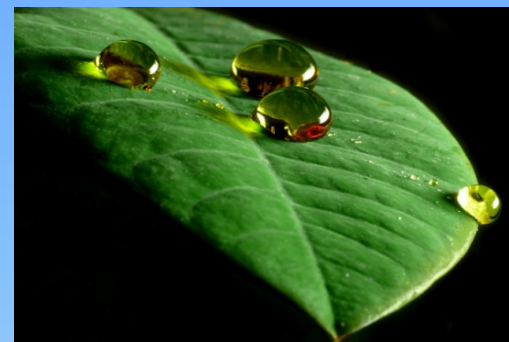


Workshop

The “Mysteries” of Surface Phenomena



Regina Rüffler, Georg Job



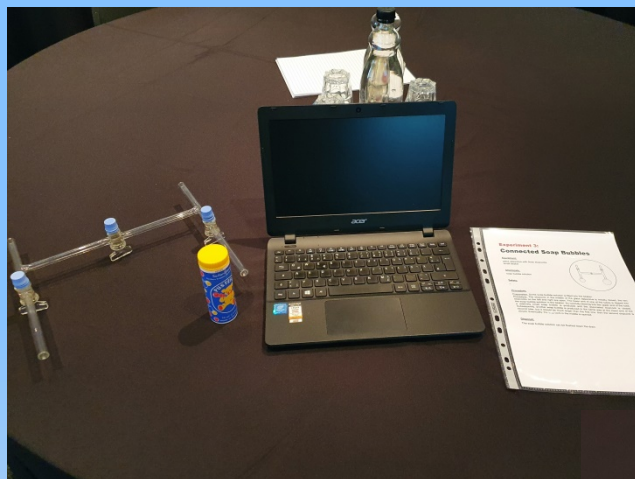
c/o. Institute of Physical Chemistry,
University of Hamburg

ICCE 2022

Capetown / South Africa, 18-22 July 2022

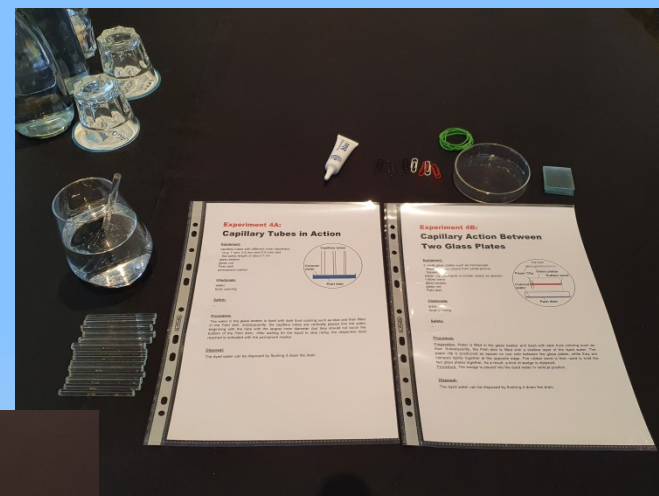
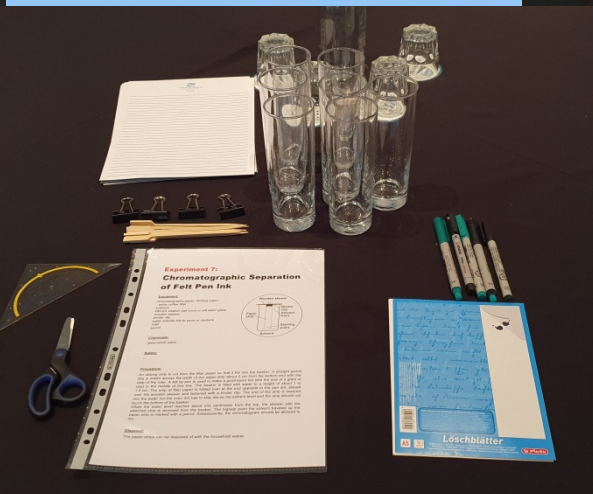
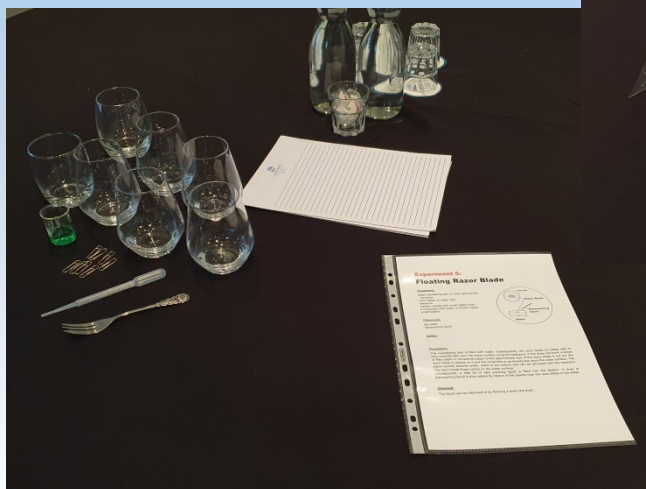
Impressions from the Workshop

“The “Mysteries” of Surface Phenomena”



Station 3

Station 5



Station 6

Station 4



Outline

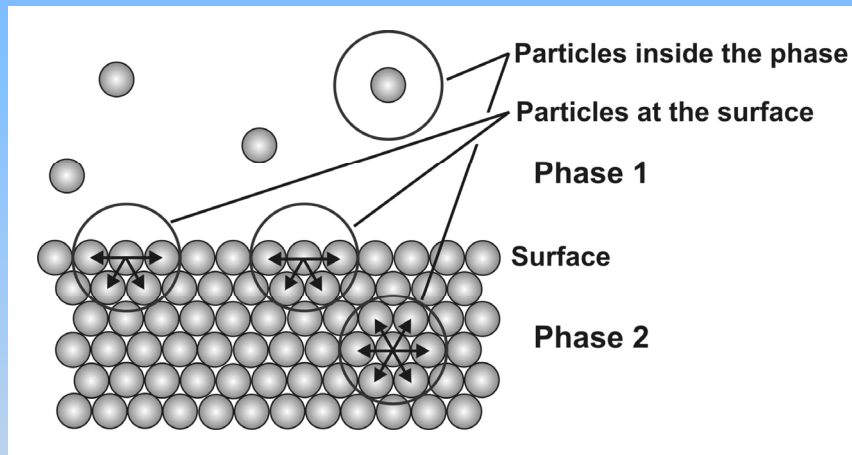
- 1. Surface Tension and Surface Energy**
- 2. Various Surface Effects**
- 3. Adsorption on Liquid Surfaces**
- 4. Adsorption on Solid Surfaces**
- 5. Outlook**

1. Surface Tension and Surface Energy



Surface Tension

chemical and physical properties at the **surface** of a solid or liquid substance differ from those in the bulk



particles at the surface are subject to different intermolecular forces than those inside the phase because they are missing part of their neighbors

(the binding forces are also referred to as *cohesion*)



one-sided pull towards the interior of the denser phase which manifests itself in the occurrence of a tensile stress in the surface layer

phenomenon known as **surface tension σ**

Illustration of Surface Tension in Nature

one possibility is to have a closer look at the insects such as water striders that are able to “walk on water”

these insects do not “float” because they are heavier than water but they are prevented from sinking because of surface tension

the surface of the water behaves like a membrane that supports the weight of the insects; their feet make indentations in the surface but do not penetrate it



Consequences of Surface Tension

surface tension results in a tendency for drops of liquid or gas bubbles to minimize their surface



spherical shape



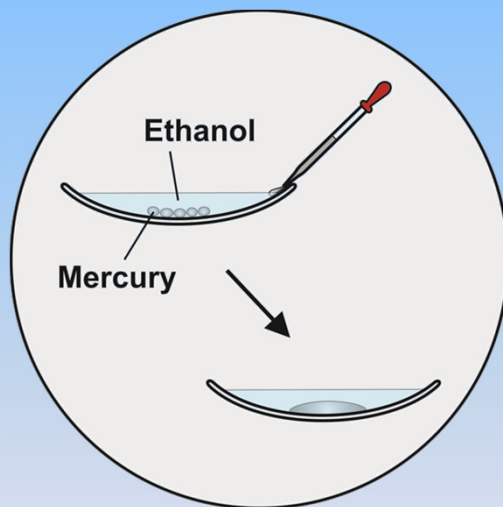
**Droplet of Liquid
in Space**

[https://www.youtube.com/
watch?v=bKk_7NIKY3Y](https://www.youtube.com/watch?v=bKk_7NIKY3Y)

Consequences of Surface Tension

for the same reason, large drops grow at the cost of smaller one

Experiment: Small droplets formed when dripping mercury in a watch-glass filled with ethanol will gradually merge to form one large drop.



<https://lp.uni-goettingen.de/get/text/2232>

Definition of Surface Tension

tensile forces F_σ that appear at the boundary lines of the surface are proportional to the length l of such a contact line

$$F_\sigma \sim l$$



surface tension := $\frac{\text{tensile force}}{\text{contact line}}$

or

$$\sigma := \frac{F_\sigma}{l}$$

SI unit: N m^{-1}

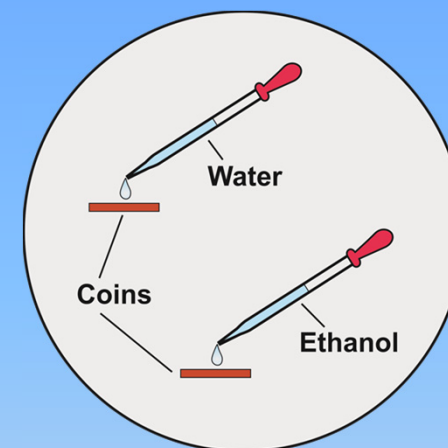
surface tension is a *substance-specific quantity*

Drops on Coins



Procedure:

Water and ethanol is dropped on two similar coins. The number of drops necessary until the respective liquid spills over the coin should be counted.



Drops on Coins

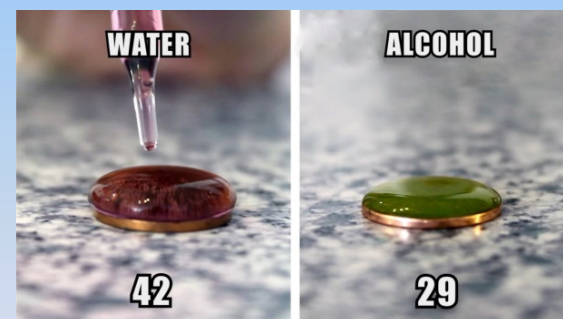
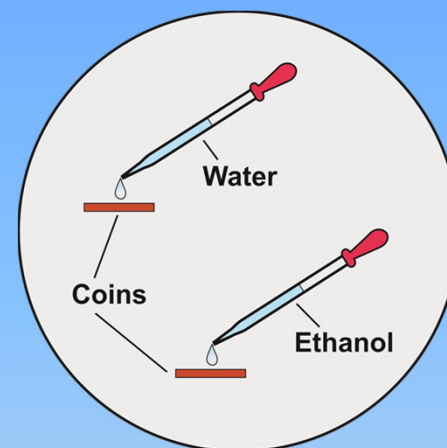


Procedure:

Water and ethanol is dropped on two similar coins. The number of drops necessary until the respective liquid spills over the coin should be counted.

Observation:

When water is dropped onto a coin a growing dome is formed even after touching the edges of the coin. But eventually, the dome breaks and the water spills over. The alcohol, however, does not form as large a bead of liquid on the coin. Therefore, many more drops of water can be added to the coin than drops of alcohol.

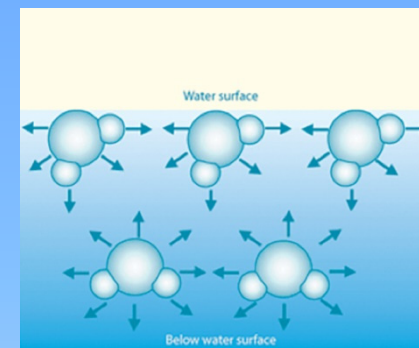


Drops on Coins

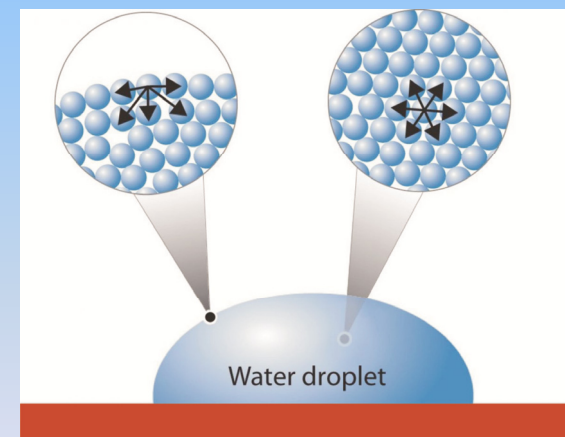


Explanation:

The surface tension of water is especially high ($\sigma = 72 \text{ mN m}^{-1}$) due to the high polarity of water molecules and the resulting relatively strong hydrogen bonds between them.



The water molecules at the surface of the drop are pulled inward and they stick together so strongly that they form a dome. Eventually, though, gravity overcomes this force and the dome breaks, spilling water over the sides of the coin.



The surface tension of ethanol ($\sigma = 22 \text{ mN m}^{-1}$) is considerably smaller than that of water. Therefore, fewer drops are able to be added to the coin.

Definition of Surface Energy

increasing of the surface area by $\Delta A \Rightarrow$ energy $W_{\rightarrow A}$ required
molecules are transported against the tensile forces from inside the phase to its surface and this costs energy

$\Rightarrow$ molecules at the surface have an amount of energy higher by the **surface energy** $W_{\rightarrow A}$ than that of the molecules inside the phase

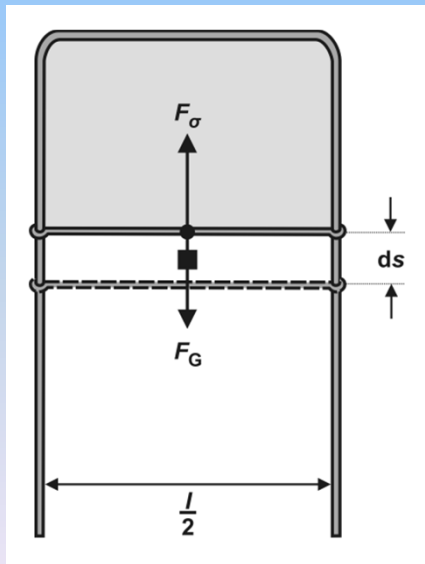


Illustration: in order to increase the liquid surface of the film by the small amount $dA = l \cdot ds$, the slider is shifted downward using only slightly more force than F_σ

energy necessary results in

$$dW_{\rightarrow A} = F_\sigma ds = \sigma \cdot l \cdot ds$$



$$dW_{\rightarrow A} = \sigma dA$$

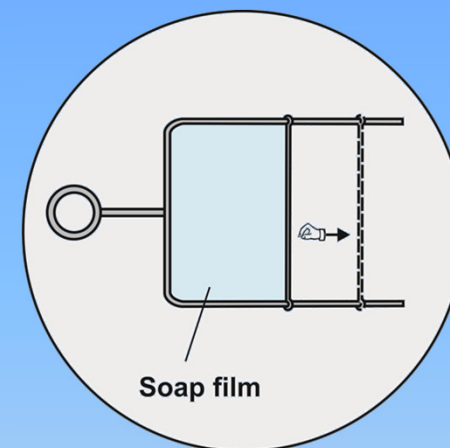
Soap Film



2A

Procedure:

A soap film is formed between a wire frame and a slider by dipping the frame into a soap bubble solution. The slider is then slowly pulled away from the end of the frame. Subsequently, one lets go of the slider.

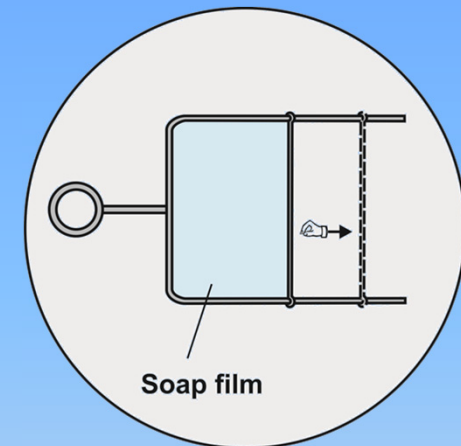


Soap Film



Procedure:

A soap film is formed between a wire frame and a slider by dipping the frame into a soap bubble solution. The slider is then slowly pulled away from the end of the frame. Subsequently, one lets go of the slider.



Observation:

The film contracts to its former size and the slider moves back to its original position.

Explanation:

In order to increase the surface area of the soap film, the energy $W_{\rightarrow A}$ has to be expended because of the surface tension. During the reverse process—when the slider moves back—this surface energy is released again.

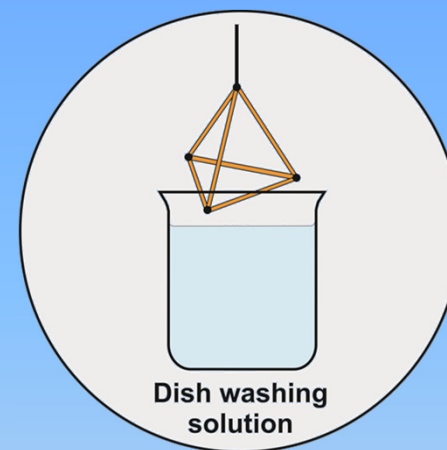
Optimal Bubble-ology



2B

Procedure:

A tetrahedral frame made by means of drinking straws and chenille stems is dipped into a dish-washing liquid containing solution and then slowly lifted out of it.



Optimal Bubble-ology



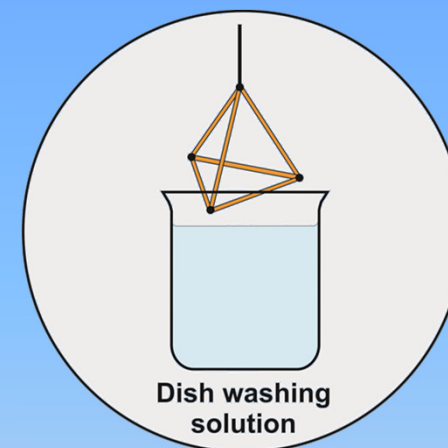
Procedure:

A tetrahedral frame made by means of drinking straws and chenille stems is dipped into a dish-washing liquid containing solution and then slowly lifted out of it.

Observation:

The soap film forms a series of plane surfaces, each of which begins at an edge of the tetrahedron and meets all the other surfaces at its center.

Depending on the direction of light incidence, the soap films shimmer in different colors.

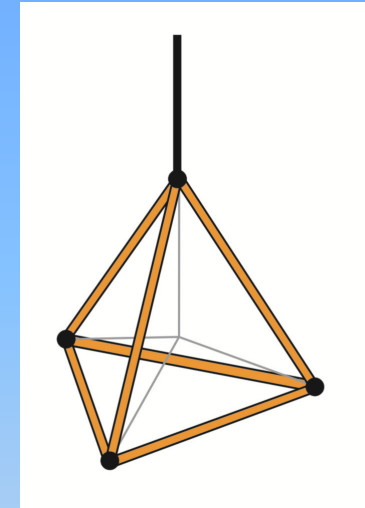


Optimal Bubble-ology



Explanation:

The soap film tends to minimize the surface energy by assuming the shape of least surface area possible taking into account the restrictions imposed by the framework. The intricate shape inside the tetrahedral frame represents this minimum area.



Since the thickness of the soap film is comparable to the wavelength of light it gives rise to interference fringes. This phenomenon is called *iridescence*.



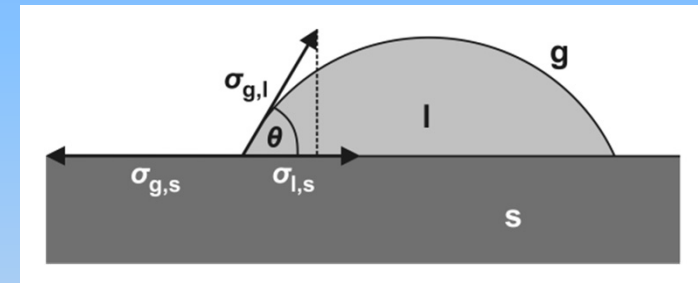
2. Various Surface Effects



Wetting

Wetting: complete covering of a solid surface by a liquid film, reason: attractive forces between different substances at a common interface (so-called *adhesion*)

liquid drop on a solid surface: three phases adjoin each other: gaseous (g), liquid (l) and solid (s) $\Rightarrow$ corresponding interface tensions



contact angle θ changes until the equilibrium of forces is attained:

$$\sigma_{g,s} = \sigma_{l,s} + \sigma_{g,l} \cdot \cos \theta \quad \text{YOUNG's equation}$$

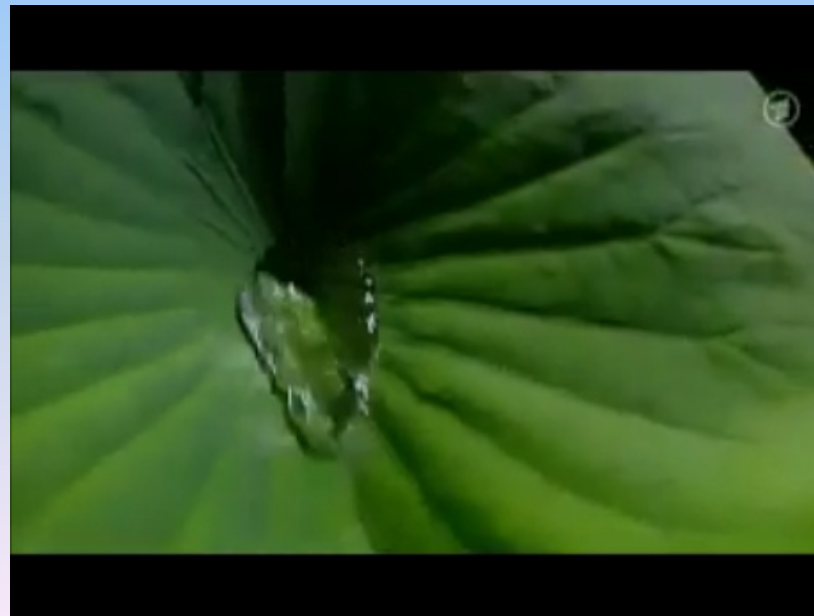
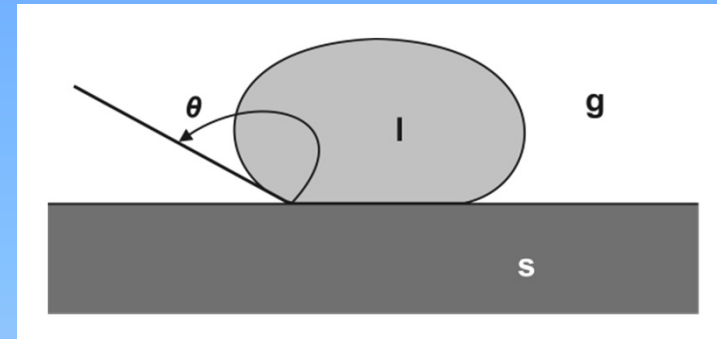
$\theta < 90^\circ$: liquid spreads across the solid surface, it *wets* it (adhesive forces stronger than cohesive forces)

$\theta \approx 0 \Rightarrow$ complete wetting; example: water on greaseless glass

Wetting

$\theta > 90^\circ$ (in the ideal case, 180°): no wetting will take place (cohesive forces stronger than adhesive forces)

Examples: mercury on glass, water on polytetrafluoroethylene fabric (Gore-Tex®), water on lotus leaves (lotus effect)



<https://www.youtube.com/watch?v=D3VvOUFesLE>

Laplace Pressure

Laplace pressure: excess pressure p_σ in a soap bubble (as well as a gas filled cavity in a liquid such as the “bubbles” in champagne or a drop of a liquid)



Does this excess pressure depend on the radius of the bubble?



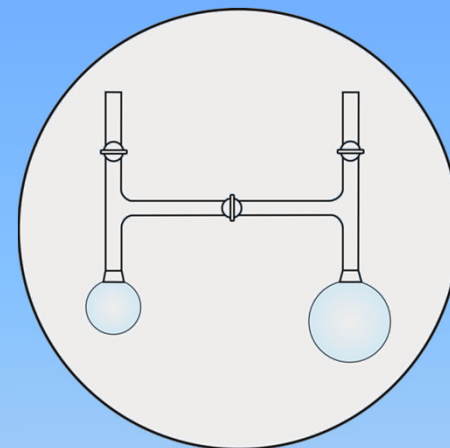
Connected Soap Bubbles



3

Procedure:

Two soap bubbles of differing sizes are connected via a closed stopcock. Subsequently, the stopcock is opened.



Connected Soap Bubbles

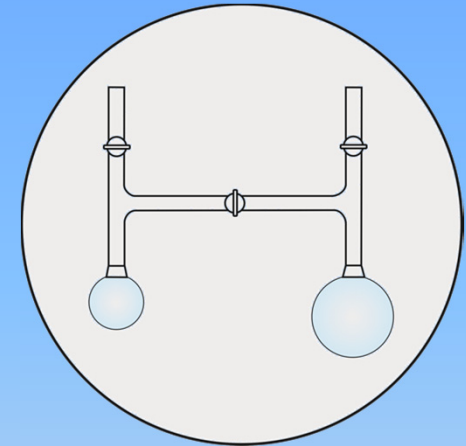


Procedure:

Two soap bubbles of differing sizes are connected via a closed stopcock. Subsequently, the stopcock is opened.

Observation:

The smaller bubble “inflates” the larger one and disappears during this process.



Apparently, the excess pressure increases as the radius decreases.

Connected Soap Bubbles

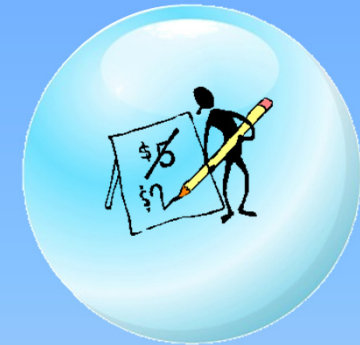


Explanation:

The excess pressure p_σ inside a soap bubble is balanced by surface tension.

If the radius r grows by dr due to further inflating, thereby increasing volume V by $dV = 4\pi r^2 dr$, the necessary energy is

$$dW = p_\sigma dV = p_\sigma \cdot 4\pi r^2 dr$$



At the same time, the surface grows by $dA = 8\pi r dr$ and the surface energy grows along with it:

$$dW_{\rightarrow A} = \sigma dA = \sigma \cdot 16\pi r dr$$

(inner and outer surface in the case of a soap bubble)

In equilibrium, the following is valid:

$$p_\sigma \cdot 4\pi r^2 dr = \sigma \cdot 16\pi r dr$$



excess pressure p_σ in a soap bubble:

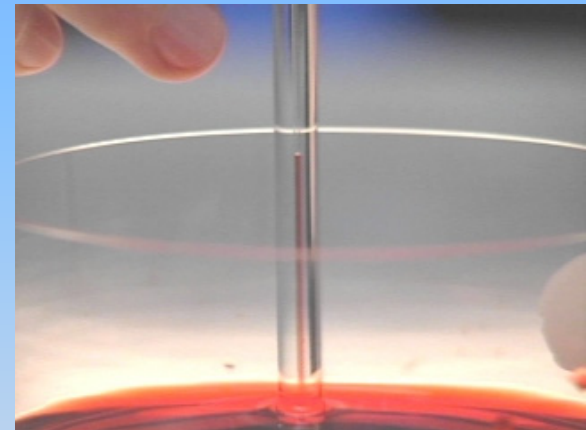
$$p_\sigma = \frac{4\sigma}{r}$$

Capillary Action

when a capillary tube is submerged in a wetting liquid, this liquid will rise in it up to a certain height defying gravity



How does the capillary rise depend upon the radius of the capillary tube?



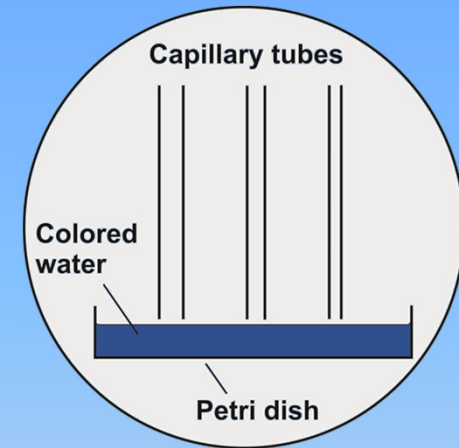
Capillary Tubes in Action



4A

Procedure:

Capillary tubes with different inner diameters are placed into colored water in a Petri dish.



Capillare Tubes in Action

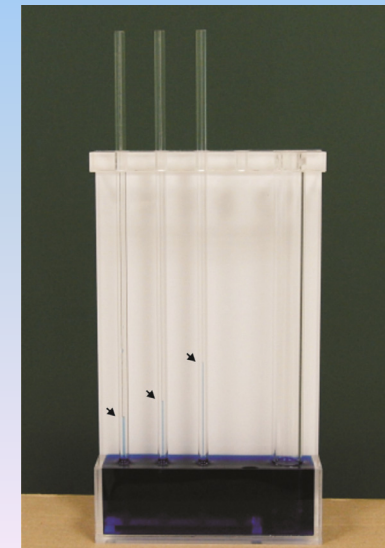
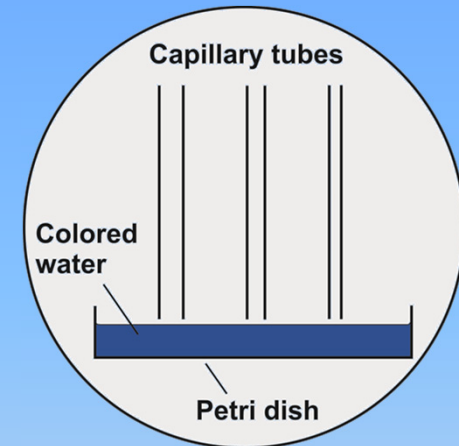


Procedure:

Capillary tubes with different inner diameters are placed into colored water in a Petri dish.

Observation:

The water rises in the capillary tubes and reaches different levels. The narrower the tube, the higher the water rises.



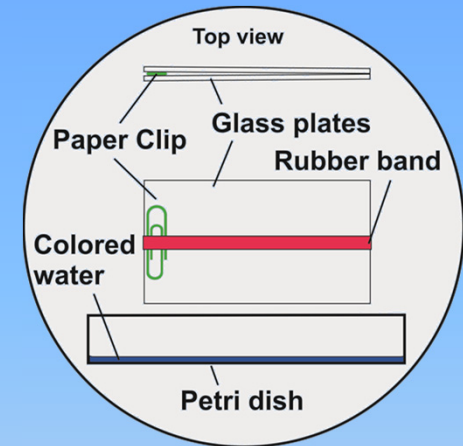
More Capillary Action



4B

Procedure:

A wedge formed by two glass plates with a paper clip as spacer and fixed together by a rubber band is placed into colored water in a Petri dish.



More Capillary Action



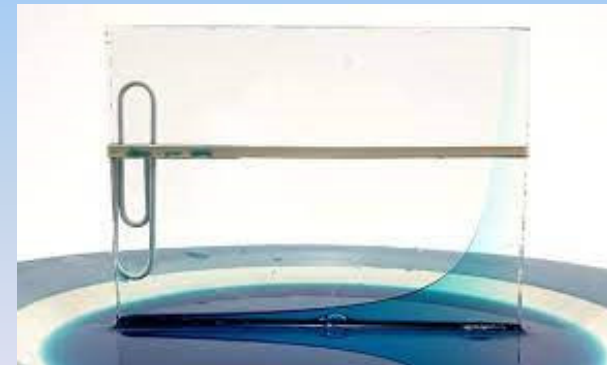
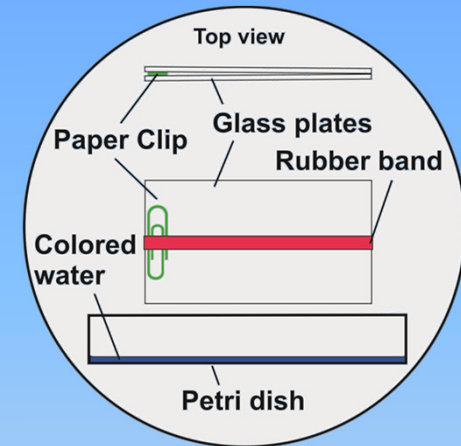
Procedure:

A wedge formed by two glass plates with a paper clip as spacer and fixed together by a rubber band is placed into colored water in a Petri dish.

Observation:

The water rises on the narrower side.

At the end, the surface of water in the wedge takes the shape of a hyperbola.



Capillary Action

Explanation:

The liquid rises in the capillary with the radius r_c until the weight $F_G = mg = \rho Vg$ of the liquid drawn up the tube just compensates for the force F_σ resulting from surface tension along the capillary circumference:

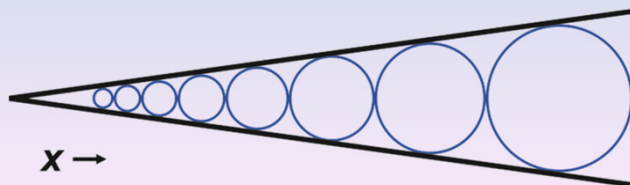
$$F_\sigma = 2\pi r_c \sigma = \rho \pi r_c^2 h g = F_G$$



$$h = \frac{2\sigma}{\rho r_c g}$$

The capillary rise h of a liquid is directly proportional to the surface tension and inversely proportional to the capillary radius.

The wedge-shaped space between the glass plates can be imagined as filled with a series of vertical capillary tubes whose radius increases with the distance x from the edge.



hyperbolic relationship
between h and x

Capillary Action in Nature

Have you ever thought about how a tree transports the ten to several hundred liters of liquid a day from the roots up to the leaves at a height of up to 120 m, where the water is needed for photosynthesis and to maintain the leaf structure?

water transport determined by *three* processes, which complement each other and have different importance during the year and in different climates

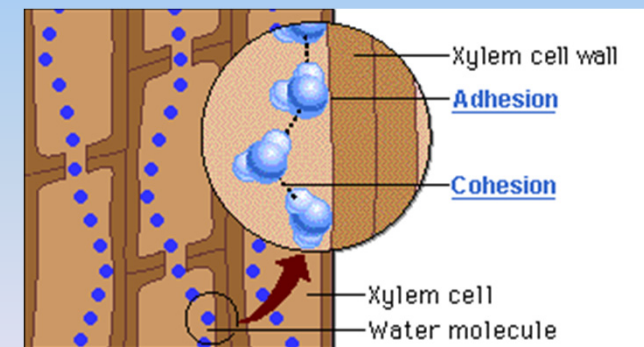
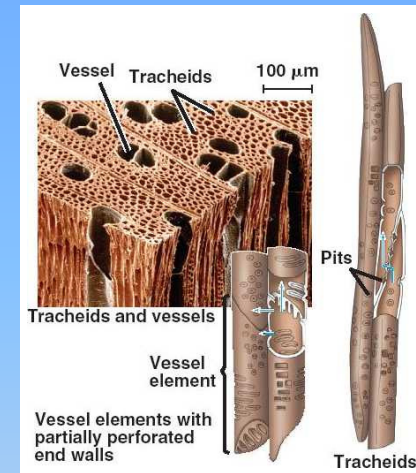
- *transpiration pull*
- *capillary action*
- *root pressure*



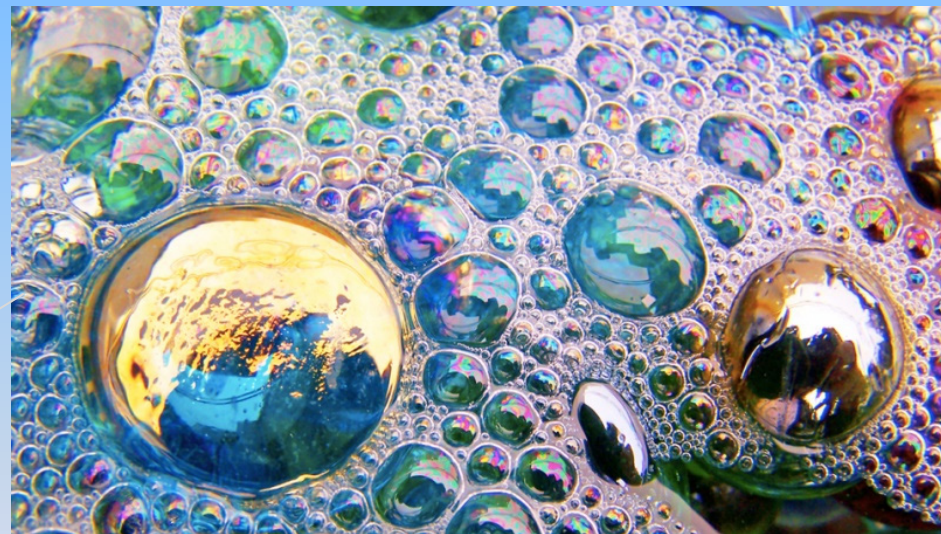
Capillary Action in Nature

supporting function of the *capillary action* in the water transport of a plant by facilitating the gravity defying transport processes: water rises within thin tubes (xylem conduits) in the wood as if by itself, and it rises higher, the thinner these tubes are

adhesion between the water molecules and the inner walls of the xylem conduits causes an upward movement of the liquid; cohesion between the water molecules themselves keeps the water column together during the transport process



3. Adsorption on Liquid Surfaces



Adsorption on Liquid Surfaces

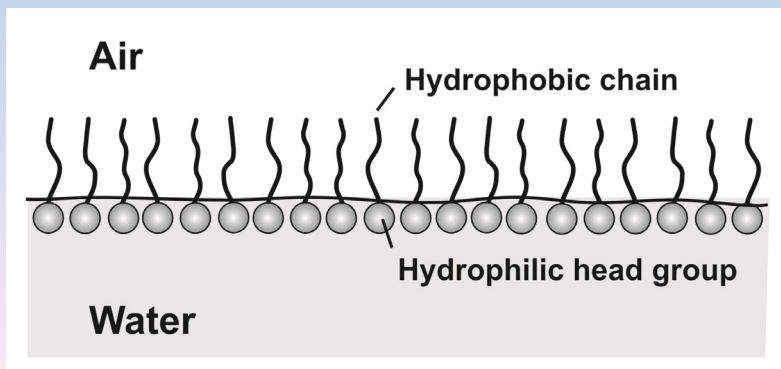
dissolved substances (*surfactants*) can influence interface tension by enriching themselves in the interface



phenomenon called *adsorption*

surfactants in aqueous solutions mainly organic compounds with long hydrophobic hydrocarbon chains and hydrophilic head groups [hydroxyl group, sulfonic acid group (SO_3^-), etc.]

surfactant molecules slip between the water molecules and the hydrophobic residue of these molecules extends out of the water



attraction between the H_2O molecules due to the strong hydrogen bonds decreases along with surface tension

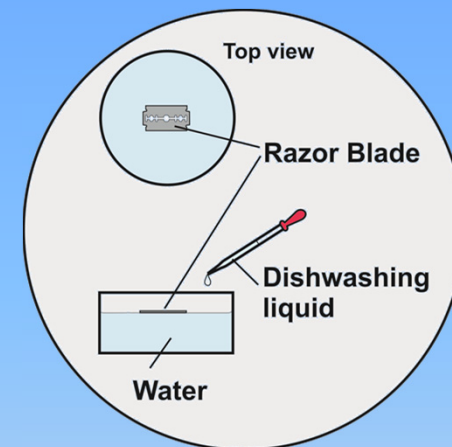
Floating Razor Blade



5

Procedure:

When a razor blade (or paper clip, etc.) is carefully laid upon a water surface, it will sink slightly, but continues to float. Then, a drop of dish-washing liquid is added near the object.



Floating Razor Blade



Procedure:

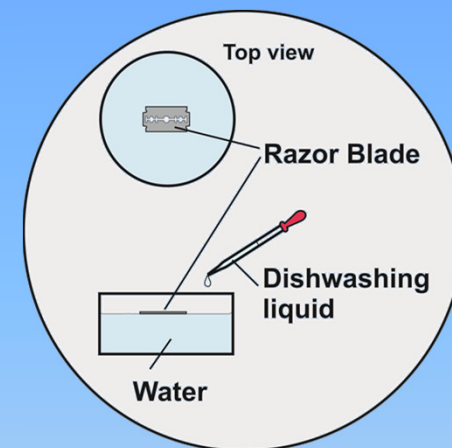
When a razor blade (or paper clip, etc.) is carefully laid upon a water surface, it will sink slightly, but continues to float. Then, a drop of dish-washing liquid is added near the object.

Observation:

The blade is first pushed slightly to the side, but finally it sinks to the bottom of the container.

Explanation:

The razor blade initially floats on the water due to its quite high surface tension. When dishwashing liquid is added, the surface tension decreases and the razor blade can no longer be supported by the surface tension.



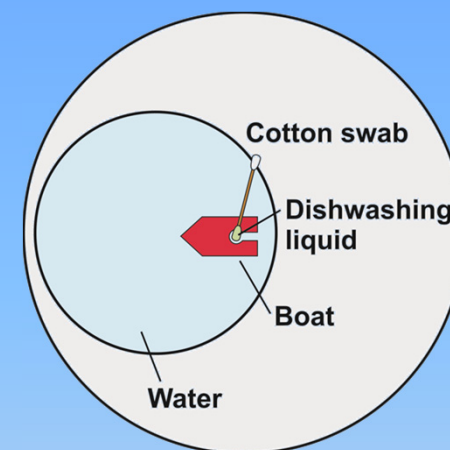
Soap-Powered Boat



6

Procedure:

The “boat” made from cardboard is placed on the water. A cotton swab is used to collect a small amount of dishwashing liquid. Subsequently, the end of the cotton swab is dipped into the water in the notch of the boat.

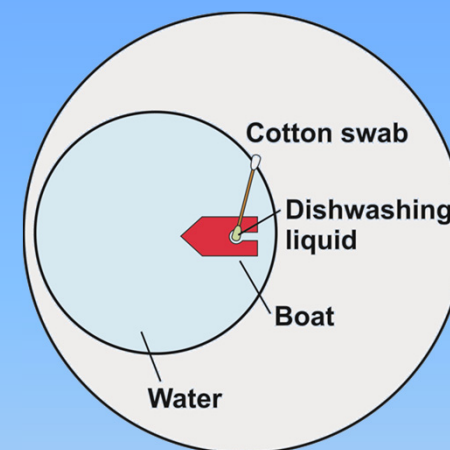


Soap-Powered Boat



Procedure:

The “boat” made from cardboard is placed on the water. A cotton swab is used to collect a small amount of dishwashing liquid. Subsequently, the end of the cotton swab is dipped into the water in the notch of the boat.



Observation:

The boat zooms forward in the water.



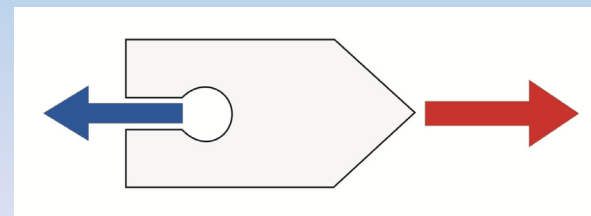
Soap-Powered Boat



Explanation:

The soap boat experiment makes use of the “Marangoni effect,” the tendency of molecules to migrate from a region of low surface tension to a region of high surface tension.

When a drop of dishwashing liquid is placed in the notch, a soapy film spreads out on the water surface from the back of the boat, thereby “pushing” the boat forward.



This is similar to a rocket.

Marangoni Effect in Nature

small aquatic insects such as the rove beetles *Microvelia* can rapidly (up to 70 cm/s) skim over the water surface to escape potential predators without employing the oscillatory movements of legs by using the Marangoni effect

for this purpose they secrete chemicals that momentarily reduce the surface tension to the rear



4. Adsorption on Solid Surfaces



Adsorption on Solid Surfaces

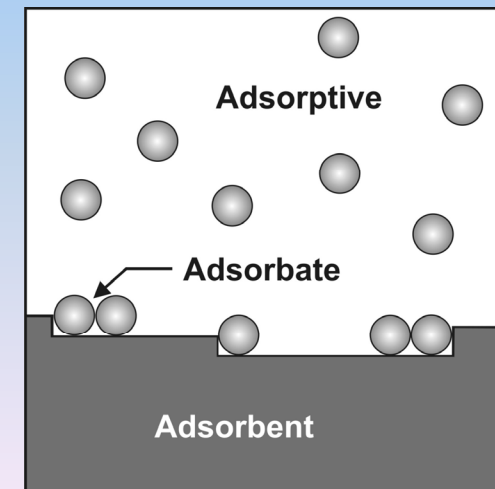
Experiment: soft drink containing food coloring is poured on activated carbon $\Rightarrow$ clear filtrate

real adsorption process varies between two extreme adsorption forms, which differ from each other primarily by the strength of the bonding of the *adsorptive* (free particles before adsorption, gas molecules for example) to the *adsorbent* (the molecules of the solid surface such as activated carbon)

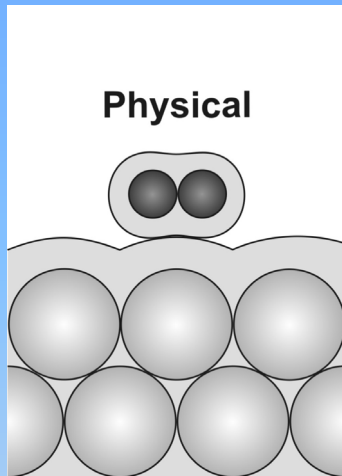


- *physical adsorption*
- *chemical adsorption*

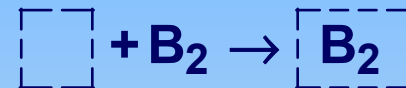
extent of adsorption depends directly upon the surface area of the adsorbent



Physisorption



physisorption (physical adsorption): molecules of a gaseous or dissolved substance B that have accumulated on a solid adsorbent are loosely “physically” bound, for example by VAN DER WAALS’ forces



$\boxed{}$: site on the surface

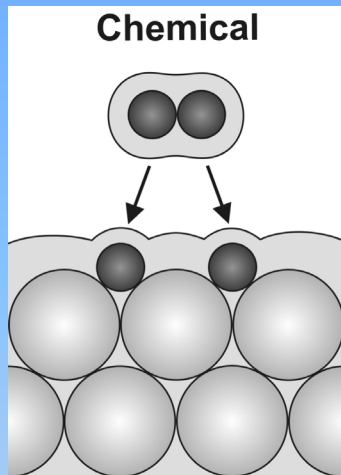
physical adsorption has the character of a *condensation*.

chemical drive (GIBBS energy) almost exclusively determined by the type of substance being adsorbed

adsorbed particles can attach into several layers, one on top of the other (*multilayer adsorption*), and essentially keep their structure

Example: noble gases at low temperatures

Chemisorption

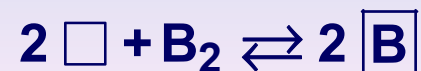


chemisorption (chemical adsorption): a stable “chemical” bond is formed $\Rightarrow$ chemical adsorption has the character of a *chemical reaction*

chemical drive (GIBBS energy) depends also significantly upon the adsorbing solid substance involved

molecular bonding in the adsorbate [deposited, at most, in a single layer on the adsorbent (*monolayer adsorption*)] strongly altered so that the particles are in a very reactive state and can even dissociate

Example: adsorptive bonding of hydrogen to surfaces of transition metals such as Pd or Fe; hydrogen is not adsorbed in molecular form but in atomic form

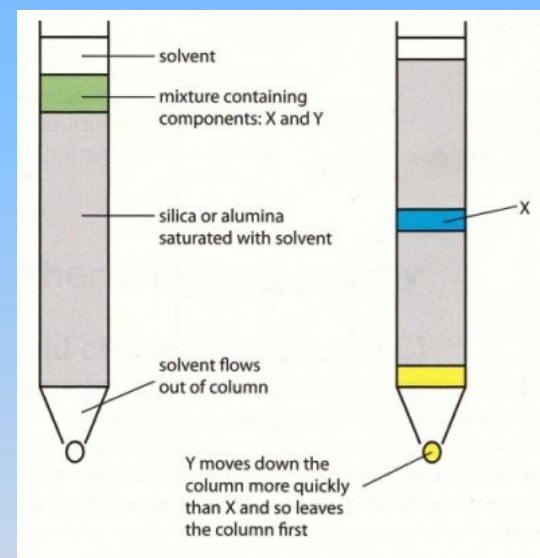


Adsorption Chromatography

adsorption plays a major role in separation of substances, especially in *adsorption chromatography*

method based upon the difference of adhesion probabilities of the substances being separated which, being in a mobile phase (liquid, gas), are passed along a stationary phase (solid material, for example, Al_2O_3 , SiO_2)

the greater the attraction of a substance for the stationary phase compared to the mobile phase, the slower this substance moves up



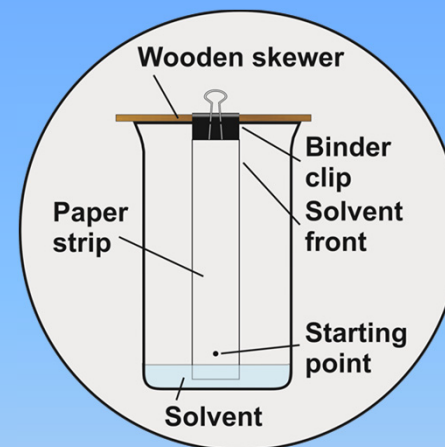
Chromatographic Separation of Felt Pen Ink



7

Procedure:

A felt tip pen is used to make a dot at one end of an oblong filter paper strip. The strip is then attached to a wooden skewer with a binder clip and the end of the strip is lowered into the water but the dot should not be submerged.

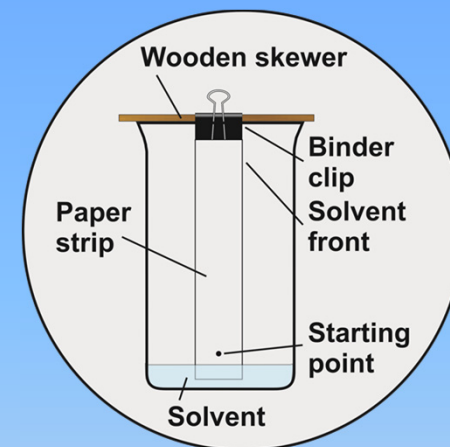


Chromatographic Separation of Felt Pen Ink



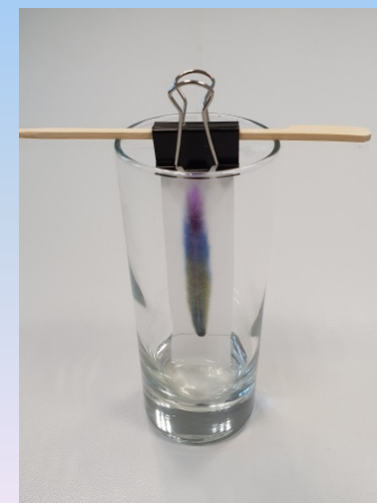
Procedure:

A felt tip pen is used to make a dot at one end of an oblong filter paper strip. The strip is then attached to a wooden skewer with a binder clip and the end of the strip is lowered into the water but the dot should not be submerged.



Observation:

The solvent immediately starts moving up the paper strip, carrying the ink pigments with it. The dot separates into variously colored components.

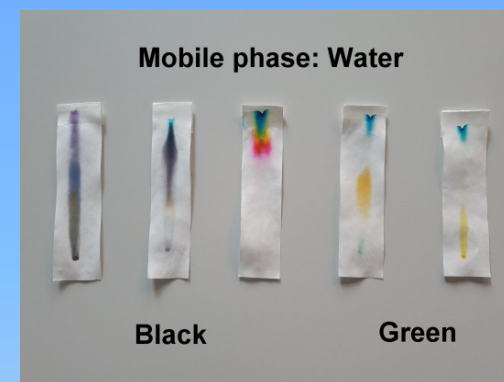


Chromatographic Separation of Felt Pen Ink



Observation (continued):

Depending on the brand of the felt tip pen and its color, different color patterns are created.



Explanation:

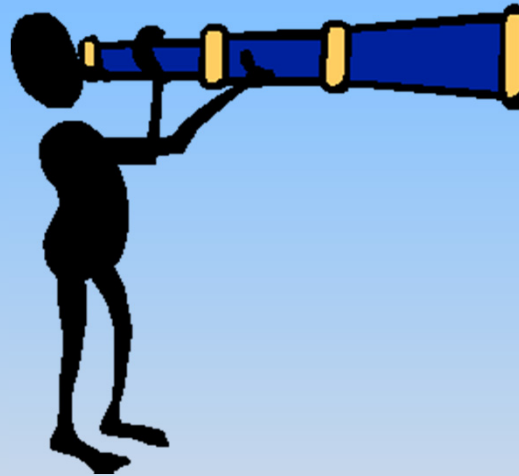
In the present case of paper chromatography, the mobile phase is water and the stationary phase is paper (or rather the water trapped between the cellulose fibers). The mobile phase moves up the paper by capillary action, carrying the different components with it. The various types of dye molecules in the ink migrate with a different speed depending on their preference to be adsorbed onto the stationary phase versus being carried along with the mobile phase. In this way the components are separated from one another.

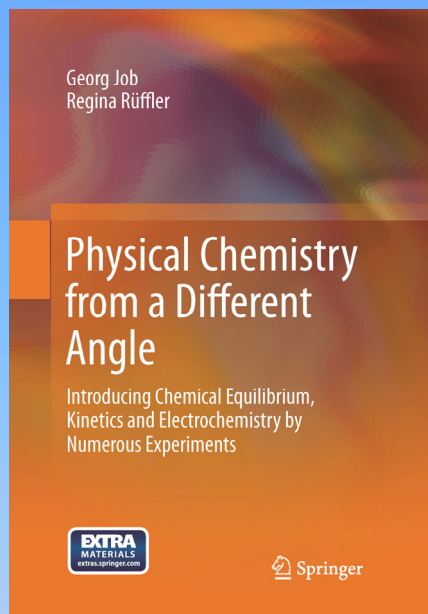
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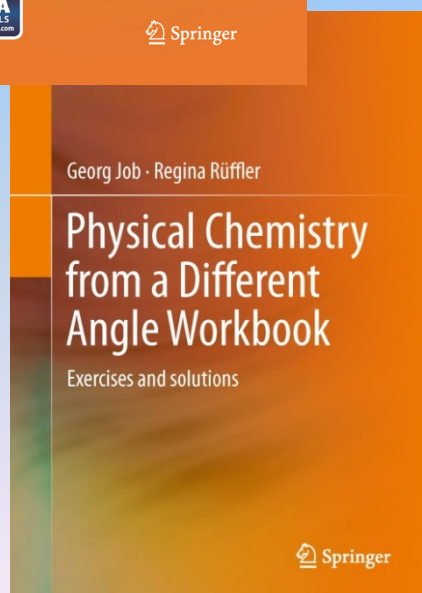


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**Thank you very much for
your friendly attention.**

