Science For Diplomats

Starring the OPCW Laboratory

Illuminating Chemical Reactivity

Tuesday 9 July 2019
13:30 – 14:45
Doms Room

Light lunch available at 13:00

...an event guaranteed to brighten up your day!
Illuminating Chemical Reactivity

*an event guaranteed to brighten up your day*

**Science for Diplomats at EC-91**

*The Hague, 9 July 2019*

Starring

Dr Marc-Michael Blum, Head OPCW Laboratory

With supporting cast

Mr Cheng Tang (SAB Chair), Mr Lucas Benderitter (OSP), Mr Peter Brud (OSP), Dr Jonathan E. Forman (Science Policy Adviser and SAB Secretary), Ms Giovanna Pontes (OSP), Ms Ayah Wafi (OSP) and special guest Ms Andrea Dymytrova
Let us Know You are Here!

Periodic Table of States Parties to the Chemical Weapons Convention
In Honour of the International Year of the Periodic Table of Chemical Elements 2019

<table>
<thead>
<tr>
<th>Country Element</th>
<th>Date of Deposit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Order of Entry into Force</td>
<td>Country Symbol</td>
</tr>
</tbody>
</table>

LEGEND
- Western Europe and Other States (WEOG)
- Eastern Europe
- Africa
- Latin America and the Caribbean (GR/LAC)
- Asia
Let us Know You are Here!

Collect your “element” from the Periodic Table of States Parties outside the Ooms Room.
Scheduled Chemicals under the Chemical Weapons Convention (CWC)

**Schedule 1**

Guidelines for Schedule 1
The following criteria shall be taken into account in considering whether a toxic chemical or precursor should be included in Schedule 1:
(a) It has been developed, produced, stockpiled or used as a chemical weapon as defined in Article I.
(b) It poses otherwise a high risk to the object and purpose of this Convention because of its high potential for use in activities prohibited under this Convention because one or more of the following conditions are met:
(i) It possesses a chemical structure closely related to that of other toxic chemicals listed in Schedule 1, and has, or can be expected to have, comparable properties;
(ii) It possesses such lethal or incapacitating toxicity as well as other properties that would enable it to be used as a chemical weapon;
(iii) It may be used as a precursor in the final single technological stage of production of a toxic chemical listed in Schedule 1, regardless of whether this stage takes place in facilities, munitions or elsewhere;
(c) It has little or no use for purposes not prohibited under this Convention.

Schedule 1 Part A. Toxic Chemicals

Schedule 1 Part B. Precursors

**Schedule 2**

Guidelines for Schedule 2
The following criteria shall be taken into account in considering whether a toxic chemical not listed in Schedule 2, or a precursor to a chemical listed in Schedule 2, or a chemical listed in Schedule 2, part A should be included in Schedule 2:
(a) It poses a significant risk to the object and purpose of this Convention because of its high potential for use in activities prohibited under this Convention because one or more of the following conditions are met:
(i) It possesses such lethal or incapacitating toxicity as well as other properties that would enable it to be used as a chemical weapon;
(ii) It may be used as a precursor in one of the chemical reactions in the final stage of production of a chemical listed in Schedule 2 or Schedule 3, part A;
(c) It poses a significant risk to the object and purpose of this Convention by virtue of its importance in the production of a chemical listed in Schedule 2 or Schedule 3, part A;
(d) It is not produced in large commercial quantities for purposes not prohibited under this Convention.

Schedule 2 Part A. Toxic Chemicals

Schedule 2 Part B. Precursors

**Schedule 3**

Guidelines for Schedule 3
The following criteria shall be taken into account in considering whether a toxic chemical or precursor not listed in other Schedules, should be included in Schedule 3:
(a) It has been developed, stockpiled or used as a chemical weapon;
(b) It poses otherwise a high risk to the object and purpose of this Convention because of its high potential for use in activities prohibited under this Convention because one or more of the following conditions are met:
(i) It possesses such lethal or incapacitating toxicity as well as other properties that would enable it to be used as a chemical weapon;
(ii) It may be used as a precursor in the final single technological stage of production of a toxic chemical not listed in Schedule 3, part B.
(c) It may be produced in large commercial quantities for purposes not prohibited under this Convention.

**Organisation for the Prohibition of Chemical Weapons**
Working Together for a World Free of Chemical Weapons

Published Year

Schedules 1, 2, and 3 can have scientifically and economically important uses. This chart captures the number of yearly scientific publications that refer to them.
Scheduled Chemicals under the Chemical Weapons Convention (CWC)

Guidelines for Schedule 1
The following criteria shall be taken into account in considering whether a chemical or precursor should be included in Schedule 1:
(a) It has been developed, produced, stockpiled or used as defined in Article II;
(b) It poses otherwise a high risk to the object and purpose of this Convention because one or more of the following conditions is met:
(i) It possesses a chemical structure closely related to chemicals listed in Schedule 1, and has, or can be easily modified to have, comparable properties;
(ii) It possesses such lethal or incapacitating toxic properties that would enable it to be used as a chemical weapon;
(iii) It may be used as a precursor in the production of a toxic chemical listed in Schedule 1, or a precursor takes place in favor of a precursor.

“Connecting Atoms!”

“Shorthand” structures

3D Models

Sarin

Nitrogen mustard (HN-3)

Organisation for the Prohibition of Chemical Weapons
Working Together for a World Free of Chemical Weapons

Translation

Sarin

Nitrogen mustard (HN-3)
Scheduled Chemicals under the Chemical Weapons Convention (CWC)

ORGANISATION FOR THE PROHIBITION OF CHEMICAL WEAPONS

THE "SCIENCE FOR DIPLOMATS" ANNEX ON CHEMICALS
A user friendly and scientifically annotated version of the Chemical Weapons Convention Annex on Chemicals

Nitrogen mustard:

HN2: Biocides, 2-chloroethyl ether (HN2)
(RPAC Name: 2-chloro N,N-dimethylaminoethane)

Scientific Advisory Board recommendation: including corresponding protonated salts.

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Scientific Advisory Board recommendation: including corresponding protonated salts.

Nitrogen mustard (HN-3)

Sarin

Rein

Rein is a protein composed of toxic (A-chain) and cell-negating (B-chain) subunits, illustrated in red (A-chain) and blue (B-chain) in the structure on the left. The right structure is an interactive ribbon model of the virus particles.

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Note: The diagrams and images in the document are scientifically accurate and should be used for educational and informational purposes.
E. GLOSSARY

Acetylcholinesterase (AChE)

Acetylcholinesterase (AChE) is an enzyme [see also] responsible for breaking down the neurotransmitter acetylcholine (ACH) into choline and acetate. AChE is inhibited by the action of nerve agents [see also].

Crystal structure of the dimer of acetylcholinesterase (AChE) in complex with Xeonon (Protein Data Bank 3M21B). [1]

Break down of ACH to acetate and choline by AChE:

\[
\text{Acetylcholine (ACH)} \quad \xrightarrow{\text{AChE}} \quad \text{Acetate} + \text{Choline}
\]


Glossary Version 1.0 – 27 May 2019
Scheduled Chemicals under the Chemical Weapons Convention (CWC)

E. GLOSSARY

Acetylcholinesterase (AChE) is an enzyme responsible for the catalysis of acetylcholine (ACh) in cholinergic synapses and is a key target for nerve agents (see also).

Crystal structure of the dimer of acetylcholinesterase (AChE) in complex with ethylmaleimide (EM). Breakdown of ACh to acetate and choline by AChE:

Acetylcholine (ACh) → Acetate

Acetylcholinesterase (AChE)

ORGANIC CHEMICAL FUNCTIONAL GROUPS

Chemicals are defined by the functional groups they contain within their molecular structures. A functional group is a particular group of atoms in a molecule that defines reactivity, and influences chemical properties and behavior. Complex molecules can contain multiple types of functional groups. This table provides descriptions of many of the types of functional groups found in organic chemistry, it is not intended to be comprehensive.

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Nomenclature</th>
<th>General Structure</th>
<th>Substructures</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>[substructure: -acetic acid]</td>
<td>R₂C(OH)₂⁻</td>
<td>R⁻ = hydrogen atoms or alkyl group, R²⁻ = alkyl group</td>
<td>Acetates are chemical structures containing a carbon atom connected to two oxygen atoms (which serve as bridges to alkyl groups), and to either two hydrogen atoms or to a hydrogen atom and an alkyl group. Acid anhydrides are chemical structures in which an oxygen atom serves as a bridge between two carbon groups in carbon connected to an oxygen atom through a double bond, each of which is further connected to a hydrogen atom or alkyl group.</td>
</tr>
</tbody>
</table>
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Illuminating Chemical Reactivity

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The Elephant in the Room...

Molecules don't actually look like this...

Colourless liquids...

How do you know which one is which?
The Elephant in the Room...

shine IR light at the liquid (IR Spectrum)

colourless liquids...
How do you know which one is which?
The Elephant in the Room...

shine IR light at the liquid (IR Spectrum)

“weigh” the molecules (mass spectrum)
The Elephant in the Room...

“weigh” the molecules (mass spectrum)
The Elephant in the Room...
Degradation and Environmental Fate of Sulfur Mustard

Darcy van Eerten

Environmental fate in:
- Cement & Soil
- Sea Water
- Synthesis Routes
- Toxicology
- Reported Impurities
- Decontamination
- Scheduled Chemicals

Metabolic pathway for TDS utilization by bacteria isolated from the Baltic Sea

Present in ton containers

Levinstein mustards

Formed in containers and munitions
Under “real-world” conditions, we are surrounded by chemicals and chemistry!
“mixture of chemicals” (including “reaction products”)

“delivery device”
Today’s Briefing:

What does chemistry really look like?
(and how does it actually relate to the world you see and feel?)
What you see may not look exactly like the chemists Explanation! (“language” describes things, but objects do not always look like words!)
What you see may not look exactly like the chemists’ Explanation! (“language” describes things, but objects do not always look like words!)

Today’s Briefing:
What does chemistry really look like?
(and how does it actually relate to the world you see and feel?)
Before we Begin...

Science for Diplomats 2014
Dr. Blum presented to 5 delegations
Before we Begin...
Before we Begin...

Science for Diplomats 2017
Standing room only!
Before we Begin...

Sci...

Dr Blum

OPCW
Before we Begin…

THE BOOK OF
TOTALLY
IRRESPONSIBLE
SCIENCE

FEATURING
★ How to Grow a
Frankenstein Hand!
★ How to Turn Milk
into Stone!
★ How to Make a
Potato Gun!

PLUS
★ Cola Geysers!
★ Burning Ice!
★ DIY Blubber!
★ Homemade
Lightning!
★ And More…

64 DARING
EXPERIMENTS

Have a Blast!
Chemical reactivity

or why
Chemistry is basically the same as Politics

Marc-Michael Blum, Ph.D.
Head, OPCW Laboratory
Politics is more difficult than physics

Albert Einstein
Chemistry is basically the same as politics

Marc-Michael Blum
Head, OPCW Laboratory

(somehow implying that Chemistry is more difficult than Physics)
Chemistry:

Chemistry is the study of matter, its properties, *how and why substances combine or separate to form other substances*, and how substances interact with energy.
The Chemical Weapons Convention is quite focused on chemicals themselves:

• Declarations based on production, consumption and/or transfers of chemicals
• Annex on Chemicals of the CWC listing those chemicals for which special verification measures are in place
• Sampling & Analysis is conducted to confirm the presence or absence of a CWC relevant chemical
• ...
But we also deal with REACTIONS of chemicals:

- We discuss the meaning of “production by synthesis”
- We discuss the productions of DOCs via biomediated processes
- Sampling & Analysis is looking for precursors and degradation products of chemical agents in IAUs
- Reaction products of agents with biomolecules ("adducts") are valuable biomarkers and important in biomedical verification
- ...
So why do chemicals react with each other?
What are the laws that determine in what direction a chemical reaction is proceeding?

KEEP CALM AND FOLLOW THE LAWS OF THERMODYNAMICS
The **first law** of thermodynamics is a version of the law of conservation of energy, adapted for thermodynamic systems. The law of conservation of energy states that the total energy of an isolated system is constant; energy can be transformed from one form to another, but can be neither created nor destroyed.
The **second** law of thermodynamics states that the total entropy of an isolated system can never decrease over time. The total entropy of a system and its surroundings can remain constant in ideal cases where the system is in thermodynamic equilibrium. In all processes that occur, including spontaneous processes, the total entropy of the system and its surroundings increases and the process is irreversible in the thermodynamic sense. The increase in entropy accounts for the irreversibility of natural processes, and the asymmetry between future and past.
Chemical equilibrium

\[ \text{A} + \text{B} \rightleftharpoons \text{C} + \text{D} \]

Thermodynamics determine if A and B or C and D are the favoured products and where the equilibrium is located. It does NOT determine reaction rates.

\[ \text{A} + \text{B} \rightleftharpoons \text{C} + \text{D} \]

\[ \text{A} + \text{B} \rightleftharpoons \text{C} + \text{D} \]
Activation Energy and reaction rates
A practical example
Fritz Haber (1868-1934)

“Father” of chemical warfare in World War I

But also Nobel Laureate in Chemistry 1918
Carl Bosch (1874-1940)
Chemist and Industrialist
Nobel Laureate in Chemistry 1931
The Haber-Bosch process

Making ammonia with nitrogen from the air

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

- Nitrogen is a very stable and unreactive molecule.
- Process has high activation barrier.
- Raising the temperature makes reaction faster but shifts equilibrium from ammonia towards starting products
Reaction rate and temperature
The Haber-Bosch process

The solution:

• **Lowering activation energy** a using metal catalyst
• **Temperature for reasonable reaction rates** now lower but still favouring the starting products
• **Shifting the equilibrium towards ammonia** by applying high pressure.
The Haber-Bosch process

Major technological breakthrough (high pressure reactions in industry). Uses about 1-2% of world energy consumption.
• Enabled Imperial Germany to continue to fight World War I despite being blocked from accessing natural nitrate deposits. Enabled the mass production of nitrogen fertilizers.
• Enabling massive growth of agricultural production.
• Without the Haber process the current world population would not be possible.
• About half of all nitrogen atoms in the human body are derived from air nitrogen via the Haber process.
Chemical warfare and reactivity

- Nerve agents should have high reactivity with the biological target (Acetylcholinesterase) but low reactivity towards water (hydrolytic stability). Fluoridates better than chloridates.
But back to Chemistry and Politics....

\[ A + B \rightleftharpoons C + D \]

How can this be similar to politics? Clearly defined start and end states? Predictable reaction rates and equilibrium? No room for negotiations?

Chemistry can be a little bit more complicated.....
Part 1
Metabolic Pathways

Carbohydrate Metabolism
Acidic Carbohydrate Derivatives
Carbohydrate Metabolism
Pentoses and Pentose Cycle
Carbohydrate Metabolism
Amino Sugar Derivatives
Carbohydrate Metabolism
Glycolysis and Gluconeogenesis

Amino Acid Metabolism
Histidine
Amino Acid Metabolism
Lysine
Amino Acid Metabolism
Serine, Threonine, Cysteine, Methionine

Bacterial Metabolism
Nucleotide Sugars
Bacterial Metabolism
Methane Oxidation
Bacterial Metabolism
Pyruvate Turnover

C1-Metabolism
Lipid Metabolism
Glyco- and Phospholipids
Lipid Metabolism
Fatty Acids
Lipid Metabolism
Sphingolipids

Lipid Metabolism
Carotenoids and Isoprenoids
Steroid Metabolism
Phytosterols
Steroid Metabolism
Cholesterol Synthesis

Nucleotide Metabolism
Purines
Nucleotide Metabolism
NAD, NADP
Antibiotics
Penicillin, Cephalosporin

Bacterial Metabolism
Butanol, Butyrate, Fermentation
Bacterial Metabolism
Penicillin, Cephalosporin

Cofactors and Vitamines
Coenzyme A
Steroid Metabolism
Adrenocorticoids and Glucocorticoids
Steroid Metabolism
Androgens and Estrogens
Looks like the org chart of the UN? Reminds you of political decision making?
Sometimes even a chemical reaction does not know in what direction it wants to run...
Sometimes even a chemical reaction does not know in what direction it wants to run...
Ok you say. Colour changes are nice but I need a green light from capital. How can chemistry help me with that?
Ok you say. Colour changes are nice but I need a green light from capital. How can chemistry help me with that?
Captured on Video!

https://www.youtube.com/watch?v=shZtgWBWFAA&feature=youtu.be
Your kit contains:

- 1 Lego laboratory bench
- 1 flow chemistry assembly (consisting of three fluidic blocks with 5 connecters, tubing and a stopcock)
- 2 syringe to tubing connecters
- 1 syringe (3 ml) containing precursor A (blue)
- 1 syringe (3 ml) containing precursor B (yellow)
- 1 product collection container

Your kit includes all the parts you will need to safely mix component chemicals (precursors) together to produce and collect a new chemical product.
You are in possession of a DIY flow chemistry kit!

Your kit contains:
- 1 Lego laboratory bench
- 1 flow chemistry assembly (including tubing and a stopcock)
- 2 syringe to tubing connectors
- 1 syringe (3 ml) containing precursors
- 1 syringe (3 ml) containing product
- 1 product collection container

YOUR TURN!

Your kit includes all the parts you will need to safely mix component chemicals (precursors) together to produce and collect a new chemical product.
A fully assembled flow chemistry system should look like this:

Your task:
1. Figure out how to assemble the system
2. Mix precursors A and B
3. Collect the product (without spilling, leaking or otherwise contaminating your work space!)

Prizes will be awarded for the perfect combination of system assembly, chemical containment, product purity and product yield. Good luck diplochemists!

Assembly instructions?
We keep hearing how easy it is to produce chemicals using DIY approaches, now you can show us how!

... in case you really want instructions... just ask! A cheat sheet is available upon request.
A fully assembled flow chemistry system should look like this:

Your task:
1. Figure out what chemicals you need to mix.
2. Mix the chemicals.
3. Collect the products.

Prizes will be awarded to those who can produce chemicals using the approach that you can share with others...

Assembly:
We keep helping you every time you express enthusiasm using our approach. Then you can start to show...

...in case you really want instructions... just ask! A cheat sheet is available upon request.
Chemistry Lessons

Science for Diplomats at EC-SS
The Chemical Universe: Scheduled and Unscheduled

Tuesday, 15 July 2019
Qoms Room, OPCW
13:30 - 14:45
Light lunch served at 13:00

Science for Diplomats at EC-90
The Expanding Chemical Universe: From C1 to C10 and beyond

Tuesday 12 March 2019
Qoms Room 13:30 - 14:45
Light Lunch Available at 13:00

A lunch time mission to boldly go
where no delegation has gone before...

OPCW
ORGANISATION FOR THE PROHIBITION OF CHEMICAL WEAPONS

THE "SCIENCE FOR DIPLOMATS"
ANNEX ON CHEMICALS

A user friendly and scientifically annotated version of the Chemical Weapons Convention Annex on Chemicals

What is missing?
How can we make the "Unofficial" Annex on Chemicals more informative?

From the audience:

- Rule
- Ses explanations of cemic
- More real chemical exerci
- Hal compositions
- Links

What is missing?
Scientific Advisory Board Update

28th Session of the OPCW Scientific Advisory Board
Briefing to States Parties
Friday 14 June 2019
Ieper Room 13:30 - 15:00
Light lunch served at 13:00
Scientific Advisory Board Update

Temporary Working Group on Investigative Science and Technology

Reporting to the Scientific Advisory Board (SAB), the Temporary Working Group (TWG) will in particular consider the following questions:

Question 1: Which methods and capabilities used in the forensic sciences could usefully be developed and/or adopted for Chemical Weapons Convention-based investigations?

Question 2: What are the best practices and analysis tools used in the forensic sciences for effectively cross-referencing, validating, and linking together information related to investigation sites, materials collected/analyzed, and individuals interviewed?

Question 3: What are the best practices for management of data collected in investigations, including compilation, curation, and analytics?

Question 4: What are the best practices for the collection, handling, curation and storage, and annotation of evidence?

Question 5: Which technologies and methodologies (whether established or new) can be used in the provenancing of chemical and/or material samples collected in an investigation?

Question 6: Which technologies and methodologies (whether established or new) can be used to ensure the integrity of an investigation site?

Question 7: Which methods are available (or are being developed) for the sampling and analysis of environmental and biomedical materials and can be used in the detection of toxic industrial chemicals relevant to the Chemical Weapons Convention?

Question 8: Which technologies and methodologies (whether established or new) can be used in ensuring chain of custody and verifying authenticity (especially in regard to digital images and video recordings)?

Question 9: Are there stakeholders that the Technical Secretariat could usefully engage with to leverage their capabilities on investigative matters?

In addition, the TWG will provide advice on Technical Secretariat proposals for methodologies, procedures, technologies, and equipment for investigative purposes.

Third report now available.

TWG will meet twice more, then produce a final report.
Some Acknowledgements: Interns!
Thank you for Joining Us!
Good Luck Dr Blum, we will miss you!
OPCW

Organisation for the Prohibition of Chemical Weapons

Organisation pour l'Interdiction des Armes Chimiques

Организация по запрещению химического оружия

Organización para la Prohibición de las Armas Químicas