

r

H

NH

R

O

H R

R

R

R

C C N C C N C C N

H

**Polypeptide e**

found enzyme-catalysed the stomach in food

R

hydrolysis in

**Dipeptides**

enzyme-catalysed hydrolysis in the intestine

R

Amino acids absorbed into the bloodstream from the small intestine

**FIGURE 18.3.8**

H

H

R o

o

f

C

C

H O

H O

H

O

H

C C g N C

H

2

O

N R

H

R

C C N C C N C

C N

H

R

H

H

H P R

a H

O

O

C OH H

H O

H

2

O

CC N

C OH H O

H

H

H O

H

H O

H

OH H OH H OH H

C OH H

Digestion of protein in food. The blue dashed lines indicate where peptide links are broken during hydrolysis of the polypeptide.

501 CHAPTER 18 | USES OF PROTEINS

C

O

C

O

s

**502**

AREA OF STUDY 7 | BIOCHEMISTRY

The products of hydrolysis are shorter polypeptide chains or individual amino acids. Note that water is a reactant in this process. One water molecule is consumed for each peptide bond broken.

In the laboratory, extreme conditions are required to hydrolyse a protein. Typically, the protein sample is heated in 6 mol L–1 hydrochloric acid for 24–72 hours.

P

CHEMFILE

Denaturing egg white When egg white is heated, the clear everyday example of the denaturing albumin. The denatured protein has from the original protein. The protein in egg white can be denatured such as the cooking of an egg; others If you add salts such as ammonium proteins is drawn away and forms the protective layer of water stabilising and precipitates out of solution. If protein strands, the protein refolds denaturation of the protein is reversible. When denaturation disrupted, the process as when you boil or acids such as nitric side chains that were aggregate together the egg e white.

occurs acid. by fry hidden forming is an When irreversible. P egg because within (Figure dispersion an ion–dipole you egg and the the sulfate very liquid of This are 18.3.9), add white a its r hydrogen dissolves folded protein. different reversible. forces, can tertiary turns in enough to is bonds a egg happen albumin or heated, variety into o Egg back changing when bonds structure, chemical white, water with an white of when into the molecules protein opaque in the the ways. to the hydrophobic the solution. contains and hydrate the the water ions o protein texture Some is solid. physical protein protein mixed of are that the the In a are This exposed molecules protein and this surrounds denatures ions salt. is amino with properties irreversible, heated, is colour instance, f an

and Without

strong

called

and acid

the

are

of the

such s

the

a

g

When an egg white is heated, the hydrogen bonds maintaining the tertiary structure are disrupted and the protein albumin irreversibly unfolds (denatures).

**FIGURE 18.3.9**

**18.3 Review**

SUMMARY

• Enzymes operate over an extremely mild and narrow set of conditions when compared with inorganic catalysts.

• Enzymes are very sensitive to changes in pH and temperature.

• An enzyme is said to be denatured if its tertiary structure is disrupted; for example, by high temperatures or pH changes.

• When an enzyme is denatured, the shape of its active site is changed and its catalytic activity is lost.

• During the hydrolysis of a protein, the primary structure is broken down as peptide links are broken. This occurs during digestion of food.

• The temperature at which the enzyme activity is greatest is the enzyme’s optimum temperature.

• High temperature denatures an enzyme because the increased kinetic energy of the polypeptide chain disrupts the enzyme’s tertiary and quaternary structure.

KEY QUESTIONS

1 The structure of proteins can be disrupted by

denaturation or hydrolysis. Describe each process and the bonds that are disrupted for each. 2 Enzyme activity is influenced by changes in pH.

Changing pH can alter the charge on some functional groups because they act as weak acids or bases. The side chains of a polypeptide chain are important in maintaining the enzyme’s tertiary structure. Complete the following table for each of the side chains listed.

**Structure of side chain**

• At lower temperatures, fewer, less energetic collisions occur per unit time between the enzyme and substrate so the rate of reactions is slower.

• The pH at which the enzyme activity is greatest is the enzyme’s optimum pH.

• The charges on some side chains in the polypeptide chain of an enzyme depend on the pH of the solution.

• Changes to the charges on the side chains that occur as pH changes can result in a new tertiary structure for an enzyme.

• The optimum pH and temperature of an enzyme usually match the conditions in which the enzyme operates.

P

**a Is side acidic basic neither? the**

**chain**

**or**

**or**

**g Is charged, charged In the a solution of pH e side chain positively**

**negatively or neutral?**

**2**

P

r

o

o

f

s

**In a solution of pH 11**

−CH

2

COOH

−CH

2

CH(CH

3

)

2

−CH

2

OH

−(CH

2

)

4

NH

2

3 The enzyme carbonic anhydrase catalyses the

decomposition of carbonic acid molecules to carbon dioxide and water in the lungs. When heated above 60°C, the enzyme becomes denatured. a What is meant by ‘denatured’? b Describe what usually occurs to the structure of an

enzyme when the enzyme is denatured. c Does the primary structure of the carbonic

anhydrase enzyme change during the process? d Why is the function of the enzyme closely related to

its tertiary structure? 4 One of the key differences between enzymes and

inorganic catalysts is how they are affected by their environment. a How can a change in pH effect enzyme activity? b What effect does decreasing the temperature have

on enzyme activity?

503 CHAPTER 18 | USES OF PROTEINS

**504**

**a**

**b**

**c**

**FIGURE 18.4.1**

Enzymes are used in a number of different commercial applications. (a) Malted barley the break (b) produce rise. biological enzymes that The brewing may (c) down is enzymes A carbon mixed that have scanning washing the of break stained beer. with P starch dioxide, in powder. yeast electron down water Enzymes the into causing consume fats, clothing.

and simple The micrograph in heated oils capsules the bread sugars. sugars or malt

proteins during

to of contain and

a

AREA OF STUDY 7 | BIOCHEMISTRY

a

**18.4 Enzymes in industry**

Enzymes have been used for thousands of years to produce food such as cheese, wine and bread. More recently, they have been increasingly used in industrial processes and in a range of commercial applications (Figure 18.4.1). For example, washing powders often contain enzymes such as proteases, lipases and amylases, which break down proteins, fats and starches respectively. These enzymes are able to break down many of the molecules found in common stains and have the advantage of being biodegradable.

Enzymes are also being used increasingly in industrial processes to catalyse reactions. For example, several companies are using the enzyme lipase to catalyse the production of biodiesel as an alternative to the traditional base-catalysed process. This process is discussed in greater detail in Chapter 16. ADVANTAGES AND DISADVANTAGES There are advantages and disadvantages to using enzymes as catalysts in industrial processes. These are summarised in Table 18.4.1.

**TABLE 18.4.1**

o

f

s

Advantages ∙ ∙ Advantages and disadvantages of r

**using Disadvantages enzymes o**

as industrial catalysts

∙ ∙ Enzymes catalyse reaction. In biological This temperatures required. Enzymes reaction, period Enzymes general, saves of one so are are are time.

temperatures energy enzymes they particular biodegradable specific not and can consumed and pressures are be so cost reaction and effective used that P as and in pH are they for high the or levels.

not

therefore

at a only type long of

cause less environmental pollution.

∙ Enzymes are very sensitive to changes in temperature and pH. Reaction conditions must therefore be tightly controlled. ∙ Certain chemicals can also change the

structure of enzymes and cause them to lose their function. ∙ Enzymes can be expensive to produce. ∙ Enzyme-catalysed reactions generally g they pressures reducing addresses unique reaction in are that The The very function e side-reactions shape, key major or sensitive the some and type advantage energy optimally temperatures enzymes disadvantage of of to the reaction. changes costs do ideas of under are not using and of This also to take of to green biological be safety pH using enzymes can extremely place.

used chemistry and increase considerations enzymes to temperature. conditions. as maintain specific, take be the industrial the discussed difficult reaction as place efficiency industrial This a catalysing involved As in fast to catalysts mixture.

in aqueous separate removes discussed rate Chapter of the catalysts in of only solutions. is the industrial the the reaction, that, 12. in products one need process. section Due is in particular It that for general, can

thereby

process to from

18.3, This their high

they

changes in temperature and pH affect the interactions between amino acids on the surface of the enzyme. This can lead to a change in the enzyme’s three-dimensional shape and a loss of enzyme function. The presence of other molecules in the reaction mixture may also adversely affect the shape of the active site and hence the function of the enzyme. PRODUCTION OF ETHANOL The production of ethanol is a large global industry. In 2015, over 100 billion litres of ethanol were produced worldwide. Ethanol has many uses, including industrial solvents, antiseptics, precursors for other chemical reactions, and in alcoholic beverages. However, its major use is as a fuel source, particularly in Brazil and the United States. It can be produced by two different processes: by fermentation, which is an enzymatic process using corn, sugar cane or other grains as a starting material; or by the hydrolysis of ethene, which uses crude oil as a starting material.

Fermentation For thousands of years, humans have used enzymes to convert starches from grains and sugars to ethanol in the process known as fermentation. In this process, amylase enzymes are used to catalyse the breakdown of the polysaccharide starch to glucose. Then the fermentation process uses other enzymes from yeast organisms to convert small sugar molecules, such as glucose and fructose, into ethanol and carbon dioxide, according to the following equation:

C

6

H

12

O

6

(aq) → 2CH

3

CH

2

OH(aq) + 2CO

2

(g) In wine-making, yeasts are found naturally present on the surface of grapes and in wine cellars and do not need to be added to the fermentation mixture. However, in beer brewing, yeast is added to the barley mixture to catalyse the fermentation process. Margaret River, in the south of Western Australia, is a region known for its winemaking (Figure 18.4.3). Many boutique breweries have also opened recently in the region.

r

FIGURE of used which for to burning. ethanol produce The The fermentation. as 18.4.3 is the fermentation grains found for raw ethanol Palmer other and in materials Aside biomass Wines reduces other purposes, process is from for matter in such the the fermentation, is such producing Margaret need also as g

used as woody used to as for River dispose a a commercially industrial fuel. plants, another Region, valuable e

While of Western can waste polysaccharide chemical, fermentation starches also to materials Australia.

produce serve and the P as are sugars use in called purified a landfill raw prepared of forms are often

grinding of present undergo cellulase After in fermentation.

and being the and crushing, raw amylase cooled, materials a

adding the enzymes. into processed water simple This and process raw then sugars materials heating breaks called to monosaccharides down undergo 85–105°C the fermentation polysaccharides in the cellulose, material cellulose or by fermentation which mixture the resulting point then P

the undergoes liquid tanks. yeast The contains cells repeated process and about their stops distillations enzymes 96% when ethanol can to the no purify and ethanol longer 4% the function. content water. ethanol. This The is When 15–18%, fermented process presence that cooled, can by

in at

is depicted in Figure 18.4.4.

o

505 CHAPTER 18 | USES OF PROTEINS

CHEMFILE

Producing enzymes for industry Industrial applications generally require large quantities of enzymes that are only produced naturally in tiny quantities. Scientists use microorganisms such as yeast and bacterial cells to produce the quantities of enzymes required (Figure 18.4.2). The microorganisms are genetically modified so that the enzyme of interest is expressed (synthesised) at much higher concentrations than usual. After sufficient enzyme has been produced, the cells are removed from the reaction mixture and the enzyme is purified.

**A FIGURE 18.4.2**

microbe fermentation unit for the production of drugs, hormones and enzymes for medical and industrial use. It is used to ferment microbes that have been genetically engineered to produce a drug or enzyme.

Enzymes that are to be used for industrial applications require very little processing and purification. However, if they are to be used for medical or therapeutic applications, a far more rigorous purification process is needed. Enzymes such as lipase, used to catalyse the production of biodiesel, is manufactured by industrial means. Similarly, the protein insulin, used to treat diabetes, is also produced for medicinal use by a microbial system.

o

f

s

**506**

processed grain mixture

fermentation tank

**FIGURE 18.4.4**

The industrial process for manufacturing ethanol. The products of the fermentation process are separated by distillation.

Once the fermentation and distillation processes are complete, the 96% ethanol mixture is then dehydrated, leaving ethanol that is 99.7% pure. If the ethanol is not being used for alcoholic beverages, the final ethanol is then poisoned by adding up to 5–10% of another chemical such as methanol, to make it unsuitable for consumption as drinking alcohol.

CHEMISTRY IN ACTION

**Brewing beer**

Beer is one of the world’s oldest alcoholic drinks, dating back to over 5000 years ago. Indeed, during the building of the Great Pyramids in Giza, Egypt, there are reports that workers were given a daily ration of 4–5 litres of beer to help them perform their work.

There are four major ingredients in beer: barley, hops, water and yeast, although other additives are often used. The first step in the process of brewing beer involves extracting the sugars from the barley. To do this, the barley is heated and dried a number of times (a process called malting), before being steeped in hot water for about an hour (a process called mashing). Hops, the small fruit of a vine plant, are then added to provide bitterness to the mixture, balancing the sugar content. Other spices are often added at this stage. After the mixture is filtered, yeast is then added and the fermentation process begins (Figure 18.4.5). Enzymes in the yeast convert the sugar to ethanol and carbon dioxide. This process may take place over a period of up to several weeks, depending on the type of beer being made. Some beer is artificially carbonated to produce its fizz, whereas other beer is left to age for a period of time, allowing the carbon dioxide from the fermentation process to build up.

AREA OF STUDY 7 | BIOCHEMISTRY

P

a

g

96% ethanol solution

carbonated drinks

distillation process (separating ethanol and water)

(g) + solid waste

CO

2

(g)

solid waste processed for use as stock feed

e

CO

2

**FIGURE 18.4.5**

P

Copper kettles at Becks Brewery in Bremen, Germany

r

o

o

f

s

Industrial production of ethanol by hydration of ethene While the fermentation process is the most common way of producing ethanol industrially, it is not the only method. Around 7% of the total ethanol produced is produced by the hydration reaction between ethene and water.

Ethene is obtained from the catalytic cracking of larger hydrocarbon molecules in crude oil. The ethene is then reacted with steam to produce ethanol according to the following addition reaction:

H

H C C +

H H

H

H

H

OH The conditions for this reaction must be carefully selected to ensure a compromise is reached between the reaction rate and yield. The forward reaction in this process is exothermic and there are more reactant gas particles than product gaseous particles. A moderate temperature of 270–300°C is used together with a catalyst of phosphoric acid coated on a porous solid.

A relatively high pressure of 6000–7000 kPa is used, as the cost associated with maintaining the reactants at higher pressures is outweighed by the increases to reaction rate and yield.

Each pass of the reaction mixture through the reactor only yields a conversion of about 5% of the ethene to ethanol. The reaction mixture is cooled to liquefy the ethanol, but this also liquefies unreacted water, meaning that a solution of ethanol and water is collected. Unreacted ethene is heated and cycled back into the reactor as depicted below in Figure 18.4.6.

phosphoric acid catalyst coated on porous silicon dioxide

water

furnace

furnace

H

2

O H C C H

H = –45 kJ mol–1

reactor

P

r

o

water in (coolant)

**FIGURE 18.4.6**

gaseous

a

g

e

unreacted ethene

mixture

liquefied water and ethanol solution

water out (coolant)

**ethene Comparison The two P**

methods Steps in of the for industrial industrial production process methods of for ethanol, the hydration by for of fermentation ethene ethanol to ethanol

production of glucose and hydration of ethene, have advantages and disadvantages. Table 18.4.2 summarises the major differences between the processes.

The use of enzymes as catalysts in fermentation, as opposed to inorganic phosphoric acid, means that fermentation is run at much lower temperatures and pressures. The reduced temperatures and pressures for fermentation result in a significant saving in costs, compared to the hydration of ethene.

507 CHAPTER 18 | USES OF PROTEINS

o

f

s

**508**

Comparison of fermentation process and hydrolysis of ethene

**Factor Fermentation process Hydrolysis of ethene**

has process, Temperature Pressure Catalysts Purification required

Raw used Renewable Cost The no materials by-products, advantage many different of producing so Low Normal Amylase produce yeast Many Monosaccharides and Yes—plant Low the organic other temperatures enzymes distillations products pressures simple and plant matter ethanol molecules cellulase for sugars material are from required is fermentation from renewable only to and

grains are the ethanol produced hydration Moderate High Phosphoric Limited Ethene No—crude High and or pressures of water. from present o distillations ethene temperatures oil acid crude is In in not is the that small oil

required

renewable f

fermentation the quantities reaction s

due to the many different enzymes in yeast and the different compounds present in the starting mixture. Also, in some locations there are limited crops to source raw materials for fermentation, whereas crude oil may be readily available.

Fermentation is usually the preferred method for production due to the renewable nature of the process and lower cost of the ethanol produced.

**18.4 Review**

SUMMARY

• The general advantages using enzymes versus chemical industry - enzymes are effective whereas inorganic function well at the cost of maintaining KEY QUESTIONS

1 What is the percentage yield if 100 g of ethene is

converted into 150 g of ethanol using the hydrolysis of ethene reaction? 2 A moderate temperature of around 300°C is used in

a reactor when producing ethanol using the hydration process. What is the reason for using a moderate temperature?

are: low catalysts inorganic temperatures. and at high low disadvantages usually temperatures, temperatures catalysts This do e not in reduces of

the

P

r

o

- enzymes catalyse specific reactions, whereas inorganic catalysts often catalyse multiple reactions, generating unwanted by-products and reducing yields - enzymes have to be cultivated and collected,

which can be a lengthy and expensive process.

• The main differences between the fermentation

P

a

g

process and the hydration of ethene for producing ethanol are: - fermentation uses enzymes as the catalyst,

whereas hydration of ethene uses phosphoric acid - fermentation uses lower temperatures and

pressures, but requires more distillation cycles - the raw materials used for fermentation are

renewable, usually a local grain, whereas the hydration of ethene uses crude oil, which is a non-renewable source of chemicals.

3 There is a significant cost involved in maintaining the

high pressures used in the hydration process. Use your knowledge of chemical equilibrium to explain why high pressures are employed.

AREA OF STUDY 7 | BIOCHEMISTRY

**TABLE 18.4.2**

**Chapter review**

KEY TERMS

active site denaturation enzyme enzyme activity

optimum pH optimum temperature Protein Data Bank substrate

Investigating proteins 1 Indicate whether the following statements are true or

false. If false, explain why. a Proteins with similar tertiary structures are likely to

have a similar function. b The Protein Data Bank enables protein structures to

be visualised in different ways. c A mutation that causes one amino acid in a protein

to be exchanged will always result in a loss of protein function. 2 Protein structures need to be determined

experimentally. They cannot be predicted from the primary structure. X-ray crystallography analyses often reveal that amino acids that are far apart in the primary structure of a protein are very close to each other in the protein’s three-dimensional shape. Explain the process by which this occurs.

Enzymes 3 a Explain why the action of enzymes justifies the statement ‘Enzymes make life possible’. b Why is the action of an enzyme often described as

operating like a lock and key? 4 Indicate whether the following statements summarising

the properties of enzymes are true or false. a Enzymes are made of proteins. b Enzymes do not change the position of equilibrium. c Enzymes are consumed by the reaction. d Enzymes increase the activation energy of a

reaction. e Enzymes increase the rate of reaction. f Enzymes are sensitive to conditions such as pH

changes or temperature increase which denatures the enzyme. g Enzymes are highly specific for the biochemical

reactions they catalyse because of the shapes of their active site. 5 There is a mutation that causes one of the amino acids in the active site of an enzyme to be substituted for another. Although the mutation does not dramatically alter the three-dimensional shape of the protein, it causes a reduction in enzyme activity. Account for this observation.

enzyme–substrate complex fermentation induced fit model lock-and-key model

6 On a b c identify label the draw this the first process.

diagram the and the two parts label model steps o in of a Figure diagram the of of enzyme enzyme diagram 18.5.1:

o to model

show action action as indicated the shown f next s to show

step in

P

a

g

e

**P FIGURE Enzymes—dependence 18.5.1 r**

on pH and temperature 7 Medicinal proteins such as insulin are administered

by injection, rather than being ingested. Suggest why insulin cannot be given orally as tablets or capsules. 8 Jellied pineapple dessert cannot be made by using

gelatine and fresh pineapple because an enzyme in the pineapple causes molecules in the gelatine to break down instead of setting. Suggest how jellied pineapple might be prepared. 9 Which one of these formulas gives the correct structure

of tyrosine (NH

2

OH)COOH) in the highly acidic conditions present in the human stomach? A +NH

3

CH(C

6

H

4

OH)COOH B NH

2

CH(C

6

H

4 CH(C

6

H

4

OH)COO− C +NH

3

OH)COO− D NH

2

CH(C

6

H

4 CH(C

6

H

4

OH)COOH 10 Draw the structure of the zwitterion form of the amino

acid valine. You should refer to the table of amino acids (Table 17.1.1, page 460).

509 CHAPTER 18 | USES OF PROTEINS

CHAPTER REVIEW CONTINUED

11 The graph in Figure 18.5.2 shows the effect of

temperature on the enzyme activity for a metabolic reaction. For each of the parts of the graph labelled A, B and C, explain the variation in enzyme activity with temperature.

10

P

A

y

C

20 30 40 50 60 70 80 Temperature of reaction (°C)

**FIGURE 18.5.2**

Enzymes in industry 12 Give the chemical equation that describes the

fermentation of glucose. 13 Describe three differences between the two processes

for the formation of ethanol, the fermentation of glucose and the hydration of ethene. 14 The equation for the reaction for the hydration of

ethene is: CH

2

t i v i t c a e m y z n E

B

Use equilibrium listed reaction a b = your CH 2

(g) knowledge + H

2

O(g) of  Le CH

Châtelier’s 3

CH

2

OH(g) principle,

ΔH = −45 e kJ mol−1

Increasing Decreasing changes rate.

and pressure

temperature will collision a affect both theory the g

to equilibrium predict how yield the

and

**510**

AREA OF STUDY 7 | BIOCHEMISTRY

15 Give two disadvantages and two advantage of using

16 Connecting 17 18 P enzymes than In fermentation process can ethanol Biological as break disadvantages over Unless maximum because enzymes denaturation that order lipases be ethanol a inorganic down traditional distillation used and of to high as in the washing (to ethanol distillation purify r yeast catalysts proteins). water. is to and of break concentrations main of likely catalysts. purify glucose using washing the describe to is content powders down ideas used, denature. to o ethanol for is ethanol Evaluate form a used. or industrial biological oil) powder. beer the the of contain with of produced roughly and from Explain Explain hydration types the and ethanol o the proteases processes, advantages a washing wine enzymes of mixture protein. ∼15%. how this interactions by can of both distillation process either ethene, cause powder (to This f of

such rather

have and is

the of the

a s

UNIT 4 • ORGANIC CHEMISTRY AND

CHEMICAL SYNTHESIS

**Section 1: Multiple choice**

1 The systematic name for CH

3

s

REVIEW QUESTIONS

f 7 The volume of carbon dioxide (in L) collected at STP when

6.32 g of ethane undergoes complete combustion is: A 4.77 B 9.25 C 9.55 D 18.5

8 Which of the following molecules is most likely to undergo an addition polymerisation reaction? A FCH

2

CH

2

CH

2

CH(CH

3

)

2

is: A 1,1-dimethylbutane. B 2-methylpentane. C 2-methylpentene. D propyldimethylmethane.

2 Oxidation of a secondary alcohol produces:

A an aldehyde. B a ketone. C a carboxylic acid. D an ester.

3 Which of the following compounds would be expected to

have the highest boiling point? A CH

3

o 9 B C HOCH C

6

H

5

CHCHOH CH

2

CONH

2

COOH

o 2

D Listed organic I II III IV Which hydrocarbon CH alcohol amide aldehyde ketone 3 r COCH

below of compounds. these 2 are CH

chain? groups 3 the names of groups found in some

are always found at the end of a

A I and II only B III only C I, II and III only D I, III and IV only

10 Consider the following reaction pathway.

ethene — →—

CH

2

CH

2

OH B CH

3

P

CH

2

CH

2

CH

3 C CH

3

CH

2

CH

2

Cl D CH

3

CH

2

CH

3 4 Which of the following statements are true of the

homologous series of primary alcohols? I The members differ by one CH

2

unit. 5 II They are all strong bases.

III They can be oxidised to form carboxylic A I and II B II and III C I and D I, II Chloroform and III

III (trichloromethane, g CHCl

3 e acids.

II

ethanol — →——

III

ethanoic acid The reactions that occur in steps I, II and III of the pathway are: A substitution, addition, hydrolysis B chlorination, substitution, addition C addition, substitution, oxidation D addition, reduction, hydrolysis.

11 A triglyceride molecule with a molar mass of 878 g mol−1,

when fully hydrolysed, yields a single type of fatty acid molecule. The molar mass of this fatty acid (g mol−1) is closest to: A 262 B 280 C 292 D 310

I

chloroethane — →—

) is synthesised commercially by the chlorination of methane. Reaction occurs CH The chloroform 4

final + 3Cl

according mixture 2

→ along CHCl a contains to with 3 + the 3HCl

chloromethane, equation:

hydrogen chloride dichloromethane

and

6 and of obtained. to A B C D The together P the generate 101 134 179 197 ester tetrachloromethane. chloroform, which What methyl 1.0 kg of mass ethanoate the of and chloroform, of following?

at methane Distillation one could plant assuming (in be yields allows g) made would of separation 75% by 75% be reacting yield?

needed

are

A CH

3

CH

2

OH and CH

3

COOH B CH

3

CH

2

OH and HCOOH C CH

3

OH and CH

3

CH

2

COOH D CH

3

OH and CH

3

COOH

545 REVIEW QUESTIONS

**546**

UNIT 4 | ORGANIC CHEMISTRY AND CHEMICAL SYNTHESIS

UNIT 4 • REVIEW

12 The industrial production of chemical Z proceeds in the

presence of a catalyst according to the equation:

X(g) + 2Y(g) → zZ(g) The graph below shows the variation in the equilibrium yield of Z with pressure at a range of temperatures

100

80

200°C

300°C

60

400°C

%

40

500°C

20

600°C

200 400 600

Pressure (kPa)

800 1000

It can be deduced that the production of Z is an: A endothermic reaction and the value of z could be 2. B endothermic reaction and the value of z could be 4. C exothermic reaction and the value of z could be 2. D exothermic reaction and the value of z could be 4. Section 2: Short answer 1 Enzymes be example using produced can petrol a b Write for reaction i ii iii used be Write formulas hydrolysis suitable Which used part condensation? The in atmospheric 300°C. reaction, P enzymes organic for used industry a for is are synthesis use b(i): by balanced to a the of industrial one as In balanced the biological describe catalyst. in glucose compounds, account substitution, for synthesis terms derived a of existing or at catalysed fuel a organic pressure, ethene. more pressures reaction equation, in of scale to the equation, for catalysts, from modified the vehicles. produce of of compounds, type Include the hydration for ethanol synthesis addition, the and rate in yeast. of using g use the part of following around using a and some ethanol. vehicles, reaction enzyme-catalysed of the temperature Ethanol b(i) from molecular acid–base, such extent of reactions. name semistructural of for ethene. takes 60 glucose, terms which high occurring the or e times can of of mixed place the catalysed formulas

a

near

pressure. could Ethanol One

also redox, can

with be

in

be

c Suggest two reasons why the enzyme catalysed

synthesis reaction in part a may be the preferred method for large scale, long term synthesis of ethanol for use as a fuel.

2 A triglyceride molecule found in a fat is shown in the

following diagram.

triglyceride H

C

C

s

H

O

H

H

H

C O

O

C O C (CH 2

)

16

CH

3

(CH

2

)

16

CH

(CH

2

**f a i O**

O C Draw the structures and the anionic form produced by the base of of catalysed the the o glycerol long hydrolysis chain 3 molecule

fatty acid

of this triglyceride. ii The saponification reaction in part a(i) produces

soap. Name the functional group in the anionic particle drawn in part a(i). b The semistructural formula of a synthetic detergent which can be used in place of soap is shown below.

H

CH

3

)

16

CH

3

P

r

C CH 3

o

CH

2

H

C (CH

2

)

5

C

6

H

4

SO

3

Na

CH

3

i Is the detergent shown cationic, anionic or polar? ii Name the type of bonding which occurs between

the detergent ions and water molecules. iii Name the type of bonding which occurs between

the detergent ions and oil molecules from a greasy plate. c Synthetic detergents have replaced natural detergents

such as soap for many cleaning purposes. i State one advantage of detergents over soap. ii State one disadvantage of detergents over soap. d Biodiesel is an increasingly important alternative fuel which is synthesised from triglycerides and methanol using either a hydroxide catalyst or a lipase catalyst. i Draw the structure of a biodiesel molecule

containing a total of 18 carbon atoms ii Name the types of bonding which exist between

biodiesel molecules.

3 a For each of the following structures, write a condensed (semistructural) formula.

H

H C H

C

H

H

H

H H H

C

C

H

H

H

C

H

C

C

C H

H

H

H H

H

C

H

H

H

H

H

C

C

C

C

C H

H H

H

O

H

H H H

H

C C H

O

O

N

C

C H

b Give the correct IUPAC names for each of the

following structures.

CH

2 P H

3

C

H

3

C a C

H

H

C

g CH

3 e

H

3

C

CH

2

CH CH

2 CH

2

HC CH

3

NH

2

O

H

3

C

C CH

2 O

CH

2

CH

3

c State appropriate reagents and conditions to effect

the conversion of: i butan-2-ol to butanone ii cyclohexene to cyclohexane. d Write balanced chemical equations (excluding states)

using semi-structural formulas for the: i condensation reaction of ethanol and propanoic

acid

4 An When 1.00 under obtained. 3CH a ii i experiment 3 mol acid–base propanoic 3.00 appropriate L−1 The g solution of reaction was ethanol reaction acid.

conditions conducted of is acidified was between represented treated 2.42 o

to potassium synthesise ethanamine g with of by ethanal 25.0 the dichromate

ethanal.

equation: mL and

was

of a

ii 5 P b Alcohols produce reaction. i ii CH State Write 2 OH(l) r the a balanced + oxidation Cr

o 2

O

7 2−(aq) half-equation 3CH number 3

+ CHO(l) 8H+(aq) of carbon + for 2Cr3+(aq) →

the + 7H 2

O(l) in ethanal. oxidation process occurring in the reaction. Calculate the percentage yield for the synthesis experiment. Suggest two reasons why the percentage yield less than 100%.

can be dehydrated by heating in acid to alkenes, as shown in the following generalised

OH

is

R

1

CH

2

CH R

2

H

3

PO

boil

4

R

1

CH

CH R

2

When hexan-3-ol was heated with acid, the resultant mixture was found to contain four distinct isomeric products. a i Draw a structural formula for hexan-3-ol.

ii What type of alcohol (primary, secondary or

tertiary) is hexan-3-ol? iii Hexan-3-ol has a very low solubility in water compared with ethanol, which is completely miscible in water. Account for this difference in solubilities. b Two of the products of the dehydration of hexan-3-ol

are structural isomers, differing only in the position of the functional group. Draw and name these two isomers. c Each of the isomers drawn in part b can exhibit cis–

trans isomerism. For one of the compounds drawn in part b, draw and label the cis and trans isomers.

547 REVIEW QUESTIONS

f

s

**548**

UNIT 4 | ORGANIC CHEMISTRY AND CHEMICAL SYNTHESIS

UNIT 4 • REVIEW

6 A number of reactions involving sulfur containing

compounds are shown in the equations K–O. Some of these reactions occur during the production of sulfuric acid by the contact process. K S(l) + O

2

(g) → SO

2

(g) L H

2

SO

4

(aq) + MgO(s) → MgSO

4

(aq) + H

2

O(l) M 2SO

2

(g) + O

2

(g)  2SO

3

(g) N SO

3

(g) + H

2

SO

4

(l) → H

2

S

2

O

7

(l) O H

2

SO

4

(l) + 3H

2

S(aq) → 4S(s) + 4H

2

O(l) a Select the letter K–O corresponding to a reaction:

i showing sulfuric acid acting as an oxidising agent ii in which the oxidation number of sulfur is

unchanged iii in which the substance called oleum appears. b The reaction represented by the letter M is an

important step in the manufacture of sulfuric acid by the contact process. i To improve the yield of SO

3

in this reaction should the temperature be raised or lowered? Explain your choice. ii State one disadvantage of using the temperature

chosen in part b(i). iii The yield of SO

3

in this reaction would be improved by the use of high pressure. Explain why the reaction is carried out at near atmospheric pressure during industrial production of sulfuric Section 1 acid. c The reaction represented by in the presence of a catalyst. this catalyst increase, decrease the following characteristics i ΔH value ii Equilibrium yield of SO

3 iii Rate of reverse reaction

3: Extended answer A 6.500 g sample of an organic burnt carbon In g of the compound Does the or letter not the reaction?

change M presence e (C is x conducted each of

of

compound at a in excess oxygen. a

4.74 g H y

O

*z*

) was of water, and 11.60 g of

a 200°C Show C 3 separate H P 6

O dioxide that 2 and was the experiment, 1.20 were vaporised. molecular × produced.

a 5.01 g sample The vapour 102 kPa.

formula of occupied the of the

2.22 L

compound is

b Two possible molecular structures for the compound

are shown below.

H

H

C H

isomer I

O

C

H

O C

H

isomer H

II

C o H

H

f

s

i ii Give Describe results samples the H

of systematic H H of a the simple the o test, isomers H

which laboratory name I of isomer I.

test, including could distinguish and II above.

the between

iii Draw a structural formula for, and give the name

of, another isomer of C

3

O C P c Isomer II r may be C produced sequence shown below.

compound C 3

O

H

6

O

2

. using the reaction

compound A

HBr

H

7

Br

B

compound C

MnO

4 C

3

OH–

i Draw the structural formula for compound B. ii Compound C, C

3

H

8

O, has a molar mass of 60 g mol−1 and a boiling point of 97°C. Propanone (C

3

H

6

O) has a molar mass of 58 g mol−1 and a boiling point of 56°C. Account for the difference in the boiling point of these two compounds of similar molar mass. iii Write the expected observations which could be

made when substance C reacts with an acidified solution of potassium permanganate to produce isomer II. Include the appearance of reactants and products in your answer.

–

H+

isomer II H

8

O

C

3

H

6

O

2

2 Enkephalins are short polypeptides involved in the nervous system’s detection of pain and harm. The structure of met-enkephalin, so-called because it contains a methionine residue, is shown below. Met-enkephalin may undergo acid catalysed hydrolysis to release the four different amino acids. a i Refer to a table of amino acids in your Chemistry Data Booklet and use it to name the amino acids (other than methionine) present in met-enkephalin. ii On the structure shown below, circle and label two

peptide linkages.

O

O

H

2

N

C

NH

C

CH

CH

2

o O

HO

b Enkephalins are short polypeptides. Much longer

polypeptides form proteins, whose structure may be described in terms of primary, secondary and tertiary structures. Give explanations for the following facts relating to protein structure and function. i Formation of the primary structure of proteins

produces water as a by-product but formation of secondary, tertiary and quaternary structures do not. ii Despite having unique and very different amino

acid sequences, almost all proteins are able to form α-helical and β-pleated regions. iii All proteins are denatured by extreme pH changes,

but some enzymes can lose their activity as a result of even relatively small pH changes without being fully denatured. iv The tertiary structures of some proteins are more easily disrupted by an increase in temperature than are those of others.

iii On the structure shown below, circle and label the

terminal carboxyl and amino groups. iv Draw the structure of the methionine amino acid as it would exist in the acidic hydrolysis solution. v At a particular pH, an amino acid has both a

positive and negative charge and is known as a zwitterion. Draw the zwitterion structure for one of the amino acids in met-enkephalin other than methionine.

O

NH

C

CH

2

NH

r CH

CH

2

O o CH NH

S

H

3

2

CH

CH

2

f

s

CH

2

P c C

Proteins are formed by condensation polymerisation

P

a

g

H N e CH

2

of amino acids. Another similar condensation polymer is nylon. The structure of one nylon molecule is shown below. This nylon is composed of two alternating monomers. One of these monomers shows a strongly basic character. i Draw the structural formula of this basic monomer. ii Write an equation to show the reaction of this

monomer with excess hydrochloric acid (states are not required). iii State one structural similarity between proteins

and nylon. iv State one structural difference between proteins

and nylon.

O

CH

2

CH

2

C

CH

2

CH

2

CH

2

CH

2

CH

2

N

CH

2

CH

2

C

H O

*n*

549 REVIEW QUESTIONS

C

OH