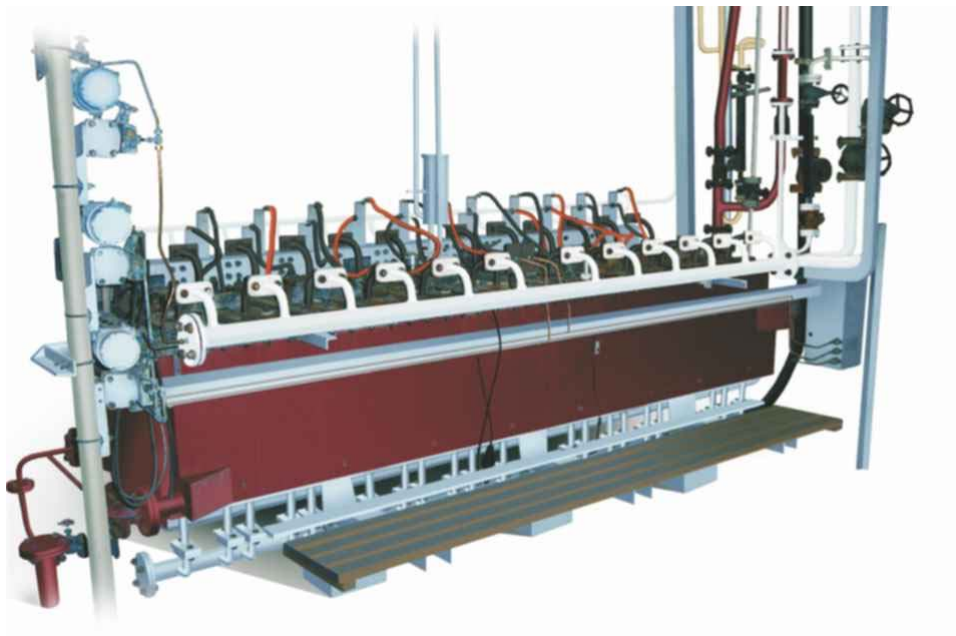


World Production of halogens

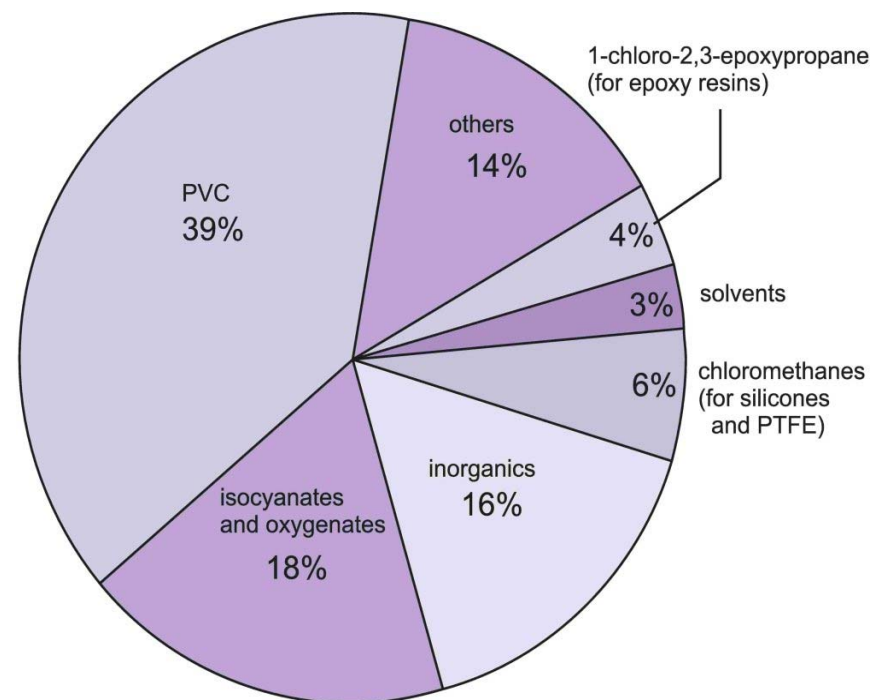


Fluorine

Fluorine is the 13th most common element on the earth's crust.

World	F_2	20,000 tonnes
-------	-------	---------------

World	Br_2	556,000 tonnes
-------	--------	----------------



Chlorine

World	Cl_2	56,000,000 tonnes
-------	--------	-------------------

World	I_2	19,000 tonnes
-------	-------	---------------

Every kilogram (roughly one litre by volume) of seawater has approximately **35 grams of dissolved salts (predominantly sodium(Na^+) and chloride (Cl^-) ions).**

Salt Ion	Ions in Seawater	%
Chloride (Cl^-)	18.980	55.04
Sodium (Na^+)	10.556	30.61
Sulfate (SO_4^{2-})	2.649	7.68
Magnesium (Mg^{2+})	1.272	3.69
Calcium (Ca^{2+})	0.400	1.16
Potassium (K^+)	0.480	1.10
Bicarbonate (HCO_3^-)	0.140	0.41
Bromide (Br^-)	0.065	0.19
Boric acid (H_3BO_3^-)	0.026	0.07
Strontium (Sr^{2+})	0.013	0.04
Fluoride (F^-)	0.001	<0.01
Other ions	<0.001	<0.01

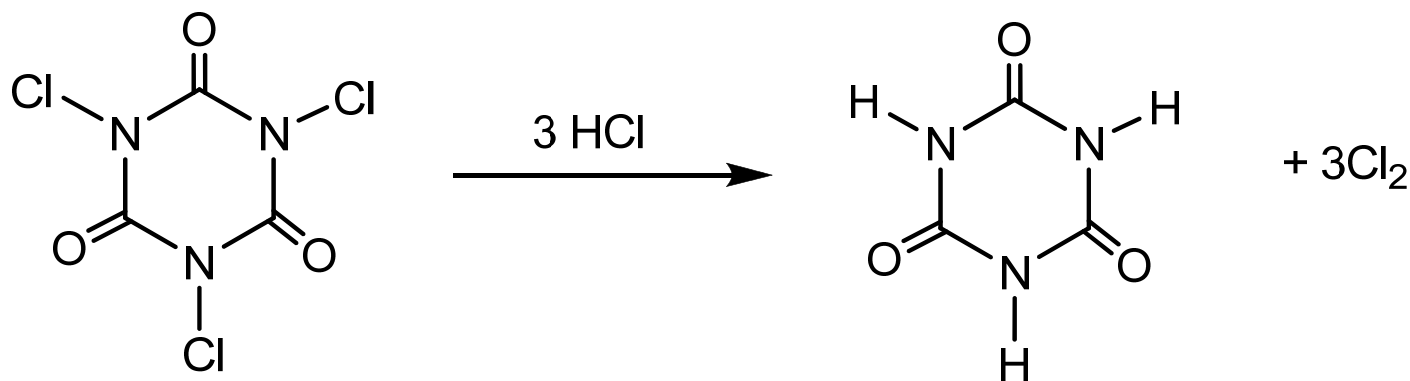
Earth's oceans together contain about 2.6×10^{16} metric tons of chlorine

- Chlorine is not only abundant in our oceans; it is the sixth most abundant element in Earth's crust.

- Chlorine has the highest electron affinity (348.6 kJ/mol) and the third highest electronegativity (3.16) of all the reactive elements. The Cl-Cl bond dissociation energy (58 kcal/mol) is the highest among dihalogen molecules.
- Chlorine gas and many of its compounds are chemicals useful in water purification. Cl₂ reacts with water giving a mixture of HCl and HClO and the latter is responsible for breaching the bacterial cell wall and killing of the bacteria
- Gastric juices of stomach of human beings have 0.3 to 0.4 % hydrochloric acid. White blood cells kill bacteria by producing HClO (hypochlorous acid) inside their cells.
- Naturally occurring chlorine is a mixture of its two stable isotopes ³⁵Cl and ³⁷Cl with natural abundances of 75.8% and 24.3% respectively.
- It is used in the manufacture of house hold bleaches, disinfectants, mostly chlorinated phenols for killing bacteria and is used for bleaching paper pulp. Chlorine is also used for the manufacture of chlorates and it is important in organic chemistry, forming compounds such as chloroform, carbon tetrachloride, polyvinyl chloride, and neoprene.
- Chlorine chemistry is essential for the manufacture of about 93% of the top-selling drugs.
- Polychlorinated dibenzodioxins, known as PCDDs are some of the most toxic compounds known to mankind which are also formed during burning of organo chlorine compounds.
- From its first use as a germicide to prevent the spread of "child bed fever" in the maternity wards of Vienna General Hospital in Austria in 1847, chlorine has been one of society's most potent weapons against a range of life-threatening infections, viruses, and bacteria for over 150 years

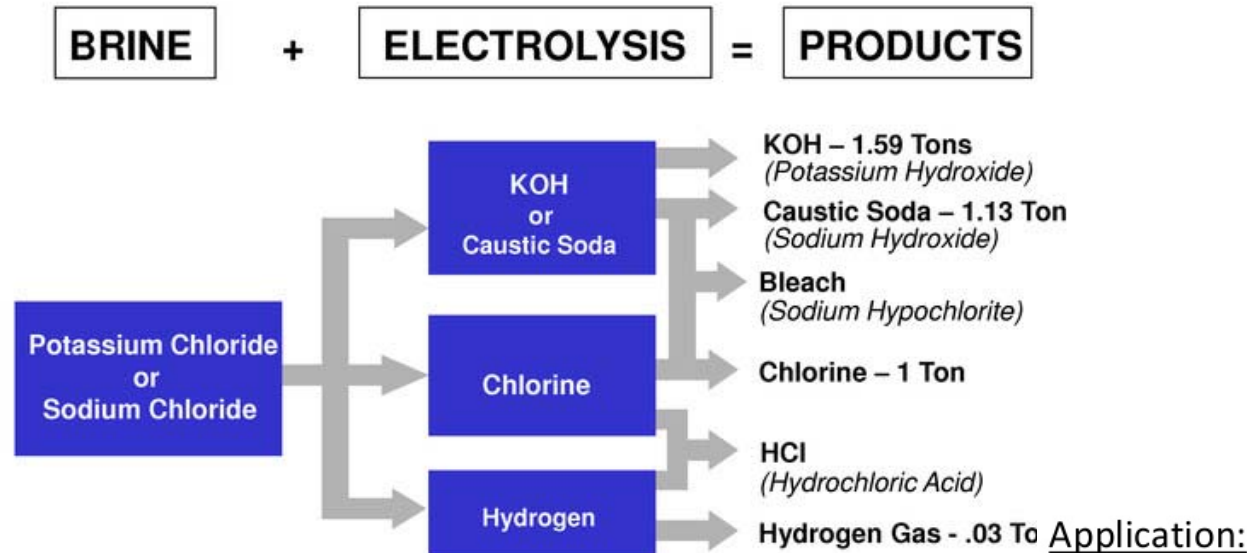
Laboratory synthesis of chlorine

There are many methods of synthesizing chlorine gas in the laboratory and almost all of them use hydrochloric acid. A reaction of HCl with KMnO_4 , MnO_2 , PbO_2 , Pb_3O_4 , O_2 , $\text{NaClO}(\text{aq})$ readily gives Cl_2 but often with water vapor. The most efficient method used nowadays is by the reaction of trichloroisocyanuric acid (TCCA or TCICA) with hydrochloric acid, the former being a highly stable free flowing and high melting white powder.



Chlor Alkali Process

Raw Materials



Chlor-alkali process: Chlor for chlorine and Alkali for sodium hydroxide.

At cathode

- H₂ Gas is evolved
- Fuel
- Margarine
- ammonia

At anode

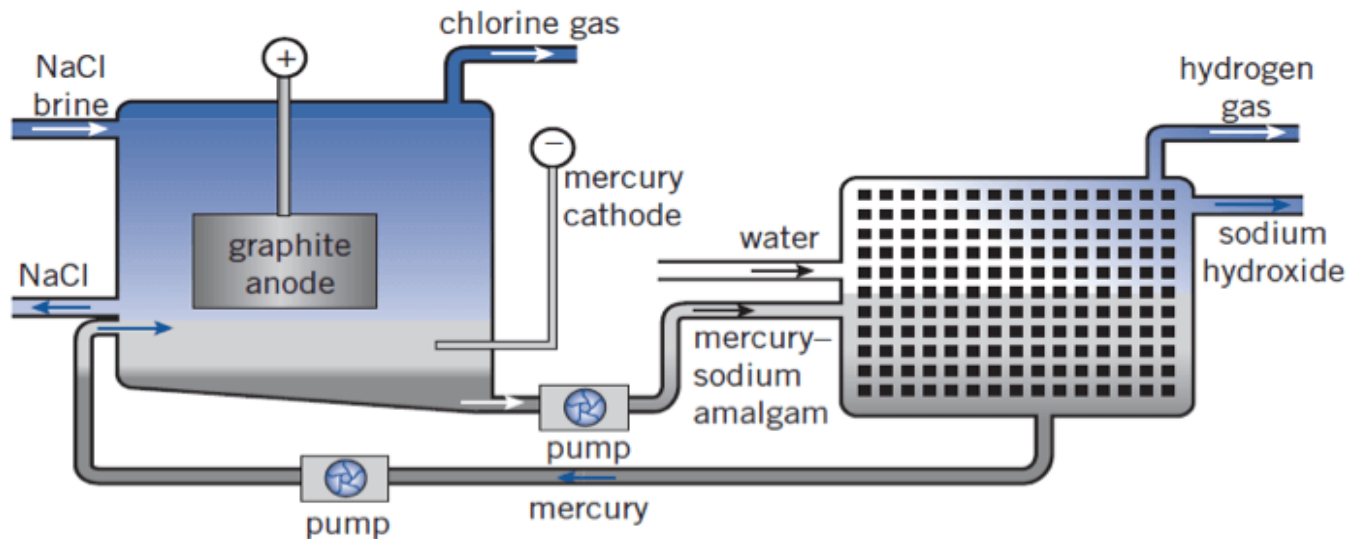
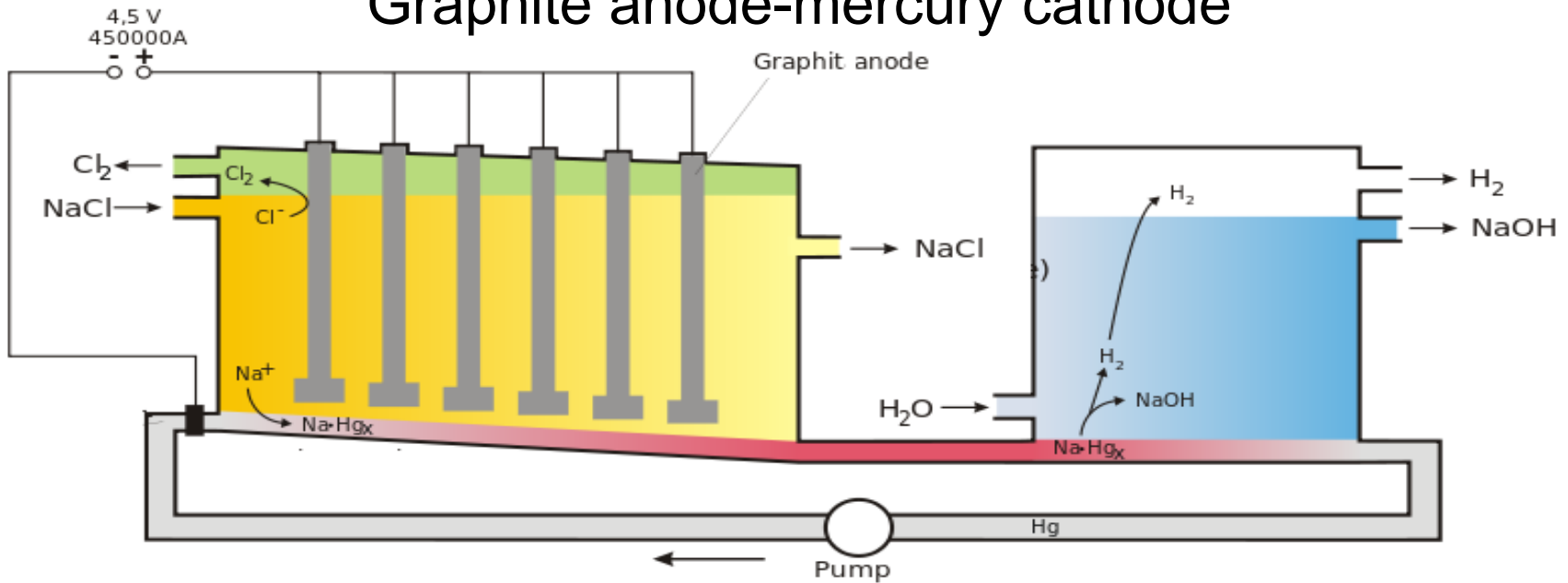
- Cl₂ Gas is evolved
- Water treatment
- PVC
- CFC's
- Disinfectants
- pesticides

Near cathode

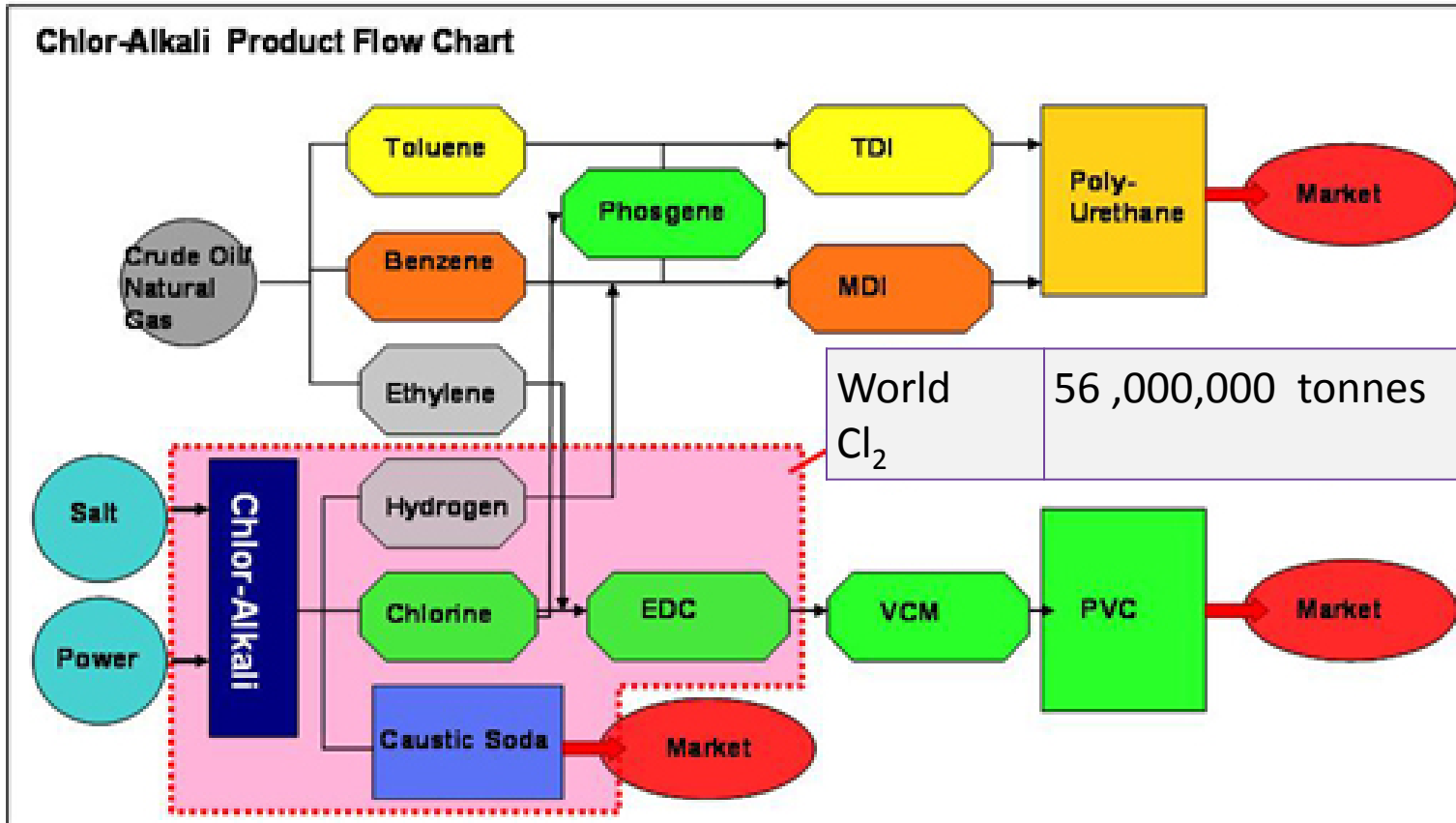
- NaOH is formed
- Degreasing metal
- Soap
- Papermaking
- Artificial fibers

Castner-Kellner Process

Graphite anode-mercury cathode



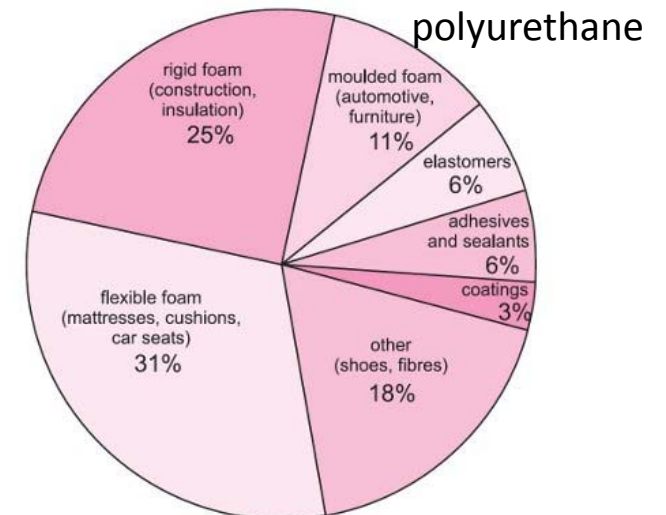
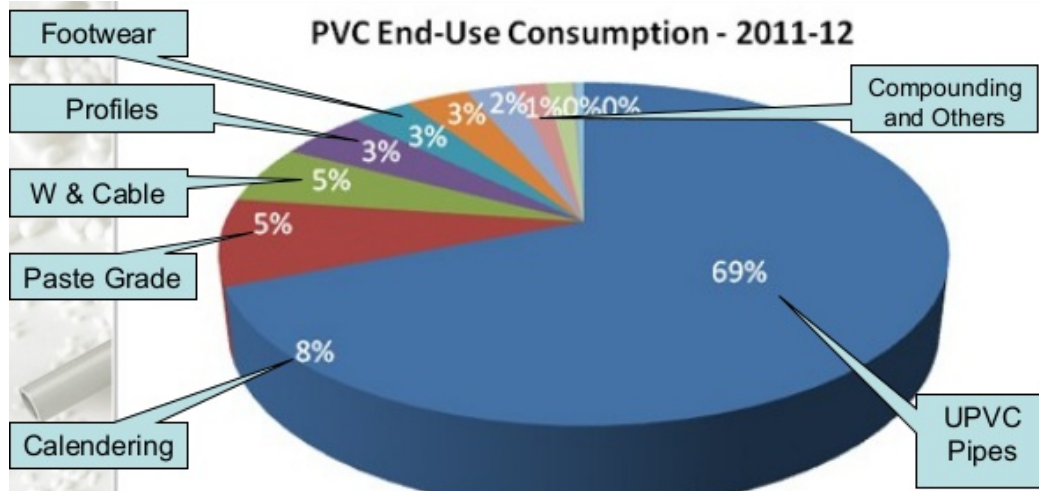
Chlor-Alkali Product Flow Chart



Toluene Di Isocyanate
Methylene Diphenyl di Isocyanate

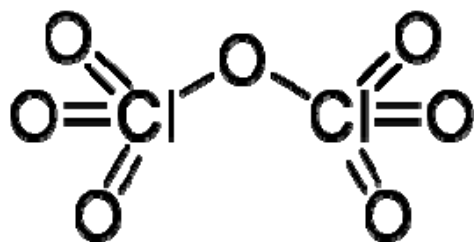


Ethylene Di Chloride
Vinyl chloride monomer

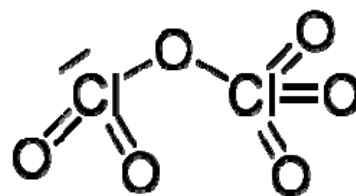


Chlorine: Unique properties

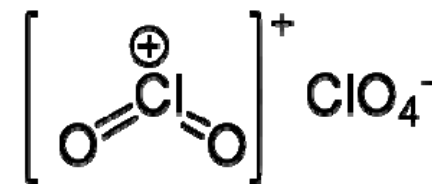
Chlorine shows oxidation states 7, 6, 5, 4, 3, 2, 1, 0, -1 and is also a good oxidizing agent.



Dichlorine heptoxide

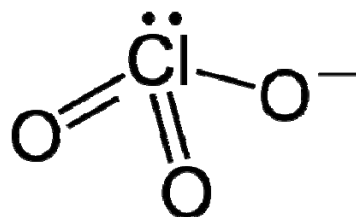


(a)

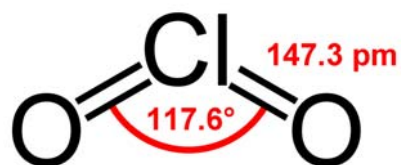


(b)

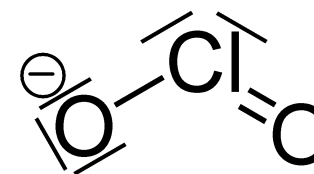
Dichlorine hexoxide



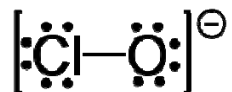
Chlorate



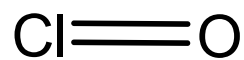
Chlorine dioxide



Chlorite



hypochlorite



Chlorine monoxide



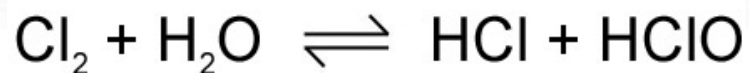
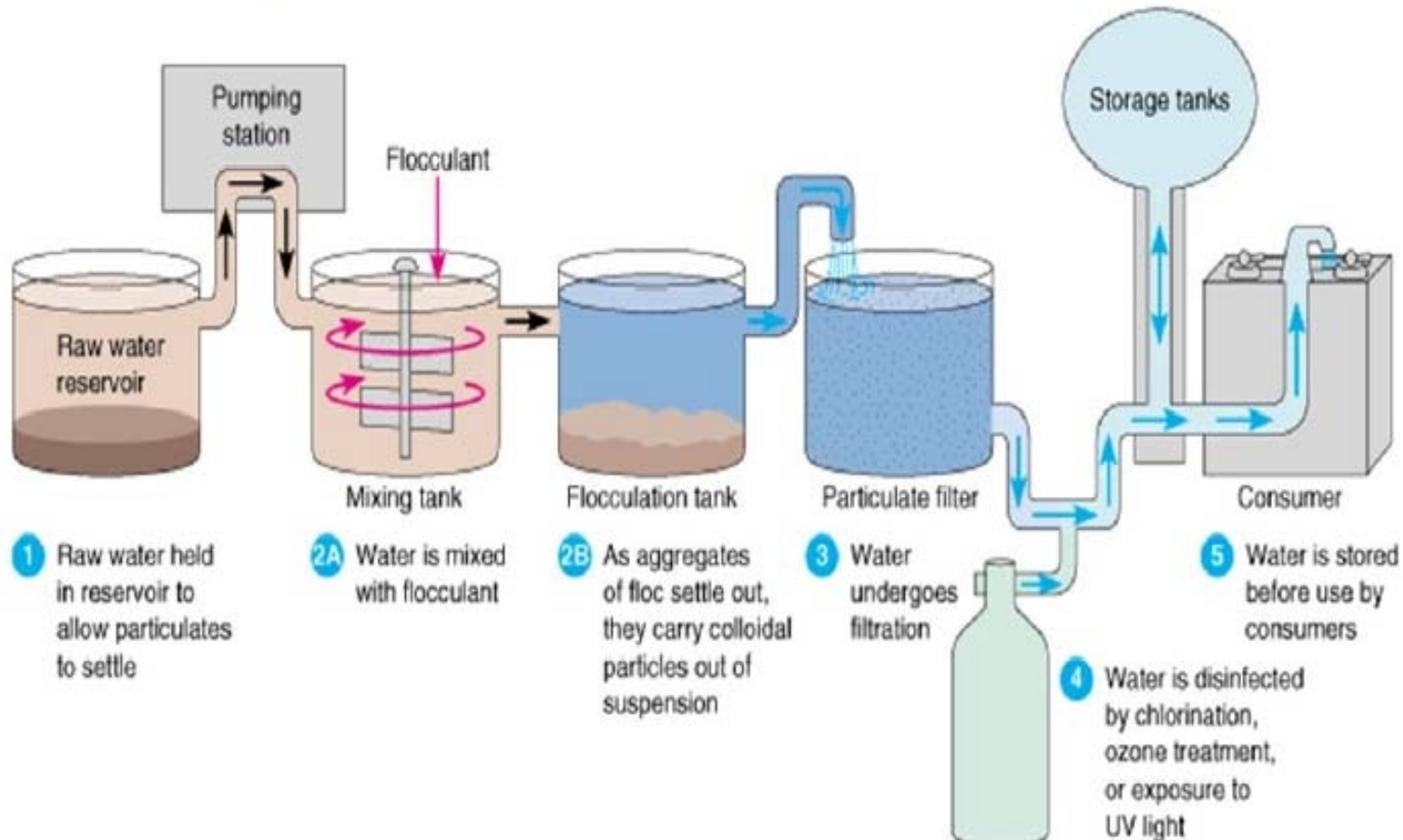
Chlorine

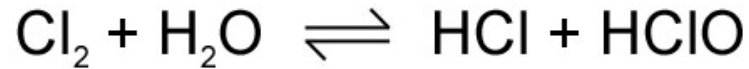


Chloride

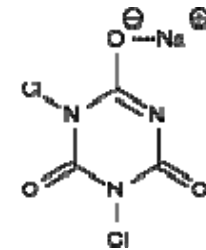
Chlorine gas in water purification

Municipal Water Purification Plant

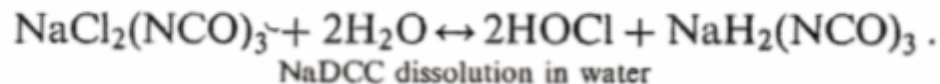
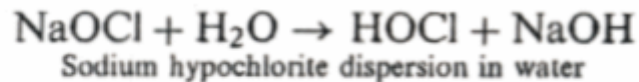




	Chlorine Dioxide (Potable Aqua)	Chlorine NaDCC (Oasis Plus)
Cryptosporidium	Highly Effective	Highly Effective
Giardia	Highly Effective	Highly Effective
Viruses	Highly Effective	Highly Effective
Bacteria	Highly Effective	Highly Effective
Protozoa (most)	Highly Effective	Highly Effective
pH required	Any pH	5.5- 9
Water Temperature	Above 64 deg. F	Above 64 deg. F
Treatment Time	4 hours- (30 min. min.)	10 Minutes



Sodium dichloro
Isocyanurate
NaDCC



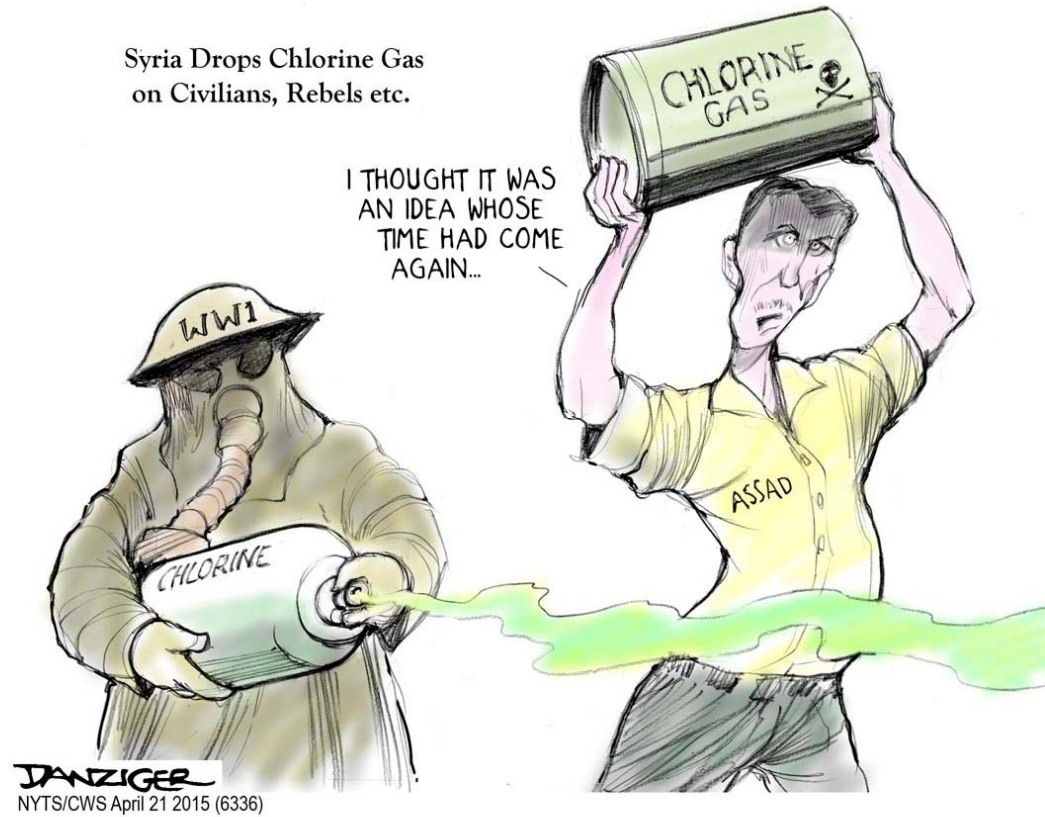
Compound	Reaction with Cl₂	Reaction with ClO₂
Water	HClO and HCl	No reaction

Cl₂ as a chemical warfare agent



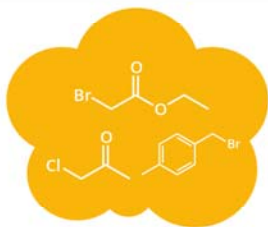
Haber=Dr "Evil"

Syria Drops Chlorine Gas
on Civilians, Rebels etc.



CHEMICAL WARFARE WORLD WAR I

WORLD WAR I IS SEEN AS THE DAWN OF MODERN CHEMICAL WARFARE, WITH A VARIETY OF DIFFERENT CHEMICAL AGENTS BEING EMPLOYED ON A LARGE SCALE, RESULTING IN APPROXIMATELY 1,240,000 NON-FATAL CASUALTIES, AND 91,000 FATALITIES. A VARIETY OF POISONOUS GASES WERE USED THROUGHOUT THE CONFLICT, WITH EACH HAVING DIFFERING EFFECTS UPON VICTIMS.



TEAR GASES

(ethyl bromoacetate, chloroacetone & xylyl bromide)

SMELL & APPEARANCE

Both ethyl bromoacetate and chloroacetone are colourless to light yellow liquids with fruity, pungent odours. Xylyl bromide is a colourless liquid with a pleasant, aromatic odour.

EFFECTS

Tear gases are what is known as 'lachrymatory agents' - they irritate mucous membranes in the eyes, mouth, throat & lungs, leading to crying, coughing, breathing difficulties, and temporary blindness.

FIRST USED

1914

In August 1914, the French forces used tear gas grenades against the German army, to little effect.

ESTIMATED CASUALTIES

0 These gases were used to incapacitate enemies rather than to kill; symptoms commonly resolved within 30 minutes of leaving the affected area.



CHLORINE

SMELL & APPEARANCE

Chlorine is a yellow-green gas with a strong, bleach-like odour. Soldiers described its smell as 'a distinct mix of pepper and pineapple'.

EFFECTS

Chlorine reacts with water in the lungs, forming hydrochloric acid. It can cause coughing, vomiting, and irritation to the eyes at low concentrations, and rapid death at concentrations of 1000 parts per million.

FIRST USED

1915

Used by German forces at Ypres in April 1915. British forces used it for the first time at Loos in September.

ESTIMATED CASUALTIES

>1,100 Chlorine was devastating as troops were initially unequipped to deal with it. Later, gas masks limited its effectiveness.

Number of fatalities in first use of chlorine at Ypres



PHOSGENE & DIPHOSGENE

(carbonyl dichloride & trichloromethane chloroformate)

SMELL & APPEARANCE

Phosgene is a colourless gas with a musty odour comparable to that of newly mown hay or grass. Diposgene is a colourless, oily liquid.

EFFECTS

React with proteins in lung alveoli, causing suffocation. Cause coughing, difficulty breathing and irritation to the throat & eyes. Can cause delayed effects, not evident for 48hrs, including fluid in the lungs & death.

FIRST USED

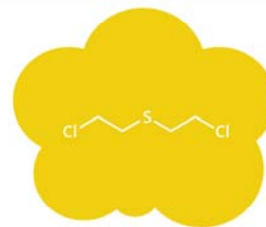
1915

In December 1915, the German forces used phosgene against the British at Ypres.

ESTIMATED CASUALTIES

85% It's estimated 85% of all gas-related fatalities in World War I resulted from phosgene and diposgene, which were both used to fill artillery shells.

of all gas-related fatalities in WWI



MUSTARD GAS

(bis(2-chloroethyl) sulfide)

SMELL & APPEARANCE

When pure, mustard gas is a colourless and odourless liquid, but it's used as a chemical agent in impure form. These are yellow-brown in colour and have an odour resembling garlic or horseradish.

EFFECTS

Powerful irritant and vesicant (blistering agent) that can damage the eyes, skin, & respiratory tract. Causes chemical burns on contact with skin. Forms intermediates that react with DNA leading to cell death.

FIRST USED

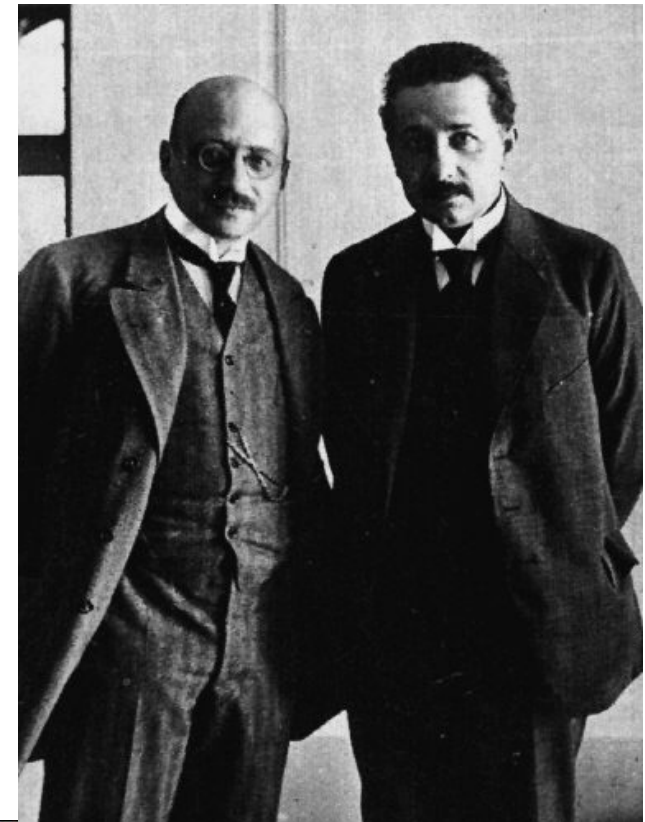
1917

On 12th July 1917, German forces used mustard gas against the British at Ypres.

ESTIMATED CASUALTIES

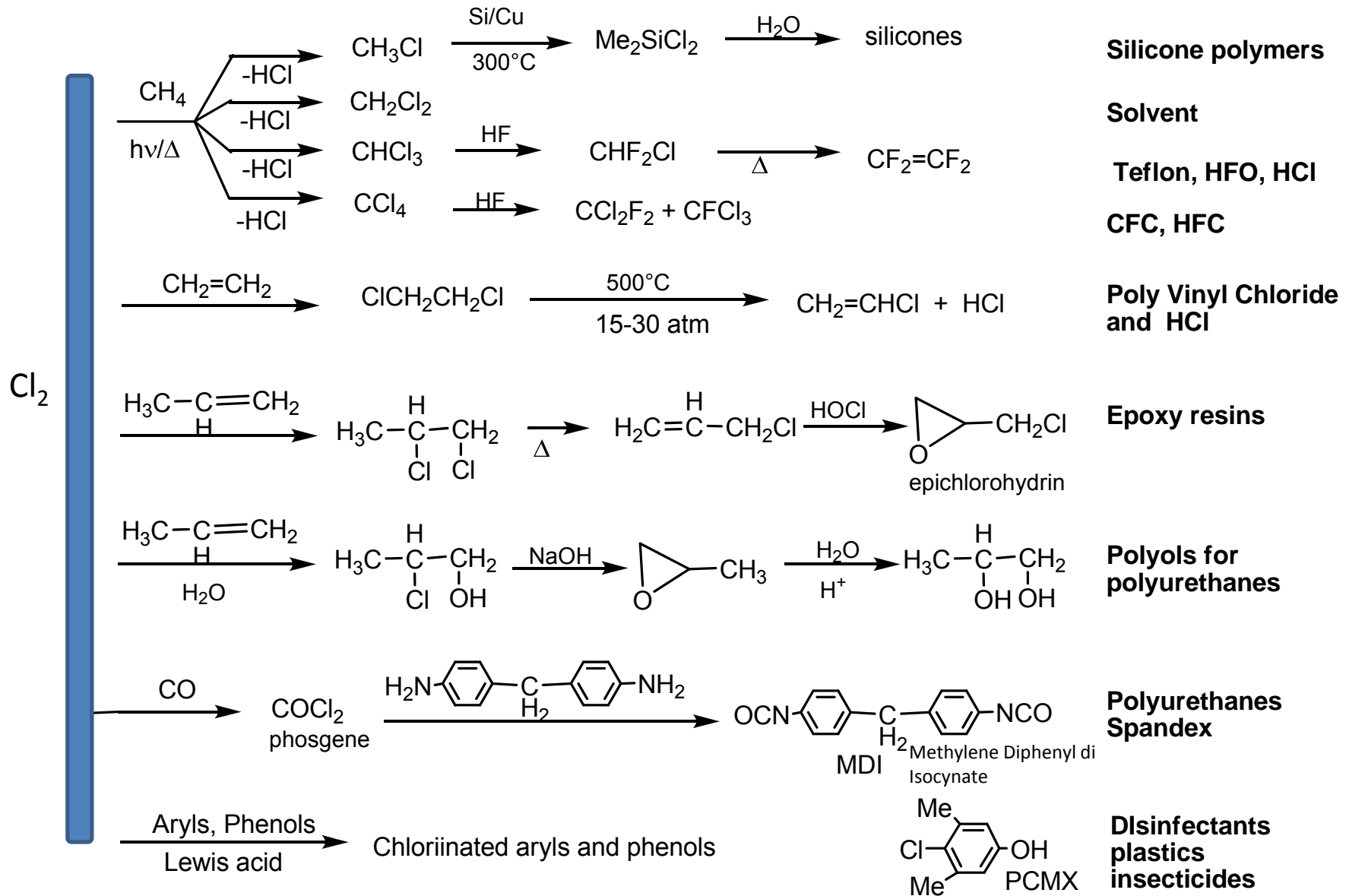
2-3% The mortality rate of mustard gas casualties was low, but its effects were debilitating, and patients required elaborate care.

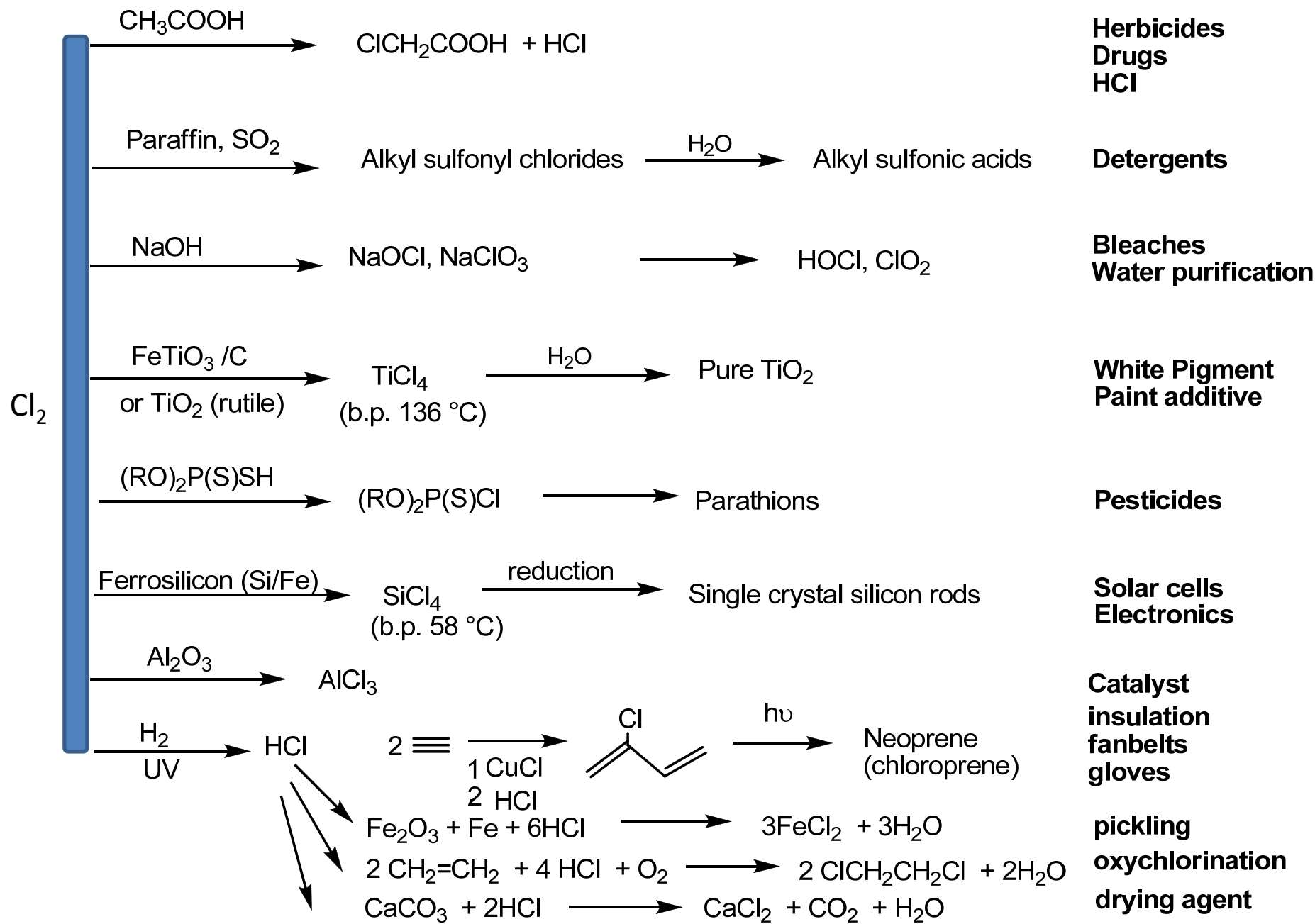
mortality rate of mustard gas casualties



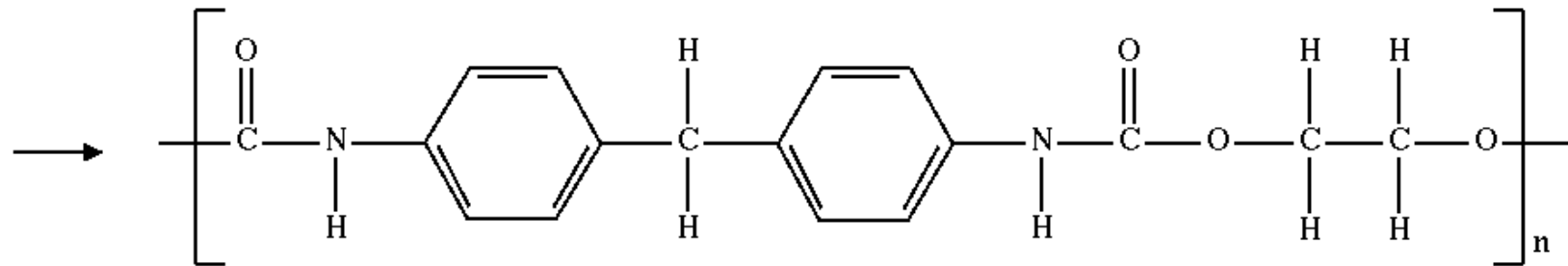
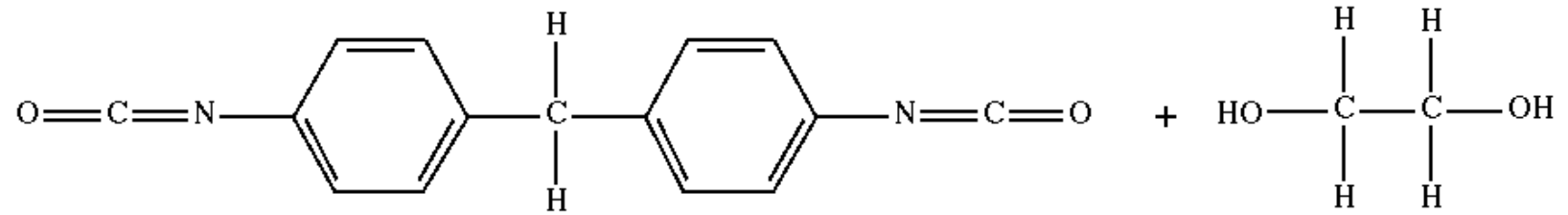
Cl



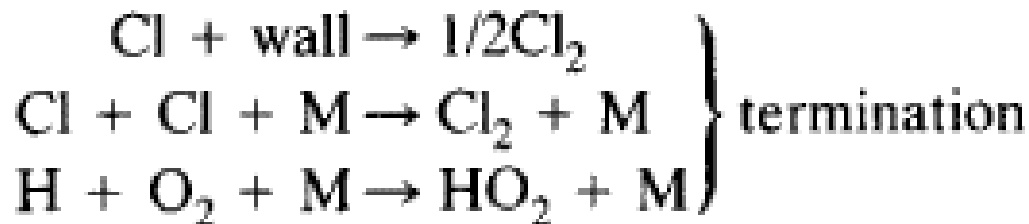
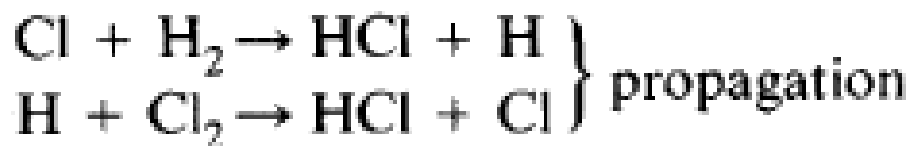




Polyurethane synthesis



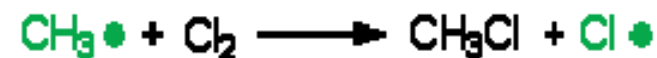
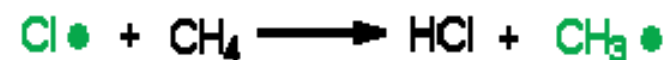
•The first chain reaction discovered was not a nuclear reaction; it was a chemical chain reaction. It was discovered in 1913 by Max Bodenstein, who saw a mixture of chlorine and hydrogen gases explode when triggered by ultra violet light of 470 nm or stronger. The chain reaction mechanism was fully explained in 1918 by Walther Nernst.



1. Initiation reaction

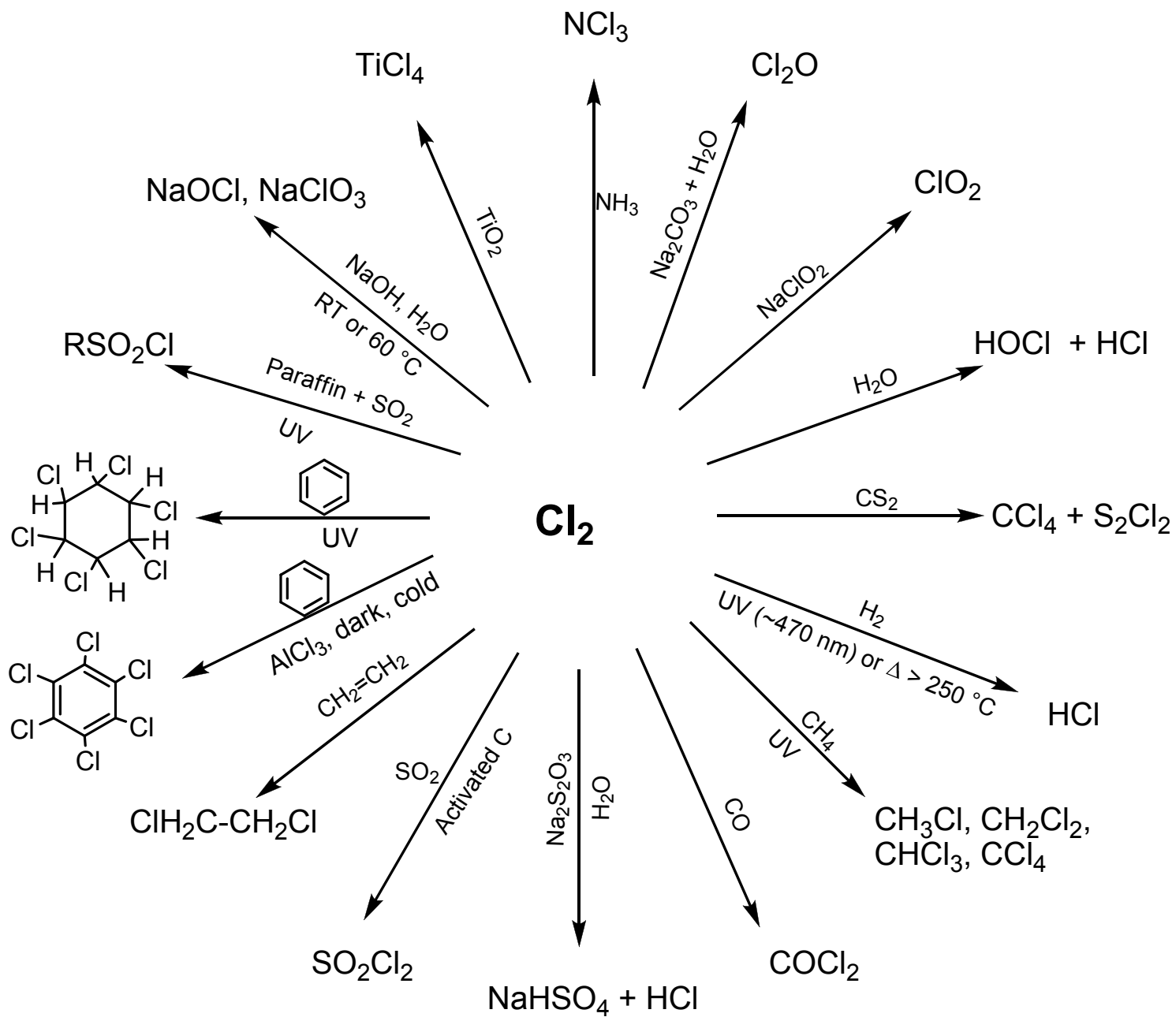


2. Chain propagation



3. Chain termination reactions



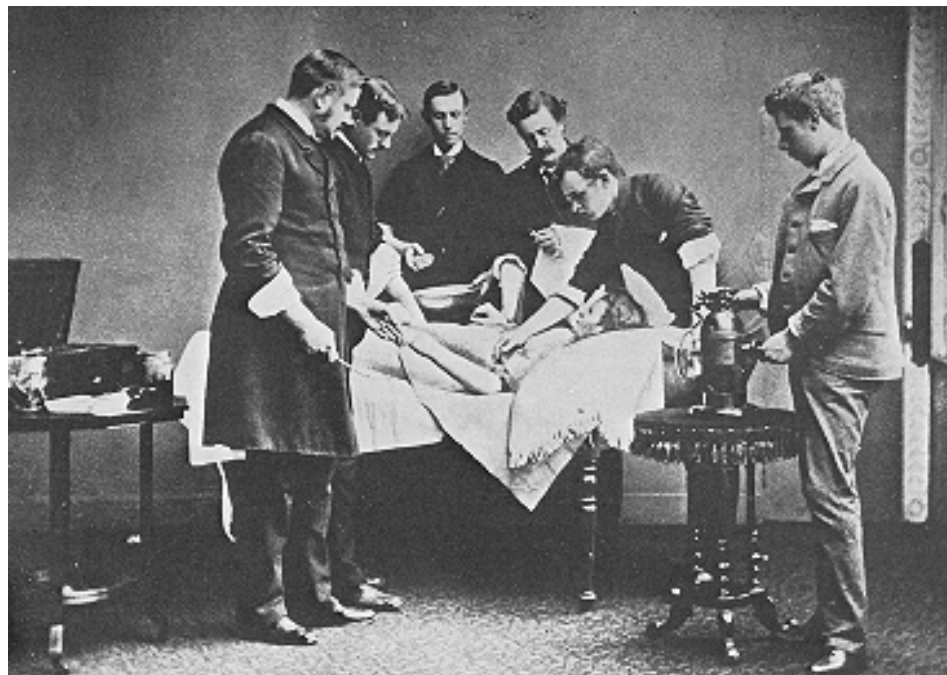


The Story of Dettol

Antiseptics and disinfectants

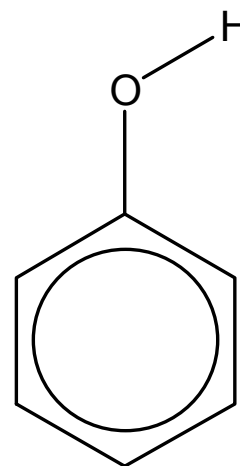
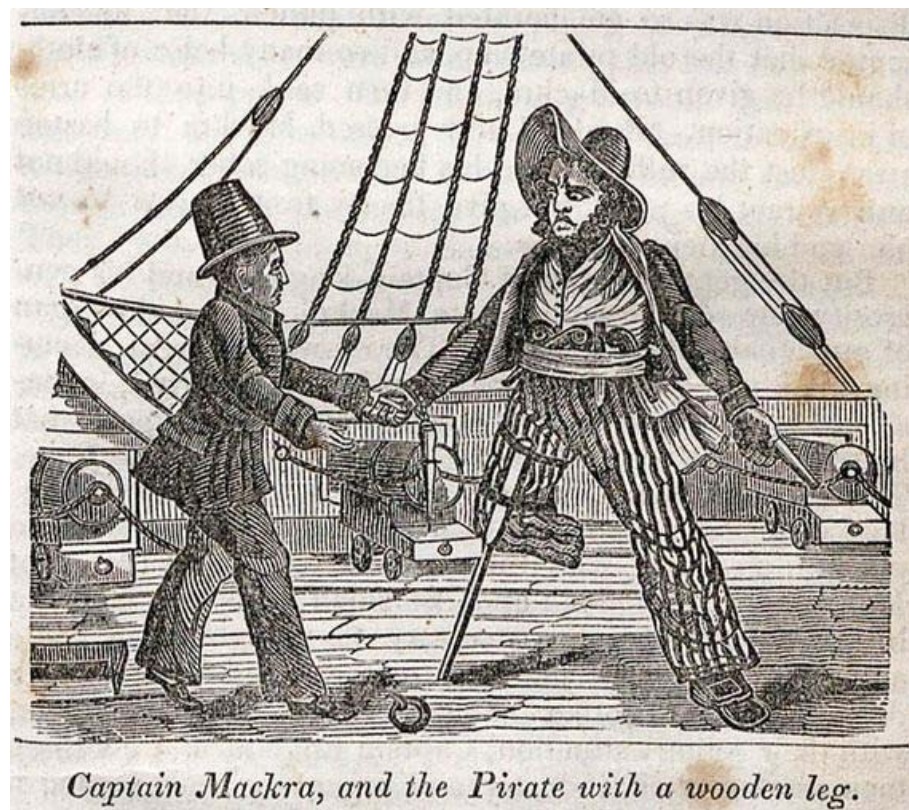
Before the mid-1800s, major surgery was often a death sentence. Amputations of damaged limbs were carried out as a last resort but patients frequently died from post-operative infections.

This changed in the 1860s when Joseph Lister developed antiseptic surgery using carbolic acid to sterilise wounds and instruments. Lister was aware of the germ theory of infections developed by Louis Pasteur and others, and knew that carbolic acid (which we now call phenol) was able to kill germs



Adapted from Chemistry in the cupboard; RSC chemistry, UK , 2010

It is reputed that phenol's germ-killing power first came to notice in a bizarre way. Sailors who underwent amputations at sea appeared to have a higher survival rate than patients in hospital. This seemed to be due to the practice at sea of dipping the stump into molten tar to seal the wound. Tar contains, among other things, phenol

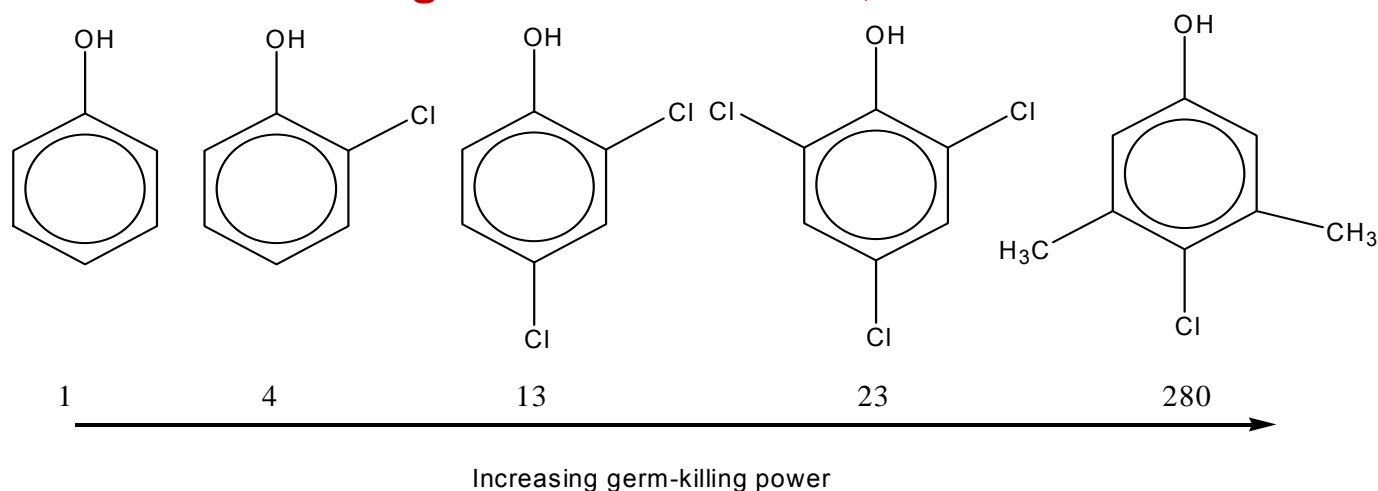


Adapted from Chemistry in the cupboard; RSC chemistry, UK, 2010

Structure activity relationships

Phenol is effective at killing germs but is otherwise a far from ideal antiseptic as it causes nasty skin burns. One technique used by pharmaceutical chemists when faced with this sort of situation is to synthesise a number of compounds related to the substance that is known to be effective. This is in the hope that one or more of these compounds will be as active, or better, than the original but with fewer side effects (such as skin burning). Even better is the possibility of establishing a structure-activity relationship. This is a pattern which links some structural feature of the molecule with its pharmacological efficiency

- the more methyl groups attached to a benzene ring, the better the germ-killing power, or
- the more electronegative a substituent, the less harmful to the skin.



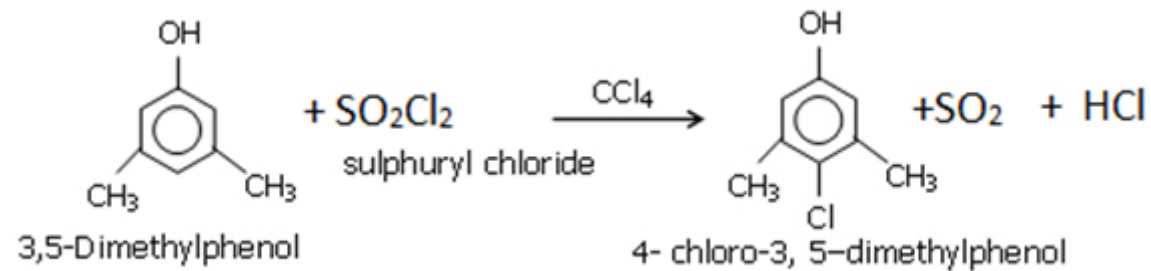
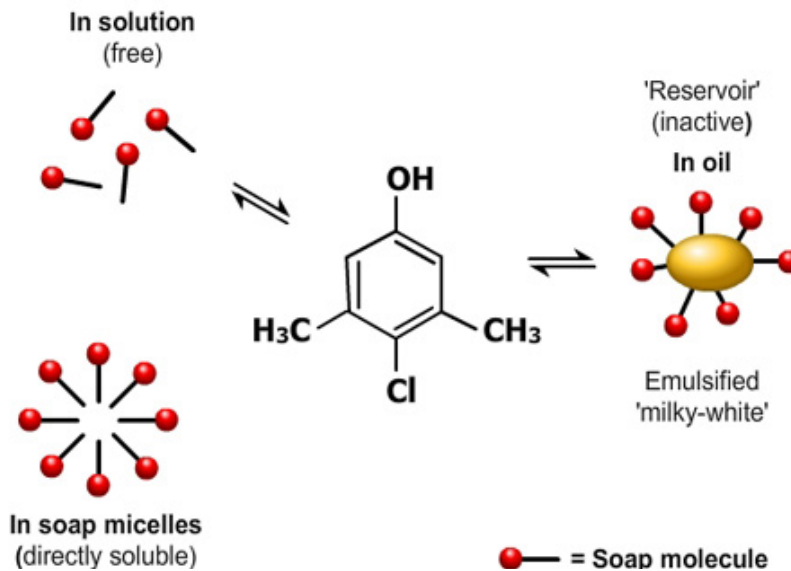
In fact the structure-activity relationships that have been established for derivatives of phenol are:

- the –OH group is required for activity;
- activity increases with a halogen in the 4- position (ie opposite the –OH group in the ring);
- activity increases with alkyl substituents of increased chain length;
- increased substitution makes the compound less water-soluble; and
- increased substitution decreases toxicity to humans when taken by mouth.

Phenol is already an effective germicide, so a greater killing power is not really needed. What the greater efficiency of 4-chloro-3,5-dimethylphenol means is that much smaller concentration can be used and therefore fewer side-effects will be expected.

The active germ-killing ingredient in Dettol is in fact 4-chloro-3,5-dimethylphenol, also known by its non-systematic name *para*-chloro-*meta*-xylenol or PCMX

Para chloro meta xylenol- PCMX



Chemical Name

CAS No

Proportion (%w/w)

Chloroxylenol

88-04-0

4.8 (%w/v)

Pine Oil

8002-09-3

<10

Isopropyl alcohol

67-63-0

10 - 30

Other ingredients classified as not hazardous according to NOSCH

to 100

Adapted from Chemistry in the cupboard; RSC chemistry, UK, 2010

How does PCMX kill bacteria?

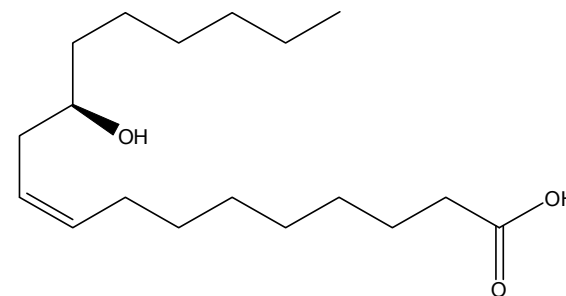
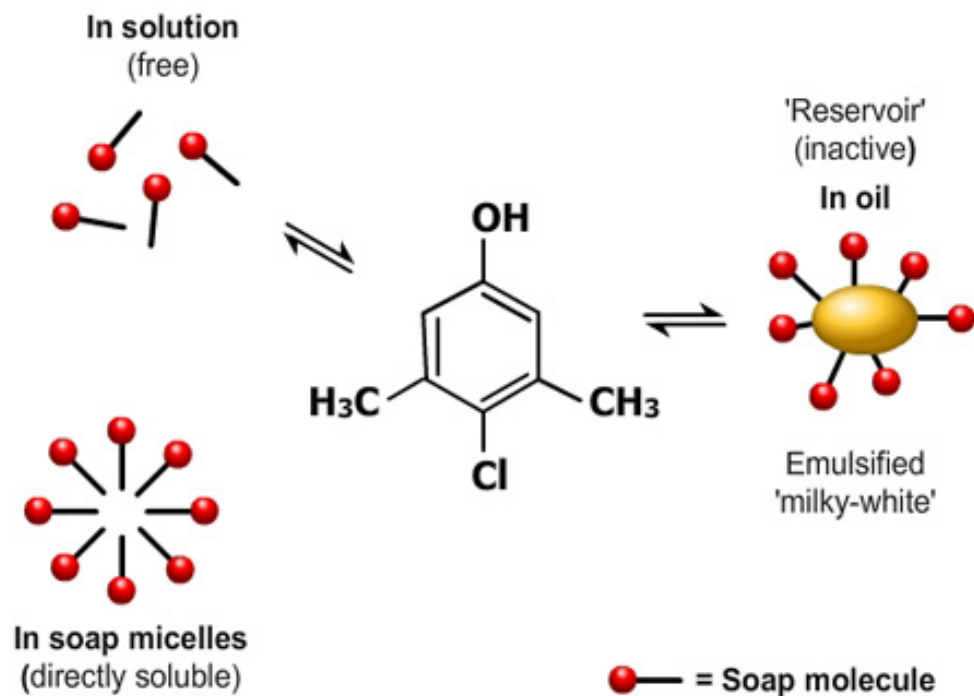
The detailed biochemistry of the action of PCMX and other phenol-based antibacterial agents is complex. However, very simply, they are understood to work by the -OH group of the molecule **binding to proteins present on the cell membrane of bacteria, disrupting the cell membrane and allowing the contents of the cell to leak out.**

This allows more PCMX to enter the cell, binding further with proteins and enzymes, and effectively shutting down the cell's functions. At high concentrations of PCMX, the proteins and nucleic acids in the cell are coagulated and cease to function, leading to rapid cell death.

The $\text{p}K_a$ value is a measure of the strength of an acid. The larger the $\text{p}K_a$ value, the weaker the acid.

- PCMX $\text{p}K_a = 9.7$; $K_a = 1.99 \times 10^{-10} \text{ mol dm}^{-3}$
- phenol $\text{p}K_a = 9.9$; $K_a = 1.28 \times 10^{-10} \text{ mol dm}^{-3}$
- ethanol $\text{p}K_a = 15.9$; $K_a = 7.9 \times 10^{-15} \text{ mol dm}^{-3}$

In the phenoxide ion, PhO^- , the negative charge is spread over the benzene ring due to overlap of a p-orbital on the oxygen atom with the delocalised π -system of the benzene ring,



The soap used in Dettol is made from castor oil which contains ricinoleic acid

On dilution in water, however, a cloudy liquid forms. This consists of droplets of pine oil containing dissolved PCMX. These are held dispersed in water by a layer of soap molecules arranged with their tails in the pine oil and their heads in the water, Figure 13. These droplets are big enough to scatter light, hence the cloudiness of the suspension which is called an emulsion. The PCMX in the droplets of pine oil is not available to kill bacteria - it is the free aqueous PCMX that does this. However, an equilibrium exists between the emulsified PCMX in the droplets and free PCMX dissolved in the water. As PCMX is used up in killing bacteria, more is released from the droplets to keep the aqueous PCMX concentration essentially constant.

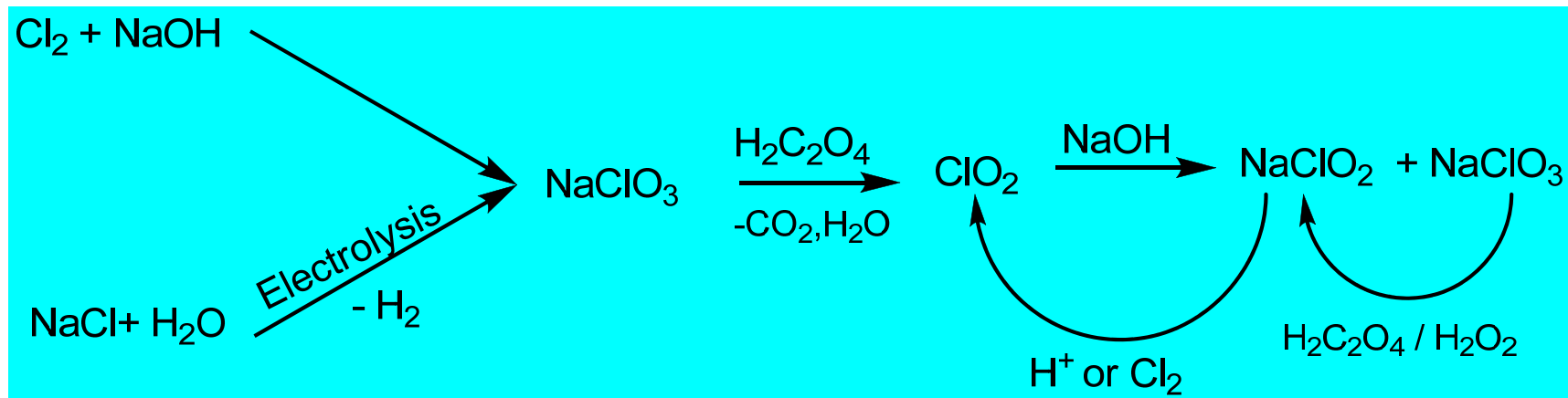
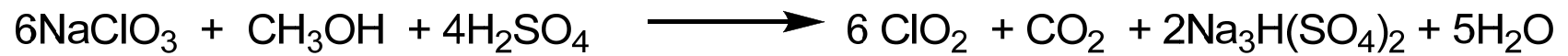
Chlorine dioxide ClO_2



This yellowish-green gas crystallizes as bright orange crystals at $-59\text{ }^\circ\text{C}$. As one of several oxides of chlorine, it is a potent and useful oxidizing agent used in water treatment and in bleaching. The molecule ClO_2 has an odd number of valence electrons, and therefore, it is a paramagnetic radical. **It can explode at gas-phase concentrations greater than 30% volume in air decomposing into chlorine and oxygen.** The decomposition can be initiated by light, hot spots, chemical reaction, or pressure shock. Thus, chlorine dioxide gas is never handled in concentrated form.

Compound	Reaction with Cl_2	Reaction with ClO_2
Water	HClO and HCl	No reaction
CH_3CHO	Cl_3CCHO	$\text{H}_3\text{CC}(\text{O})\text{OH}$
NH_3	NH_2Cl , NHCl_2 , NCl_3	No reaction
R_3N	R_3NCl^+	Oxidative dealkylation R_2NH_2^+ , RCHO , HClO_2
Cyanide	$(\text{ClCN})_3$, Cyanuric chloride	CNO^- (below pH 10) or $\text{CO}_2 + \text{N}_2$ (above pH10)
H_2S	Colloidal Sulfur	SO_4^{2-}
RSH	RSO_2Cl or RSSR	Sulfonic acid and Sulfonates

Chlorine Dioxide ClO₂



Since ClO₂ is difficult to handle and is also an explosive, for all practical purposes it is generated from NaClO₂. NaClO₂ is produced worth over 18 million USD per year.