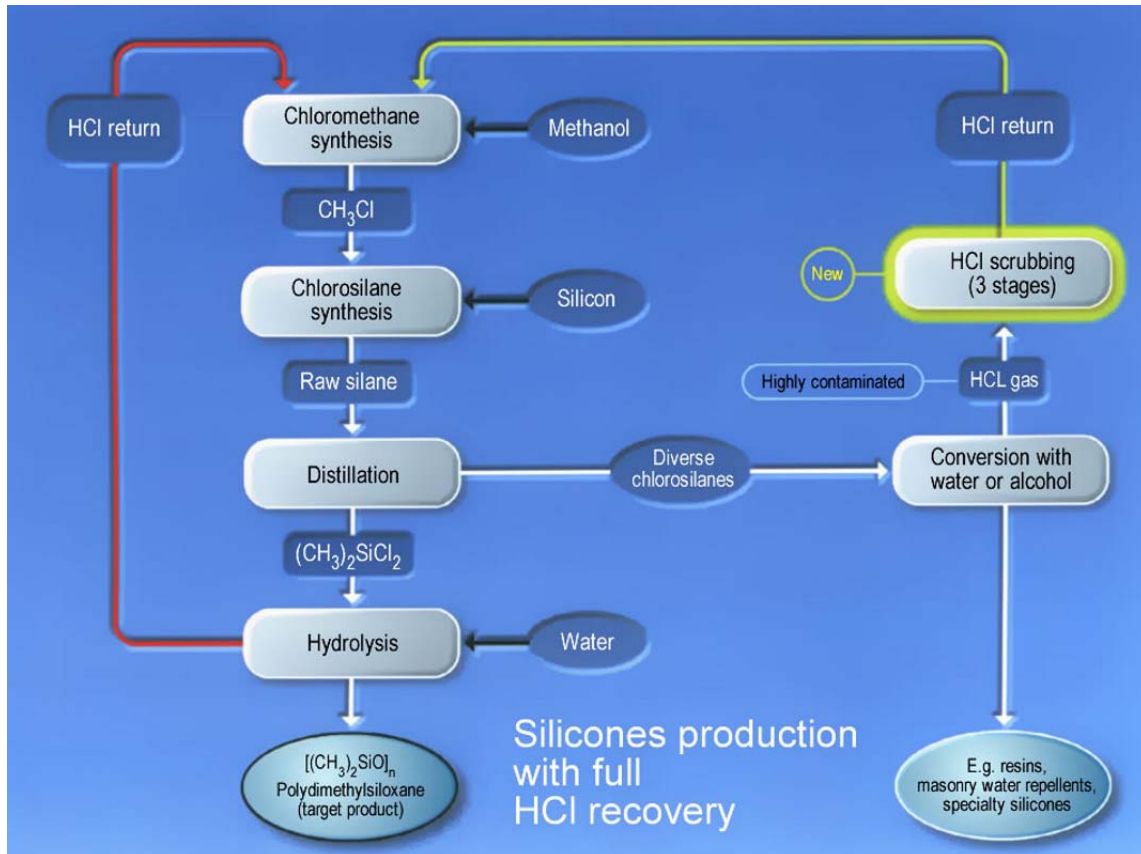


Worksheet 1.1
Manufacture of silicones

Name:

Class:

Date:



1. Write down the chemical equations for the numbered processes in the diagram:

① Chloromethane synthesis:

② Chlorosilane synthesis (mono-, di-, trichlorosilane):

Worksheet 1.2 Manufacture of silicones	Name:
	Class:
	Date:

③ Hydrolysis of dichlorodimethylsilane:

④ Condensation of dihydroxydimethylsilane:

2. Name the starting materials and end products in this industrial process.

3. Explain the two HCl loops. How do they differ with regard to the recycled hydrogen chloride gas?

Worksheet 1.3 Manufacture of silicones	Name:
	Class:
	Date:

4. Which chlorine compounds are used in silicones production? Write down their names and formulas.

5. Why is "chlorine chemistry" necessary in this process, even though the silicone products do not contain chlorine?

6. How can chlorine emissions be avoided during silicones production? What are the advantages of this?

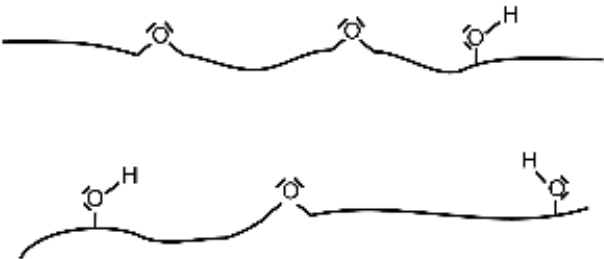
Worksheet 2.1 Water-repellent treatment	Name:
	Class:
	Date:

1. The surface of paper is hydrophilic whereas that of polyethylene (PE) is hydrophobic. Why?

- Paper is of natural origin (cellulose), whereas PE is a synthetic material.
- Water molecules interact more strongly with paper molecules than with the molecules of a PE film.
- Paper is white whereas PE is transparent.
- Paper has a rougher surface than PE.

2. On the left of the following diagram are some highly simplified structural elements from cellulose molecules.

a) Draw a schematic diagram of PE molecules in the right-hand box.

Schematic diagram of cellulose molecules	Schematic diagram of PE molecules
	

b) What kind of intermolecular bonds are formed between water molecules and cellulose molecules? Draw them in the left-hand box above.

Worksheet 2.2
Water-repellent treatment

Name:

Class:

Date:

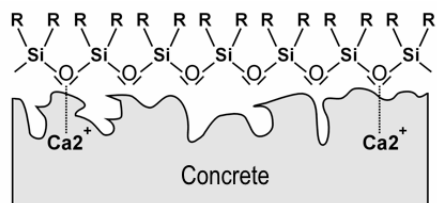
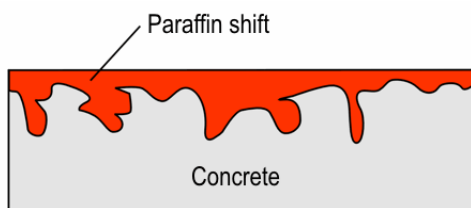
c) Which of these intermolecular interactions are also possible between water molecules and silicone molecules?

d) How can a polar surface be made water-repellent (hydrophobic)?

3. A piece of concrete (consisting mostly of calcium carbonate) can be rendered water-repellent

- with paraffin (which is a mixture of alkenes) or
- with silicone fluid

(see sketches).



Worksheet 2.3 Water-repellent treatment	Name:
	Class:
	Date:

Name similarities and differences regarding:

a) Thickness of the coating

b) Adhesion of the water-repellent coating

c) Resistance of protective layer to mechanical and thermal stress

Worksheet 2.4 Water-repellent treatment	Name:
	Class:
	Date:

d) Consumption of coating material per square meter (coverage)

e) Coating method

4. Which of the two methods is better in your opinion? Why?

Worksheet 3.1
Emulsions and antifoam agents

Name:

Class:

Date:

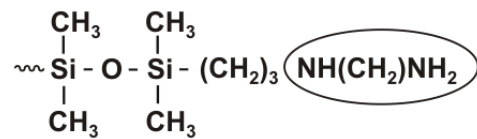
Highly simplified diagram of a surfactant particle



a) Conventional surfactant
sodium salt of fatty acid; soap



b) Silicone surfactant
(aminosilicone fluid)



1. Label the two main parts of a surfactant particle and then describe how the surfactant works.

2. What are the similarities and differences between the two surfactants a) and b) shown above on the right?

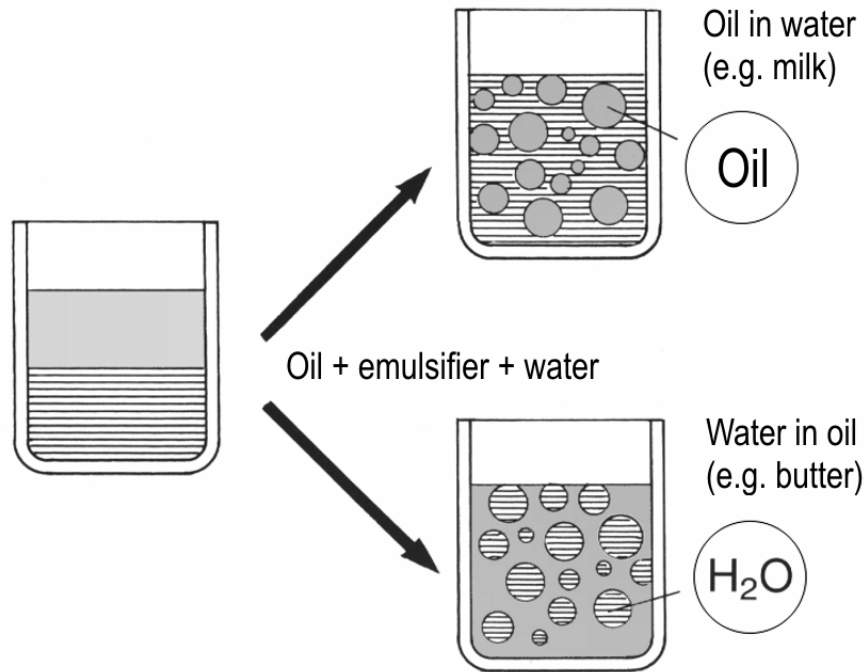
Worksheet 3.2
Emulsions and antifoam agents

Name:

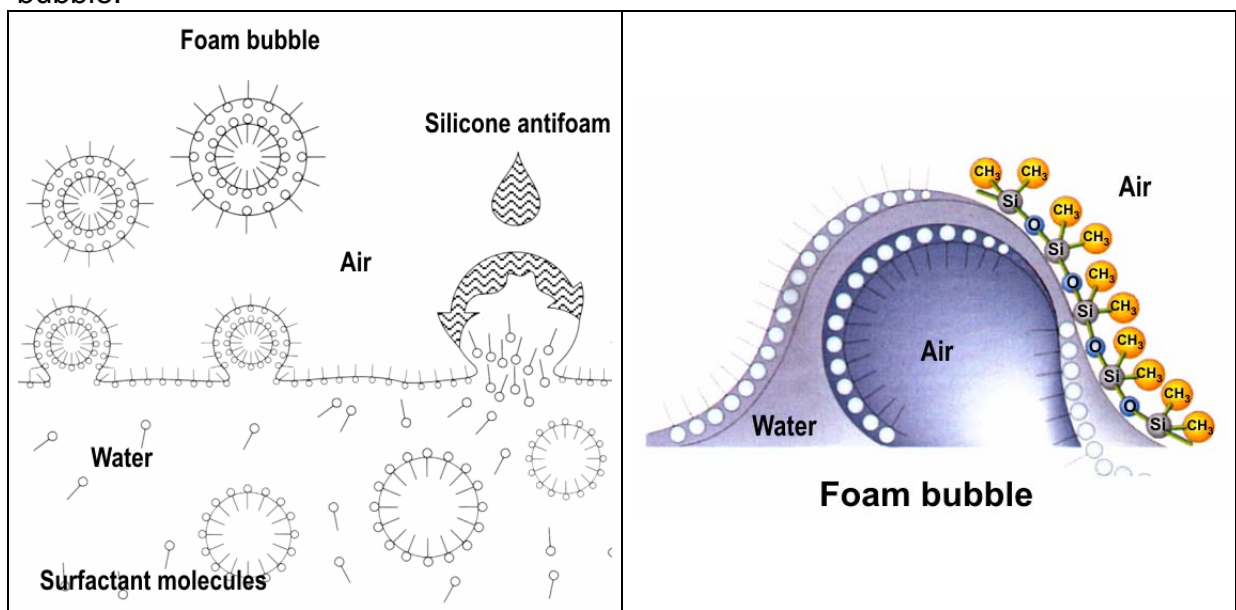
Class:

Date:

3. Draw an oil drop and a water drop, showing each surrounded by surfactant molecules in the proper orientation.



4. Use the diagram on the left below to describe the formation and the structure of a bubble.



Worksheet 3.3 Emulsions and antifoam agents	Name:
	Class:
	Date:

5. Using both diagrams, explain how a bubble bursts under the influence of the silicone antifoam.

6. What kind of forces are at work in the case of the
- bubble?
- defoaming process?

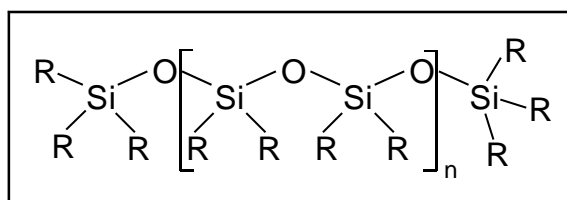
Worksheet 4.1 Silicone fluids, resins and rubbers	Name:
	Class:
	Date:

1. Starting materials for the manufacture of silicones are:

"Monofunctional units" (monochlorosilane)	"Difunctional units" (dichlorosilane)	"Trifunctional units" (trichlorosilane)
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{Si}-\text{Cl} \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{Cl}-\text{Si}-\text{Cl} \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{Cl} \\ \\ \text{H}_3\text{C}-\text{Si}-\text{Cl} \\ \\ \text{Cl} \end{array}$

Fill in the correct names of the compounds shown.

2. The typical structure of a silicone fluid is shown in the following diagram. (R stands for any organic group or radical.)



a) Which of the three silane units in question 1 has to be used manufacturing a silicone fluid?

b) Create a 2-step synthesis for a silicone fluid that has the molecular structure shown above and name the types of reaction involved.

Step 1:

Worksheet 4.2 Silicone fluids, resins and rubbers	Name:
	Class:
	Date:

Type of reaction:

Step 2:

Type of reaction:

c) What is the function of the silane units in the silicone fluid chain?

d) The length of the molecule can be controlled by varying the number of functional units. Explain why this is so.

Worksheet 4.3 Silicone fluids, resins and rubbers	Name:
	Class:
	Date:

2. Assign the following properties to the terms “silicone resin”, “silicone fluid”, and “silicone rubber”:
solid, hard, elastic, liquid, water-repellent, electrically conducting, insulating, chemically resistant.

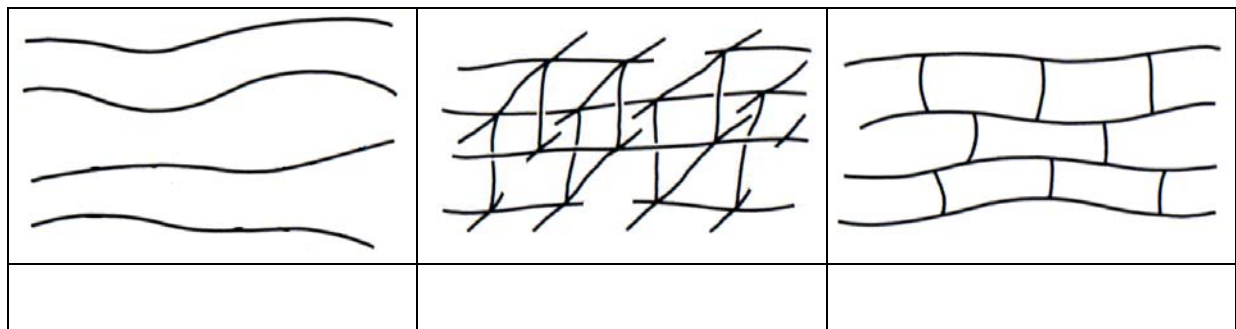
(Note: Any property may be used more than once).

Silicone fluid:

Silicone resin:

Silicone rubber:

3. The following three schematic diagrams show typical silicone products:



a) Match the right silicones (rubber, oil, resin) with the pictures.

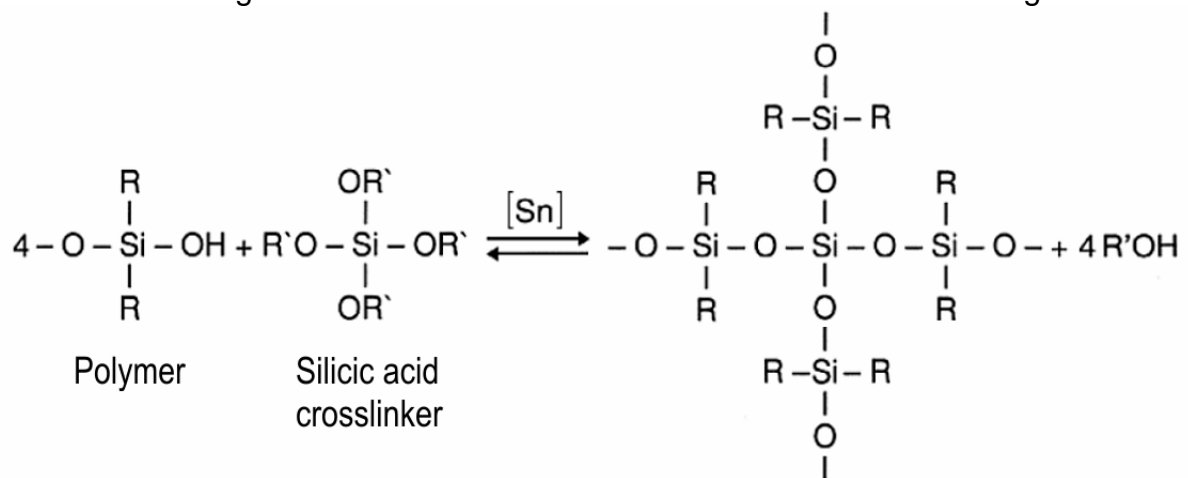
b) Explain the properties from question 2 with the help of the structural models above.

Worksheet 4.5 Silicone fluids, resins and rubbers	Name:
	Class:
	Date:

c) Which substituent on the Si atom is necessary for the molecule of crosslinking agent?

.

5. The crosslinking reaction shown below is known as condensation curing.



a) Explain this term.

b) Mark the new bonds and the cleaved molecules.

c) What structural feature must the molecule of crosslinking agent have?

6. Which of the two types of crosslinking (see exercises 4 + 5) is more likely to cause the material to cure completely? Explain.

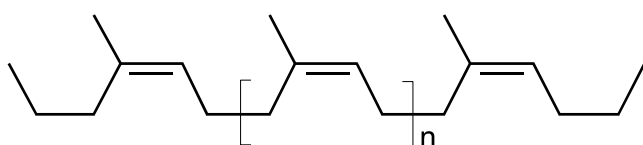
Worksheet 4.6

Silicone fluids, resins and rubbers

Name:

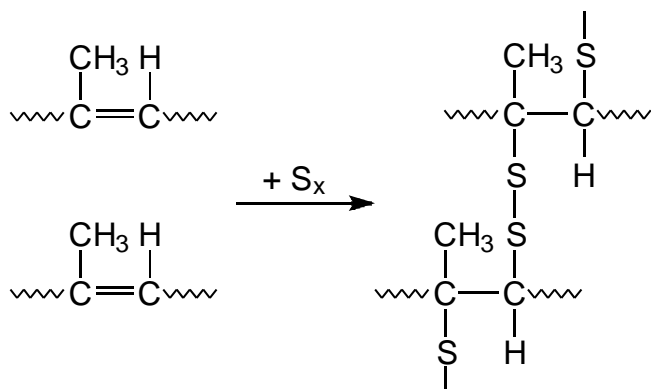
Class:

Date:



cis-1,4-Polyisoprene

7. The box on the left shows the structure of natural rubber (cis-1,4-Polyisoprene) and its curing reaction.



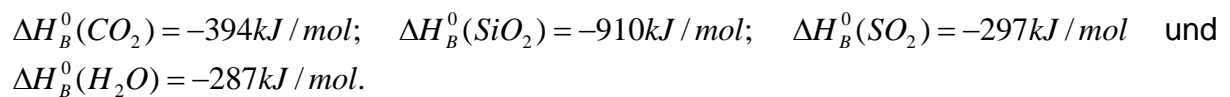
a) Comment on the compositions of vulcanized natural rubber and silicone rubber.

b) Which of the two types of silicone crosslinking does curing of natural rubber resemble more? Explain.

Worksheet 4.7 Silicone fluids, resins and rubbers	Name:
	Class:
	Date:

8. What products are formed when natural rubber and silicone rubber undergo complete combustion? Write down their names and formulas.

9.) The enthalpies of formation for carbon dioxide, silica, sulfur dioxide and water are:



Can this information be used to predict the different quantities of heat evolved during combustion of rubber and silicone rubber? Explain in detail.

10.) What property of silicone rubber is an advantage over natural rubber in a fire?

.

Worksheet 5.1

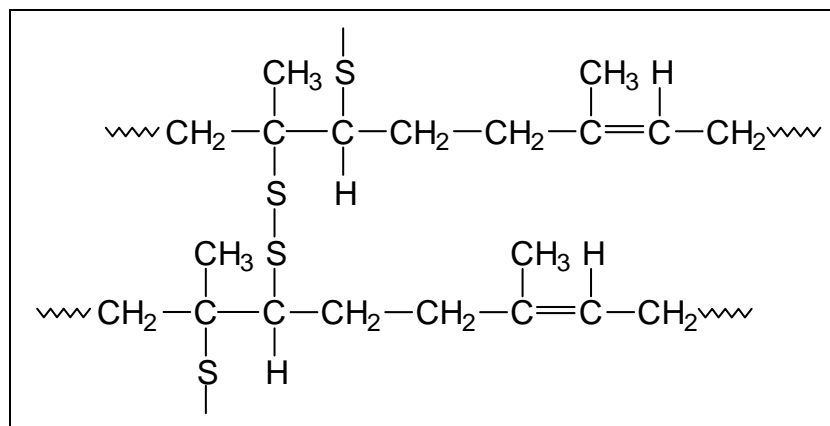
Comparison: Silicone rubber –
Natural rubber

Name:

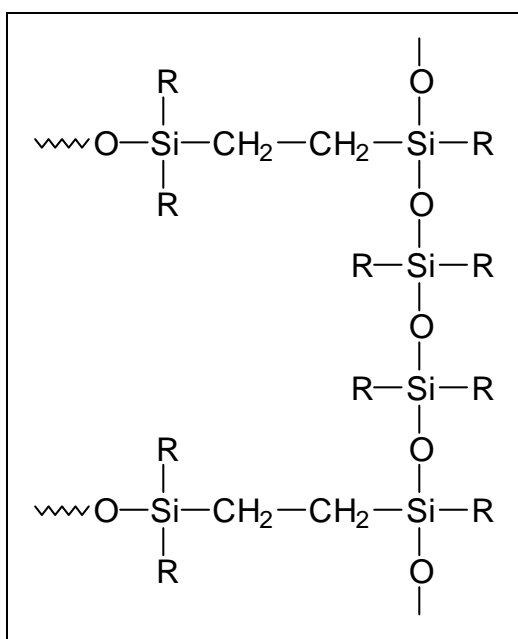
Class:

Date:

Structure of natural rubber



Structure of silicone rubber



1. Natural rubber gradually dissolves in paraffin oil (mixture of alkanes), whereas silicone rubber doesn't. Give reasons for this difference using the structures shown.

Worksheet 5.2 Comparison: Silicone rubber – Natural rubber	Name:
	Class:
	Date:

2. Exposure to ozone gas causes natural rubber to crack. Silicone rubber is not affected by ozone. Look up the term "ozonolysis" in a textbook on organic chemistry and then explain the difference using the structures shown.

3. The bond energies of the C-C bond, the C-H bond and the Si-O bond at 298 K are as follows:

C-C: 607 kJ/mol

C-H: 338 kJ/mol

Si-O: 800 kJ/mol

Using this information and the structures shown above, explain why silicone rubber has greater heat resistance than natural rubber.

Worksheet 6.1 Properties of tetrachlorosilane	Name:
	Class:
	Date:

Chlorine forms the following compounds with the elements of the second row in the periodic table:

	NaCl	MgCl ₂	AlCl ₃	SiCl₄	PCl ₃	SCl ₂	Cl ₂
	Solid	Solid	Solid	Liquid	Liquid	Liquid	Gas
Mp	800 °C	712 °C	192.5 °C (under pressure)	- 67.7 °C	- 92 °C	-78 °C	- 101 °C
Bp	1465 °C	1418 °C	sub. 180 °C	56.7 °C	74.5 °C	59 °C	- 34.1 °C
Δ EN				1.2			

1. Calculate the missing electronegativity differences Δ EN (and write them in the corresponding table fields).

On the left and right of the arrow, write in the type of bond that applies to NaCl and Cl₂.

2. Explain the connection between the electronegativity difference, the partial ionic nature and the physical state at room temperature.

Worksheet 6.2 Properties of tetrachlorosilane	Name:
	Class:
	Date:

3. Complete the following table. Check either "Yes" or "No" and, where necessary, write in the ions or the products of hydrolysis.

	Ions?		Hydrolysis?	
NaCl <small>Think of a table salt solution.</small>	Yes <input type="radio"/>		Yes <input type="radio"/>	
	No <input type="radio"/>		No <input type="radio"/>	
AlCl ₃	Yes <input type="radio"/>		Yes <input type="radio"/>	
	No <input type="radio"/>		No <input type="radio"/>	
SiCl₄ <small>Hydrolysis of tetrachlorosilane (see expt)</small>	Yes <input type="radio"/>		Yes <input type="radio"/>	
	No <input type="radio"/>		No <input type="radio"/>	
PCl ₃	Yes <input type="radio"/>		Yes <input type="radio"/>	
	No <input type="radio"/>		No <input type="radio"/>	
Cl ₂ <small>Think of chlorine water.</small>	Yes <input type="radio"/>		Yes <input type="radio"/>	
	No <input type="radio"/>		No <input type="radio"/>	

4. Explain why the chlorides behave differently in water.

Worksheet 7.1

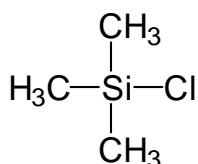
Hydrolysis and rate of hydrolysis of chloromethylsilanes

Name:

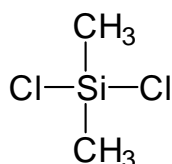
Class:

Date:

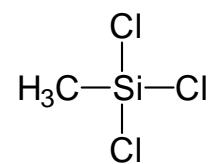
The “Hydrolysis of chloromethylsilanes” and “Rate of hydrolysis of chloromethylsilanes” experiments revealed similarities and differences in the three chloromethylsilanes.



Chlorotrimethylsilane



Dichlorodimethylsilane



Trichloromethylsilane

1. Name the similarities and differences.

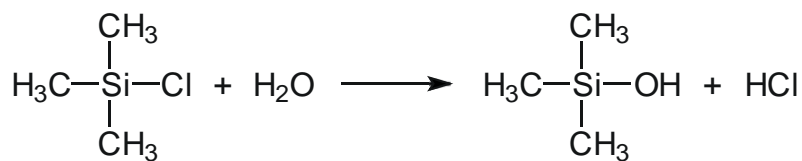
Similarities:

Differences:

2. Explain the different properties of the hydrolysis products using the equations.

a) Chlorotrimethylsilane

Hydrolysis:



Chlorotrimethylsilane

Trimethylsilanol

Worksheet 7.2

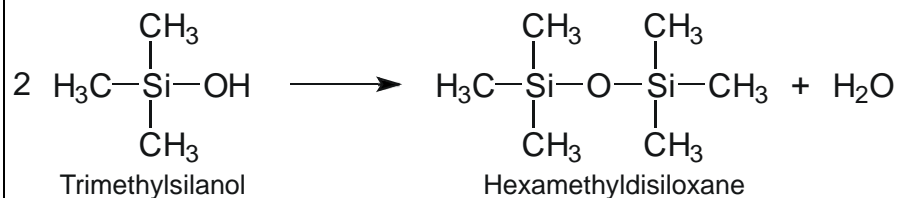
Hydrolysis and rate of hydrolysis of chloromethylsilanes

Name:

Class:

Date:

Condensation:

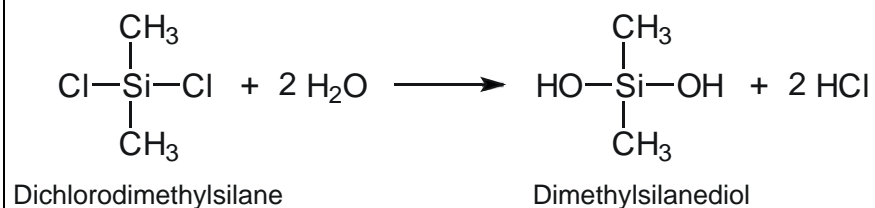


Product: Properties

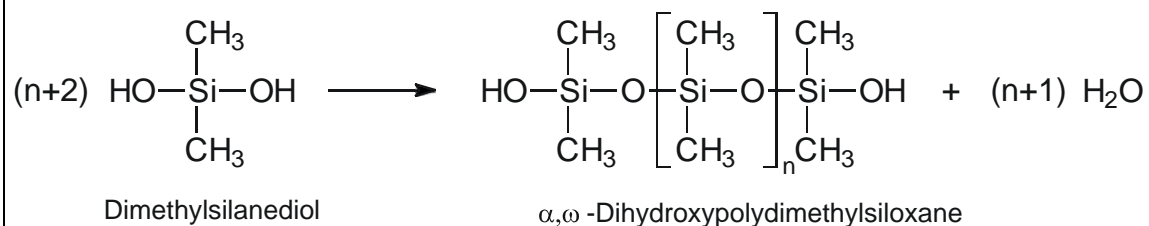


b) Dichlorodimethylsilane

Hydrolysis:



Condensation:



Worksheet 7.3

Hydrolysis and rate of hydrolysis of chloromethylsilanes

Name:

Class:

Date:

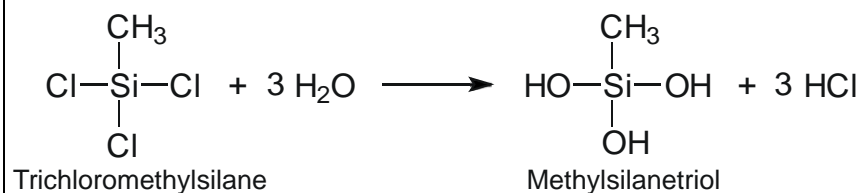
Product:

Properties

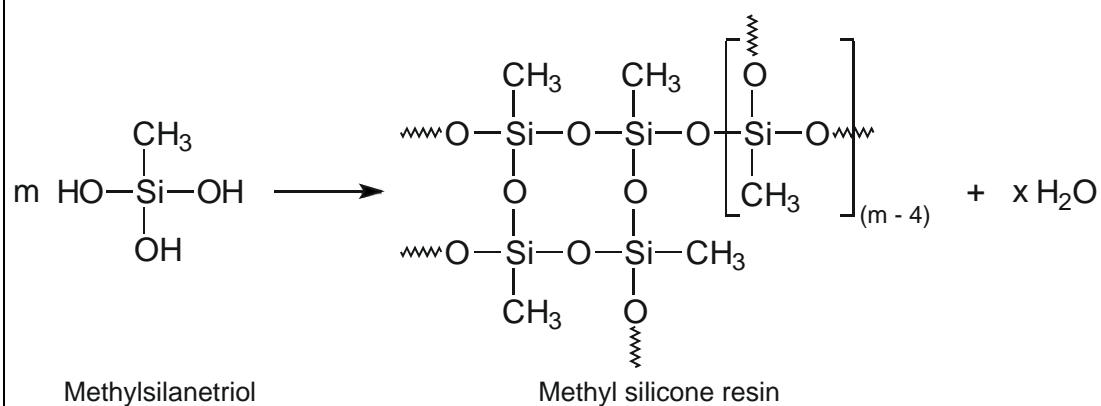


c) Trichloromethylsilane

Hydrolysis:



Condensation:

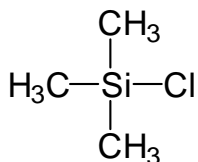
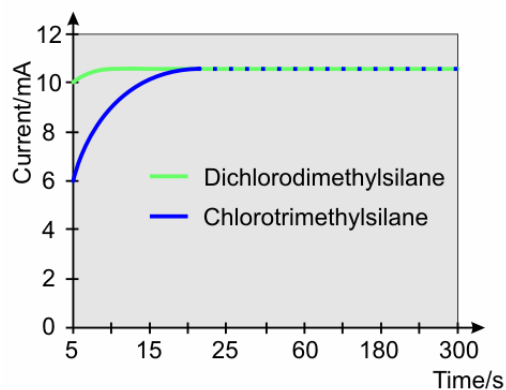


Worksheet 7.4 Hydrolysis and rate of hydrolysis of chloromethylsilanes	Name:
	Class:
	Date:

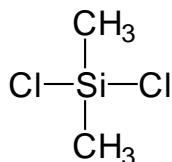


Properties

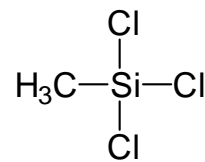
3. The experiment "Rate of hydrolysis of chloromethylsilanes" revealed different rates of hydrolysis for the chloromethylsilanes. What do you attribute the different rates of hydrolysis to?



Chlorotrimethylsilane



Dichlorodimethylsilane



Trichloromethylsilane

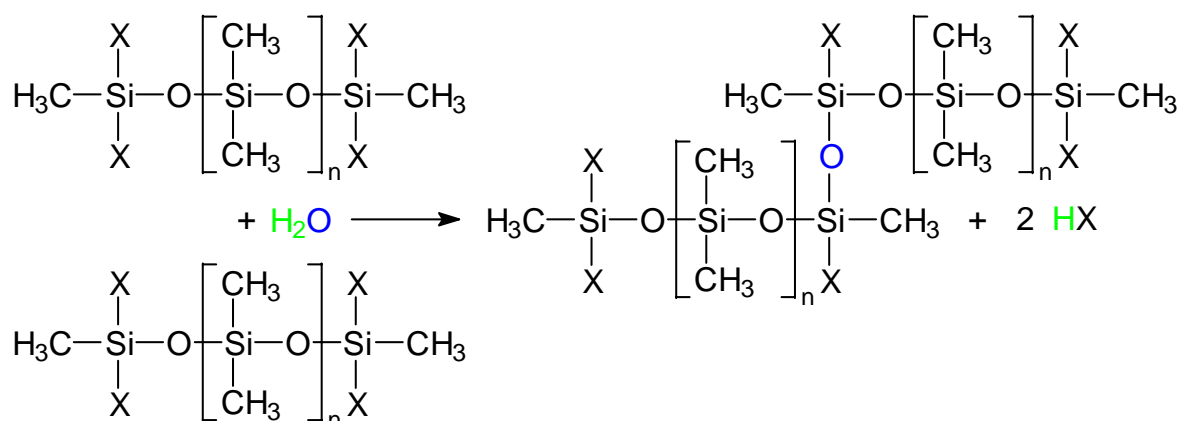
Worksheet 7.5 Hydrolysis and rate of hydrolysis of chloromethylsilanes	Name:
	Class:
	Date:

4. What happens when tetrachlorosilane is hydrolyzed?

5. Illustrate the same type of chemical reactions as shown in question 2 for the hydrolysis and condensation of tetrachlorosilane.

Worksheet 8.2 RTV-1 silicone rubbers	Name:
	Class:
	Date:

3. The following general reaction illustrates the curing of the silicone rubber from exercise 1 when it is exposed to atmospheric humidity. Circle the reacting groups and name X and HX.



X =	HX =
-----	------

Experiment: Cover the ends of two U-shaped profiles with adhesive tape. Fill one with ELASTOSIL[®] E43 and press the compound down with a wet finger. Do the same with the second profile, using ELASTOSIL[®] N199. Fill the third profile with gypsum, and scrape off the excess with a spatula. Now place a moistened strip of pH paper on the edge of each U profile and allow the compound to cure. What happens?

After final curing, check the samples for impact strength, consistency and ease of overpainting with watercolors.

4. Write your observations into the following table and compare the properties of the samples.

	ELASTOSIL [®] E43	ELASTOSIL [®] N199	Gypsum
Odor			
pH paper			
Impact strength			
Consistency			
Paintability with watercolors			

Worksheet 8.3 RTV-1 silicone rubbers	Name:
	Class:
	Date:

5. Explain the different odors as well as the different colors of the pH strips when the different samples cure.

ELASTOSIL[®] E43:

ELASTOSIL[®] N199:

Gypsum:

6. Using the structure of the samples, explain why gypsum breaks when subjected to strong mechanical force whereas the two other samples behave elastically.

Worksheet 8.4 RTV-1 silicone rubbers	Name:
	Class:
	Date:

7. How do you explain the different adhesion of the watercolor to the various samples?

8. Silicone rubbers and gypsum are used as jointing materials in the building industry. Which of the two materials would you use for joints subject to permanent movement and stresses?

9.) Explain why ELASTOSIL[®] E43 is unsuitable for joining two pieces of marble.

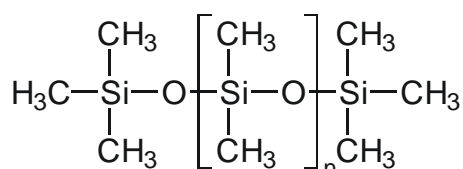
Worksheet 9.1 Properties of silicone fluids	Name:
	Class:
	Date:

Water-repellent properties of silicone fluids

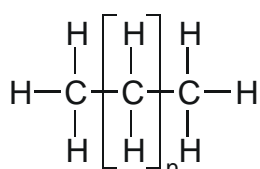
Experiment 1: Brush Silicone Fluid AK 5000 from the WACKER lab set over different smooth, clean surfaces, such as glass, copper, a wooden panel, a paper tissue and then do the same to identical surfaces with glycerol. Then apply a layer of candle wax to piece of paperboard. Place a drop of water dyed with methylene blue on the treated and untreated surfaces. What happens?

Observation:

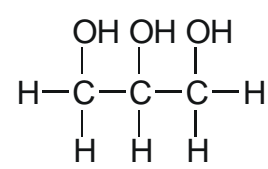
1. Try to explain the observations using the structural formulae for silicone fluid, glycerol and paraffin from experiment 1.



Silicone fluid (Polydimethylsiloxane)



Paraffin (higher alkane)



Glycerol

Explanation:

Worksheet 9.2

Properties of silicone fluids

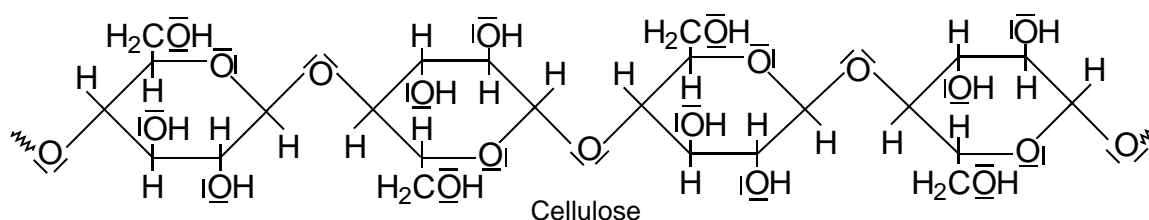
Name:

Class:

Date:

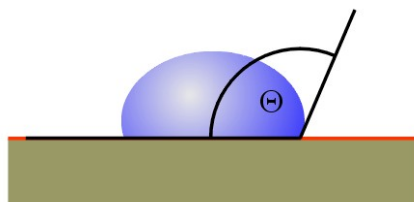
2. While the paraffin coating can be scratched off relatively easily, the silicone fluid adheres comparatively well to surfaces such as glass, building materials and textiles (e.g. cellulose) due to intermolecular interactions (electrostatic forces of attraction, hydrogen bonds).

Draw a section of a silicone molecule in the following space and use dotted lines to show the interactions between the cellulose surface and the silicone molecule.



Baking silicone fluids on glass surfaces

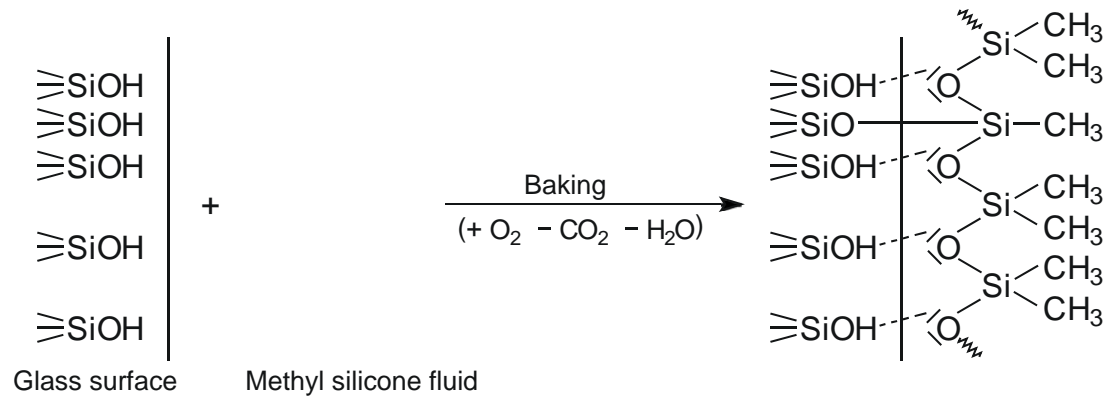
The adhesion and film-formation of the silicone layer can be fundamentally strengthened by chemical reactions with functional groups, such as hydroxyl groups, on the surface. Thus, it is possible that, at high baking temperatures, polydimethylsiloxane molecules on glass surfaces become anchored on the surface by primary valences through occasional scission of a Si-CH₃ bond under the influence of oxygen and water as well as subsequent condensation with siloxy groups (SiOH). It can be observed that (see diagram) this treatment causes the contact angle which forms between water and the silicone-treated glass surface to rise to 100-110°.



Contact angle θ of a water drop on a (water-repellent) surface

Worksheet 9.3 Properties of silicone fluids	Name:
	Class:
	Date:

3. Using the explanation above, draw the hydrogen bonds and the primary valences in different colors for the product formed by anchorage of a methyl silicone fluid to a glass surface. Write down the equation part of the silicone molecule on the reagent side.



Viscosity of silicone fluids

Experiment 2: Measure the time it takes for a metal ball to travel between two marks on a glass tube (glass beaker viscometer) in olive oil, sewing machine oil, Silicone Fluid AK 1000 and Silicone AK 5000 from the WACKER lab kit at five different temperatures.

4. Plot the natural logarithm of the fall time (y-axis) against the temperature. Do you notice anything?

Worksheet 9.4 Properties of silicone fluids	Name:
	Class:
	Date:

5. Explain why the calculated viscosity depends on the temperature.

6. Imagine you had the task of selecting one of these four oils for use in hydraulic equipment subjected to major temperature fluctuations, e.g. in an airplane. Explain your choice of oil.

Worksheet 9.5 Properties of silicone fluids	Name:
	Class:
	Date:

Viscosity determinations

The viscosity of a substance depends on the molecular mass, the molecular shape and the intermolecular bonds in addition to the temperature. Given standardized conditions, it is therefore possible to make inferences about the mean molar mass of the dissolved polymer from the viscosity. For example, viscosity measurements are used, in production monitoring to check how far a polymerization has progressed, i.e. whether the synthesised polymer has already reached the desired molar mass.

7. Explain why viscosity measurements are suitable for routine tests.

8. Think of possible application areas for silicone fluids on the basis of the properties you have determined.

Worksheet 10.1 Surfactants and antifoam agents	Name:
	Class:
	Date:

Experiment 1: Fill a medium-sized glass dish with water and carefully place a paper clip on the surface of the water. Then add several drops of water from a pipette at the edge of the glass dish followed by several drops of dish soap. What happens?

Observation:

1. How would you interpret and explain your observations from Experiment 1?

Interpretation:

Explanation:

2. Using what you learned from experiment 1, explain the special abilities of the water strider (see photo).



Worksheet 10.2 Surfactants and antifoam agents	Name:
	Class:
	Date:

Explanation:

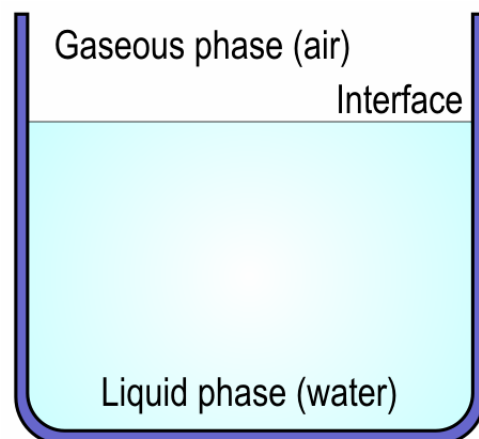
3. The real active substances in detergents are surfactants. These may be anions, cations, zwitter ions or molecules. A characteristic of surfactant particles is that they all have a hydrophilic end and a hydrophobic end.

Using this information, draw the model of an anionic surfactant that has the following formula: $\text{H}_3\text{C}(\text{CH}_2)_n\text{COO}^-\text{Na}^+$ ($n = 9$ to 19).

Drawing:

4. Another name for a surfactant is surface-active agent. In the diagram on the right, show how the surfactant particles are aligned on the water surface and in the water and explain how this lowers the surface tension of the water.

Explanation:



Worksheet 10.3 Surfactants and antifoam agents	Name:
	Class:
	Date:

Experiment 2: Take a small vial with a snap-on lid, add water until it is 2/3rds full and then add several drops of dish soap. Close the lids and shake the vials vigorously. What happens? How does the foam change in the course of time?

Observation:

5. How would you explain your observations from Experiment 2?

Explanation:

Experiment 3: Place some surfactant solution in a vessel, shake it and then add one drop of Antifoam Emulsion AS-EM SRE from the WACKER lab kit. What happens? What do you see when it is shaken again?

Observation:

Worksheet 10.4
Surfactants and antifoam agents

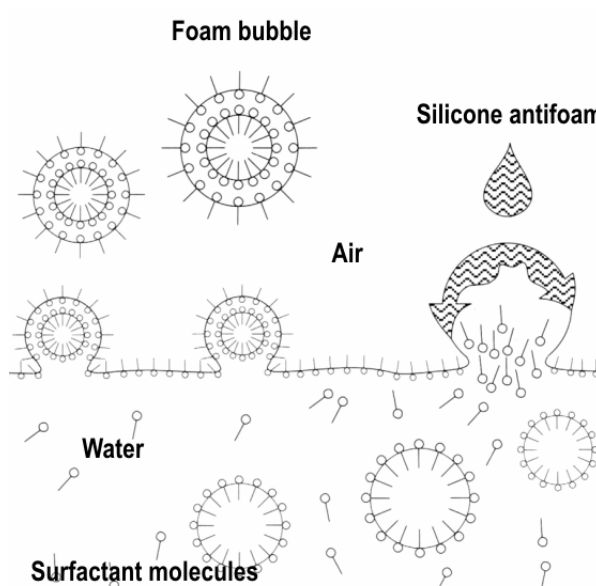
Name:

Class:

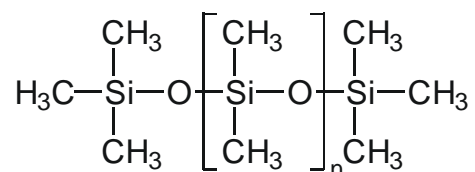
Date:

6. Explain your observations from experiment 3 with the help of the diagram on the right.

Explanation:



7. To be effective, an antifoam agent needs to have a very low surface tension, to be insoluble in the liquid that is foaming and to have high spreading power. At the same time, the tendency of a liquid to foam is also based on low surface tension. A methyl silicone fluid served as antifoam agent in the experiment (see diagram). Using the structure of the methyl silicone fluid, explain why it works as an antifoam agent even though its surface tension is lower than that of surfactants (surface tension of methyl silicone fluid: approx. 20 mN/m; surfactants: approx. 30 mN/m).



Structural formula of a methyl silicone fluid

Explanation:

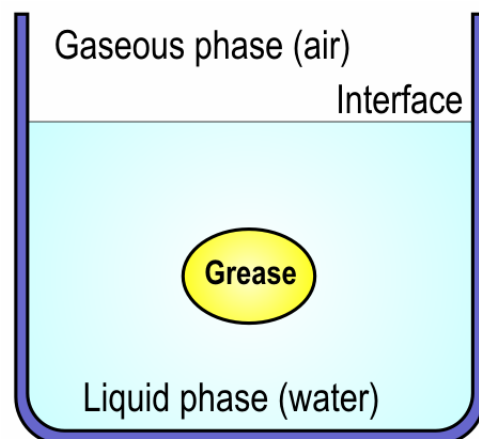
Worksheet 10.5 Surfactants and antifoam agents	Name:
	Class:
	Date:

Experiment 4: Vigorously shake 2 ml water, 0.5 ml olive oil and 1 ml surfactant solution in a test tube, place the test tube in the stand and observe separation in the test tube. Carry out the same test on the surfactant solution from Experiment 3 but without adding surfactant solution.

Observation:

8. Use the surfactant model to explain your observations from Experiment 4. Draw the orientation of the surfactant particles at the interface between the air and the water, and between the water and the oil.

Explanation:



Worksheet 11.1 Müller-Rochow synthesis	Name:
	Class:
	Date:

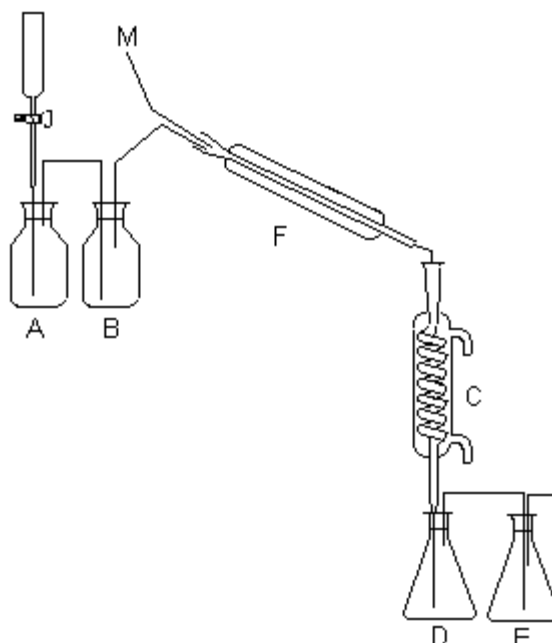
Background

The chemist E. G. Rochow conducted an experiment on the manufacture of silicones on May 9th and 10th, 1940 that went down in the annals of chemistry as the direct or Müller-Rochow synthesis (R. Müller arrived independently at the same results as Rochow three-quarters of a year later). Rochow made the following entry about the experiment in his lab journal:

May 9, 1940

I crushed a 50/50 mixture of Cu-Si from the Niagara Falls Smelting Co. in the jaw crusher and filled a Nonex pipe with the material (particle size: 6-7 mm down to fine powder). I placed the pipe in the furnace and attached it to CH₃Cl & HCl lines. Only a CO₂ cool trap at the outlet end.

- A = Hydrogen chloride source
 - B = Bubble counter
 - C = Cooler for reaction products
 - D = Flask cooled to 0 °C
 - E = Flask cooled to -80 °C
 - F = Furnace with
Reaction tube
- M = Chloromethane



Rochow's original apparatus for the reaction of chloromethane and silicon

May 10, 1940 I heated up the tube to 370 °C in the furnace and kept it at this temperature. First, I introduced some HCl to etch the surface of the alloy, and then I introduced a slow current of CH₃Cl. Apparatus ran the whole day.

4:40 p.m. I interrupted the CH₃Cl flow. About 5 cm³ of liquid had accumulated in the cool trap and there was some liquid at the cold pipe end. I transferred everything to ice-water, which was covered with ether, and stirred. The material hydrolyzed with some cloudiness, but no great quantity of silica formed; it also seems to contain little CH₃Cl.

I decanted some of the ethereal solution into a Petri dish and drove off the ether. A clear, viscous glycerol-like substance remained. This fluid feels sticky, and is very similar to methylsilicone.

Worksheet 11.2 Müller-Rochow synthesis	Name:
	Class:
	Date:

1. Explain which reactions occurred in the experiment up as far as hydrolysis. (Note: The copper is not consumed in the reaction!)



2. Which reactions occur during the hydrolysis? (Write down the non-stoichiometric reaction equation).



3. As already mentioned, the copper is not consumed in the reaction. On the other hand, the test will not occur with just pure silicon. Explain why this is so.

4. Describe the effect of increasing the temperature or pressure on the course of the chemical reaction in exercise 1.

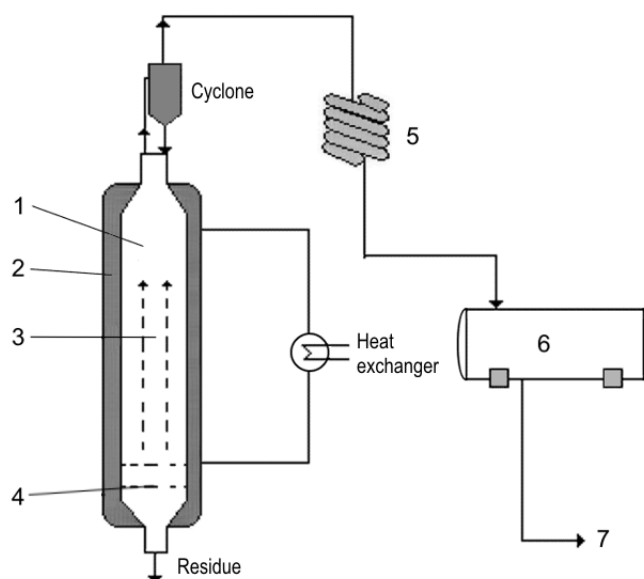
(Tips: 1. All reagents are gaseous at the reaction temperature, except silicon. 2. The reaction is exothermic).

Industrial production

The significance of the experiment described above may be gauged from the fact that industrial synthesis of chloromethylsilanes is based solely on the reaction of between chloromethane and silicon in the presence of a copper catalyst.

Worksheet 11.3 Müller-Rochow synthesis	Name:
	Class:
	Date:

In the industrial version of the direct synthesis, finely ground silicon dust (with a little copper as catalyst) is introduced into a fluid bed reactor where, at 280 °C and a pressure of 1-5 bar, it is agitated by a stream of chloromethane fed in at a tangent. The resultant mixture of chloromethylsilanes is condensed and fractionally distilled to separate it into its individual components. Hydrolysis of the chloromethylsilanes yields the corresponding silanols, which condense immediately and are processed in various ways to different silicone products.



5. Match the numbers 1 to 7 in the above diagram of the industrial-scale production of chloromethylsilanes with the following terms:

Cooling jacket	CH_3Cl	Condenser	Si/Cu
To distillation	Fluid bed reactor	Raw silane mixture	

6. Chloromethane and silicon serve as reagents in the direct synthesis. The silicon is obtained from quartz (SiO_2) and carbon in the electric furnace. Write down the corresponding general reaction and state how the requisite chloromethane can be produced.

I) Production of silicon: $+$ \longrightarrow $+$

II) Production of CH_3Cl : $+$ \longrightarrow $+$