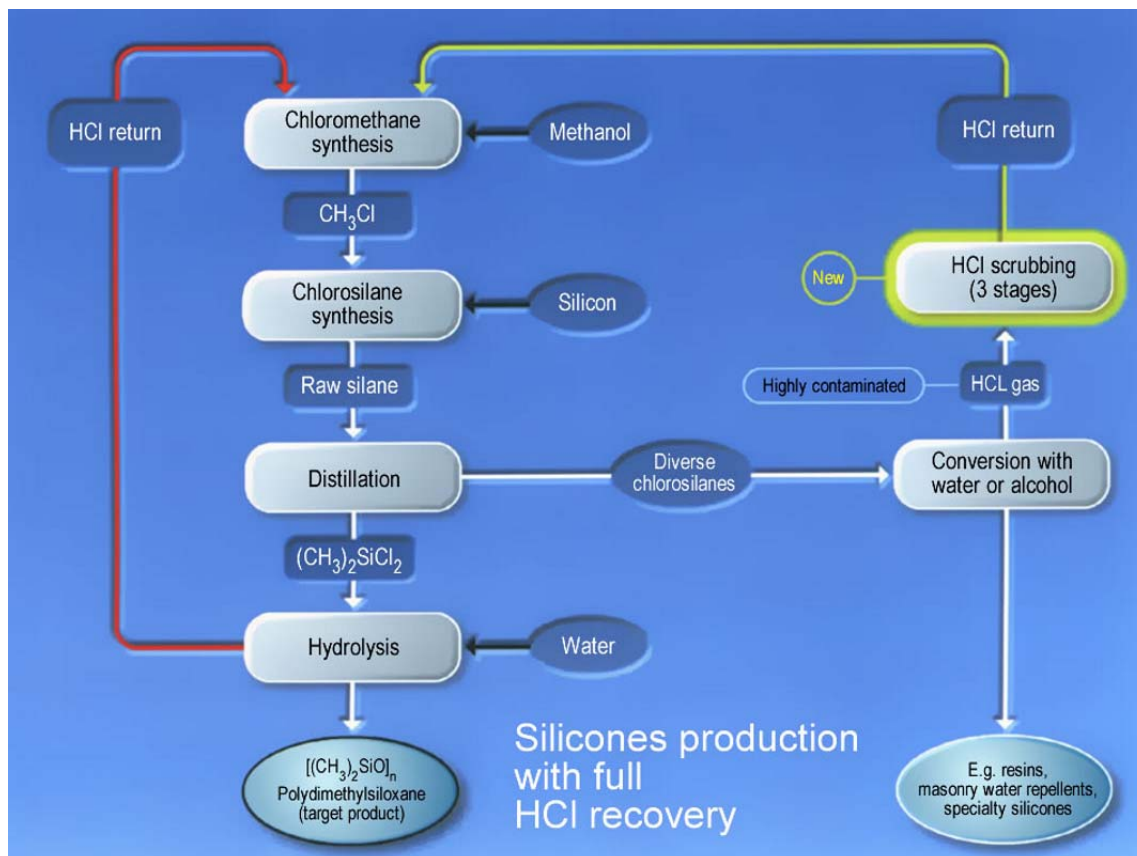


Worksheet 1.1
 Manufacture of silicones
Sample answer key

Name:

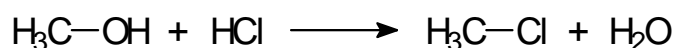
Class:

Date:

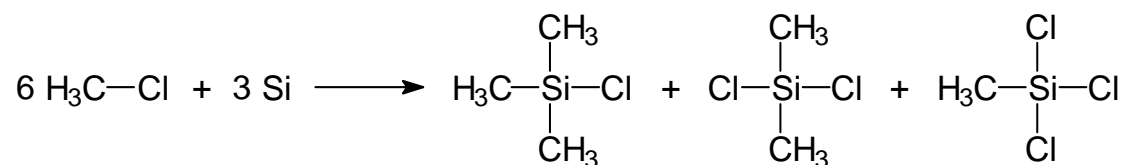


1. Write down the chemical equations for the numbered processes in the diagram:

① Chloromethane synthesis:



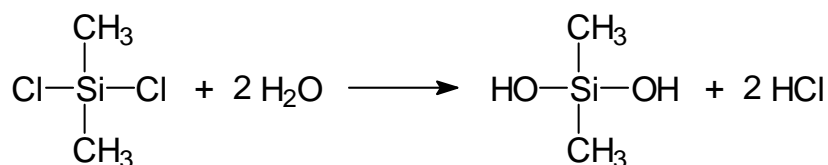
② Chlorosilane synthesis (mono-, di-, trichlorosilane):



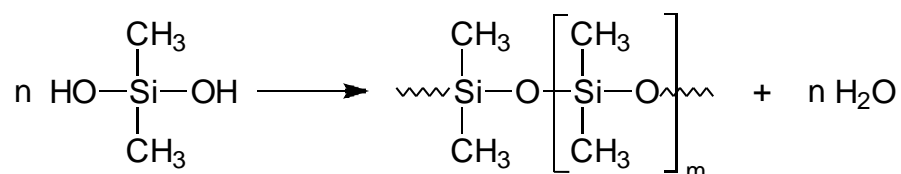
(Note that the stoichiometry of this reaction as shown is not correct. Other silanes are formed as well.)

Worksheet 1.2 Manufacture of silicones Sample answer key	Name:
	Class:
	Date:

③ Hydrolysis of dichlorodimethylsilane:



④ Condensation of dihydroxydimethylsilane:



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

Methanol, hydrogen chloride as well as elemental silicon are the starting materials.

The initial end products are mono-, di- and trichlorosilanes, which can be converted by hydrolysis and then condensation into the corresponding polysiloxanes (silicones.)

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

The HCl loop on the left in the diagram returns the hydrogen chloride formed by the hydrolysis of chlorosilanes back to the process while the loop on the right ensures that unconsumed hydrogen chloride from the silane synthesis is returned to the process.

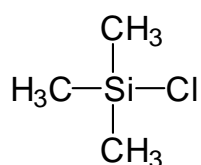
Worksheet 1.3 Manufacture of silicones Sample answer key	Name:
	Class:
	Date:

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

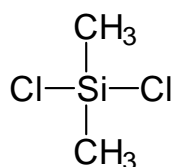
The following chlorine compounds play an important role in silicones production:

Hydrogen chloride HCl *Chloromethane* H₃C—Cl

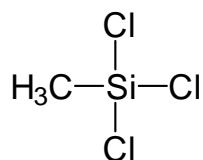
Chlorotrimethylsilane



Dichlorodimethylsilane



Trichloromethylsilane



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

“Chlorine chemistry” is necessary in this process because reactive chlorine compounds are needed as intermediates. Without these, the desired product could not be produced economically.

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

The hydrogen chloride generated by hydrolysis of the chlorosilanes during the production of silicones can be returned to the process. On one hand, this greatly eases the burden on the environment and, on the other, it can save resources and money.

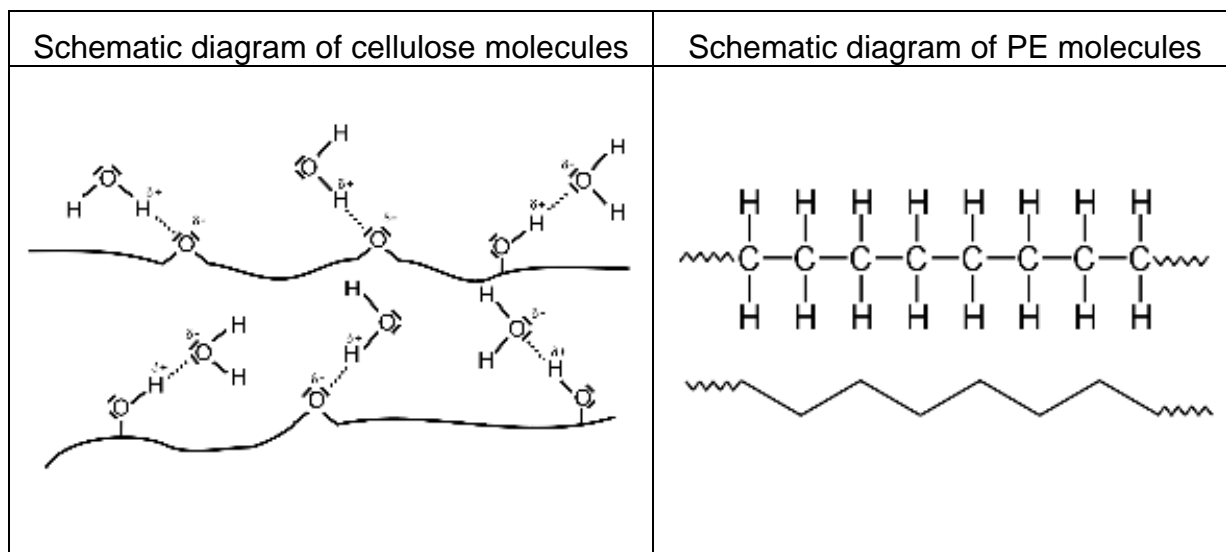
Worksheet 2.1 Water-repellent treatment Sample answer key	Name:
	Class:
	Date:

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.



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

Hydrogen bonds can form between water molecules and cellulose molecules. This is why water is able to wet paper well.

Worksheet 2.2 Water-repellent treatment Sample answer key	Name:
	Class:
	Date:

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

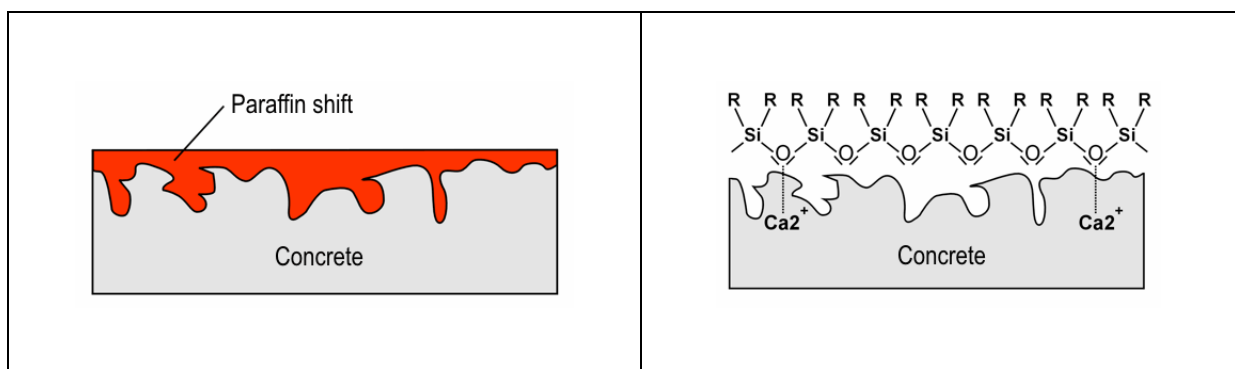
In principle, hydrogen bonds could form between the water molecules and the oxygen atoms of a silicone molecule. However, the numerous nonpolar methyl groups in the silicone group would counteract this. That is why water beads and runs off silicone-treated surfaces instead of wetting them.

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

For a surface to be rendered hydrophobic, it only needs to be coated with a nonpolar substance.

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	Name:
Water-repellent treatment	Class:
Sample answer key	Date:

Name similarities and differences regarding:

a) Thickness of the coating

The paraffin coating in the left diagram is much thicker than the silicone coating in the right diagram. Whereas the paraffin coating is millimeters thick, the silicone coating is just nanometers thick.

b) Adhesion of the water-repellent coating

In the case of the silicone coating, relatively strong forces of attraction develop between the silicone molecule and, for example, the calcium ions, which are a component of the concrete; the result is particularly strong adhesion.

c) Resistance of protective layer to mechanical and thermal stress

The silicone coating is clearly more resistant than the paraffin coating to thermal and mechanical stress. Not only does the silicone have high heat resistance, but the thinness of the coating (just molecules thick) enables it to act like an elastic skin.

Worksheet 2.4	Name:
Water-repellent treatment	Class:
Sample answer key	Date:

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

Because the silicone coating is only several molecules thick, much less of it is needed per square meter than of the paraffin.

e) Coating method



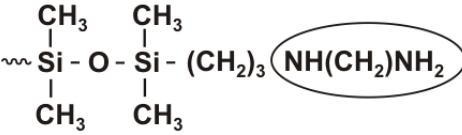
The paraffin wax would have to be melted before use. It is also doubtful whether it would penetrate into all nooks and crannies in the surface of the material to be treated – yet that is indispensable for proper protection. The silicone is a liquid and can therefore get into and wet all irregularities on the surface.

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

I think the silicone coating is better because of points a) to e) listed above. Aside from the small quantity used for coating (which keeps the cost of the coating down), I think it is also important that the appearance of the treated material is not changed. With the paraffin wax coating, the natural color of the material would be hidden by the color of the paraffin wax .

(Answers may vary.)

Worksheet 3.1 Emulsions and antifoam agents Sample answer key	Name:
	Class:
	Date:

<p>Highly simplified diagram of a surfactant particle</p>  <p><u>Hydrophobic</u> <u>Hydrophilic</u> <u>tail</u> <u>head</u></p>	<p>a) Conventional surfactant sodium salt of fatty acid; soap</p>  <p>b) Silicone surfactant (aminosilicone fluid)</p> 
--	---

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

As shown in the diagrams above, surfactant molecules consist of a hydrophilic head and a hydrophobic tail. Greasy or oily substances (grime) interact with the hydrophobic tail, while the water molecules hydrate the hydrophilic head. This forms the basis of the cleaning effect. The surfactant molecules act as bridges that link the grime (nonpolar) to the water (polar). Rinsing then removes (cleans) the “grime-surfactant-water” molecule from the object or garment.

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

Both surfactant molecules have a polar head and a nonpolar tail.

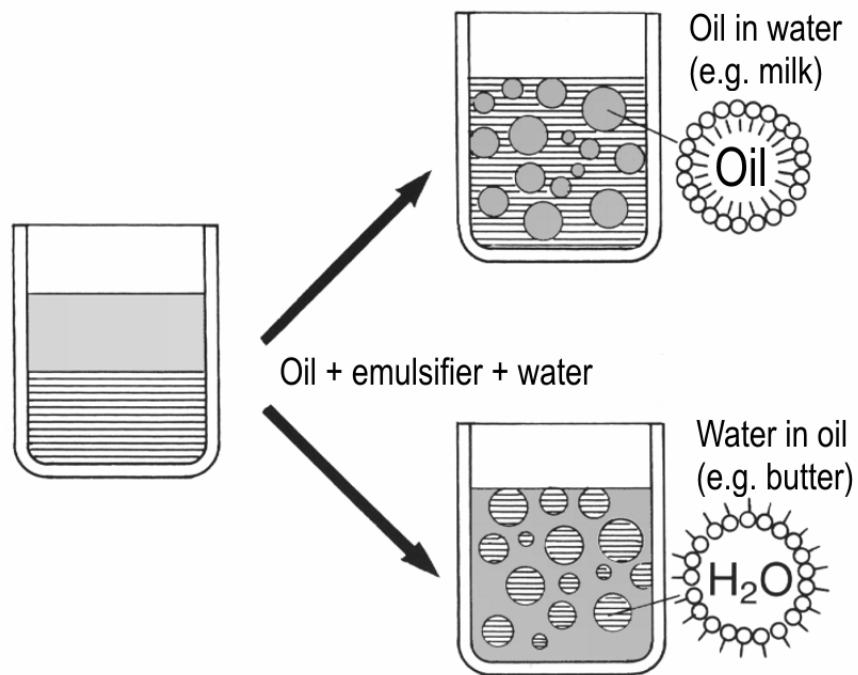
a) The polar head of the conventional anionic surfactant is a carboxylate or sulfonate group, and the nonpolar tail consists of a hydrocarbon chain.

b) The silicone surfactant, however, has a polar head consisting of an amino group and a nonpolar tail of concatenated polydimethylsiloxane units.

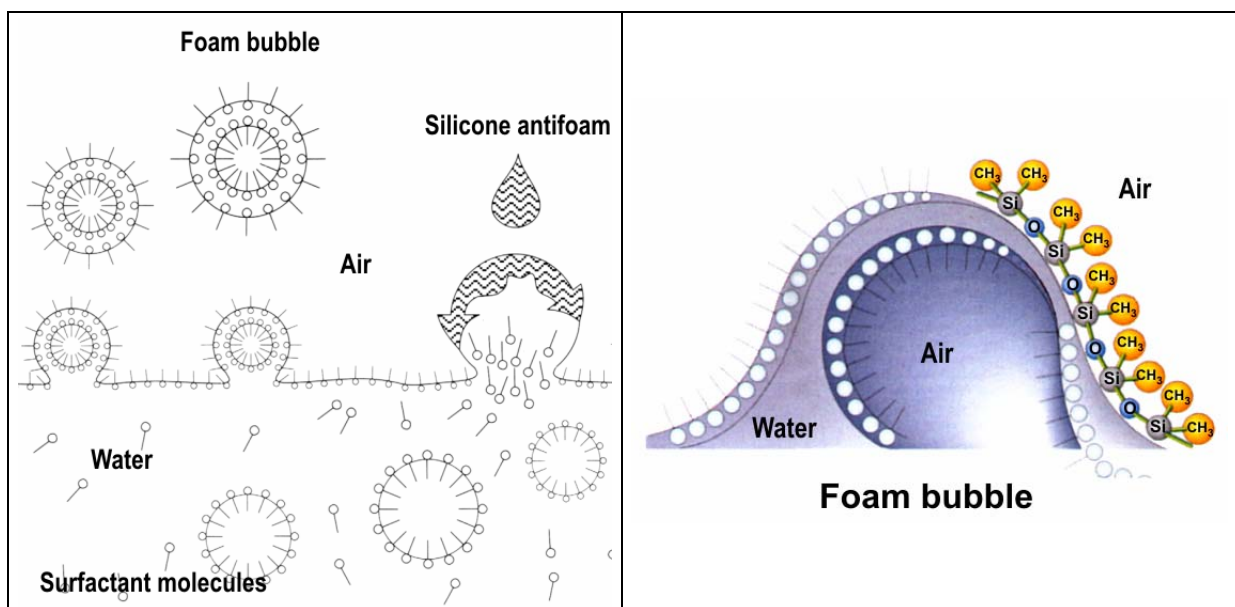
Worksheet 3.2
Emulsions and antifoam agents
Sample answer key

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	Name:
Emulsions and antifoam agents	Class:
Sample answer key	Date:

Bubble formation takes place at the interface between water and air. If surfactant molecules have accumulated at the surface of a solution and air is then blown in, bubbles will be formed. They consist of air trapped inside a film of water, which is covered on each side by a layer of surfactant molecules whose heads are facing one another.

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

The silicone antifoam interacts with the outer layer of surfactant on the bubble and displaces the surfactant particles from the surface. The film of water drains away, and the bubble becomes unstable and collapses.

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

When a bubble is forming, the surfactant molecules initially lower the surface tension of the water. When air is blown in, electrostatic forces of attraction cause the surfactant molecules to form bubbles. Antifoam molecules have a lower surface tension than surfactants and can thus displace them from the air/water interface by electrostatic repulsion. As a result, the foam lamella becomes thinner and thinner until finally it collapses.

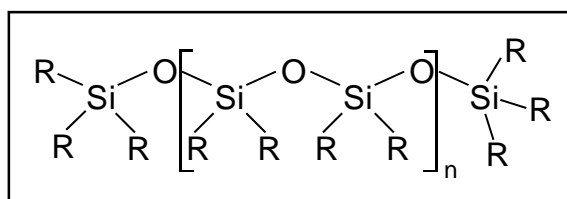
Worksheet 4.1 Silicone fluids, resins and rubbers Sample answer key	Name:
	Class:
	Date:

1. Starting materials for the manufacture of silicones are:

„Monofunctional units“ (monochlorosilane)	“Difunctional units” (dichlorosilane)	“Trifunctional units” (trichlorosilane)
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{Si}-\text{Cl} \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{Cl}-\text{Si}-\text{Cl} \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{Cl} \\ \\ \text{H}_3\text{C}-\text{Si}-\text{Cl} \\ \\ \text{Cl} \end{array}$
<i>Chlorotrimethylsilane</i>	<i>Dichlorodimethylsilane</i>	<i>Trichloromethylsilane</i>

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.)

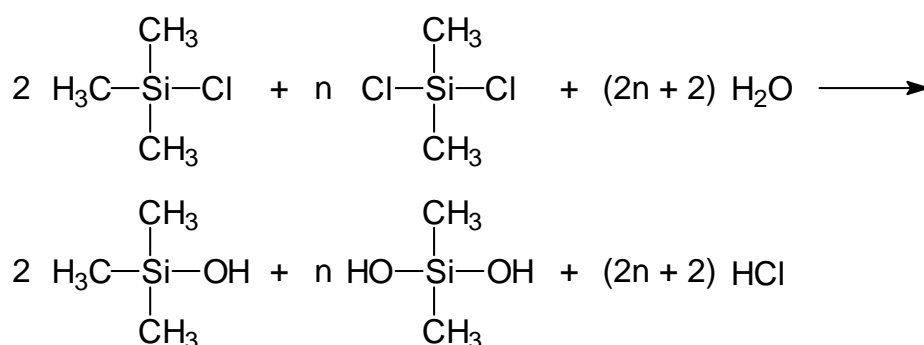


a) Which of the three silane units in question 1 has to be used manufacturing a silicone fluid?

Difunctional silane units (chain segments) and monofunctional silane units (chain terminators) are needed for the manufacture of 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.

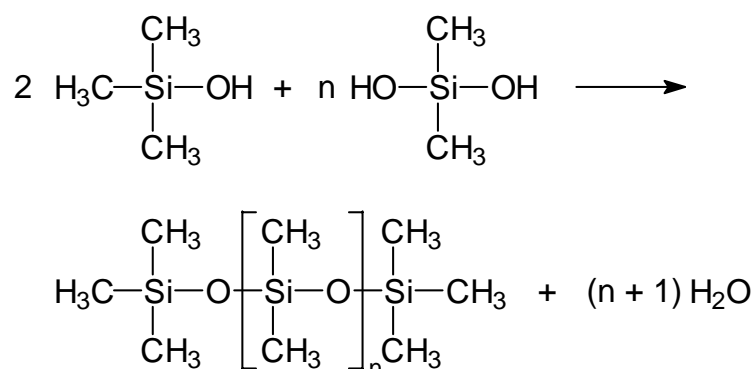
Step 1: *Making the silanes react with water*



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

Type of reaction: *Nucleophilic substitution*

Step 2: *Silanol condensation*



Type of reaction: *Polycondensation*

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

Difunctional silane units function as segments in a silicone fluid chain while the monofunctional units terminate the individual chains (i.e. act as end groups).

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

Adding a large excess of difunctional units leads predominantly to the formation of long-chain polymers. If, however, the concentration of monofunctional units is increased, short-chains polymer form predominantly.

Reason: Since the monofunctional units can only bond to one neighboring unit, they act as terminal groups. At high concentrations, the polycondensation reaction terminates quickly, and short-chain polymers are predominantly formed.

On the other hand, the difunctional units can form two bonds, which is why high concentrations of difunctional silane units lead to long polymer chains. The polymer chain only stops growing when a monofunctional unit has bonded to both ends of it.

Worksheet 4.3 Silicone fluids, resins and rubbers Sample answer key	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.

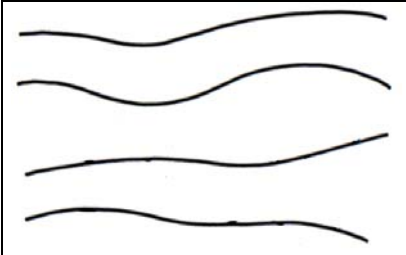
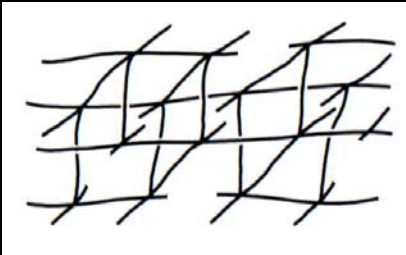
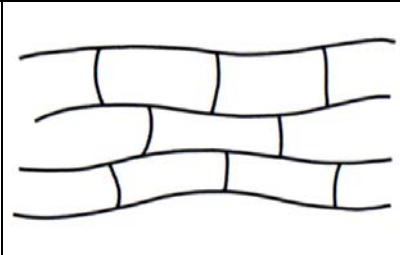
(Note: Any property may be used more than once).

Silicone fluid: *Liquid, water-repellent*

Silicone resin: *Hard, water-repellent, insulating, chemically resistant*

Silicone rubber: *Solid, elastic, water-repellent, insulating, chemically resistant*

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

		
<i>Silicone fluid:</i>	<i>Silicone resin:</i>	<i>Silicone rubber:</i>

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.

The silicone fluid is composed of long, more or less linear, polymer chains. The chain length governs the viscosity of the silicone fluid.

Due to this fact, silicone fluids may be used as lubricants.

Silicone resins, by contrast, consist of three-dimensionally crosslinked macromolecules. This structure renders the material hard and sparingly soluble because the molecule parts cannot be moved against each other and because solvent molecules can penetrate only slightly or not at all. Since the macromolecules do not contain any delocalized electrons, silicone resins are not electrical conductors.

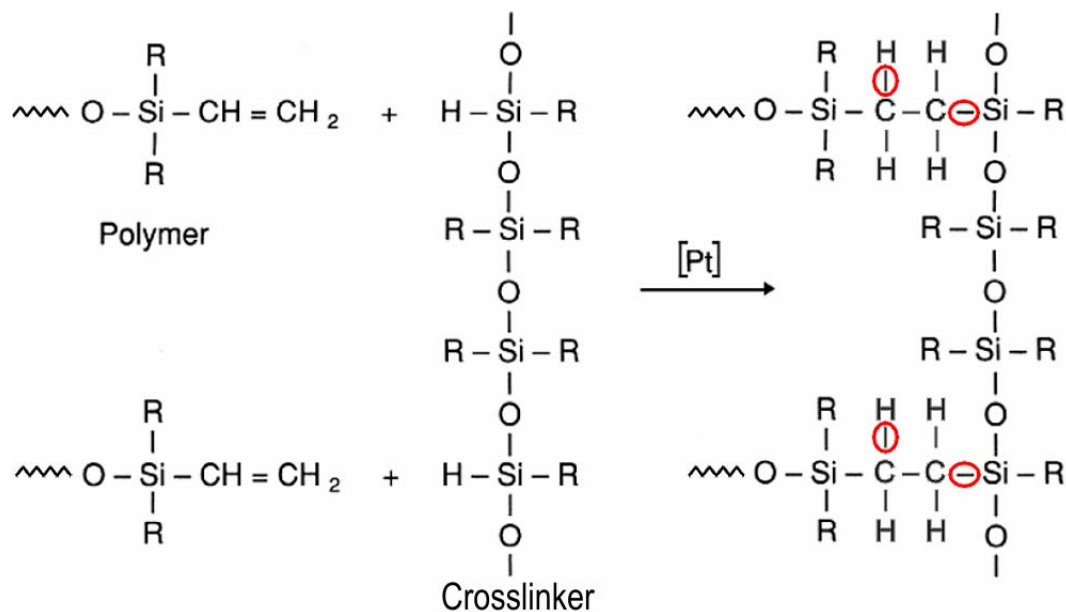
Silicone rubber is a solid because it crosslinks in many layers.

Worksheet 4.4 Silicone fluids, resins and rubbers Sample answer key	Name:
	Class:
	Date:

However, the “vertical” crosslinks” (see general reaction below) between the long horizontal silicone chains allow a certain degree of movement. Accordingly, the material is elastic. Since no reactive groups are present in most cases, silicone rubber is chemically resistant.

The hydrophobic properties of all silicone grades stem from the high content of hydrocarbon groups in their molecules.

4. The crosslinking reaction of linear polymers to form elastomers (silicone rubber) shown below is called addition curing.



a) Explain this term.

In this type of crosslinking of silicone molecules, two different silicone units (polymer and crosslinking agent) are joined together (added). This type of reaction typically involves a reagent with a double bond to which another molecule can be added.

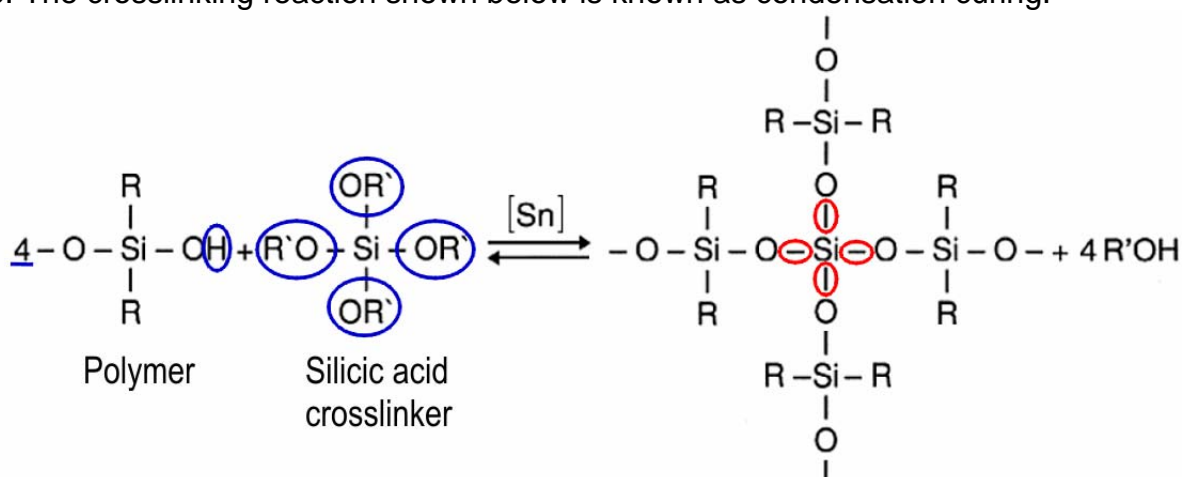
b) Mark the new bonds.

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

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

A hydrogen atom must be present as a substituent on the Si atom of the crosslinking agent so that addition crosslinking can take place.

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



a) Explain this term.

The name polycondensation stems from the fact that in this reaction alcohol molecules (small particles) are cleaved off and the remaining molecular groups become attached to each other.

b) Mark the new bonds and the cleaved molecules.

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

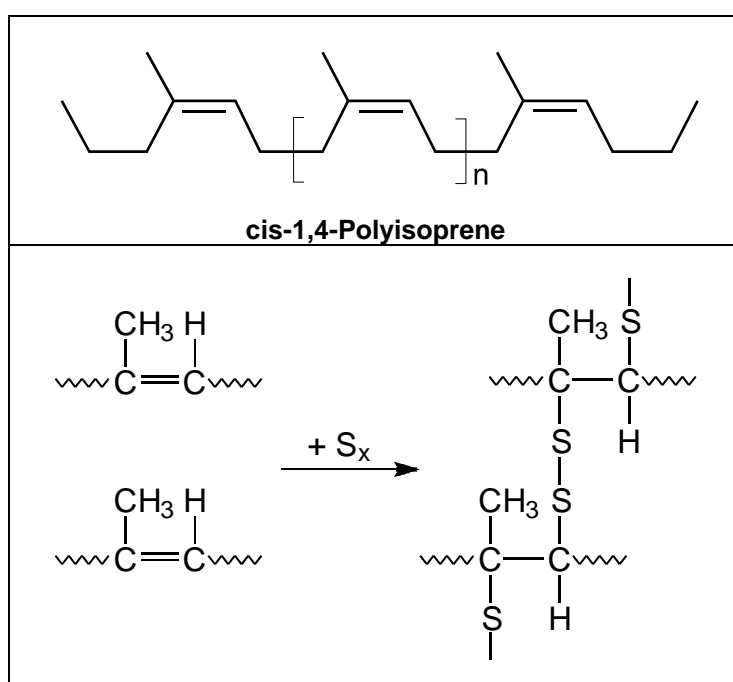
The molecule of crosslinking agent needs the Si-O-R' group in order for condensation curing to occur.

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

Addition curing is more likely to lead to complete curing of the material as it is an irreversible reaction.

Worksheet 4.6 Silicone fluids, resins and rubbers Sample answer key	Name:
	Class:
	Date:

Condensation is an equilibrium reaction in which the conversion rate is heavily dependent on the concentration of the alcohol formed. The alcohol has to evaporate before the equilibrium can shift in the direction of the products.



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.

Sulfur is used as a crosslinking agent for natural rubber. No sulfur is needed for addition curing of silicones.

The elemental composition of the silicone therefore does not change during curing, whereas sulfur is incorporated as a further element during curing of natural rubber.

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

Curing of natural rubber is more similar to addition crosslinking. Like addition crosslinking, curing with sulfur utilizes the presence of double bonds to crosslink individual monomer units into a network. No small molecules are released or cleaved.

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

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

Carbon dioxide (CO₂), water (H₂O) and sulfur dioxide (SO₂) are formed during total combustion of natural rubber.

Carbon dioxide (CO₂), water (H₂O) and silicon dioxide (SiO₂) are formed during total combustion of silicone rubber.

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

$$\Delta H_B^0(\text{CO}_2) = -394 \text{ kJ/mol}; \quad \Delta H_B^0(\text{SiO}_2) = -910 \text{ kJ/mol}; \quad \Delta H_B^0(\text{SO}_2) = -297 \text{ kJ/mol} \quad \text{and} \\ \Delta H_B^0(\text{H}_2\text{O}) = -287 \text{ kJ/mol}.$$

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

From the information, it may be inferred that combustion of silicone rubber releases more heat than the combustion of natural rubber. This is due to the much higher enthalpy of formation of SiO₂ in comparison with the enthalpies of formation of all other combustion products. In addition, the percentage of silicon in silicone rubber is higher than the percentage of sulfur in natural rubber.

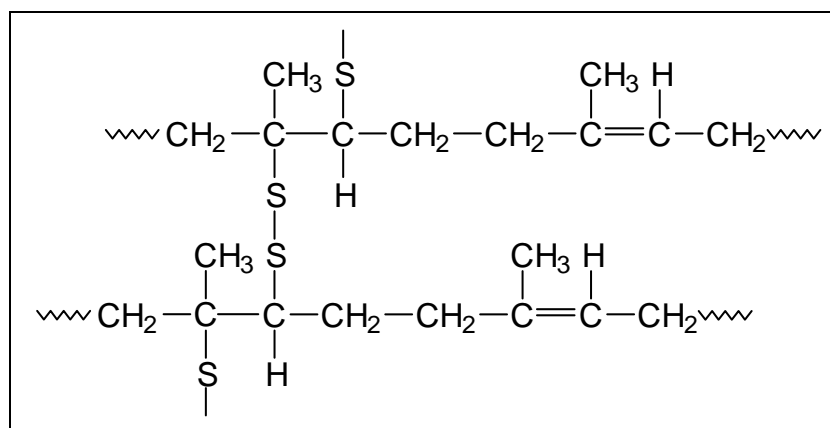
However, this ignores the fact that the elements are already bound both in the natural rubber and in the silicone rubber. For a more precise assessment, the corresponding bond energies (C-C, C-H, Si-O etc., would have to be considered.

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

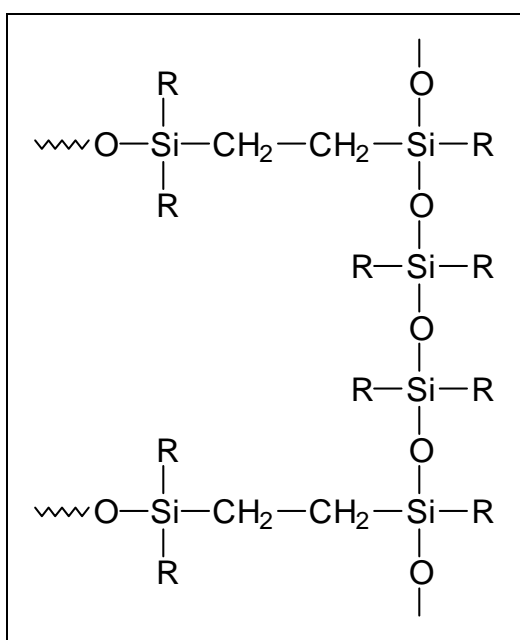
Silicone rubber releases no poisonous fumes in a fire whereas natural rubber releases considerable quantities of sulfur dioxide.

Worksheet 5.1 Comparison: Silicone rubber – Natural rubber Sample answer key	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.

Since rubber consists of virtually nonpolar macromolecules, it dissolves readily in paraffin oil, which also consists of nonpolar molecules. Silicone rubber, in contrast, contains strong polar sequences (Si-O linkages), that interact with the nonpolar molecules from the paraffin oil.

At the same time, silicone rubber is swelled by alkanes because the silicone molecules contain numerous methyl groups. However, complete dissolution does not occur.

Worksheet 5.2 Comparison: Silicone rubber – Natural rubber Sample answer key	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.

The ready susceptibility of rubber to ozone stems from the carbon-carbon double bonds. These are attacked by ozone. The molecule is subsequently split into two fragments, each containing terminal carbonyl groups. The critical factor at this stage is whether the rubber is additionally subjected to mechanical stress. If so, the surface layer tears and the underlying layers are exposed to further ozonolysis. Since silicone rubber generally does not contain double bonds, it is unaffected by ozone.

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

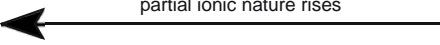
Using this information and the structures shown above, explain why silicone rubber has greater heat resistance than natural rubber.

The crucial factor here is the relatively high bond energy of the Si-O linkage. Since it is the only type of bond in the principal chain of the silicone molecule, it makes a substantial contribution to the high heat resistance of silicones. Accordingly, a great deal of energy has to be applied before silicone rubber is destroyed thermally.

In contrast, the corresponding bond energies in natural rubber are comparatively low. Accordingly, natural rubber thermally decomposes at lower temperatures.

Worksheet 6.1 Properties of tetrachlorosilane Sample answer key	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
ΔEN	<i>2.1</i>	<i>1.8</i>	<i>1.5</i>	1.2	<i>0.9</i>	<i>0.5</i>	<i>0</i>
<i>Ionic bond</i>						<i>Covalent bond (nonpolar)</i>	

1. Calculate the missing electronegativity differences ΔEN (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.

The partial ionic nature increases in line with the electronegativity difference. The corresponding compounds always have higher melting and boiling temperatures, i.e. they become “more solid” at room temperature.

Salts such as NaCl and MgCl₂ are purely ionic compounds. Strong forces of electrostatic attraction act between the ions, which are arranged in a lattice. A large quantity of energy is needed to overcome these forces; the melting temperature is therefore high. At the other extreme, molecular compounds consist of nonpolar molecules. The forces between the molecules are much lower than the bonding forces between atoms within the molecules. Such compounds are gases even at room temperature.

The borderline between the two extremes is “fluid.”

Worksheet 6.2 Properties of tetrachlorosilane Sample answer key	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 checked="" type="checkbox"/>	$Na^+ (aq) + Cl^- (aq)$	Yes <input type="checkbox"/>	
	No <input type="checkbox"/>		No <input checked="" type="checkbox"/>	
AlCl ₃	Yes <input checked="" type="checkbox"/>	$Al^{3+} (aq) + 3 Cl^- (aq)$	Yes <input checked="" type="checkbox"/>	<i>Some</i> $Al(OH)_3 (s, aq) + 3 HCl (aq)$
	No <input type="checkbox"/>		No <input type="checkbox"/>	
SiCl ₄ <small>Hydrolysis of tetrachlorosilane (see expt)</small>	Yes <input type="checkbox"/>		Yes <input checked="" type="checkbox"/>	$SiCl_4 + 4 H_2O \rightarrow Si(OH)_4 + 4 HCl$ <i>Orthosilicic acid condenses to polysilicic acid</i>
	No <input checked="" type="checkbox"/>		No <input type="checkbox"/>	
PCl ₃	Yes <input type="checkbox"/>		Yes <input checked="" type="checkbox"/>	$H_3PO_3 (aq) + 3 HCl (aq)$
	No <input checked="" type="checkbox"/>		No <input type="checkbox"/>	
Cl ₂ <small>Think of chlorine water.</small>	Yes <input type="checkbox"/>		Yes <input type="checkbox"/>	
	No <input checked="" type="checkbox"/>		No <input checked="" type="checkbox"/>	

4. Explain why the chlorides behave differently in water.

When sodium chloride dissolves in water, the ionic lattice is broken down, and the ions become hydrated and enter solution. No hydrolysis occurs.

Chlorine (which consists of nonpolar molecules) only dissolves slightly as Cl₂ (aq).

With the other compounds, hydrolysis is either partial (AlCl₃) or complete (SiCl₄, PCl₃), the governing factor being whether and to what extent the hydrolysis products separate out as precipitates or enter solution as stable ions.

Worksheet 7.2

Hydrolysis and rate of hydrolysis of chloromethylsilanes

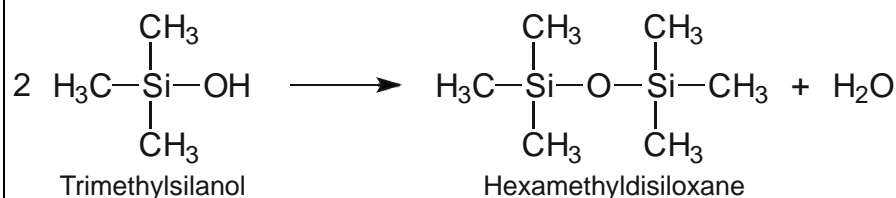
Sample answer key

Name:

Class:

Date:

Condensation:



Product:



Properties

Hydrolysis of chlorotrimethylsilane yields trimethylsilanol. This has only one functional group, namely the hydroxyl group. For this reason, there is only one possible condensation product, hexamethyldisiloxane.

The relatively small, symmetrical molecule is nonpolar and therefore is immiscible with water. Because it has few

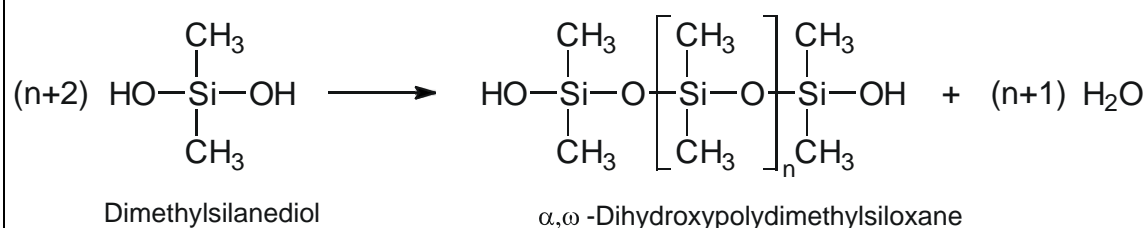
opportunities for molecular interaction, it has a low viscosity.

b) Dichlorodimethylsilane

Hydrolysis:



Condensation:



Worksheet 7.4

Hydrolysis and rate of hydrolysis of chloromethylsilanes

Sample answer key

Name:

Class:

Date:

Product:



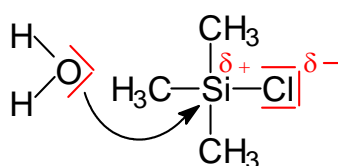
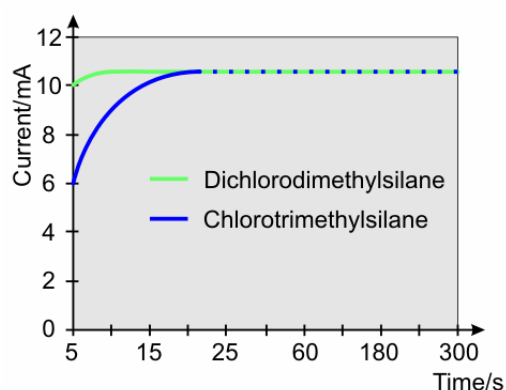
Properties

Hydrolysis of trichloromethylsilane yields methylsilanetriol. This has three functional hydroxyl groups. For this reason, it can condense to highly crosslinked three-dimensional molecules.

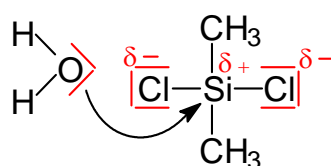
These macromolecules form solids. Due to a lack of space, not every hydroxyl group inside the molecule can condense, and there are enough free hydroxyl groups available at the outer interface for further condensation; consequently, the molecule can continue growing. The giant molecules, which contain few polar hydroxyl groups in relation to their size, form solids that are insoluble in water.

3. The experiment "Rate of hydrolysis of chloromethylsilanes" revealed different rates of hydrolysis for the chloromethylsilanes.

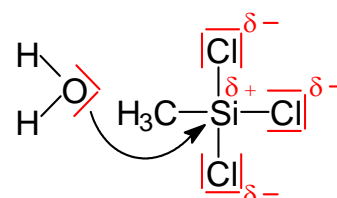
What do you attribute the different rates of hydrolysis to?



Chlorotrimethylsilane



Dichlorodimethylsilane



Trichloromethylsilane

The water molecule initiates nucleophilic attack of the silicon atom using the free electron pair on the oxygen atom. Since the chlorine atom is much more electronegative than the silicon atom, it attracts electrons (inductive effect). That is why the chloromethylsilanes react increasingly faster with water as the chlorine content rises.

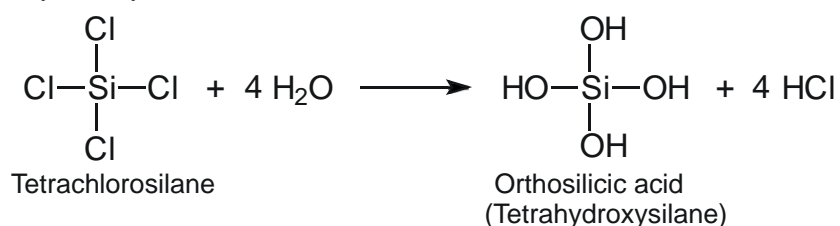
Worksheet 7.5 Hydrolysis and rate of hydrolysis of chloromethylsilanes Sample answer key	Name:
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4. What happens when tetrachlorosilane is hydrolyzed?

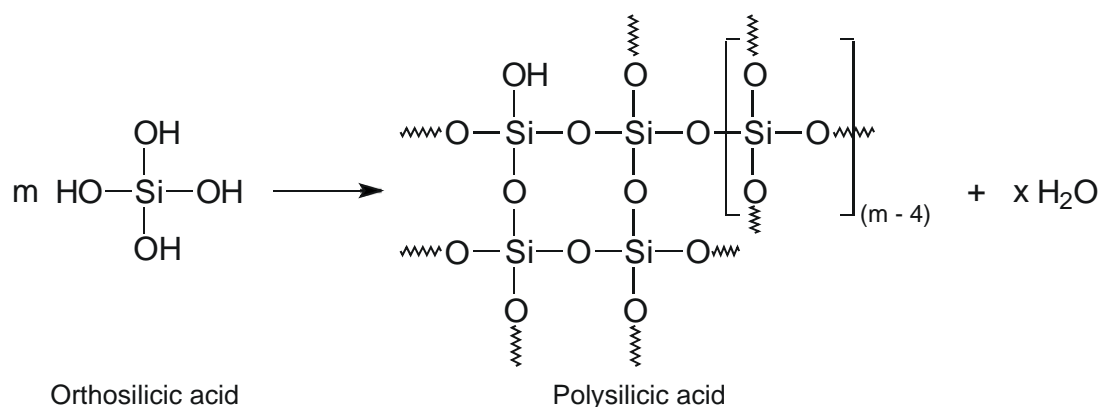
In this case, the silicon atom gains the strongest positive charge. Accordingly, tetrachlorosilane should react very violently with water. Since the silicon atom is well shielded by the large, partially negatively charged chlorine atoms, it is relatively hard for water molecules to reach it and initiate nucleophilic attack. Hydrolysis of tetrachlorosilane is therefore comparable to that of dichlorodimethylsilane.

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

Hydrolysis:



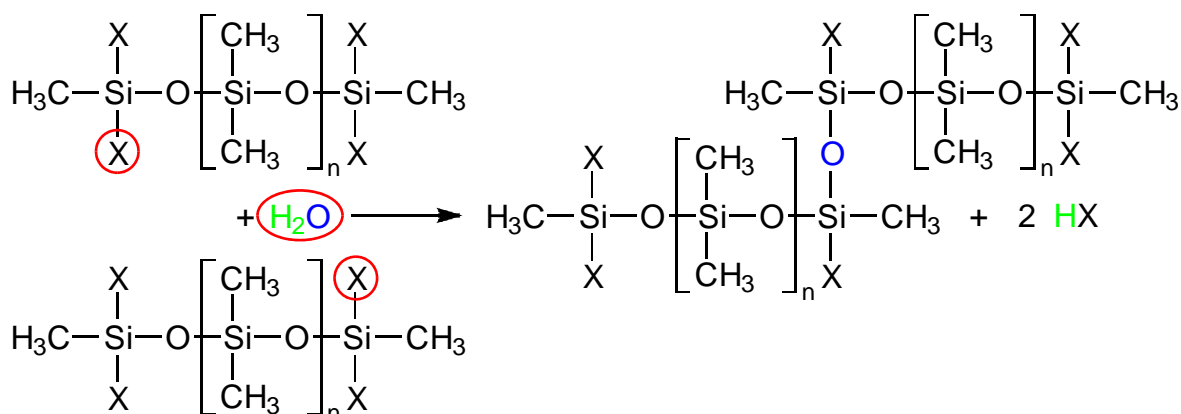
Condensation:



Note: Gelatinous high-molecular silicic acid is formed initially. After dewatering, this is converted into a highly crosslinked, white solid that is sparingly soluble in water. Ignition of polysilicic acid at temperatures above 1,000 °C yields silicon dioxide (quartz).

Worksheet 8.2 RTV-1 silicone rubbers Sample answer key	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.



$X = \textit{Ethoxy group}$	$\text{HX} = \textit{Ethyl alcohol}$
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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	<i>Vinegar odor</i>	<i>Indeterminate</i>	<i>Odorless</i>
pH paper	<i>Red coloration</i>	<i>No change</i>	<i>No change</i>
Impact strength	<i>Elastic</i>	<i>Elastic</i>	<i>Breaks into small pieces</i>
Consistency	<i>Soft, rubbery</i>	<i>Soft, rubbery</i>	<i>Solid</i>
Paintability with watercolors	<i>Poor adhesion; can be washed off</i>	<i>Poor adhesion; can be washed off</i>	<i>Very good adhesion; cannot be washed off</i>

Worksheet 8.3 RTV-1 silicone rubbers Sample answer key	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:

The vinegar odor and the acidity of ELASTOSIL[®] E43 stem from the fact that this system contains an acetoxy-based crosslinking agent that releases acetic acid during curing.

ELASTOSIL[®] N199:

The indeterminate odor and the neutral pH of ELASTOSIL[®] N199 stem from the fact that this system contains an oxime-based crosslinking agent that releases an oxime during curing.

(Note: The pupils can only give this explanation if the product description is shown to them and explained.)

Gypsum:

When gypsum cures, water molecules are incorporated into the ionic lattice of the calcium sulfate. The calcium sulfate CaSO_4 is thereby converted into calcium sulfate dihydrate (gypsum) $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$. Since no cleavage products are formed, no change is observed, especially where odor is concerned.

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

When silicone rubbers cure, crosslinks are formed between the molecular chains of the silicone rubber. These are responsible for the elastic behavior.

Gypsum is a salt-like solid that breaks on mechanical impact (a blow).

Worksheet 8.4	Name:
RTV-1 silicone rubbers	Class:
Sample answer key	Date:

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

Silicones are extremely hydrophobic. The water-color therefore cannot penetrate into the silicone rubber and is easily removed. Gypsum, in contrast, is extremely hydrophilic, which is why the water-color can penetrate easily and adheres strongly to the surface.

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?

It is best to use the silicone rubber because the gypsum is destroyed by the constant stress. The silicone rubber can compensate for some of the movement because it is elastic.

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

ELASTOSIL[®] E43 is unsuitable because acetic acid is released during curing and would attack the marble.

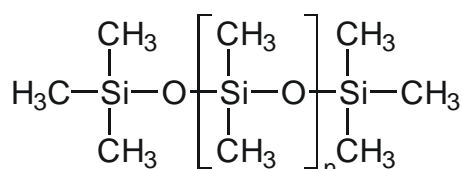
Worksheet 9.1	Name:
Properties of silicone fluids	Class:
Sample answer key	Date:

Water-repellent properties of silicone fluids

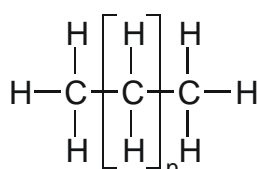
Experiment 1: Brush Silicone Fluid AK 5000 from the WACKER lab set over different smooth, clean surfaces, such as glass, copper, a wooden panel, a paper tissue and then do the same to identical surfaces with glycerol. Then apply a layer of candle wax to piece of paperboard. Place a drop of water dyed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

Observation: *The water droplets form comparatively spherical drops that do not run off the siliconized surfaces or paperboard treated with candle wax. Viewed from the side, the drops on the treated surfaces are much higher than those on the untreated surfaces. The water is absorbed more slowly by the paper tissue, the card and the wood than by the untreated surfaces. The water drops on the surfaces treated with glycerol spread out extensively and are quickly absorbed.*

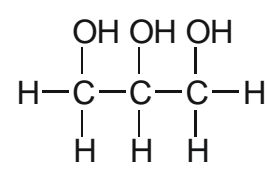
1. Try to explain the observations using the structural formulae for silicone fluid, glycerol and paraffin from experiment 1.



Silicone fluid (Polydimethylsiloxane)



Paraffin (higher alkane)



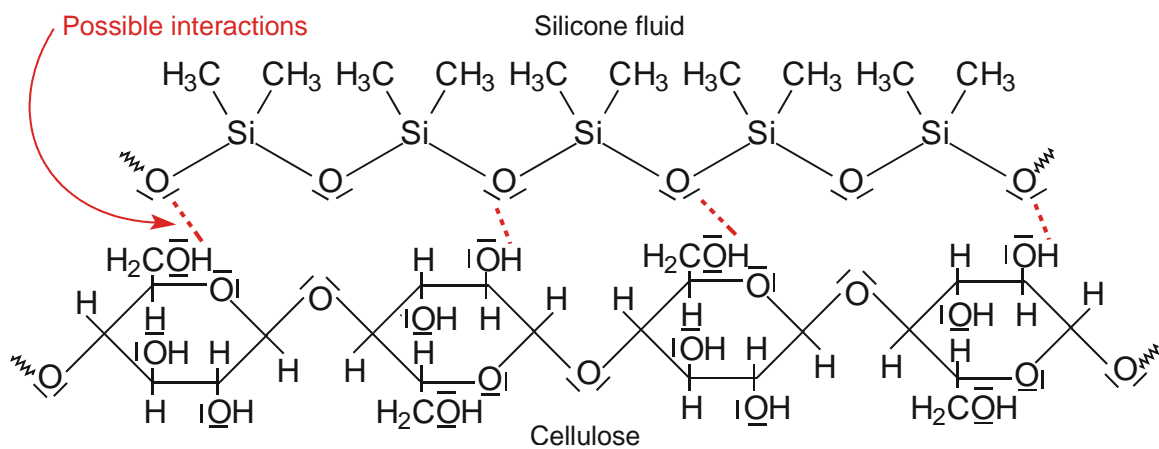
Glycerol

Explanation: *Only weak interactions can occur between the nonpolar alkane molecules and the polar water molecules. The paraffin therefore exhibits pronounced hydrophobicity. Similarly, the hydrophic effect of the silicone fluid may be explained in terms of the content of nonpolar methyl groups. In contrast, the glycerol has three hydroxyl groups that lead via hydrogen bonds to strong interactions between the glycerol and water molecules. These strong interactions are responsible for the hydrophilic nature of the surfaces treated with glycerol.*

Worksheet 9.2 Properties of silicone fluids Sample answer key	Name:
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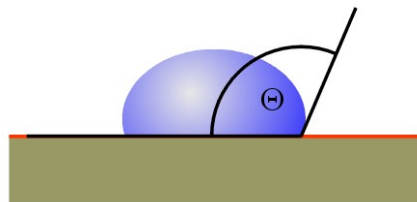
2. While the paraffin coating can be scratched off relatively easily, the silicone fluid adheres comparatively well to surfaces such as glass, building materials and textiles (e.g. cellulose) due to intermolecular interactions (electrostatic forces of attraction, hydrogen bonds).

Draw a section of a silicone molecule in the following space and used 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

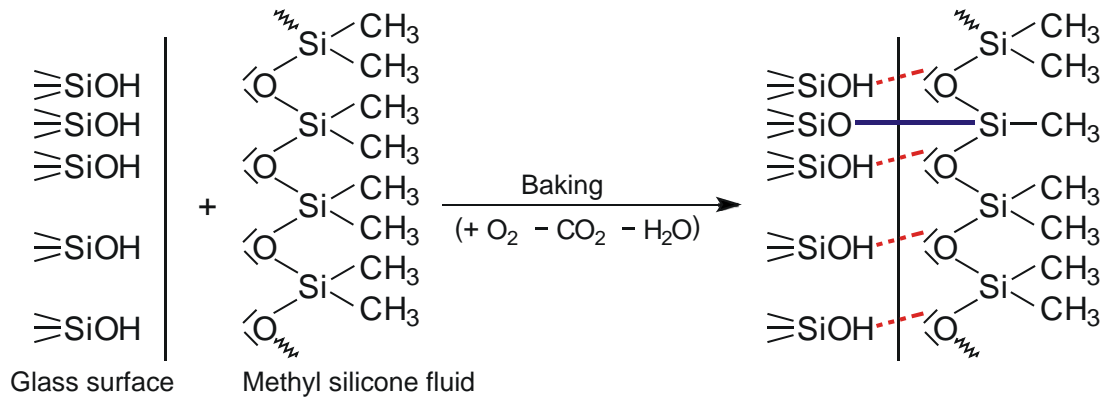
Sample answer key

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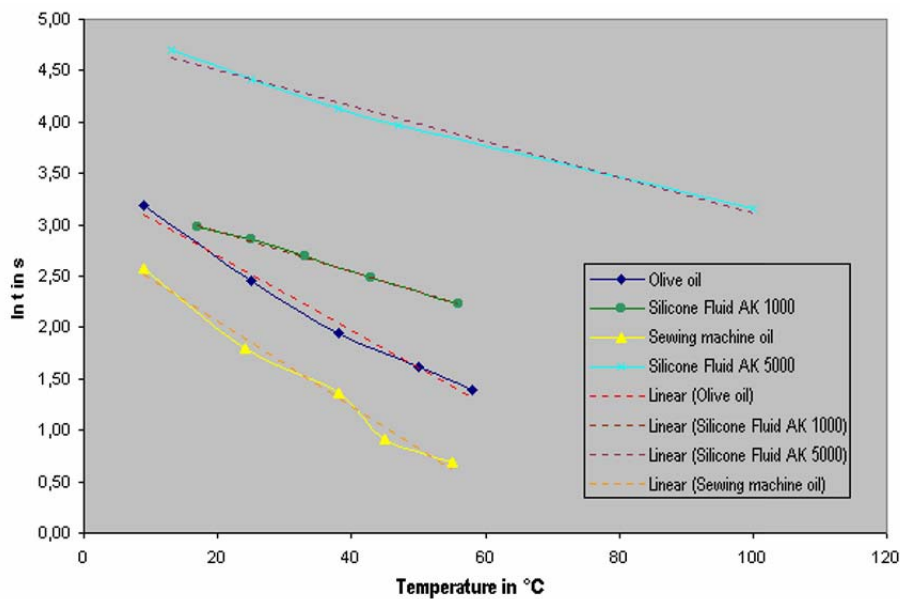
3. Using the explanation above, draw the hydrogen bonds and the primary valences in different colors for the product formed by anchorage of a methyl silicone fluid to a glass surface. Write down the equation part of the silicone molecule on the reagent side.



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	Name:
Properties of silicone fluids	Class:
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It is noticeable that the natural logarithm of the fall time decreases linearly with the temperature. Additionally, it may also be seen from the slope of the curves that the viscosity (fall time) is not so dependent on the temperature in the case of the silicone fluids as it is with the other oils. Furthermore, the viscosity increases with increase in chain length or rise in molecular weight.

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

With increase in temperature, the energy of the system increases and the mean velocity of the individual molecules increases. This leads to an increase in the random movements by the various molecules. The liquid becomes more mobile and the viscosity drops.

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.

I would choose a silicone fluid because its viscosity would not vary as much with the temperature as it would with the other oils studied. Thus, at an altitude of 10 to 12 kilometers (where the temperatures are -50 to -60 °C), a mineral oil could turn solid and would no longer perform its task.

Worksheet 9.5	Name:
Properties of silicone fluids	Class:
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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.

Viscometry is suitable because it is simple, quick and cheap to carry out.

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

On account of their properties, silicone fluids would be suited for impregnating agents, polishes and hydraulic fluids that operate under extreme conditions.

Worksheet 10.1 Surfactants and antifoam agents Sample answer key	Name:
	Class:
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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: *When the surfactant solution is added, the paper clip sinks further and further into the water with each drop of surfactant until it suddenly sinks to the bottom.*

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

Interpretation: *Presumably, a force is acting on the water surface that prevents the paper clip from sinking. The surfactant solution reduces the force, and the paper clip gradually sinks.*

Explanation: (Teacher helps with explanation)

Surface tension acts at the interface of a liquid. It shows up as the attempt by the liquid to minimize its surface area. In the experiment, the surface tension is greater than the gravity acting on the paper clip, and that is why the paper clip floats. The surfactant solution lowers the surface tension, and the paper clip sinks.

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



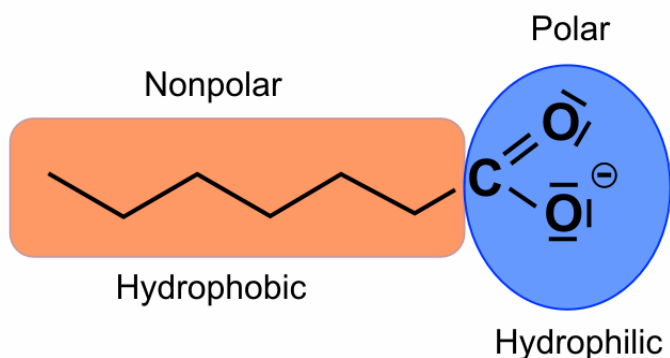
Worksheet 10.2 Surfactants and antifoam agents Sample answer key	Name:
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Explanation: *The water strider is able to walk on the water because of the surface tension of the water. In this case, too, the surface tension is greater than the force of gravity acting on the water strider.*

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.

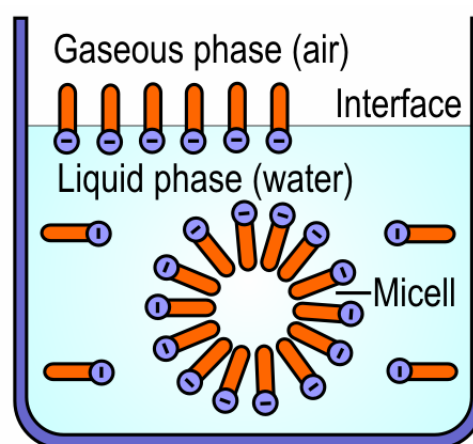
Using this information, draw the model of an anionic surfactant that has the following formula: $\text{H}_3\text{C}(\text{CH}_2)_n\text{COO}^-\text{Na}^+$ ($n = 9$ to 19).

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: *On the surface of a soap solution, the surfactant particles align themselves so that the hydrophobic ends are sticking out of the water surface.*



Since the forces of attraction between the nonpolar hydrocarbon ends of the surfactant particles are much lower than between the water molecules, the surface tension of the water is lowered.

Worksheet 10.3 Surfactants and antifoam agents Sample answer key	Name:
	Class:
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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: *When the vials are shaken, the upper third fills with foam. This initially consists of small spherical bubbles that gradually unite to form larger polyhedral bubbles.*

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

Explanation: *Foam is formed when surfactants at the interface with air accumulate in the solution and thereby lower the surface tension of the water. The foam bubbles remain stable, provided too much surfactant does not drain away. Increasing drainage causes the bubbles to become increasingly thinner, they huddle more closely together, causing mutual deformation and turning into polyhedra.*

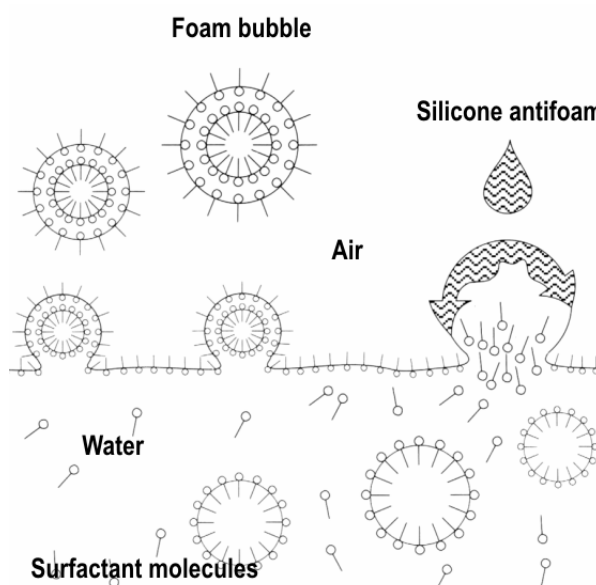
Experiment 3: Place some surfactant solution in a vessel, shake it and then add one drop of Antifoam Emulsion AS-EM SRE from the WACKER lab kit. What happens? What do you see when it is shaken again?

Observation: *The foam collapses when the antifoam emulsion is added. The foam can be heard popping. A slightly hazy solution is formed. Shaking the vial again causes some foam to form, but it collapses immediately.*

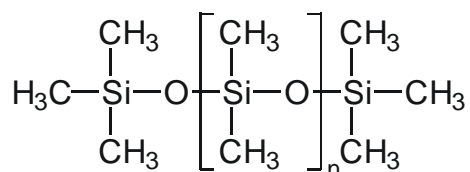
Worksheet 10.4 Surfactants and antifoam agents Sample answer key	Name:
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6. Explain your observations from experiment 3 with the help of the diagram on the right.

Explanation: *The silicone fluid particles also accumulate on the surface of the water. There they displace the surfactant particles, and this causes the bubbles to collapse.*



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: *Unlike the surfactant particles, the silicone fluid molecules are nonpolar. That is why they cannot trap water in the skin of the foam bubbles. The interaction between them and the surfactant particles results in displacement of the surfactant from the bubble skin, and the bubbles collapse.*

Worksheet 10.5 Surfactants and antifoam agents Sample answer key	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: *Yellowish emulsions are formed when the test tubes are shaken.*

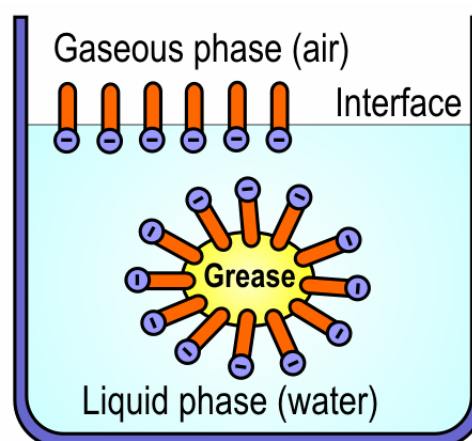
Without surfactant solution, the emulsion separates relatively quickly and an oil phase and a water phase are formed.

With surfactant solution, the emulsion lasts longer and no obvious separation occurs.

The same observation is made for the surfactant solution containing added antifoam agent. However, no foam is formed in this case.

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: *Surfactants stabilize grease/water emulsions through the formation of grease/surfactant micelles. The surfactant particle orients its hydrophobic (lipophilic) side toward the grease and its hydrophilic side toward the H₂O dipoles.*



Worksheet 11.1 Müller-Rochow synthesis Sample answer key	Name:
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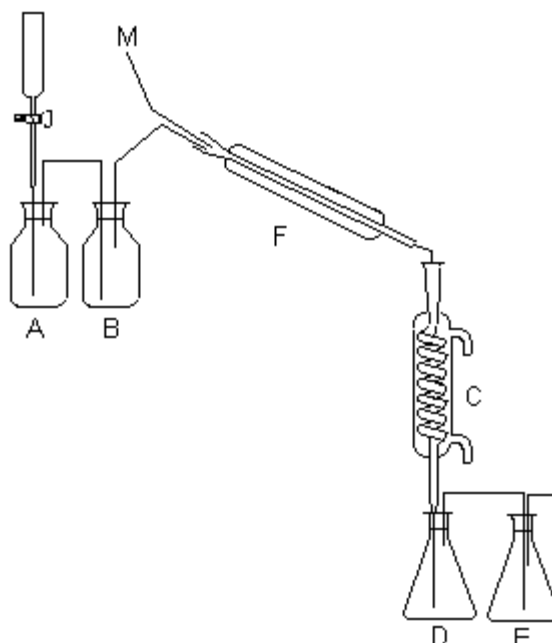
Background

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.

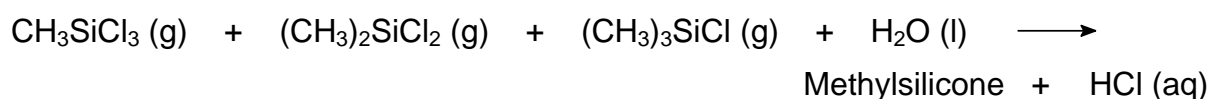
I decanted some of the ethereal solution into a Petri dish and drove off the ether. A clear, viscous glycerol-like substance remained. This fluid feels sticky, and is very similar to methylsilicone.

Worksheet 11.2 Müller-Rochow synthesis Sample answer key	Name:
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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.

The copper acts as a catalyst for the reaction. It therefore participates in the reaction, but is not consumed. The reaction does not proceed in the absence of a catalyst, as its activation energy is too high.

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).

When the pressure is increased, the equilibrium is shifted to the right because 3 moles of chloromethylsilane are formed from 6 moles of chloromethane.

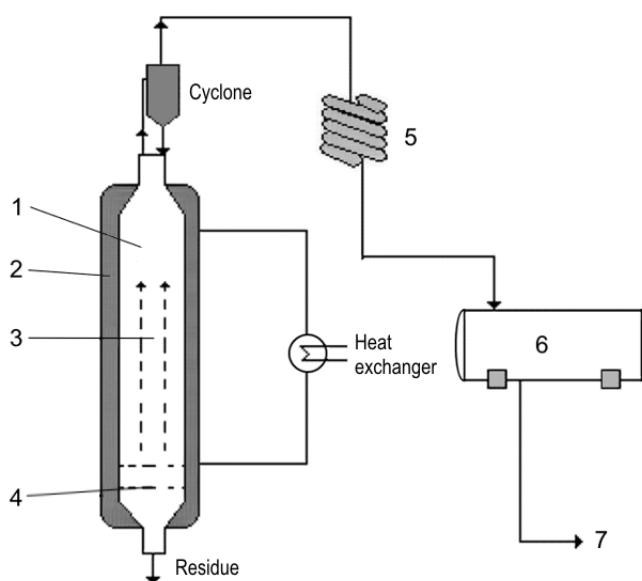
Since the reaction is exothermic, the equilibrium should shift to the left when the temperature is increased.

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 Sample answer key	Name:
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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	2	CH ₃ Cl	4	Condenser	5	Si/Cu	3
To distillation	7	Fluid bed reactor	1	Raw silane mixture	6		

6. Chloromethane and silicon serve as reagents in the direct synthesis. The silicon is obtained from quartz (SiO₂) and carbon in the electric furnace. Write down the corresponding general reaction and state how the requisite chloromethane can be produced.

