



Chemistry in Conflict

An OPCW educational module

Cover illustration

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Chemistry in Conflict



Gemeente Den Haag



**Universiteit
Leiden**
The Netherlands

Chemistry in Conflict

This module is intended as a thematic project for the IB standard level Chemistry curriculum or any comparable national chemistry program. It was produced by collaboration between the Organisation for Prohibition of Chemical Weapons (OPCW), Leiden University, the City Council of The Hague, the International School The Hague, the Johan de Witt scholengroep, the Vrijzinnig-Christelijk Lyceum, and the IB Africa, Europe and Middle East Global Centre in The Hague, the Netherlands. The OPCW, the City Council of The Hague and Leiden University funded the production of this workbook for students and supplemental educational materials.

Authors

Fiona Clark, IB Africa, Europe and Middle East Global Centre, The Hague

Hanspeter van Daalen, Johan de Witt scholengroep

Ioana Howland, the International School of The Hague

Henk de Vries, Vrijzinnig-Christelijk Lyceum

Ludo Juurlink, Leiden University, Leiden

Editing

Ludo Juurlink

Layout and design

Eva van Bemmelen

Workbook Chemistry in Conflict
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Introduction

Ypres, Belgium. April 22, 1915. Armies of French and Algerian soldiers have been stuck in trenches for many, many days. They hold on to their long rifles. It is late in the afternoon and a breeze is coming their way from the opposite side of the battle field. In the distance German soldiers have been busy moving large drums around. Suddenly a yellow-green smog appears at the horizon and heads their way. It smells odd. The cloud stings their eyes and hurts their lungs. Within seconds everyone is yelling and screaming. Breathing becomes increasingly difficult and the soldiers can't stop coughing. They drop their rifles as their vision starts to fail. They cover their eyes and hold a cloth to their mouths walking aimlessly around. But the wind doesn't stop and the smog doesn't go away. It is heavier than air and fills up the trenches. There is no option but to climb out of the trench protecting them from the hail of German bullets. They must try to escape this poison air.



Humankind's history is one that may be described by all the wars fought and recorded over more than two thousands years. Although all wars contain cruelties, World War I was special. It was the first war in which scientific progress in the field of chemistry led to the ability of armies to intentionally hurt or even kill their opponents using gaseous chemicals. The French were the first to use tear gas in 1914, but the Second Battle at Ypres in 1915 truly started a new era in which chemical weapons would be deployed on a large scale.

It is now a century later. Our ability to understand and manipulate the world in which we live through discovery, scientific and technological progress has been proven truly phenomenal. It enables us to live on planet Earth with over 7 billion people. However, it has also led to the development of more powerful nuclear, chemical and biological weapons that hurt or kill more people in a shorter time, destroy larger areas, giving

the owner of these weapons a better chance of winning a war. In only a couple of decades, humankind went from fighting with rifles and guns, often still in close combat, to developing, stock piling and employing weapons of mass destruction.

This booklet is intended to help you learn the basics of one subset of such weapons. You will study chemical weapons, how they are made and analyzed, what their effects are, but also how people are now trying to dispose of them through international collaboration. More importantly, you will come to understand that scientific progress often occurs without much attention to ethical questions connected to new technologies that are made possible from our increased understanding. Therefore it is time to add an ethical perspective to your study of the sciences.



1

Chemical Weapons

“With its high viscosity and low volatility, VX has the texture and feel of motor oil. This makes it especially dangerous, as it has a high persistence in the environment. It is odorless and tasteless, and can be distributed as a liquid, both pure and as a mixture with a polymer in the form of thickened agent, or as an aerosol.”



- 1 Chemical warfare
- 2 Detection and synthesis
- 3 Physiological effects

Learning objectives

Chemical warfare

After studying this section, you should be able to explain the differences between various types of warfare, name at least five chemical warfare agents, explain what dual use chemicals are and how this is relevant to prohibition of chemical weapons, and classify chemical weapons according to a useful scheme.

Detection and synthesis

After studying this section, you should be able to explain how chemical warfare agents are generally detected and identified, apply your knowledge of MS and molecular structures to relate a mass spectrum to a chemical warfare agent, and analyze important reaction steps in the synthesis of such agents using your knowledge of organic chemistry.

Physiological effects

After studying this section, you should be able to name various symptoms exhibited by casualties of sulfur mustard and sarin and discuss the biochemical mechanism underlying the symptoms.

1. Chemical warfare

Introduction

This lesson deals with the distinction of chemical, biological and nuclear weapons. In addition it discusses what chemical weapons are and how they may be classified.

Weapons of mass destruction

Weapons used to kill or harm large numbers of humans and/or cause great damage have been termed Weapons of Mass Destruction (WMD). We distinguish four different types. Nuclear weapons are generally thought of as explosive devices that derive their destructive force from nuclear reactions. Examples are the H-bomb and the atomic bomb. Besides their enormous explosive force, these weapons result in the spreading of radioactive material that is harmful to all forms of life. Radiological weapons, such as 'dirty bombs', have only the latter intent and use conventional explosives to spread radioactive substances. Biological weapons are not employed through large explosions. Organisms, like bacteria and viruses, that may harm humans, animals or plants would be destroyed in the explosion. Obviously, they are employed differently. Chemical weapons form the last category.

Questions and assignments

1. Name as many chemical weapons that you know without looking them up in a book or on the internet.
2. Compare your list with a classmate and discuss which ones are chemical or some other form of weaponry.
3. Do you consider a poison derived from an organism a chemical or biological weapon? Explain your answer.

Questions and assignments

4. How would you define a chemical weapon?

Single or dual use

Chemicals that are derived or isolated from organisms can be extremely toxic. An example of such a toxic chemical is ricin. It can be used to poison individuals. Ricin is extracted and further purified from the seeds of the castor oil plant. It has been found more than once in letters sent to important politicians. At the end of this chapter you can find a description of ricin and its physiological action that was released by Thomson Reuter when former US President Obama received such a letter in 2013. Even though it was never used to kill people on a large scale, ricin is a chemical weapon. It has no other use. And, although it has not been deployed, some countries have studied the use of ricin in cluster bombs or spreading it as dust clouds.



Figure 1.1.1
Botanical drawing
of the castor oil
plant

Many chemicals which can be used as weapons or are applied in the synthesis of chemical warfare

agents also have peaceful and commercial purposes. An example is thiodiglycol. This chemical can be used in the manufacture of mustard agents. It is also used as a solvent in inks. Also many herbicides and insecticides are quite toxic and could be used easily as chemical warfare agents. The nitrogen mustards are cytotoxic chemotherapy agents and similar to warfare agents known commonly as 'mustard gas'. Although nitrogen mustards can be used as medicine, in principle these compounds can also be deployed as chemical warfare agents. To complicate matters even further, some chemicals are separately not harmful but upon mixing become a chemical weapon. The chemicals methylphosphonyl difluoride and a mixture of isopropyl alcohol and isopropyl amine are held in separate chambers within the weapon. When the weapon is fired, acceleration and rotation causes these chemicals to mix producing Sarin nerve gas. The dual use of many chemicals is obviously an issue if one wants to control or ban chemical weapons from our planet.

Questions and assignments

5. Discuss whether Ricin is truly a single use chemical. Consider the plant.
6. Reconsider your definition of a chemical weapon taking into account the dual use of some chemicals. Discuss your improved definition with classmates.

Good and bad chemicals

Public dismay at the horrors of chemical warfare has spurred negotiations between nations to prevent chemical weapons from ever again being used for warfare. An international treaty on the prohibition and disarmament of chemical weapons, the Chemical Weapons Convention (CWC), is now in effect. This convention not only addresses synthetic chemicals but also toxins derived from organisms. The CWC will be an important topic of study in the second chapter.

In order to decide which chemicals should be prohibited and which chemicals need to be monitored, an unambiguous definition of a chemical weapon is required. It is seemingly easy to define a chemical weapon as a toxic chemical contained in a delivery system such as a bomb or artillery shell, but that would impose some difficulties. For

example, according to this definition, riot control agents would be chemical weapons since they produce irritation of human sensory and other physical effects. However, riot control agents are not intended to permanently harm or kill humans and their effects usually disappear within a short time after exposure. Prohibition of riot control agents would make it a lot more difficult for the police to fight riots. Whether or not riot control agents should be considered as chemical weapons resulted in much discussion during the negotiations of the CWC.



Figure 1.1.2
Exploding tear gas cans at riots in Athens, Greece in 2012

Questions and assignments

7. Reconsider your definition of a chemical weapon again. Take riot control agents into account and the usage of chemicals for peaceful and commercial purposes.

Classification of chemical weapons

Classifying means that one groups a range of items according to characteristics that may vary between the individual items. You could classify the students in your school based on a large variety of schemes. For example, you could use the colour of their eyes, whether they are your friends, which grade they attend. Depending on the purpose of grouping items, one classification scheme may be more useful than others.

Similar to classifying a group of weapons as either nuclear, chemical, radiological or biological, one may classify chemical weapons according to their physiological effects. An existing classification scheme defines them as riot control agents, choking agents, blister agents, blood agents or nerve agents. The general physiological effects for four of these are listed in table 1.1.1.

	Choking agents	Blister agents	Blood agents	Nerve agents
Mode of action	Absorption through lungs	Absorption through lungs and skin	Absorption through lungs	Absorption through lungs (G) and skin (VX)
Symptoms upon exposure	Fluid builds up in the lungs, choking the victim	Burns skin, eyes. Blisters skin, windpipe and lungs	It destroys the ability to utilise oxygen by the soft tissues.	Causes seizures, loss of body control. Paralysis muscles
Manner of dispersion	Gas	Liquid, aerosol and vapour	Gas	Liquid, aerosol and vapour



Table 1.1.1

Physiological effects of chemical warfare agents

Certain classes are subdivided. For example, the nerve gases are divided into two main classes: G-agents and V-agents. The V-agents tend to be more lethal than G-agents and they are ‘persistent’, i.e. they last for a long period. G-agents are non-persistent. They were all discovered during or soon after World War I by the Germans (hence the ‘G’). One of the most well-known chemical weapons, sarin, is a nerve agent of the G-class.

Questions and assignments



- Can you think of reasons why a classification scheme according to physiological effects may be useful?
- Classify the chemical weapons listed in the table below according to the classes mentioned above. Use internet sources.



- Can you think of another classification scheme for chemical weapons? Discuss with a class mate various classification schemes. Which one is more useful for what purpose? Work out one scheme that you think is useful and reclassify the chemical weapons mentioned above according to that scheme.

Chemical weapon	Classification		Chemical weapon	Classification
Chlorine			Tabun	
Lewisite			VX	
Cyanogen chloride			VE	
Arsine			Hydrogen cyanide	
Phosgene			Cyclosarin	
Sulfur mustard			Choropicrin	
Phosgene oxime soman			Nitrogen mustard	



Table 1.1.2

Classification of warfare agents

Questions and assignments

11. Would it be useful to include a classification scheme in your definition of a chemical weapon?
12. Now that you have thought about a definition and classification of chemical weapons, read [OPCW Fact Sheet #4](#). How close were you to the official definition?

Ricin poisoning

WHAT IT DOES

Inactivates ribosomes in cells, which prevents the body from creating proteins. This can cause widespread organ damage that can lead to pulmonary, liver, renal, and immunological failure

PRODUCTION

Can be made from waste "mash" produced when oil is extracted from castor beans



DELIVERY

Can be introduced in liquid, aerosol, powder, or pellet form

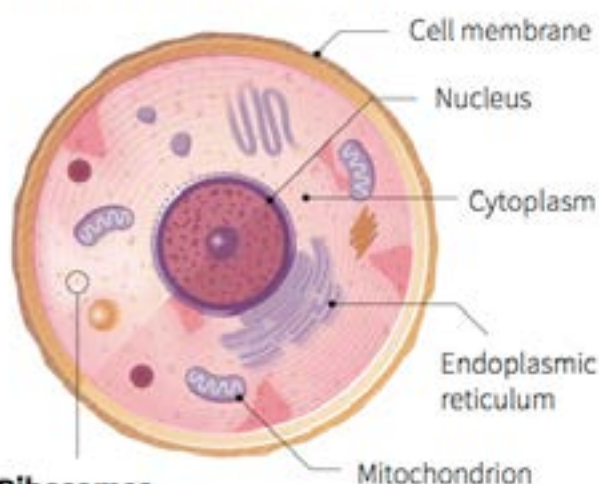
EFFECTS AFTER EXPOSURE

Within 8 hours - Pathological changes

36-72 hours - Acute respiratory failure

If exposure does not prove fatal within 3-5 days, the victim will usually recover

HUMAN CELL STRUCTURE

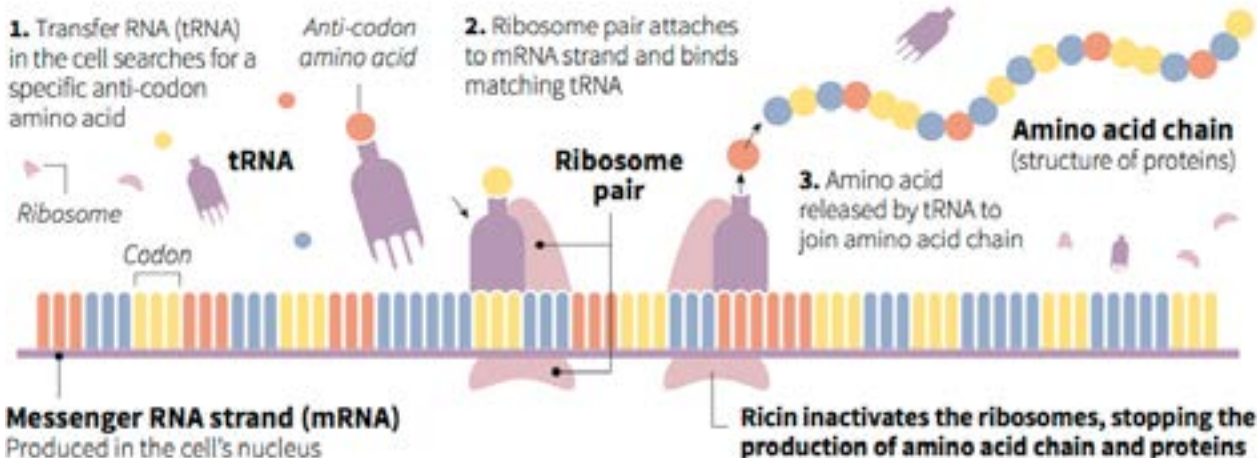


Ribosomes

- Can be found in the cytoplasm or the endoplasmic reticulum
- Bind one amino acid at a time to build chains of proteins which the body uses to perform biological functions

HOW RICIN AFFECTS PROTEIN SYNTHESIS

Note: Diagram is schematic



Sources: Reuters; How Stuff Works; Federation of American Scientists

RNA - Ribonucleic acid

C. Inton, 18/04/2013

REUTERS

2. Detection and Synthesis

Introduction

This lesson deals with the general detection method and synthesis of three well-known chemical warfare agents, i.e. sulfur mustard, tabun and sarin.

Detection with GC-MS

Although IR spectrometry is an option, mostly the combination of Gas Chromatography and Mass Spectrometry (GC-MS) is used for the detection of potential warfare agents and the intermediates used in their synthesis*, GC-MS combines two analytical techniques. Gas chromatography (GC) is used to first separate different chemicals that may be present in a sample. When a compound exits the separation column of the GC, mass spectrometry (MS) is used to create a mass spectrum of that compound.

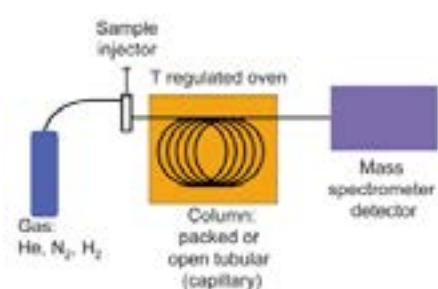


Figure 1.2.1
Schematic illustration GC-MS analysis.

A mass spectrum shows masses belonging to various fragments of a chemical compound. The original compound is first ionized in the gas phase. In this process, the created parent ion may fragment into smaller pieces. The parent ion is the entire molecule but ionized to a charge of +1. When it fragments into two pieces, one of these will be charged whereas the other fragment is neutral.

The units provided on the x-axis of a mass spectrum are atomic mass units (amu) per unit of

*as well as reaction and degradation products.

charge. It is often indicated as m/z . To separate ion fragments, MS uses electromagnetic fields. These fields yield the dependence of the signal on the mass-to-charge ratio and not just the mass of the ion. The charge is usually +1. For example, CH_3^+ will show up as $m/z=15$. Sometimes the parent ion, is present in spectrum. However, this is not always the case.

Well-known chemical weapons

Sarin and sulfur mustard are well-known chemical warfare agents, which can be readily identified by GC-MS. In figures 1.2.2 and 1.2.3 their chemical structures are shown.

During the inspection of industrial sites that are suspected of producing chemical weapons, an inspector of the OPCW can decide to take a number of samples. These different samples can be analysed on site with a bench top GC-MS. Samples may also be shipped to chemical laboratories in various countries that are qualified to do the analysis. The mass spectra of compounds found by inspectors are compared to a mass spectrum database to test whether suspected chemicals are present.

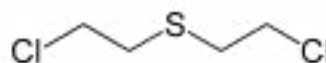


Figure 1.2.2
The structure of sulfur mustard

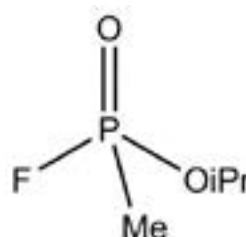
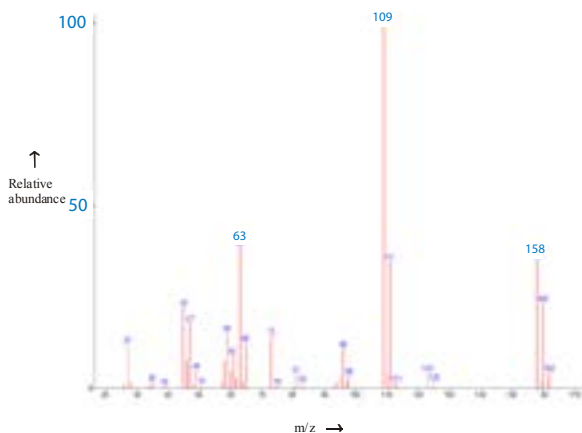


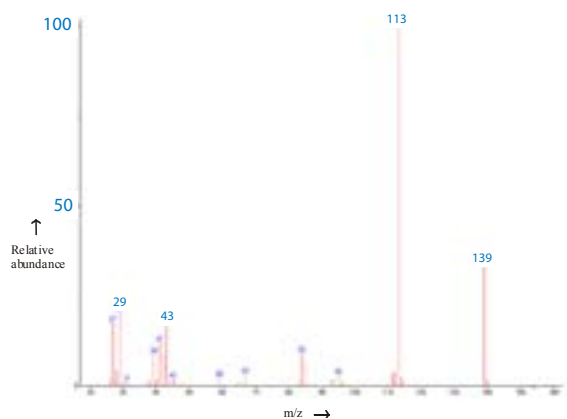
Figure 1.2.3
The structure of sarin

Questions and assignments

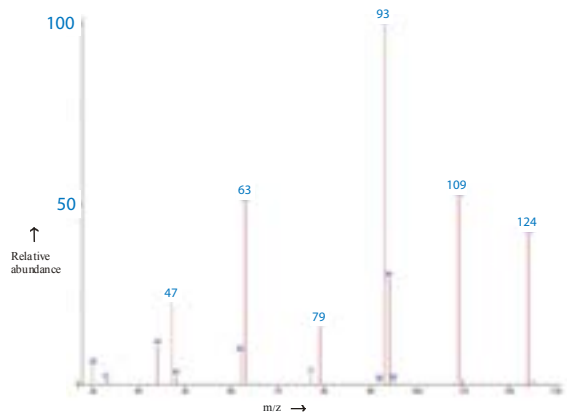
Figures 1.2.4-6 show three mass spectra.



● Figure 1.2.4 mass spectrum of sample 1



● Figure 1.2.5 mass spectrum of sample 2



● Figure 1.2.6 mass spectrum of sample 3

1. Which mass spectrum belongs to sarin? Explain your answer.
2. Explain which mass spectrum belongs to sulfur mustard.

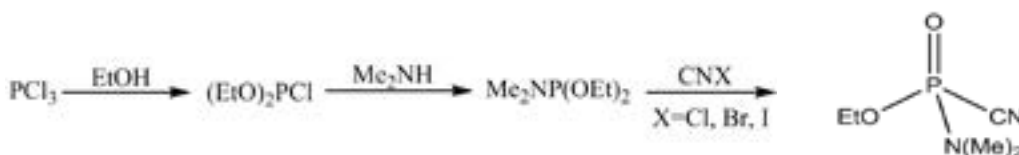
Synthesis of sulfur mustard

Sulfur mustard was possibly developed as early as 1822 by César-Mansuète Despretz (1798–1863). Despretz described the reaction of sulfur dichloride and ethylene but never made mention of any irritating properties of the reaction product, which makes the claim doubtful. In 1854, another French chemist, Alfred Riche (1829–1908), repeated this procedure and also did not describe any adverse physiological properties. In 1860, the British scientist Frederick Guthrie synthesized and characterized the sulfur mustard compound, and he also noted its irritating properties. The scientists Wilhelm Lommel and Wilhelm Steinkopf developed a method for the large-scale production of sulfur mustard in 1916.

Sulfur mustard can be made by two consecutive chemical reactions. In the first reaction sulfur dichloride is made from sulfur and chlorine. Sulfur dichloride reacts with ethylene to form sulfur mustard. Impure sulfur mustard has a colour ranging from pale yellow to dark brown, while pure sulfur mustard has no colour.

Questions and assignments

3. Write down the reaction that is the first step in the production of sulfur mustard - the reaction between sulfur and chlorine to produce sulfur dichloride.
4. Give the reaction for the second step in the synthesis of sulfur mustard from ethylene and sulfur dichloride.
5. Explain whether the reaction between sulfur dichloride and ethylene can be regarded as a substitution reaction or an addition reaction.
6. Formulate a hypothesis to explain the fact that impure sulfur mustard has a yellowish colour.
7. Design an experiment to test your hypothesis. Could you use GC-MS?



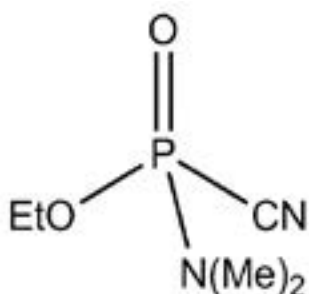
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Figure 1.2.7

A synthesis pathway for tabun

Synthesis of tabun and sarin

The beginning of modern chemical warfare begins in the German search for new pesticides in the 1920s and 1930s. Because of Germany's desire to lessen its reliance on food import, the German government searched for new insecticides to increase food production. Chemist Gerhard Schrader was tasked with finding new non-flammable, non-harmful insecticides. Schrader synthesized a series of "organophosphates" - organic molecules with a central phosphorous atom and with four covalently bound atoms or larger groups. Schrader made the organophosphates more potent by adding a cyanide group ($\text{C}\equiv\text{N}$). Organophosphates with cyanide groups had undesirable side effects on the chemists. They experienced, for example, blurred vision and dilated pupils. Eventually these side effects became severe enough to warrant hospitalization. One of these organophosphates with a cyanide group is tabun, shown in figure 1.2.8.



.....

Figure 1.2.8

The structure of tabun

Tabun proved too toxic to use as a commercial insecticide. However, the findings were passed on to the German government's war office. Tabun was produced, tested successfully in the field and declared the German chemical weapon of choice. In figure 1.2.7 a synthesis pathway for tabun is given.

Later Schrader and his team of chemists worked on a new set of organophosphates using fluorine rather than cyanide groups. In 1938 they discovered a compound that proved to be 5-10 times more lethal than Tabun and named it sarin. Sarin can be made by different chemical pathways.

Questions and assignments

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8. Give three separate complete equations of the chemical reactions shown in scheme figure 1.2.7. The organic compounds and phosphorus trichloride should be shown in complete structural formulas.
9. Describe five different synthesis pathways of sarin from various chemicals. Use sources from the internet. From a chemist's point of view, explain which of the synthesis pathways would be preferred.
10. Discuss the difficulties involved in monitoring the prohibition of the production of chemical weapons.



3. Physiological effects

Introduction

This lesson deals with the physiological effects of the known chemical warfare agents sulfur mustard and sarin.

Physiological effects

The effects that chemical weapons have on the functions and activities of living organisms and their parts vary. You have already learned that classification schemes for chemical weapons can be based on such physiological effects. Here, we look at these effects and trace their chemical and biochemical origin.

Sulfur mustard

Exposure to sulfur mustard can lead to a number of symptoms. The eyes can become red and irritated, even “burned”. In a number of cases people have been known to go blind. Small quantities of sulfur mustard cause severe yellowish blistering of the skin. If sulfur mustard is inhaled, the respiratory system is damaged. This can cause a runny bloody nose, sneezing, shortness of breath, and coughing. Some of the more serious respiratory symptoms appear anywhere from 24 to 48 hours after exposure. Sulfur mustard can be lethal even several days after exposure.

Sulfur mustard is not very soluble in water. However it is soluble in fat, which contributes to its rapid absorption into the skin. Although sulfur mustard is more soluble in fat than water, any moist area of the body, like the lungs, is especially susceptible to its effects. This is caused by the hydrolysis of sulfur mustard, liberating hydrochloric acid. Despite hydrolysis, sulfur mustard or its derived products can be detected up to 10 years in some types of soil after it has been used.

Although sulfur mustard has been shown to have long-term carcinogenic properties, it can also be used as an agent in the treatment of cancer. It was observed that the victims of sulfur mustard attacks had a low white blood cell count and bone marrow tissue growth failure. More research showed that nitrogen mustards could reduce tumor growth in experiments using mice by cross-linking DNA strands. Cross-linking prevents cellular division and generally leads directly to cell death or to the development of cancer.

In figure 1.3.1 an incomplete pathway of the cross-linking of DNA strands is shown for the reaction of sulfur mustard with the guanine bases of DNA.

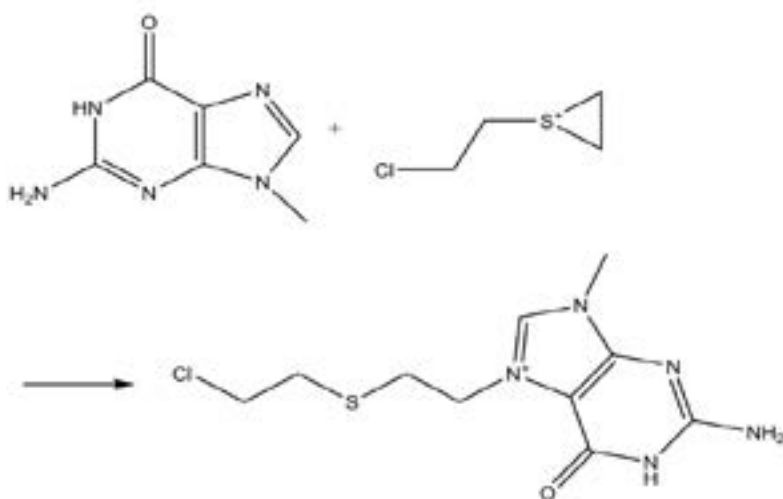
Questions and assignments

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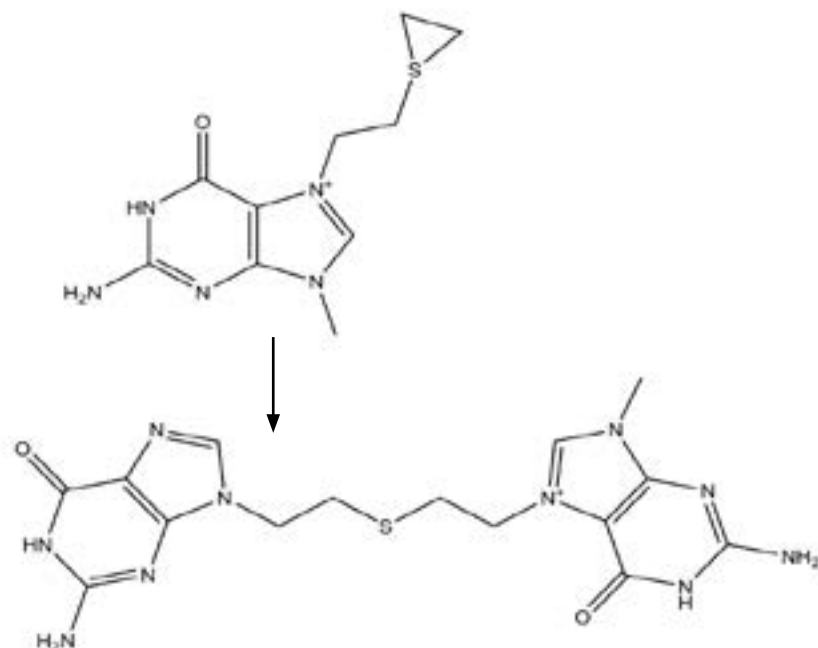
1. Explain on the basis of its molecular structure why sulfur mustard is not soluble in water, but is soluble in fat. Can you explain why exposure to sulfur mustard can cause shortness of breath?
2. In figure 1.3.1 compounds have been left out. Make the scheme complete.
3. The 1st and 2nd cyclisation reactions in figure 1.3.1 miss a product. What is it?
4. Explain why sulfur mustard in soil is a problem.



1st Cyclisation



Ethylene sulfonium ion binds to guanine



2nd Cyclisation

Cross linked guanine residues

● **Figure 1.3.1** Cross-linking of the guanine bases of the DNA strands by sulfur mustard

Sarin

Sarin is a neurotoxic agent or “nerve agent”. Contact with sarin results in various symptoms depending on the route of exposure and dose. Below, a summary is provided for various relative exposures [1-5].

In comparable degrees of exposure, people will generally first experience respiratory symptoms. After eating contaminated food or drinking con-

taminated water, gastrointestinal symptoms are usually the first.

Symptoms progressively increase and spread as more of the nerve agent is absorbed into the blood. The earliest ocular effect is pupillary constriction. Within a few minutes after exposure, redness of the eyes is observed. The earliest effects on the respiratory tract are a runny nose, tightness in the chest and occasionally prolonged wheezing.

In mild exposures, the systemic manifestations of nerve agent poisoning usually include tension, anxiety, jitteriness, restlessness, emotional instability, and giddiness. If the exposure is more marked, the following symptoms may be evident: headache, tremor, drowsiness, difficulty in concentration, impairment of memory with slow recall of recent events, and slowing of reactions. In some cases there is apathy, withdrawal and depression. The casualty begins to have increased fatigability and mild generalised weakness which is increased by exertion. This is followed by involuntary muscular twitching, scattered muscular fasciculation and occasional muscle cramps. The skin may be pale due to vasoconstriction and blood pressure is moderately elevated. Mild or moderately exposed people usually recover completely.

If the exposure has been severe, the cardiovascular symptoms will dominate and twitching movements appear in all parts of the body. Many rippling movements are seen under the skin. This is followed by severe generalised muscular weakness, including the respiratory muscles. Respiratory movements become more laboured, shallow and rapid; then they become slow and finally intermittent. If the exposure is not so overwhelming as to cause death within a few minutes, other effects appear. These include sweating, nausea and heartburn. However, if absorption of nerve agent has been great enough, there may follow abdominal cramps, vomiting, and diarrhoea. The casualty perspires profusely and may have involuntary defecation and urination. The casualty may have changes in speech, consisting of slurring, difficulty in forming words, and multiple repetition of the last syllable. The casualty may then become comatose, reflexes may disappear and generalised convulsions may ensue. With the appearance of severe central nervous system symptoms, central respiratory depression will occur and may progress to respiratory arrest. Severely exposed people are not likely to survive.

When overwhelming doses of the agent are absorbed quickly, death occurs rapidly without orderly progression of symptoms.

Inhibition of acetylcholine-esterase

Many of the previous described symptoms after exposure to sarin are caused by inhibiting the enzyme acetylcholinesterase.

Sarin can also irreversibly inhibit serine proteases by covalent bonding in the active site of serine proteases. In mammals, serine proteases perform many important functions, especially in digestion, blood clotting, and the complement system. Examples of serine proteases are chymotrypsin, trypsin and elastase.

Questions and assignments

5. What is the normal physiological role of the enzyme acetylcholine-esterase? Use sources from the internet.
6. When you go through the large number of symptoms caused by exposure to sarin, some can clearly be attributed to the inhibition of the enzyme acetylcholinesterase by sarin. Which ones are these?
7. Try to explain in a single sentence the term serine protease.
8. Formulate a possible hypothesis why sarin inhibits serine proteases.
9. Use internet sources to familiarize yourself with the enzymes chymotrypsin and trypsin. Speculate about which possible symptoms could occur if enzymes like chymotrypsin and trypsin are inhibited.

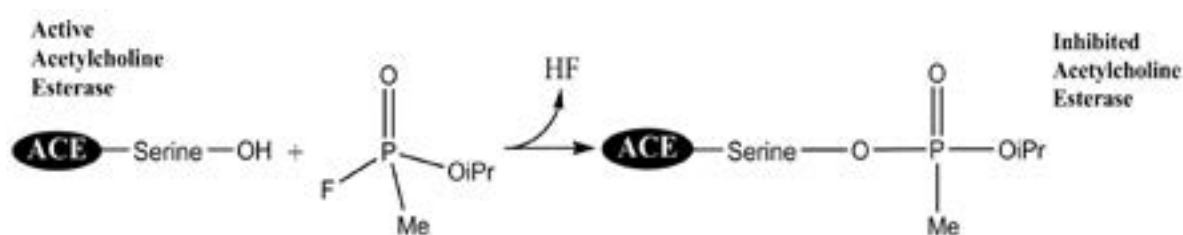


Figure 1.3.2
Inhibition of the enzyme acetylcholine esterase by sarin.



2

Chemical Weapons Convention

The main obligation under the convention is the prohibition of use and production of chemical weapons, as well as the destruction of all chemical weapons. The destruction activities are verified by the OPCW. As of August 2018, around 96% of the (declared) stockpile of chemical weapons has thus been destroyed.



- 1** Becoming a chemistry ethics teacher
- 2** Be a writer!
- 3** The Zod debate

Learning objectives

Becoming a chemistry ethics teacher

After studying this section, you should be able provide a historical perspective on the development and use of chemical weapons. You should be able to include the role of Fritz Haber in this perspective with both professional and personal aspects of his life. Finally, you should be able to argue that the history of chemical weapons demands that a study of chemistry must include an ethical perspective.

Be a writer

After studying this section, you should be able to define the key historical milestones in the ratification of the CWC, outline the main obligations of the Convention, and discuss the role the OPCW does play in the verification of the Convention and the relationship between the UN and the OPCW. You should be able to define the importance of such an intergovernmental organisation and discuss the role that the Chemical Weapon Convention Coalition plays.

The Zed debate

After executing this section, you should be able to prepare yourself for a debate on any topic related to chemical weapons.

1. Becoming a chemistry ethics teacher

Introduction

You start today by watching the OPCW produced film “[A Teacher’s Mission](#)”. The movie is meant to show chemistry teachers the importance of teaching more than just molecules and the Periodic Table in their class.

Task

Read the specific questions below prior to watching “A Teacher’s Mission”. Make notes while watching it without writing down too many details. After the film has finished, work out your own answers to these questions and then refine them by discussing them with other students.

Questions and assignments

You will watch the A Teacher’s Mission (17:51).

1. Why were chemical weapons first developed?
2. What important role did chemical weapons play in the First World War?
3. What are the benefits of developing chemical weapons?
4. Why is it important to teach chemistry? Why is it important to teach the history and ethics of chemistry – to tell a story?

Questions and assignments

5. What ‘battles’ did the scientist/chemist Fritz Haber face?
6. What role does the OPCW play?

After you have answered the questions above, individually, discuss your answers with two other classmates. How do your answers compare? How do your answers differ?



Figure 2.1.1-2
Stills from OPCW video “A Teacher’s Mission”



2. Be a Writer!

Introduction

This section uses self-study to acquaint you with the basics of the Chemical Weapons Convention (CWC). You use your writing skills to show what you have learned.

Task

As a reporter working for the local newspaper, Daily News, you have been asked by your editor to research and write an article for next week's Saturday Science section. In your article you should cover the following main points:

- The key historical milestones in the ratification of the CWC Geneva Protocol (1925) include the opening of the Convention for signature by the UN General Assembly (1993) and at present 193 countries are party to the convention.
- The main obligations of the Convention - prohibition of use and production of chemical weapons, destruction of all chemical weapons and the systematic on-site inspections of chemical and military facilities.
- The role that the OPCW plays in the verification of the Convention? What is the relationship between the UN and the OPCW? Define the importance of such an intergovernmental organisation.
- The role that the Chemical Weapons Convention Coalition plays.

Remember you want to keep the attention of your audience so you want to make the article as interesting and engaging as possible.

Beyond the assigned topics of study, you may wish to learn more on or even include in your article such topics, as the different classes of controlled substances, the world stockpile of chemical weapons, the destruction of this stockpile, and penalties for noncompliance.

You will be marked using the four categories provided on the next page.

Task Specifics

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Write a 300-400 word article.

- Use proper referencing throughout your article.
- You want to ensure that you include the terms that were listed in the glossary above.
- You will be marked using the following rubric:

Category	Level 4	Level 3	Level 2	Level 1
News article – Content	The news article is very well laid out, making use of several valuable pieces of scientific information. It contains up-to-date information regarding the topic. As well it contains many extensions, personal inferences and it relates to other chemistry, history or political topics.	The news article contains several extensions, including relationships to personal experience and other class topics. The article contains great scientific information.	The news article contains no new information. The article contains some scientific information. The article contains some errors.	The news article contains the bare minimums regarding scientific information. The article contained errors.
News Article – Originality	Article shows a large amount of original thought. Ideas are creative and inventive. Makes excellent use of interviews, resources and graphics.	Article shows some original thought. Work shows new ideas and insights. Makes good use of interviews, resources and graphics.	Uses other people's ideas (giving them credit), but there is little evidence of original thinking. Makes use of interviews, graphics, and resources.	Uses other people's ideas but does not give them credit. Interviews, resources, and graphics are used but distract from the articles' content.
Coherence and style	The article consistently uses appropriate language and shows deep insight through a natural flow of ideas and an effective conclusion.	The article achieves unity through a natural progression of ideas and the use of precise language.	The article uses only simple, generic language and has lapses in coherence.	The article does not have coherence or organization in writing.
International-Mindedness	The article is able to give several detailed examples of how the CWC influences people, countries and economies across the globe.	The article is able to give a couple of examples of how the CWC influences different people, countries and economies across the globe.	The article is able to give one example of how the CWC influences different people, countries and economies across the globe.	The article has difficulty describing how the CWC influences different people, countries and economies across the globe.

.....

Resources to get you started, but you should also find your own resources:

- **Fact Sheets**
 #1 The Chemical Weapons Convention and the OPCW — How They Came About
 #2 The Chemical Weapons Convention — A Synopsis of the Text
 #3 The Structure of the OPCW
- **Organisation for the Prohibition of Chemical Weapons (OPCW)**
<http://www.opcw.org/>
- **Chemical Weapons Convention (CWC)**
<http://www.opcw.org/chemical-weapons-convention/>
- **The Chemical Weapons Convention Fact Sheet**
<https://www.opcw.org/documents-reports/fact-sheets/>
- **CWC Coalition**
<http://www.cwccoalition.org/>
- **Obligations for the chemical and related industries**
http://www.cwc.gov/assets/pdf/outreach_industry_publications_cwc001.pdf
- **OPCW Collaboration with the UN**
<https://www.opcw.org/special-sections/syria/collaboration-with-the-un/>

3. The Zod debate

Introduction

This section intends to make you understand that many points of view can arise in a debate that may all be relevant in a decision making process.

Task

Take the stance of one stakeholder and debate why country Xanadu, who is currently no party to the Chemical Weapons Convention, should/should not ratify the Convention. You will be graded according to the categories provided below.

Category	Level 4	Level 3	Level 2	Level 1
Use of Facts/ Statistics	Major points were well supported with several relevant facts, statistics and/or examples.	Most points were supported with relevant facts, statistics and/or examples.	Some of the points were supported with facts, statistics and/or examples, but some of the points were irrelevant.	The points in the group's presentation were superficial and not supported with facts, statistics and/or examples.
Organization	All arguments were clearly tied to a point of view and organized in a logical fashion.	Most arguments were clearly tied to a point of view and organized in a logical fashion.	All arguments were clearly tied to a point of view but the organization was sometimes not clear or logical.	Arguments were not clearly tied to a point of view and the ideas were not easy to follow.
Presentation	The team clearly understood the topic in-depth and presented their point of view convincingly.	The team clearly understood the topic in-depth and presented their point of view with ease.	The team seemed to understand the main points of the topic and presented their point of view with ease.	The team did not show an adequate understanding of the topic nor had a clear point of view.
Presentation	Team consistently used gestures, eye contact, tone of voice and a level of enthusiasm in a way that kept the attention of the audience and made their point of view realistic.	Team usually used gestures, eye contact, tone of voice and a level of enthusiasm in a way that kept the attention of the audience and made their point of view realistic.	Team sometimes used gestures, eye contact, tone of voice and a level of enthusiasm in a way that kept the attention of the audience. Team did not take the task seriously	One or more members of the team had a presentation style that did not keep the attention of the audience or did not contribute to the team presentation.
Information	All information presented in their point of view was clear, accurate and thorough.	Most information presented in their point of view was clear, accurate and thorough.	Most information presented in their point of view was clear and accurate, but was not very thorough.	Information had presented was not clear or was irrelevant.
Clarifying Questions	Questions that were asked by the group displayed understanding and appreciation of the other points of view.	Questions that were asked by the group displayed understanding of the other points of view.	Questions that were asked were superficial and not based on the information presented.	Questions that were asked did not give any evidence that different points of view were considered.
Respect for team members and the stakeholders	All team members contributed ideas and valued the contributions of others. All statements and action during the debate were respectful.	Most team members contributed ideas and valued the contributions of others. All statements and action during the debate were respectful.	Most team members contributed to the teamwork. Members of the team were engaged in disrespectful behaviour during the debate.	Not all team members worked as a cohesive member of a team nor did they act respectfully to the other points of view during the debate.

Task Specifics

1. Your teacher will introduce the debate and explain the 7 categories you will be graded with.
2. Your teacher will give you the debate topic "To take the stance of one stakeholder and debate why country Xanadu, who is currently no party to the Chemical Weapons Convention, should/should not ratify the Convention."
3. You are to take the point of view of one of the stakeholders in this debate on whether Xanadu should or should not ratify the Convention. You are to provide your teacher with your top three points of view (from the list below) that you would like to be involved with. Based on these preferences, your teacher will then assign you to a different group. The points of view which will be represented in the debate include:
 - Owners of the chemical weapons company producing the chemical weapons
 - Members of Xanadu's military
 - Members of the UN peacekeeping organization
 - OPCW staff
 - Concerned citizens of Xanadu
 - Members of Doctors Without Borders
 - Chemistry students from Xanadu City High School
 - Victims of chemical weapons that were used in the recent fight between the Zods and Yods
4. You will have to work together with the group you have been assigned. You will have two class periods to research and plan your stance. You will have four minutes to present to the group. You will also be able to take part in the two minute question period that will occur at the end of each group's presentation. Remember that your score will be determined by a combination of self and teacher assessment using the 7 categories.
5. The order of presentations will be drawn from a hat. Each stakeholder will be given four uninterrupted minutes to present their point of view. At the end of each presentation, members of the other groups will have a total of two minutes to ask clarifying questions.
6. After each presentation and question period, each group will have one final minute to sum up their point of view.



3

Ethics and Science

“In his studies of the effects of poison gas, Haber noted that exposure to a low concentration of a poisonous gas for a long time often had the same effect (death) as exposure to a high concentration for a short time. He formulated a simple mathematical relationship between the gas concentration and the necessary exposure time. This relationship became known as Haber’s rule.”



- 1 Chemical warfare agents and toxic chemicals in conflicts
- 2 Ethical systems
- 3 Multiple use chemicals: A Dutch case study

Learning objectives

Chemical warfare agents and toxic chemicals in conflicts


After studying this section, you should be able to explain, using various examples, how ethical considerations are related to chemical warfare and the use of toxic chemicals in conflict.

Ethical systems

After studying this section, you should be familiar with three ethical systems/frameworks that people use when faced with ethical dilemmas, recognize that people's approach to ethical frameworks depends on their individual views and values, and use ethical frameworks to approach an ethical issue/dilemma.

A Dutch case study: supplying Syria with MEG

After preparing yourself at home, you should be able to engage in a discussion on the delivery of dual use chemicals to countries that have not ratified the Chemical Weapons Convention.



1. Chemical warfare agents and toxic chemicals in conflicts

Introduction

This lesson discusses a few examples of the use of chemical weapons and toxic chemicals in conflicts and introduces a broad variety of related ethical considerations.

World War I

In spite of The Hague Conventions of 1899 and 1907, which prohibited the use of asphyxiating and deleterious gases in war, chemical weapons were used on a massive scale during World War I. They were mostly used as slow-moving or static gas clouds to demoralize, injure and kill entrenched soldiers. The types of weapons employed ranged from riot control agents, e.g. tear gas and blister agents, to potential lethal agents, such as chlorine.

The first killing agent was employed by the German army in Belgium in 1915: chlorine. It is a powerful irritant that can inflict damage to the eyes, nose, throat and lungs. Chlorine causes death at high concentrations and prolonged exposure. German chemical companies had been producing chlorine as a by-product of their dye manufacturing. In cooperation with Fritz Haber, the German chemical industry began developing methods of discharging chlorine gas against enemy trenches. In 1918, the last year of the war, Fritz Haber received the Nobel Prize in Chemistry. This prize was founded by Alfred Nobel, a chemist, who specified in his will that his fortune had to be used to create a series of prizes for those who confer the “greatest benefit on mankind”. During and after World War I nations remained keen to develop new and more potent chemical warfare agents.

Questions and assignments

1. What did The Hague Conventions regulate and what aspect relates to chemical weapons? Use internet resources.
2. Why did Fritz Haber receive the Nobel Prize? Use internet resources.
3. Give your opinion whether it is justified that Fritz Haber received the Nobel Prize for chemistry. Support your opinion with arguments.
4. Can you think of reasons to perform research on chemical warfare agents and attempt to develop new and more potent ones?

The Italo-Abyssinian war

After World War I, a treaty called the 1925 Geneva Protocol prohibited the first use of chemical and biological weapons. It entered into force in 1928. A number of countries joined this treaty with reservations. Despite this treaty, chemical weapons were still used in a number of conflicts. For instance during the second Italo-Abyssinian war, Italy used sulfur mustard. Not only were armed forces targeted, but also the civilian population and the Red Cross. The overall military impact of the use of sulfur mustard during the war was low.

Questions and assignments

5. How did Italy justify the use of sulfur mustard, despite the fact that Italy and Abyssinia had signed the 1925 Geneva Protocol? Use internet sources.

Questions and assignments

6. Explain the reaction of France, Britain and the League of Nations (the predecessor of the UN) at the Italian invasion of Abyssinia and the use of sulfur mustard. Use internet sources.

Vietnam

A well-known example of the use of toxic chemicals is the use of herbicides contaminated with dioxins during the Vietnam War. Two of these mixtures of chemicals are known as Agent Orange and Agent Blue. Most of the spraying of these agents was intended to destroy food crops aiming to force the rural population to move to US-dominated cities, thus depriving the guerrillas of a support base. Soldiers were told that these crops had to be destroyed because they fed the Vietcong, while in fact nearly all the food was grown to support the rural population. The use of these herbicides indeed contributed to the fleeing of the rural population to escape famine and war.

The effects of herbicides like Agent Orange resulted in disruption of the ecological equilibrium. Many sprayed forest areas were invaded by pioneer species, making it likely that such forests would have difficulties regenerating. In addition, the diversity of animal species was also significantly reduced.

Dioxins from Agent Orange also settled into the soil and entered the food chain in contaminated areas. Exposed Vietnamese and US veterans have increased rates of cancer and many other health problems. In addition, those exposed to the agents have an increased risk of having children born with birth defects.

In Vietnam, US military personnel were persuaded that the sprayed chemicals were harmless. Only after returning to the US, veterans started to suspect that the exposure to those chemicals was responsible for a number of health problems. Some veterans filed lawsuits. Only in 1991, the US Congress made veterans eligible to receive compensation and treatment.

Also Vietnamese victims went to US courts. These courts, however, only considered the use of

herbicides, even though these had knowingly been contaminated with dioxins. Therefore, the agents were not considered chemical weapons and thus not a violation of international law. Furthermore, companies which produced the herbicides were not liable for the method of its use by the government. The herbicides were not intended to be used to poison humans and the US was allowed to use it as an herbicide.

Questions and assignments

7. What is your opinion about these court rulings? Discuss and summarize different points of view with fellow students.
8. Herbicides, pesticides and insecticides used in food production may also be dangerous to other living creatures and humans. Why does this complicate discussions on what to include and exclude in conventions on chemical warfare?
9. Research on such chemicals is generally intended to enhance their effectiveness and selectivity. It may also, by chance, lead to the discovery of potent warfare agents. What is your opinion on chemical research in this field?



Figure 3.1.1

UN weapons inspectors in Iran examining the use of chemical weapons by the Iraqi army during the Iran-Iraq War. (Wikipedia)

The Iran-Iraq War

A more recent international conflict in which chemical warfare was used is the Iran-Iraq war, during which the Iraqi regime at the time used chemical weapons on multiple occasions against both combatants and non-combatants. Many of these attacks had hundreds to thousand of casualties, mostly Iranian. A range of chemical weapons was used, including nerve agents and blister agents. Iraq also used mustard and nerve agents against Kurdish residents of Halabja, in Northern Iraq, in 1988. The world was shocked by the horrific pictures of chemical weapons victims at the time of the negotiations in Geneva on the Chemical Weapons Convention.

Chemical Weapons Use in Syria

Syria's civil war has seen several incidents of chemical weapon attacks. Although all chemical weapons declared by Syria were removed and destroyed outside of Syrian territory, doubts were raised as to whether Syria's chemical weapons declaration to the OPCW was complete and correct. As a result, in 2014, the OPCW Director-General established a team of experts from the Technical Secretariat, known as the Declaration Assessment Team (DAT), to resolve the identified gaps and inconsistencies in the Syrian declaration. Currently, the available information has not been sufficient enough for the Secretariat to confirm that the Syrian Arab Republic has submitted a declaration that can be considered accurate and complete. Also in 2014 the OPCW's Fact Finding Mission was formed to establish facts surrounding allegations of the use of toxic chemicals for hostile purposes in the Syrian Arab Republic. Since then, the FFM has confirmed with a high degree of confidence that chlorine, sulfur mustard, and sarin were used as weapons.

Terrorism

As knowledge becomes more easily accessible, e.g. through the internet, the risk of misuse of information on synthesis, handling and use of chemical warfare agents by terrorists or religious cults increases. For example, a Japanese cult carried out a sarin attack in the Tokyo subway killing 12 people and injuring many more in 1995.

More recently, the so-called "Islamic State" terror group was identified as the users of chemical weapons in Syria by the United Nations-OPCW Joint Investigative Mechanism (JIM).

Questions and assignments

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10. Inform yourself using internet resources on the political response of various countries to the initial claims of a chemical attack on the Kurds. Who was blamed for the attack? Compare this to the recent response to the use of chemical warfare in Syria. Do you notice similarities and differences?
11. What is your opinion on the idea that government agencies should be allowed to monitor everyone's use of the internet to search for potential terrorists informing themselves on chemical warfare synthesis?



2. Ethical systems

Introduction

This lesson familiarizes you with three ethical systems. You will apply these to the use of chemical warfare.

Three systems

When discussing an ethical issue it is very easy to jump to a conclusion and then try to justify it. A different approach would be to explore the issue first and analyze it in relation to different ethical systems. By doing this we are more likely to detach ourselves from our likes and dislikes and our personal interests and gain a better understanding of the issue and the motivation behind it. You will find that the following three ethical systems are of interest and can be applied in discussing chemical warfare: Consequentialism, Deontology (duty-based) and Virtue Theory.

Questions and assignments

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1. Prepare a short presentation with a group of students on Consequentialism, Deontology or Virtue Theory. Include a description, and the strengths and weaknesses of your system.
2. Discuss the use of chemical weapons (CW) in relation to your frameworks/systems, completing the table on the following page for your system. Make notes in the tables when other groups present their system.
3. Study one of the events of chemical warfare use mentioned in the previous section "Chemical warfare agents in conflicts", using internet sources in greater detail. Discuss your findings in relation to each one of the frameworks/systems.

Consequentialist System	
Why is it wrong to use CW?	Why can the use of CW be justified?

Duty-based system	
Why is it wrong to use CW?	Why can the use of CW be justified?

Virtue Theory	
Why is it wrong to use CW?	Why can the use of CW be justified?



3. Multiple use chemicals: A Dutch case study

Introduction

This section uses a case study to let you apply what you have learned on chemical weapons, the CWC and ethics.

Mono ethylene glycol (MEG)

Formally known as ethane-1,2-diol, ethylene glycol or MEG is an odourless and transparent liquid. It is used primarily in the manufacture of polyester fibers and polyethylene terephthalate resins (PET). Thus, most of it ends up as a fabric or a bottle. A small fraction is used for other applications, e.g. antifreeze. However, MEG is also used in the production of sulfur mustard and VX.

Delivery to Syria

In March 2011, a civil war in Syria started between the Ba'ath government headed by Bashar al-Assad and those wanting to overthrow it. In May 2013, the Dutch media reported that the Dutch branch of a company that transports bulk industrial chemicals had made large-scale deliveries of MEG to Syria since 2003.

Task

Prepare yourself for an assignment that will be explained and executed in class by studying relevant information on MEG and the delivery of MEG by a Dutch chemical company to Syria. You can use original media articles and files, such as:

- <http://www.nrc.nl/nieuws/2013/05/22/grondstof-gif-uit-nederland-naar-syrie-geimporteerd/>

Task

English summary: Syria has for years imported glycol from the Netherlands. This is a raw material for poison gas. The U.S. and Dutch authorities fear that the substance is used for the production of chemical weapons.

- <http://www.ad.nl/ad/nl/1012/Nederland/article/detail/3445329/2013/05/22/Nederland-leverde-Syri-euml-chemische-stof.dhtml>

English summary: The Netherlands has supplied Syria with a chemical from which chemical weapons can be made. It is used as a chemical coolant, but can also be used to make toxic sulfur mustard and VX.

Task

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You may also want to perform some research on MEG and the chemical company in question

- http://en.wikipedia.org/wiki/Ethylene_glycol
- <http://www.brenntag.nl>

Print out materials and make notes that prepare you for discussions on statements and questions such as

- Mono ethyl glycol is a useful chemical.
- If it is not forbidden by law, the Netherlands may in times of economic crisis deliver MEG to all countries that so request.
- Can the Netherlands provide MEG to countries that have not signed the CWC at times of internal conflict?



4 Gas masks and experiments with activated carbon

“The first use of poison gas on the Western Front was on 22 April 1915, by the Germans at Ypres, against Canadian and French colonial troops. The initial response was to equip troops with cotton mouth pads for protection. Soon afterwards the British added a long cloth which was used to tie chemical-soaked mouth pads into place, and which was called the Black Veil Respirator.”



- 1 Activated carbon and gas masks
- 2 Experiment Methylene Blue Value
- 3 Experiment Langmuir Adsorption Isotherm
- 4 Experiment Iodine Number
- 5 Research project Methylene Blue Breakthrough
- 6 Research project Pet Ether Breakthrough

Learning objectives

Activated carbon and gas masks

After studying this section, you should be able to explain the function of activated carbon in gas masks, describe how activated carbon works at the molecular level, define and explain the relevance of the methylene blue value, the iodine number, the Langmuir isotherm and breakthrough.

Experiment Methylene Blue Value

After executing this experiment, you should be able to determine the methylene blue value for a sample of activated carbon independently.

Experiment Langmuir Adsorption Isotherm

After executing this experiment, you should be able to draw an isotherm based on experimental data, determine the internal surface area for a sample of activated carbon independently, and explain the chemistry used in the acid-base titration.

Experiment Iodine Number

After executing this experiment, you should be able to determine the iodine number for a sample of activated carbon independently and explain the chemistry used in the redox titration.

1. Activated carbon and gas masks

Introduction

This introduction discusses gas masks and the function of activated carbon therein. It provides background knowledge for subsequent experiments or research projects.

Gas masks

Gas masks are devices that prevent the wearer from inhaling harmful fumes or dangerous airborne pollutants. This can be achieved by either supplying clean air from a cylinder directly to the mask or by a filter that cleans air from the surroundings drawn into the mask upon inhalation. In the latter case, activated carbon is generally used as the material that cleans the air. The activated carbon is provided in a canister carried in a separate container (figure 4.1.1). Modern gas masks are generally constructed such that the canister is screwed directly into the mask (figure 4.1.2).



.....
Figure 4.1.1
Drawing of a soldier with a gas mask and a separate container.

When the wearer inhales, air is drawn into the mask through the canister. Harmful molecules are adsorbed onto the carbonaceous surface area of the activated carbon.

How long a gas mask protects the wearer from inhaling the harmful fumes is dependent, amongst other things, on the concentration of the toxic gases in the air.



.....
Figure 4.1.2
Schematic of a gas mask with a canister that is screwed into the mask.

Activated Carbon

Activated carbon is a family of carbonaceous materials often used for filtering polluting chemicals from aqueous or gaseous streams. It is mostly produced from charcoal, which is a black residue obtained from animals or plants, when water and other volatile constituents are removed by heating the source material in the absence of oxygen. Treating charcoal in the appropriate way leaves a mostly carbon-based porous material (figure 4.1.3). Pore diameters may be as small as or even smaller than molecules. Consequently, this material has a large internal surface area.

Onto the internal surface, molecules and ions are trapped by adsorption. The bond between the material's internal surface and the trapped species can be either chemical (chemisorption) or physical (physisorption) in nature. Depending on the source of the carbonaceous material and the specific treatment, activated carbon is applied to liquid or gaseous in, e.g., automotive, food and beverage, air treatment, chemicals and catalyst industries. Activated carbon is supplied as pellets, granules or a powder, depending on the application.

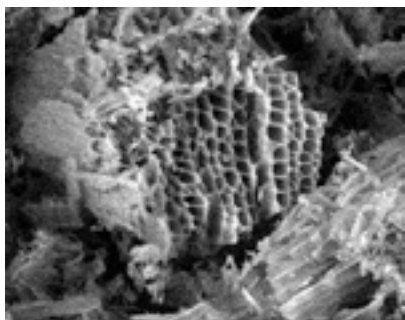


Figure 4.1.3
Scanning electron micrograph of active carbon.

Questions and assignments

1. How would the average pore size of a specific type of activated carbon and the size of polluting molecules that need to be removed from a liquid or gaseous stream be related?
2. Considering the ease with which air passes through different densities of materials, do you expect activated carbon for gas masks to be in the form of pellets, granules or powder?
3. The company Cabot Norit is one of the leading producers of activated carbon. Search their website to find out which types of activated carbon are used for gas masks. Can you find out how these types of activated carbon differ?
4. What other factors besides the concentration of the toxic fumes may determine how long a wearer of a gas mask is kept safe?

Methylene Blue Value

Methylene blue is a dye with chemical formula $C_{16}H_{18}N_3SCl$. The molecular structure is shown in figure 4.1.4. It is used, amongst others, as a redox indicator. The green powder yields a blue solution in water. Methylene blue is also used to test acti-

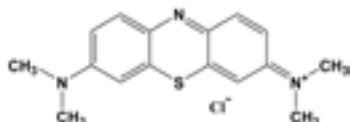


Figure 4.1.4
Molecular structure of methylene blue

vated carbon samples. In particular, the capacity of activated carbon to adsorb this dye is a measure of its quality. The Methylene Blue Value is defined as the amount of standard methylene blue solution (in mL) that can be decolorized by 0.1 g of dry activated carbon.

Questions and assignments

5. Build the methylene blue molecule using a molecular model kit.
6. How large do pore sizes need to be to allow methylene blue to be adsorbed to the internal surface of activated carbon? Base your answer on an estimate of the length and diameter of the methylene blue molecule.
7. Considering the ease with which air or liquids pass through different densities of materials. Do you expect methylene blue to be absorbed faster by granulated or pulverized activated carbon?
8. Search the Cabot Norit website to find out which types of activated carbon are used for adsorption of dyes.

The iodine number

A value commonly used to indicate the internal surface area of activated carbon is the iodine number, I_n . The name of this number refers to the chemical used to probe the internal surface area, namely iodine, I_2 . Iodine adsorbs rather strongly to the internal surface when a sample of carbon is immersed in an iodine solution. The iodine number equals the number of milligrams of iodine adsorbed from an aqueous solution by 1 g of activated carbon when the iodine concentration of the residual filtrate is 0.02 N.

Questions and assignments

9. What does 0.02 N mean?
10. Can you describe why it can be useful to use normality instead of molarity in electrochemical reactions?
11. What is $[I_2]$ expressed in molarity for a 0.02 N solution?

The Langmuir isotherm

Any surface that can adsorb molecules or ions can also become saturated with that adsorbate. At saturation, the maximum number of adsorbate molecules is reached per unit surface area. The fraction of the surface that is covered below saturation often follows a behavior described by Irvin Langmuir, who received the Noble Prize in 1932 “for his discoveries and investigations in surface chemistry”.



Figure 4.1.5
Irving Langmuir
(1881-1957)

The Langmuir isotherm, applied to a surface in contact with a liquid phase, states that the concentration C in a liquid phase is related to the fractional surface coverage, θ , at equilibrium by:

$$\theta = \frac{K_{ads} * C}{1 + K_{ads} * C}$$

Eq. 1

K_{ads} is the equilibrium constant for the adsorption and desorption of a solute molecule to a surface site.

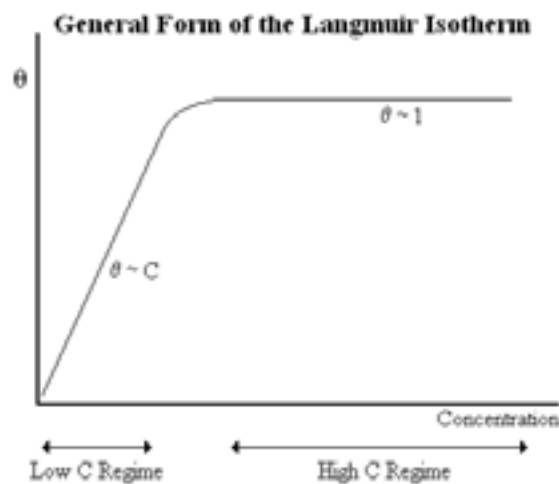
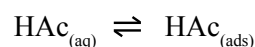
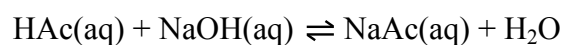


Figure 4.1.6
Relation between fractional surface coverage and concentration

To determine the surface area of a porous material such as activated carbon, we can use this relationship between concentration and surface coverage. In one of the following experiments, acetic acid adsorbs from a solution to the internal surface of pellets of *Norit RO 0.8 Extra*, a form of activated carbon used in real gas masks. After a while, equilibrium will be reached:



When the initial concentrations of HAc are varied and the concentrations at equilibrium with activated carbon are determined, the Langmuir isotherm can be constructed. For determining the concentration at equilibrium, activated carbon is first removed from the solution by filtration. The filtrate is then titrated with sodium hydroxide.



The amount of NaOH required to neutralize the solution indicates how much from the original amount of HAc was still present in the filtrate. The remainder was adsorbed to the surface of the activated carbon. When the amount that is adsorbed is referred to as Y (in moles), it can be shown that

$$\frac{Y}{C} = \frac{1}{Y_{max} K_{ads}} + \frac{C}{Y_{max}} \quad \text{Eq. 2}$$

Here, Y_{max} is the maximum amount of HAc that can be adsorbed to a sample of the activated carbon. It follows from the definition $\vartheta = Y/Y_{max}$. Plotting the data from the titrations in the appropriate way and some additional information allows one to calculate the surface area of this type of activated carbon with a unit of, for example, m^2/g .

Breakthrough

When an activated carbon filter becomes saturated, breakthrough will occur. The breakthrough point is defined as the maximum allowable concentration of a pollutant in the effluent of a gas or liquid stream that was filtered by, e.g., an activated carbon cartridge. It is often given in terms of ‘parts per million’ or ppm. For example, The National Institute for the Occupational Safety and Health (NIOSH) approves gas masks with carbon monoxide (CO) protection for escape purposes that have a breakthrough concentration of 35 ppm. For a polluted gas or liquid flowing through a packed bed, such as a column of activated carbon, the Mass Transfer Zone (MTZ) is the wave front moving through the column in which adsorption of the pollutant is still occurring. Behind the MTZ, the activated carbon is saturated and pollutants are not adsorbed anymore in that section of the column. In front of the zone, no adsorption has taken place yet. This situation is described schematically in figure 4.1.7 Upon continuation of the flow, the pollutant will at some point emerge from the packed bed. When its concentration in the effluent stream has reached the breakthrough point, use of this packed bed has become unsafe and the filter must be replaced. If this is not done, the concentration of the pollutant continues to rise up until the entire column is saturated and the effluent stream has the same concentration of the pollutant as the flow entering the filter. The filter has reached complete exhaustion.

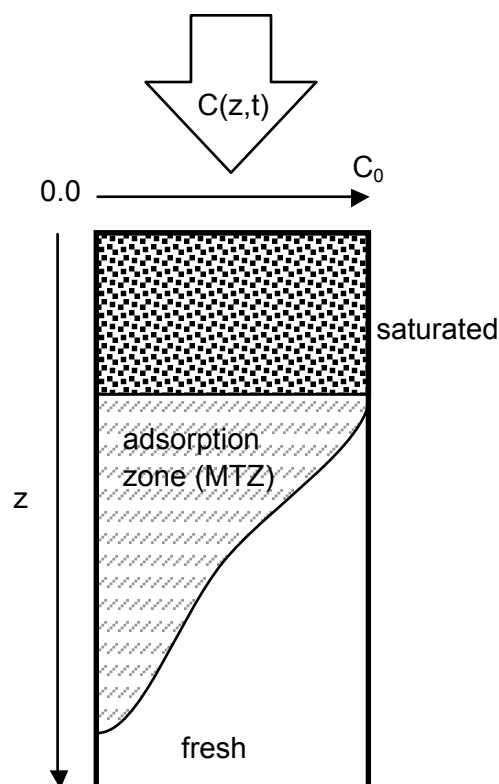


Figure 4.1.7

Schematic of the concentration profile of a pollutant in an activated carbon filter at some time t .

Questions and assignments

12. Describe in detail what is meant by all the parts and symbols in figure 4.1.7
13. Redraw the situation as shown in figure 4.1.7, but for $t=0$.
14. Redraw the situation as shown in figure 4.1.7, but for a time when the breakthrough point occurs. Assume the breakthrough point is $0.1C_0$.
15. Is it necessary to specify exact conditions of flow, temperature and such for tests that measure the breakthrough point of devices such as gas masks? Explain your answer.

2. Experiment Methylene Blue Value

Introduction

In this experiment the difference in adsorption of a dye by granulated and pulverized activated carbon is briefly and qualitatively investigated. The results are used to design a procedure for determining the methylene blue value.

Week 1 Qualitative assessment of methylene blue adsorption

Take two samples of 0.1 g of activated carbon. Pulverize one sample in a mortar. Put both samples in separate Erlenmeyer flasks (>100 mL). Add 25 mL of standard methylene blue solution (figure 4.2.1) to both and swirl the solution.

Questions and assignments

1. Is your observation in line with your prediction from question 7 in the section 4.1? If not, what may be causing the discrepancy?
2. Design for next week two experimental procedures that determine the methylene blue value accurately for your type of activated carbon. You may want to perform a couple of quick tests now.

Week 2 Determining the methylene blue value

Discuss with your teacher the methods you have chosen and determine the methylene blue value for your activated carbon sample. Compare the results of your two tests and discuss which one you believe to be more accurate. Also compare your results to those of other students.



Figure 4.2.1

Standard methylene blue solution

3. Experiment Langmuir Adsorption Isotherm

Introduction

This experiment uses a reverse acid-base titration to determine how much of a weak acid was adsorbed to the internal surface area of a known amount of active carbon. From the reverse titration the active surface area per unit weight is determined.

Determining the surface area of Norit R 0.8 Extra

We determine the surface area of a type of carbon used in real gas masks, *Norit RO 0.8 Extra*, through (partial) saturating the surface by acetic acid. To a fixed weight of pellets various amounts of acetic acid are added in separate flasks. After adsorption onto the surface has stopped with each concentration of acetic acid, the remaining amount of acetic acid in solution is quantified by reverse titration using sodium hydroxide.

Week 1 Preparation

Number six Erlenmeyer flasks from 1 through 6. Add to every flask approximately 0.38 grams of *Norit RO 0.8 Extra*. Weigh the amounts accurately and write down the exact weight in every flask.

Flask						
Mass Norit						

Prepare the following 25 mL solutions from approx. 0.4 M HAc and add then to the six numbered flasks. Leave the flasks for a week, but swirl them (at least daily) vigorously. Your teacher will provide you with the exact concentration of the HAc solution so you can calculate the exact number of moles of HAc added to every sample of Norit. The exact concentration is:

[HAc] = M

Flask						
Acetic acid	25 mL	18.75 mL	12.5 mL	6.25 mL	2.5 mL	1.25 mL
Water	0 mL	6.25 mL	12.5 mL	18.75 mL	22.5 mL	23.75 mL

Week 2 Measurements

Take aliquots from the six flasks according to the table given below and titrate them with standardized NaOH solution. Your teacher will provide you with the exact concentration of this NaOH solution. Keep track of the required amount of NaOH solution to reach equivalence in the table below.

$$[\text{NaOH}] = \dots\dots\dots \text{M}$$

Flask						
Aliquot	3.0 mL	3.0 mL	3.0 mL	7.5 mL	10.0 mL	20.0 mL
mL NaOH						

Questions and assignments

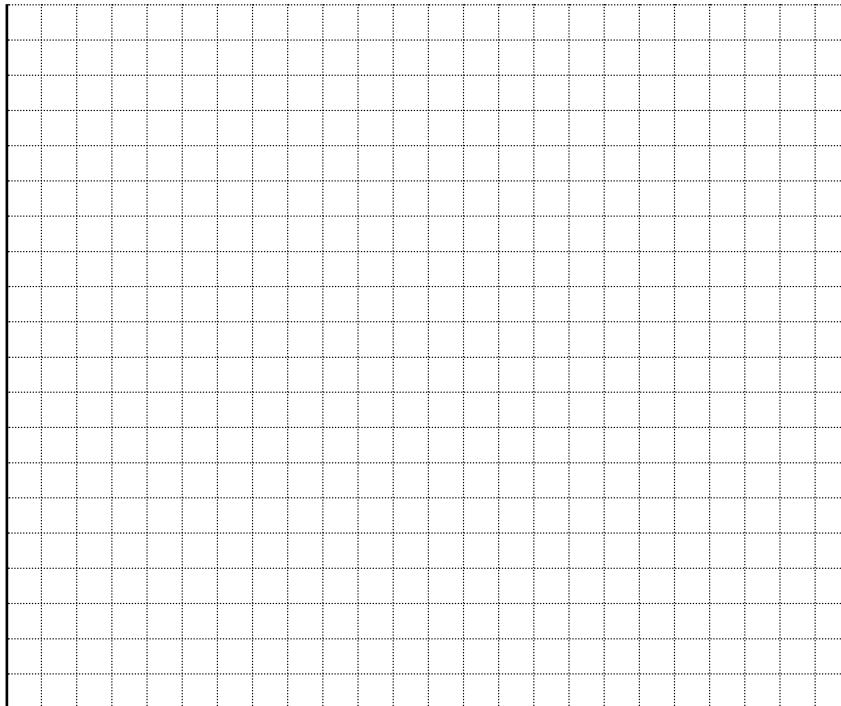
1. Perform the required calculations to fill in the table on the next page.
2. Plot your isotherm; Y vs. C . A graph is provided on the following page.
3. Plot the isotherm in the form of Equation 2 and determine the Langmuir parameters Y_{max} and K_{ads} .
4. Assume the surface area occupied by one acetic acid molecule on the surface of the charcoal is 21 \AA^2 . Determine the surface area of 1 g of charcoal. Express your result in m^2/g . Is your number reasonable? Compare your result with the one supplied by your teacher for this product.

Extra questions and assignments

5. Prove that equation 2 follows from equation 1 and the provided definitions of variables.
6. Estimate the error in your experiments and include them in your isotherm. How accurate is your determination of the Langmuir parameters Y_{max} and K_{ads} ?

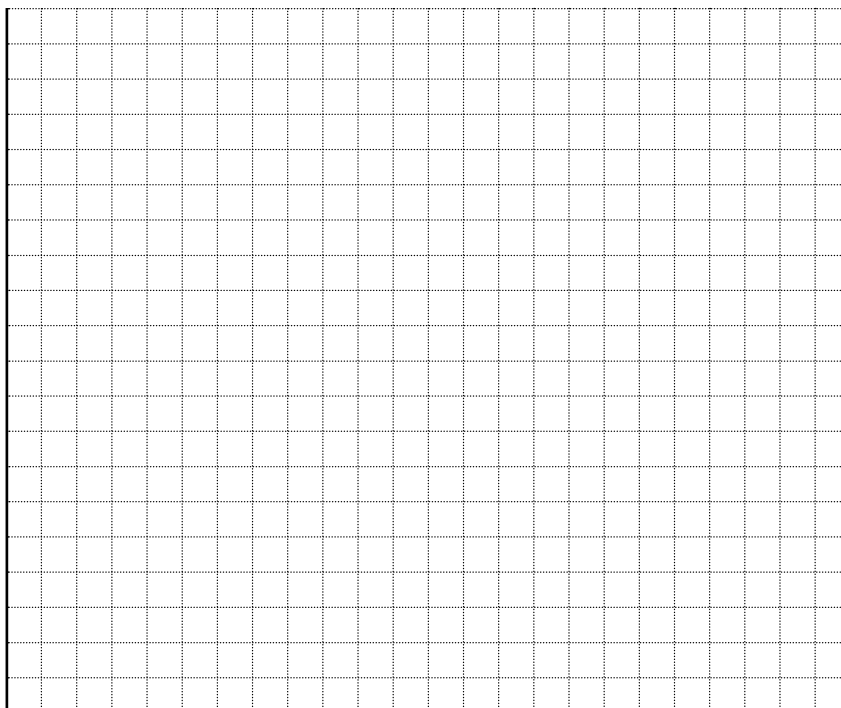
<p style="text-align: center;">flask</p> <p>[HAc] at start</p> <p>Initial moles HAc in 25 mL</p> <p>Initial moles HAc in aliquot</p>
<p>Added moles NaOH for equivalence</p>
<p>Remaining HAc in aliquot</p>
<p>Remaining HAc in 25 mL</p>
<p>Adsorbed HAc in 25 mL (Y)</p>
<p>[HAc] at equi- librium (C)</p>
<p style="text-align: center;">C/Y</p>

Y (mole)



C (mole/L)

C/Y (L^{-1})



C (mole/L)



4. Experiment Iodine Number

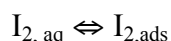
Introduction

This experiment uses a redox titration to determine how much iodine is adsorbed to the internal surface area of known amounts of active carbon. From the titration the iodine number is determined and compared to the number supplied by an OPCW approved laboratory.

The exact amount of iodine removed from the solution by adsorption to carbon is determined by iodometric titration. We measure the iodine normality of the filtrate using a redox reaction with thiosulphate, $S_2O_3^{2-}$, and a starch solution as indicator. The starch solution is added when the yellow colour of the solution starts to disappear.

Determining the iodine number

We determine the iodine number for a type of carbon used in real gas masks, *Norit RO 0.8 Extra*, using the CEFIC standard test. The determination relies on an equilibrium established between dissolved iodine, I_2 , at a concentration of 0.02 N and iodine adsorbed to the internal surface of a known amount of activated carbon.



The initial iodine solution must be of higher concentration as some of it will adsorb when the solution is brought into contact with the known amount of activated carbon. It is unlikely that the solution will be exactly 0.02 N after equilibrium has been established. However, minor deviations can afterward be accounted for using a correction term in the calculations. For your experiment, the required initial concentration of iodine is chosen such that for the activity and mass of *Norit RO 0.8 Extra* the concentration ends up near 0.02 N. The experiment starts with a known amount of carbon. It has been dried to remove all water and is then rewetted using an acidic solution. The sample is immersed into a fixed volume of an iodine solution of known normality. After a short time, the carbon is removed by filtration.

Questions and assignments

1. What are the chemical reactions of interest for an iodine-thiosulfate titration? Use the internet, your chemistry textbook and/or a redox table.
2. In the standard iodine solution, I_2 is present in combination with iodide, I^- . Why is I^- present in the iodine solution?
3. What causes the yellow colour of the solution prior to the equivalence point?
4. Why is a starch solution added?
5. Why does the blue colour disappear at the equivalence point?

¹CEFIC, Test methods for activated carbon, April 1986

Preparation and titration

- I Weigh 0.800 – 1.000 g of dried activated carbon and transfer the weighed sample to a dry glass stoppered 250 mL Erlenmeyer flask.
- II Pipette 10 mL of 5% HCl into the flask and swirl until the activated carbon is wetted.
- III Place the flask on a hot-plate in a fume hood, bring the contents to a boil, and allow it to boil for exactly 30 seconds.
- IV Allow the flask and contents to cool to room temperature. Add by pipette 100 mL of 0.10 N iodine solutions.
- V Stopper the flask immediately and shake it vigorously for 30 seconds. Filter by gravity through a filter paper immediately after the 30 seconds shaking period.
- VI Discard the initial 20-30 mL of filtrate and collect the remainder in a clean beaker.
- VII Stir the filtrate in the beaker with a glass rod and pipette 50 mL into a 250 mL Erlenmeyer flask.
- VIII Titrate the 50 mL sample with 0.10 N sodium thiosulphate solution until the yellow colour has almost disappeared. Add ~1 mL of starch solution and continue titration until the blue indicator colour just disappears. Record the volume of sodium thiosulphate used.

Calculations

Calculate the iodine number, I_n , of the carbon using the equation:

$$I_n = \frac{X}{M} A$$

• • •
Eq. 1

where

X = mass of I_2 adsorbed by activated carbon in mg
M = mass of activated carbon in g
A = correction factor, depending on the residual normality, N_r , of the filtrate.

It can be shown that

$$X = 12.693 N_1 - 279.246 N_2 V$$

• • •
Eq. 2

wherein

N_1 = normality of iodine solution

N_2 = normality of sodium thiosulphate solution

V = volume of sodium thiosulphate solution in mL.

The factor A may be applied if the residual filtrate normality, N_r , is between 0.008 and 0.0334 N.

$$N_r = N_2 \frac{V}{50}$$

• • •
Eq. 3

A is given in the table on the next page and may vary from 1.1625 to 0.925. If N_r is outside the range of 0.008 to 0.0334 N, the determination has to be repeated either with a larger amount of activated carbon if $N_r > 0.0334$ or a smaller amount if $N_r < 0.008$.

Extra questions and assignments

.....

6. Can you derive the equation that yields the iodine number?
7. Can you derive the equation for the residual filtrate normality?
8. Can you explain the rationale behind the correction term?
9. Why is starch solution added only when the titration approaches the equivalence point?

CORRECTION FACTOR FOR IODINE ADSORPTION

Residual filtrate normality	0	0,0001	0,0002	0,0003	0,0004	0,0005	0,0006	0,0007	0,0008	0,0009
0,0080	1,1625	1,1613	1,1600	1,1575	1,1550	1,1533	1,1513	1,1500	1,1475	1,1463
0,0090	1,1438	1,1425	1,1400	1,1375	1,1363	1,1350	1,1325	0,1300	1,1280	1,1275
0,0100	1,1250	1,1238	1,1225	1,1213	1,1200	1,1175	1,1163	1,1150	1,1138	1,1113
0,0110	1,1100	1,1088	1,1075	1,1063	1,1038	1,0025	1,1000	1,0988	1,0975	1,0963
0,0120	1,0950	1,0938	1,0925	1,0900	1,0888	1,0875	1,0863	1,0850	1,0838	1,0825
0,0130	1,0800	1,0788	1,0775	1,0763	1,0750	1,0738	1,0725	1,0713	1,0700	1,0688
0,0140	1,0675	1,0663	1,0650	1,0625	1,0613	1,0600	1,0588	1,0575	1,0563	1,0550
0,0150	1,0538	1,0525	1,0513	1,0500	1,0488	1,0475	1,0463	1,0450	1,0438	1,0425
0,0160	1,0413	1,0400	1,0388	1,0375	1,0375	1,0363	1,0350	1,0338	1,0325	1,0313
0,0170	1,0300	1,0288	1,0275	1,0263	1,0250	1,0245	1,0238	1,0225	1,0213	1,0200
0,0180	1,0200	1,0188	1,0175	1,0163	1,0150	1,0144	1,0138	1,0125	1,0125	1,0113
0,0190	1,0100	1,0088	1,0075	1,0075	1,0063	1,0050	1,0050	1,0038	1,0025	1,0025
0,0200	1,0013	1,0000	1,0000	0,9988	0,9975	0,9975	0,9963	0,9950	0,9950	0,9938
0,0210	0,9938	0,9925	0,9925	0,9913	0,9900	0,9900	0,9888	0,9875	0,9875	0,9863
0,0220	0,9863	0,9850	0,9850	0,9838	0,9825	0,9825	0,9813	0,9813	0,9800	0,9788
0,0230	0,9788	0,9775	0,9775	0,9763	0,9763	0,9750	0,9750	0,9738	0,9738	0,9725
0,0240	0,9725	0,9708	0,9700	0,9700	0,9688	0,9688	0,9675	0,9675	0,9663	0,9663
0,0250	0,9650	0,9650	0,9638	0,9638	0,9625	0,9625	0,9613	0,9613	0,9600	0,9600
0,0260	0,9600	0,9588	0,9588	0,9575	0,9575	0,9563	0,9563	0,9550	0,9550	0,9538
0,0270	0,9538	0,9525	0,9525	0,9519	0,9513	0,9513	0,9506	0,9500	0,9500	0,9488
0,0280	0,9488	0,9475	0,9475	0,9463	0,9463	0,9463	0,9450	0,9450	0,9438	0,9438
0,0290	0,9425	0,9425	0,9425	0,9413	0,9413	0,9400	0,9400	0,9394	0,9388	0,9388
0,0300	0,9375	0,9375	0,9375	0,9363	0,9363	0,9363	0,9363	0,9350	0,9350	0,9346
0,0310	0,9333	0,9333	0,9325	0,9325	0,9325	0,9319	0,9313	0,9313	0,9300	0,9300
0,0320	0,9300	0,9294	0,9288	0,9288	0,9280	0,9275	0,9275	0,9275	0,9270	0,9270
0,0330	0,9263	0,9263	0,9257	0,9250	0,9250					

5. Research project Methylene Blue Breakthrough Point

Introduction

In this suggestion for a research project, students investigate the dependencies of the breakthrough point of a column of activated carbon for dyes.

A simple construction to determine breakthrough points

To examine dependencies for breakthrough, one may construct a simple apparatus as shown in figure 4.9. A syringe is attached via a flexible hose to the bottom of a plastic burette. At the bottom of the burette a bit of glass wool prevents the column of activated carbon pellets from entering into the hose. On the open side of the burette, a solution of e.g. methylene blue may be added. One may drop a fixed amount of methylene blue solution onto the column, e.g. 1 mL, and then continuously add water while also pulling the solution through the column using the syringe as a suction pump. One may also continuously add a methylene blue solution. Breakthrough can qualitatively be determined by watching the colour of the effluent.

Considering how the standard methylene blue solution is defined and determined, namely through the absorption strength of the solution, you may want to make your measurements more reproducible and quantitative. For example, you could insert a cuvette into the eluent stream and determine the absorption at a fixed wavelength to follow the exact concentration profile of the dye in the effluent stream while solution is being pulled through the column. You may obviously also choose to use a different analytical technique to measure concentration.



• • • • •

Figure 4.5.1

Simple apparatus built to measure the breakthrough point

Ideas for research

- Investigate whether/how the shape of the column (length vs diameter) for a fixed amount of activated carbon influence the breakthrough point.
- Investigate how the breakthrough point depends on the flow rate for a given column shape.
- Investigate how the breakthrough point depends on the initial concentration of methylene blue.
- Investigate how the breakthrough point depends on a dye and try to relate it to molecular properties of the dyes.
- Investigate whether/how temperature of the eluate, solvent, average particle size of the activated carbon, or particle size distribution influence the breakthrough point.

You may also ask yourself whether there exists an internationally accepted, standardized test to determine the break through point. If so, how does it work and can you use this method (or a simplified version) to test some samples of activated carbon? If not, develop a standardized test.

6. Research project Pet Ether Breakthrough Point

Introduction

In this suggestion for a research project, students investigate how the different components of pet ether are absorbed by activated carbon. Research may encompass relations between molecular size, equilibrium, flow rates, pore size distributions.

Quantitative research on adsorption

The time it takes to saturate an activated charcoal filter depends on multiple variables. An obvious and important one is the concentration of the gas flowing into the filter. The flow rate, the size, shape and diameter of the filter, the type of activated carbon and its characteristics (e.g. particle size, pore size) are also important.

To investigate such dependencies, pet ether (at room temperature) can be used as the pollutant. Pet ether is a liquid substance that consists of different volatile hydrocarbons. Pet ether 40-60 consists of hydrocarbons that have a boiling point between 40 – 60 °C. Thus the mixture consists of molecules that differ in size and shape. The difference in size and shape may be expected to affect their adsorption behaviour and diffusion through the pores in the activated carbon. Thus the concentration dependence in the effluent may be different for the various molecules making up Pet ether 40-60.

To test this hypothesis, one may construct an apparatus as shown in figure 4.6.1. A small amount of pet ether is put into a round bottom flask. Equilibrium of liquid and gas exists in the head space of the flask. Using a simple aquarium pump, air is subsequently blown through the head space and guided to an activated carbon filter. At different times, samples of the effluent are taken with a syringe from the exit of the filter and analysed with a simple room temperature GC.

The peaks that are gathered from GC analysis can be used to determine the level of adsorption. The area underneath the GC peaks is a relative but quantitative measure of the amount of gas breaking through.

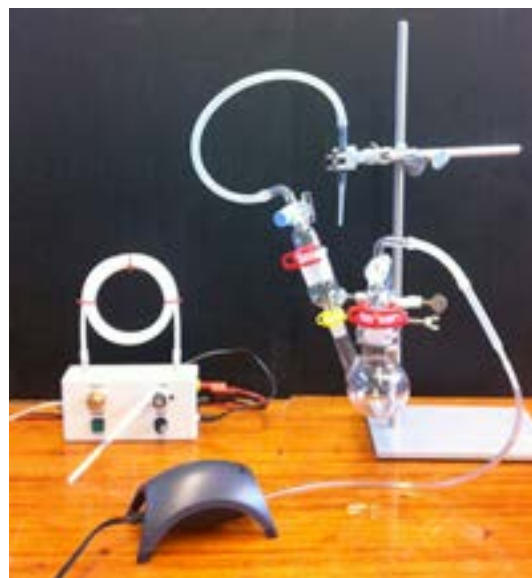


Figure 4.6.1

Apparatus to analyse the adsorption of pet ether by a column of activated carbon by GC

Ideas for research

- Investigate the absorption and saturation behaviour for the different molecules making up pet ether. Does it depend on the particular type of activated carbon used in your experiments?
- Can you relate breakthrough and saturation quantitatively to the temperature and vapour pressure of the pet ether?



Chemistry in Conflict

This module is intended as a thematic project for the IB standard level Chemistry curriculum or any comparable national chemistry program. It was produced by collaboration between the Organisation for Prohibition of Chemical Weapons (OPCW), Leiden University, the City Council of The Hague, the International School The Hague, the Johan de Witt scholengroep, the Vrijzinnig-Christelijk Lyceum, and the IB Africa, Europe and Middle East Global Centre in The Hague, the Netherlands. The OPCW, the City Council of The Hague and Leiden University funded the production of this workbook for students and supplemental educational materials.

Authors

Fiona Clark, IB Africa, Europe and Middle East Global Centre, The Hague

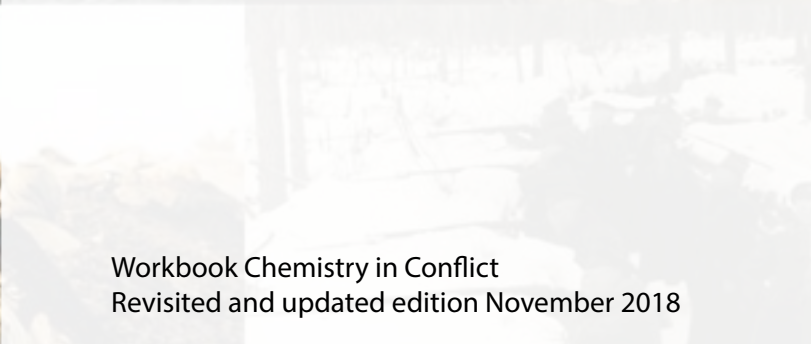
Hanspeter van Daalen, Johan de Witt scholengroep
Ioana Howland, the International School of The Hague
Henk de Vries, Vrijzinnig-Christelijk Lyceum
Ludo Juurlink, Leiden University, Leiden

Editing

Ludo Juurlink

Layout and design

Eva van Bemmelen



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