Engineering Chemistry

Fall Semester

2019 –20

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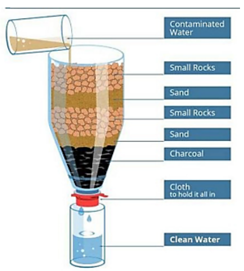
Apun Ko Zindagi Mai Kuch
Daring Karna Tha

Eng. Chem.

LTP

- 3 “sessions” per week.
- 2 theory + 1 practical
- 3 tutorials

Syllabus Structure

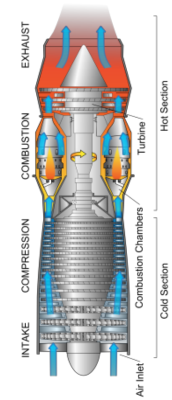


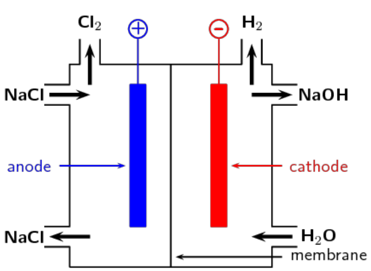
Impurities of water and its treatment

Industrial and Conducting polymers

Phase equilibria and Alloys

Energy sources





Electrochemistry - Corrosion

Energy conversion and storage

Experiments

1. Determination of total hardness of water by EDTA method.
2. Estimation of different types of alkalinity in waste water sample.
3. Estimation of Copper in an alloy by Iodometry.
4. Estimation of Iron in an alloy by Cerimetry
5. Determination of dissolved oxygen content in the Treated water sample
6. Assessment of Chemical Oxygen Demand (COD) and BOD of waste water.
7. Assessment of TDS in water samples using TDS-Conductivity method.
8. Determination of concentration of alkali metal ions (Na or K) by flame photometry
9. Analysis for percentage of Iron in steel by redox potentiometry
10. Assay of Nickel through soluble complex formation by colorimetry
11. Chloride level detection in municipal water using $AgNO_3$ by conductometry
12. Estimation of the molecular weight of a polymer by Ostwald Viscometer.

Academic Integrity

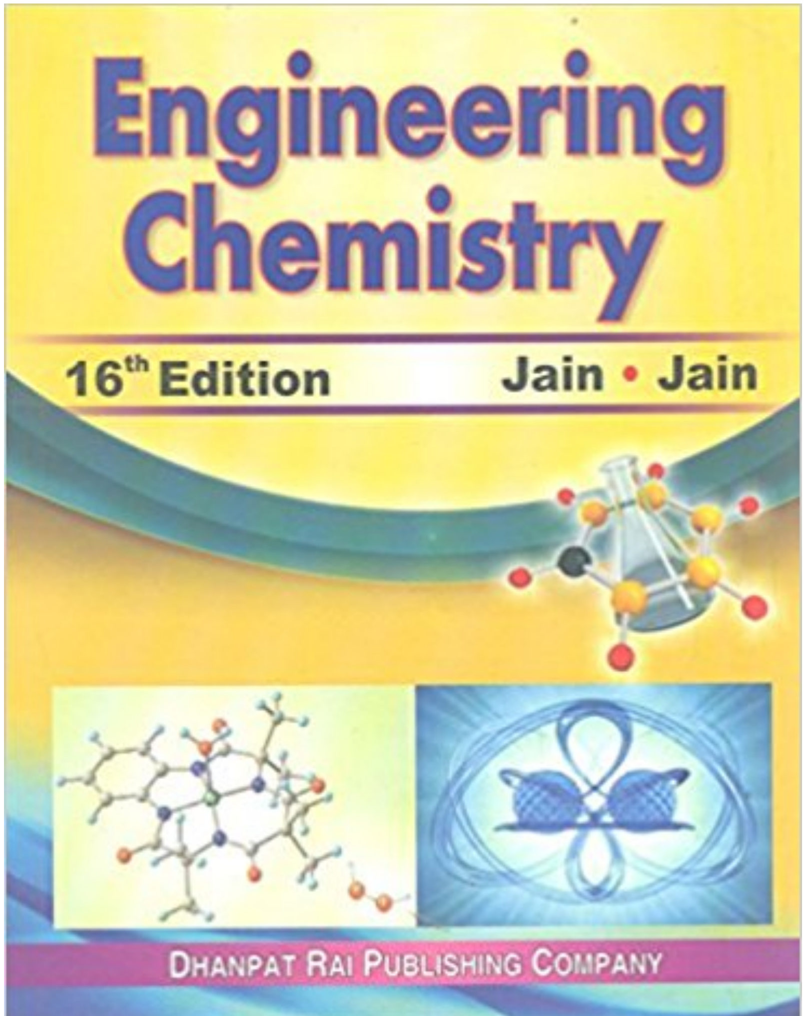
It will be the mission of teacher and students to create and maintain an academic integrity both in and out of the classroom. Therefore, all exams and activities will be proctored by the teacher and students will get different problem sets in exams. All assignments/reports/presentations/activities should result from student's own understanding and the student should agree to the following statement for a submission to be considered valid:

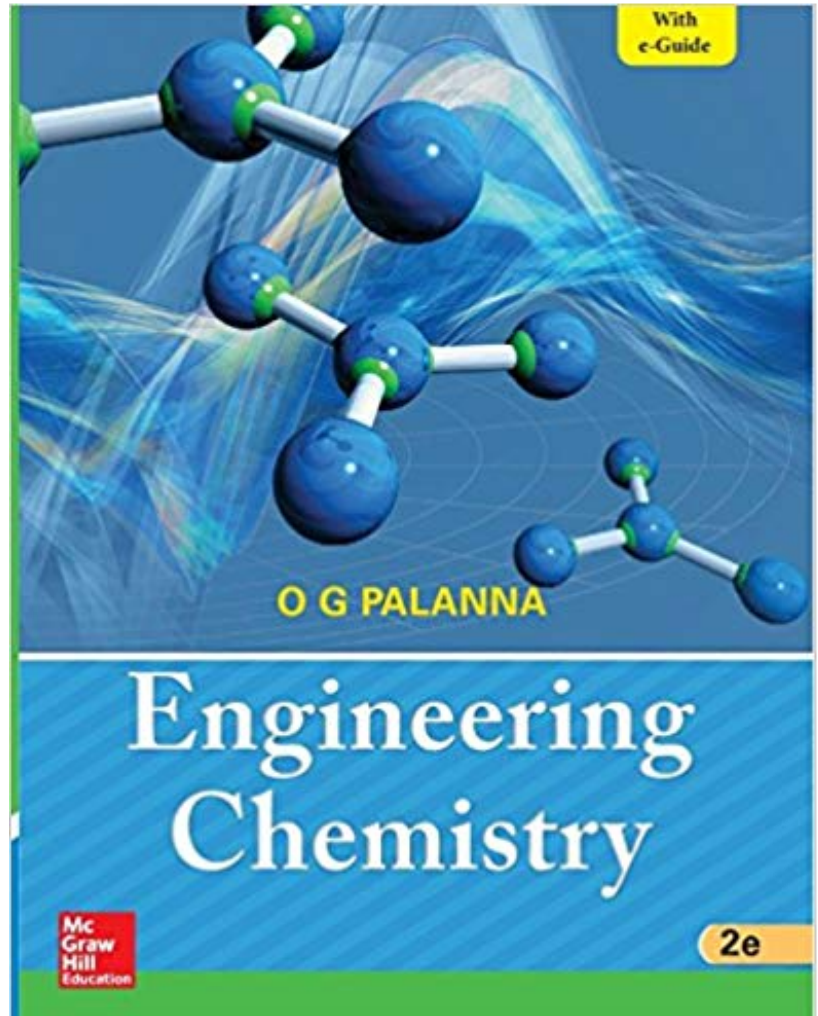
- I have not cheated or used any unauthorized material.
- I have not submitted this work for any other course without prior permission from the concerned professors.
- I have not collaborated with anyone on a take-home examination unless explicitly permitted by the instructor.
- I have not plagiarized the reports, assignments, quizzes, etc.
- I have not shared my solutions to exams/quizzes/assignments with anyone else unless specified explicitly by the instructor.

Academic misconduct improperly affects the student's evaluation and will be dealt severely as per the university regulations.

Minimum 75 % attendance!!!

Books


Engineering Chemistry
16th Edition
Jain • Jain
DHANPAT RAI PUBLISHING COMPANY


With e-Guide
O G PALANNA
Engineering Chemistry
2e
Mc Graw Hill Education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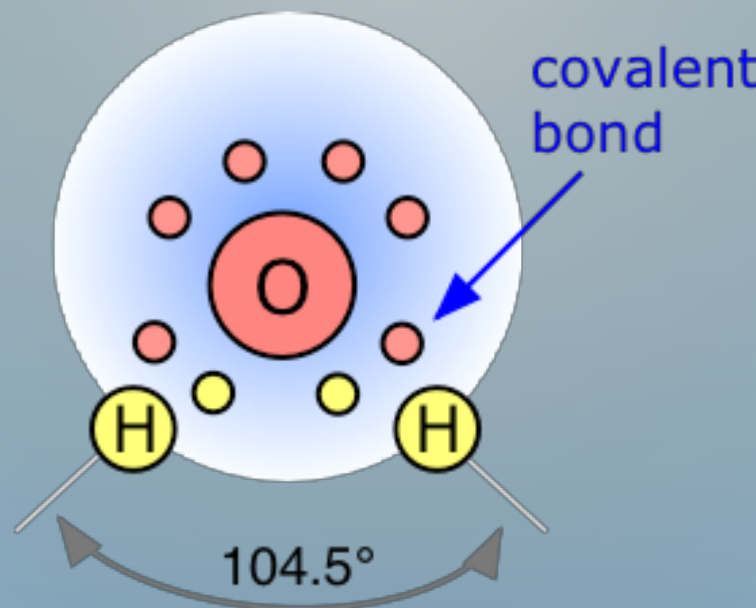
covalent
bond
O
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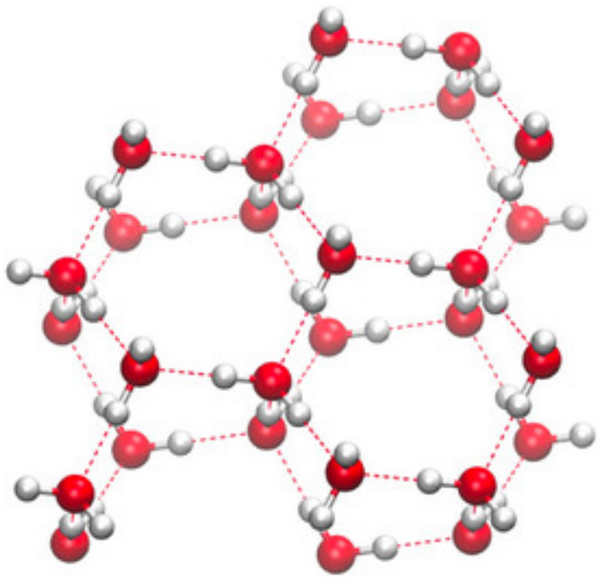
104.5°

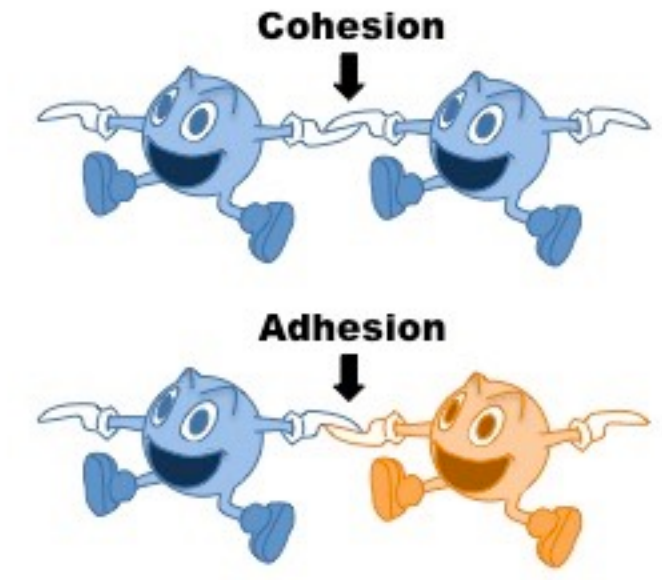
- Solid form, ice, has lower density than liquid.

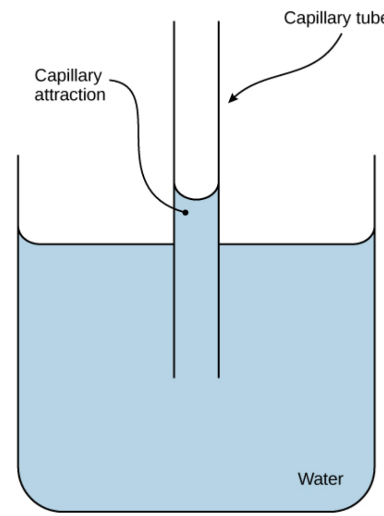
[water temp]

- Water has the highest heat capacity of all liquids.
- Water high heat of vaporization of water.

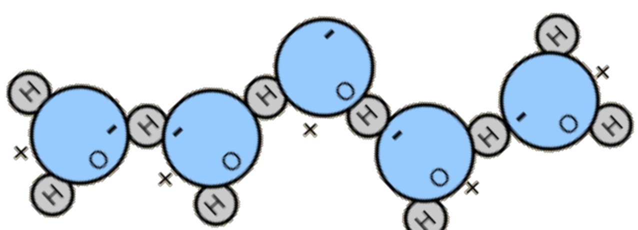
Properties of Water?

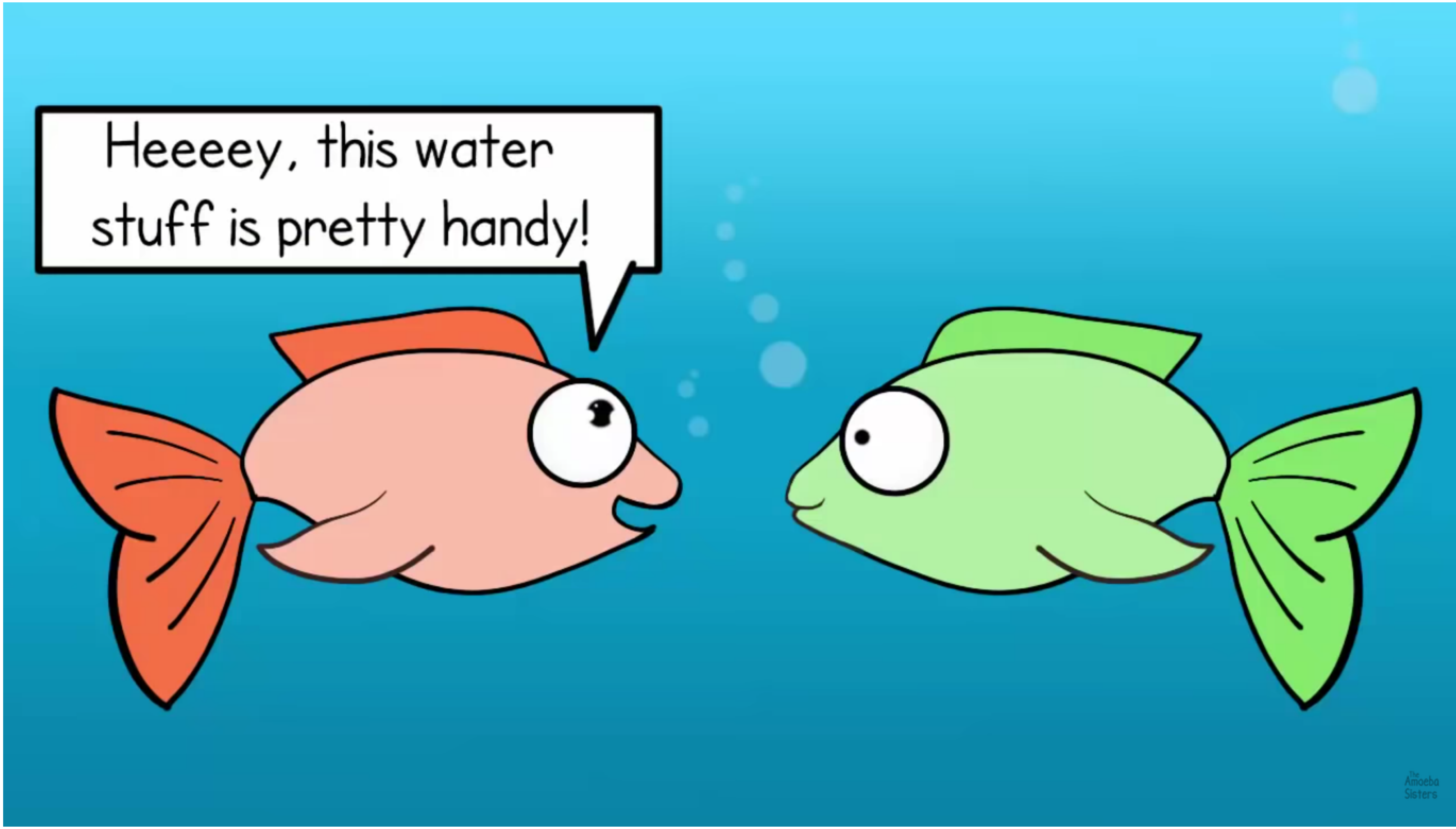
Water molecules attract or are attracted to other polar molecules.

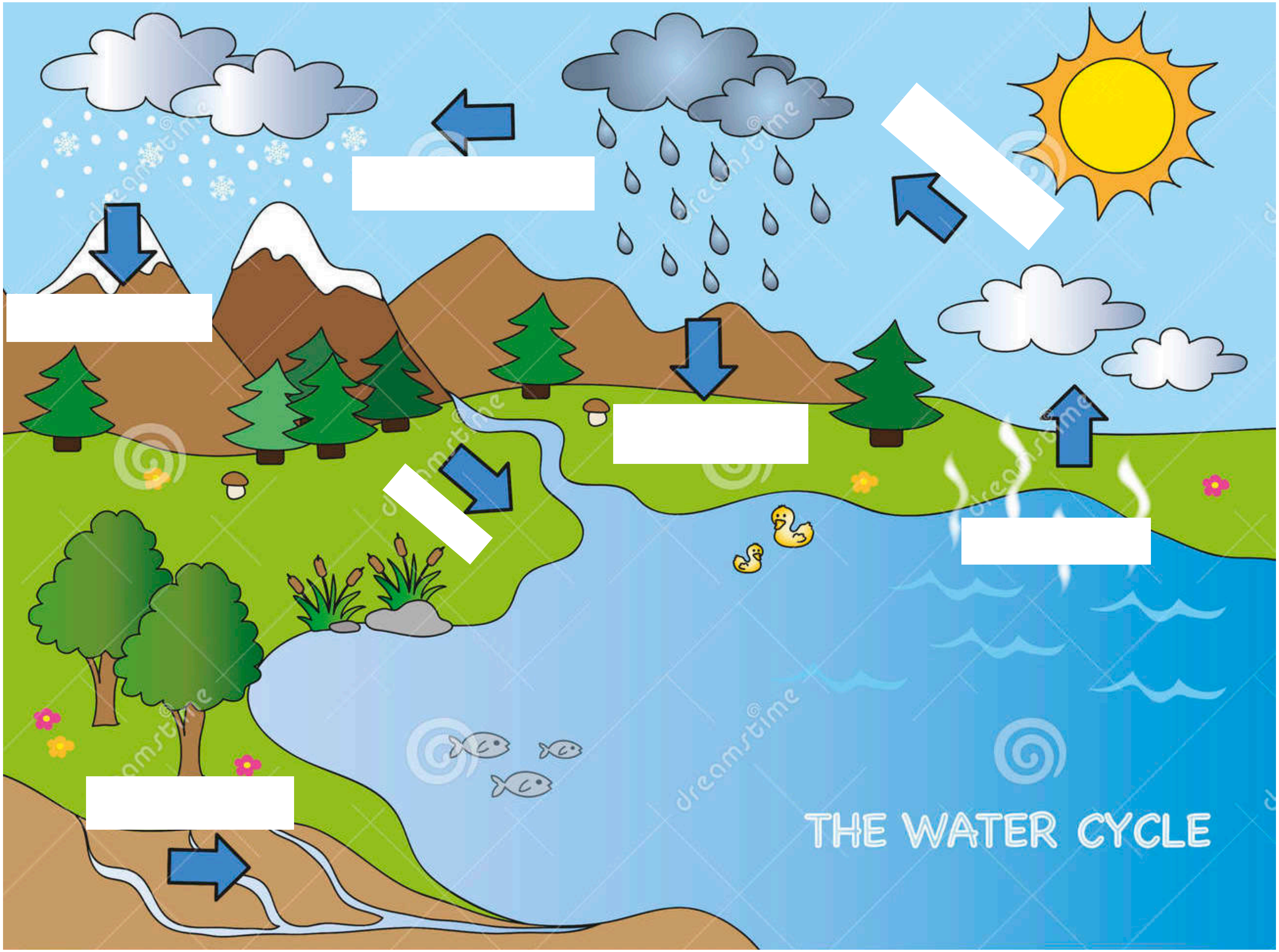




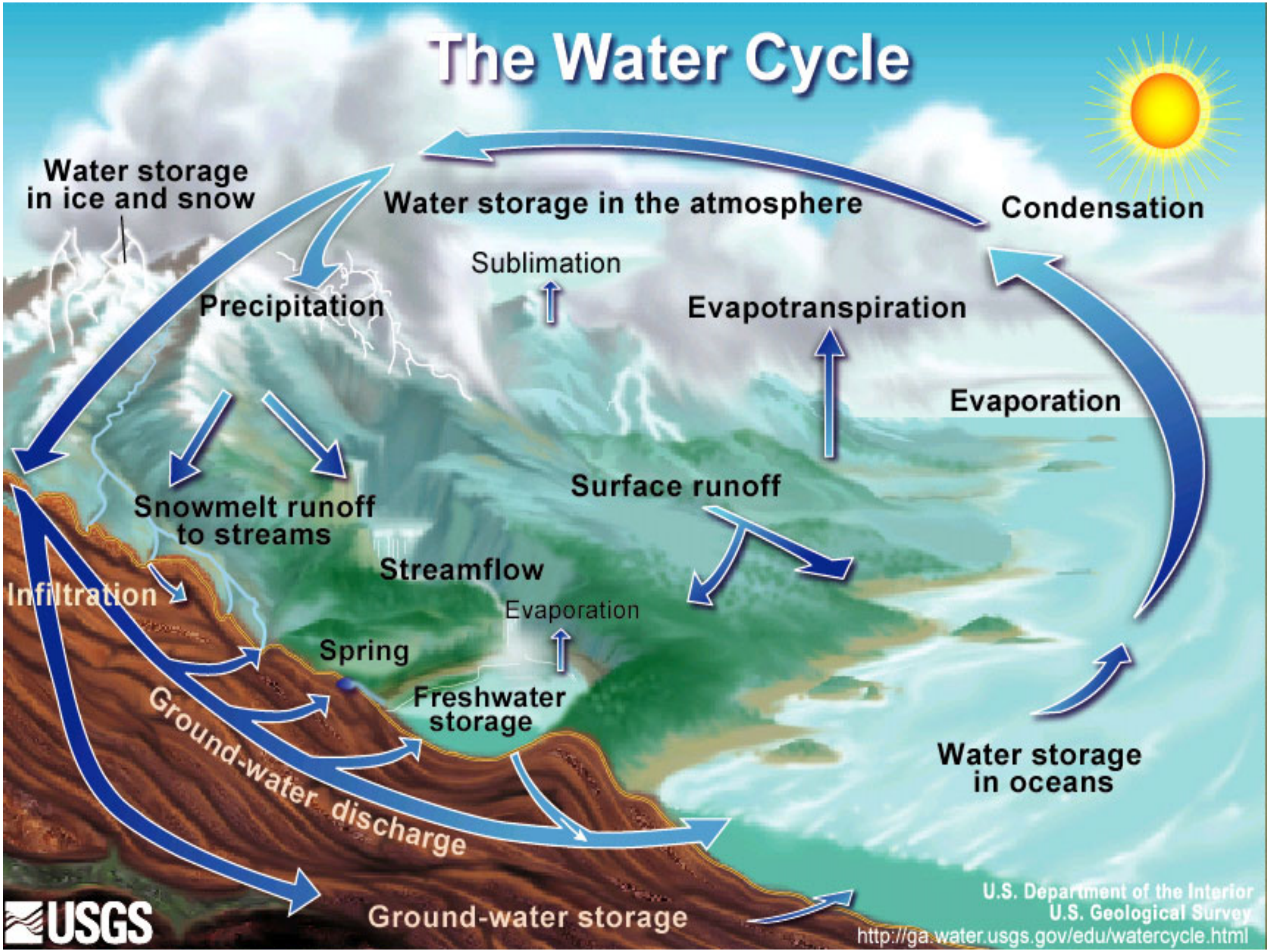
Excellent solvent.



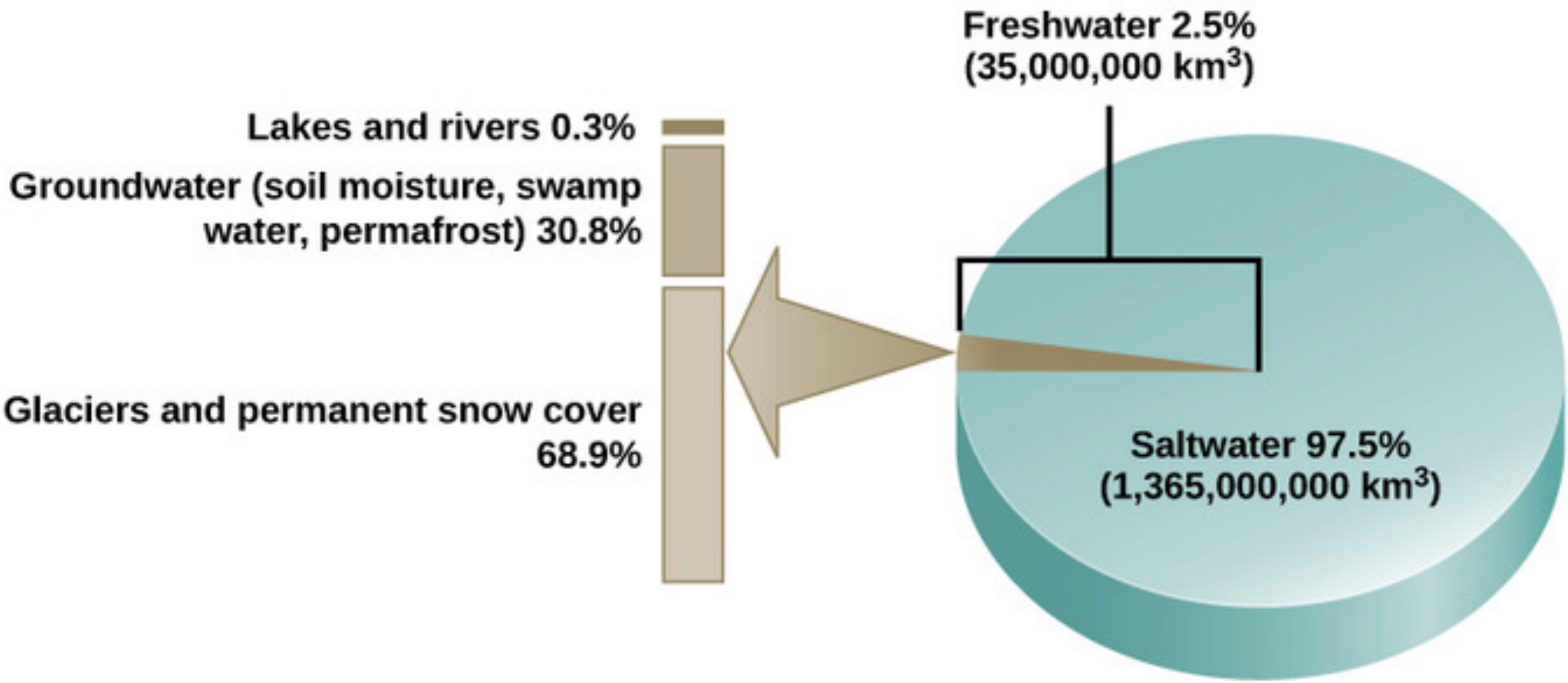

Heeeey, this water stuff is pretty handy!
The Amoeba Sisters



Processes?



US Department of the Interior



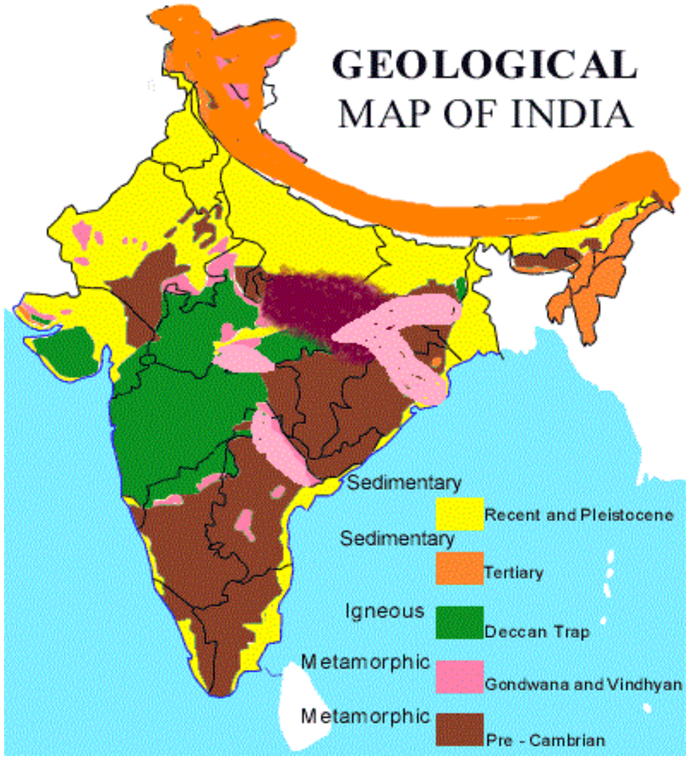
Freshwater 2.5%
(35,000,000 km3)
Lakes and rivers 0.3%
Groundwater (soil moisture, swamp water, permafrost) 30.8%
Glaciers and permanent snow cover 68.9%
Saltwater 97.5%
(1,365,000,000 km3)

Impurities In Water

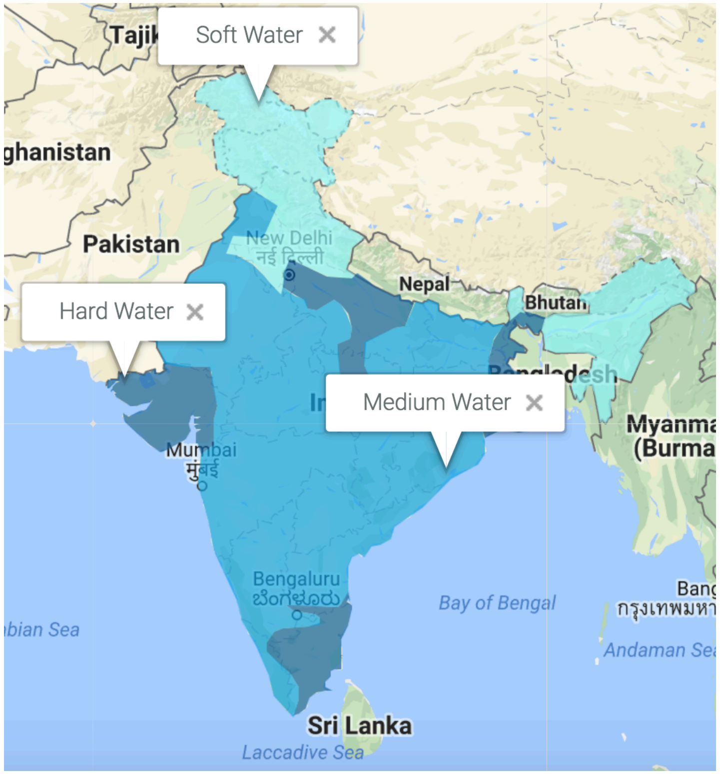
Physical Impurities
- Suspended Impurities
- Colloidal Impurities

Bacteriological Impurities
- Bacteria
- Algae
- Fungi

Chemical Impurities
- Dissolved Gases
- Dissolved Organic Salts
- Dissolved Inorganic Salts



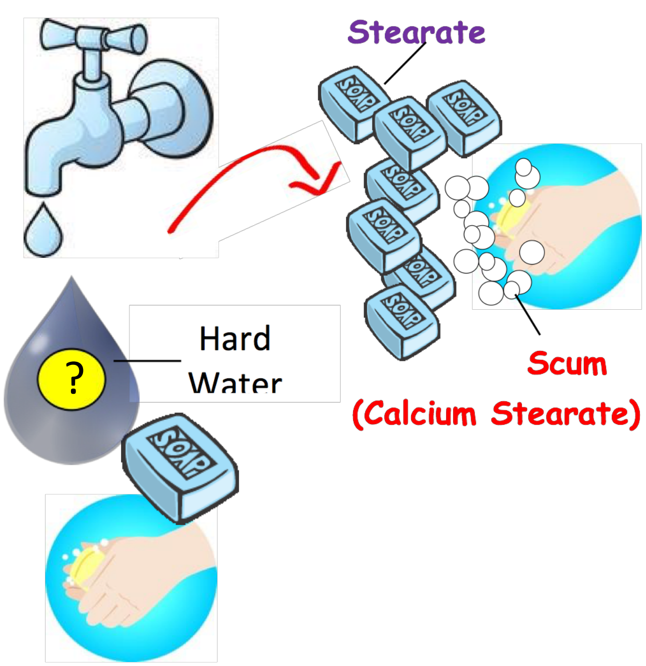
Types of rocks across India. Water types?

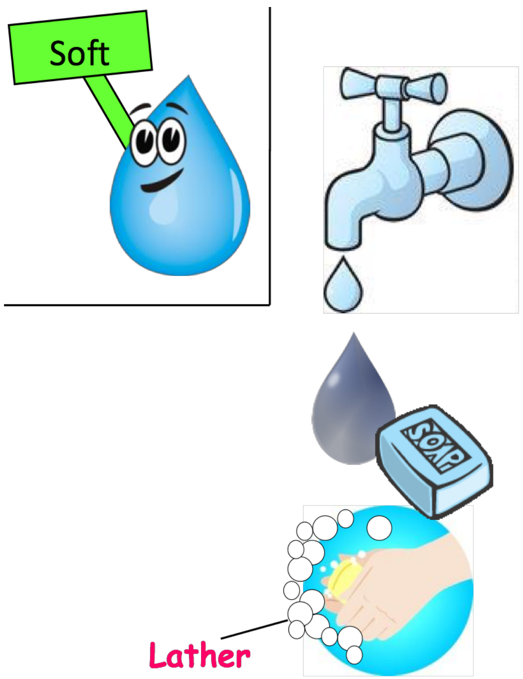


- Hard water
- Soft water

Water Hardness

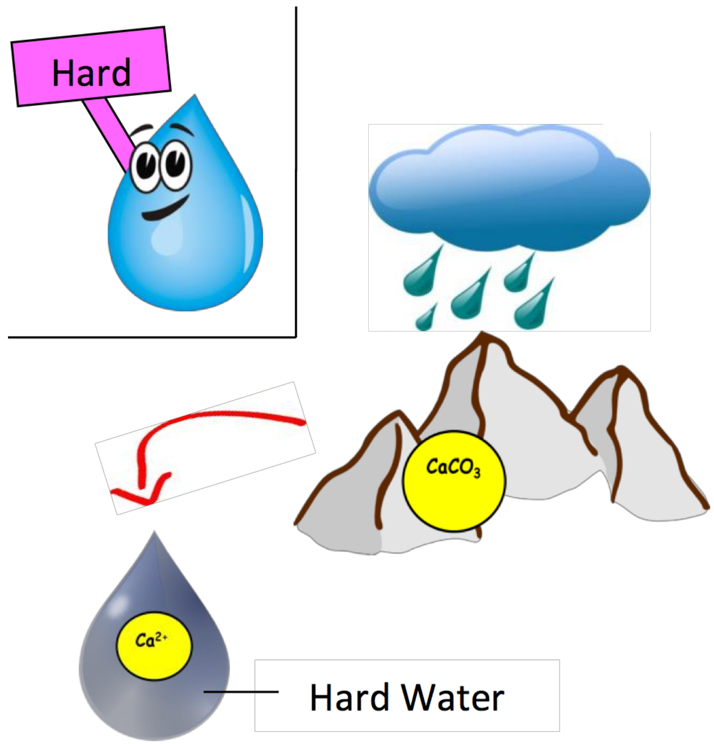
- Hardness of water refers to the quantity of dissolved salts of certain metal ions in water that reduces the tendency to form lather with soap.
- Hard water is “hard” to form lather or foam with.





Causes of Water Hardness

- Calcium (Ca^{2+}) and Magnesium (Mg^{2+}) ions.



$CaCO_3$	$CaCl_2$
$MgCO_3$	$MgCl_2$
$Ca(HCO_3)_2$	$CaSO_4$
$Mg(HCO_3)_2$	$MgSO_4$


Yeh kachra kahan se aata hai

How do Ca^{2+} and Mg^{2+} get into water?

Limestone pavement

Limestone, calcium carbonate, does not dissolve in pure water, BUT it does dissolve in acid rain.

$$CaCO_3 + H_2CO_3 \longrightarrow Ca(HCO_3)_2$$

Calcium carbonate

Carbonic Acid (acid rain)

Calcium Hydrogen carbonate

HARD

Magnesite, $MgCO_3$

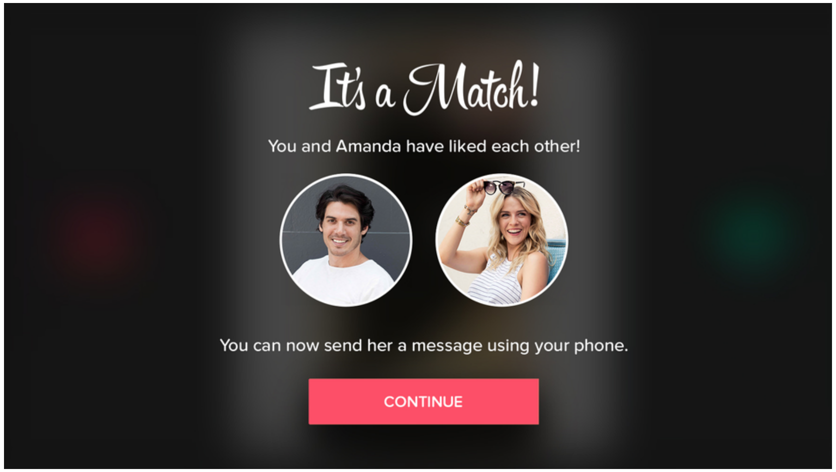
Dolomite, $CaMg(CO_3)_2$

Gypsum, $CaSO_4 \cdot 2H_2O$

Differences b/w Soft and Hard Water

Hard Water	**Soft Water**
does not produce lather with soap	produces lather with soap
contains dissolved calcium and magnesium Salts	does not contains dissolved calcium and magnesium salts.
Cleansing action of soap is suppressed	Cleansing action of soap is not suppressed
requires more material and time	does not require excess material and time

Types of Water Hardness



Temporary hardness

Permanent hardness

Temporary hardness

Causes:

Calcium hydrocarbonate – $Ca(HCO_3)_2$
Magnesium hydrocarbonate – $Mg(HCO_3)_2$

Removal: boiling the water

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 + H_2O + CO_2$$

$$Mg(HCO_3)_2 \xrightarrow{\Delta} Mg(OH)_2 + 2\ CO_2$$

Permanent hardness

Causes:

chlorides and sulphates of Ca^{2+}, Mg^{2+}, Fe^{3+}
e.g. $CaCl_2$, $MgSO_4$

Removal: not by boiling the water
Sophisticated water treatment methods

Disadvantages of Hard Water

Scale Formation

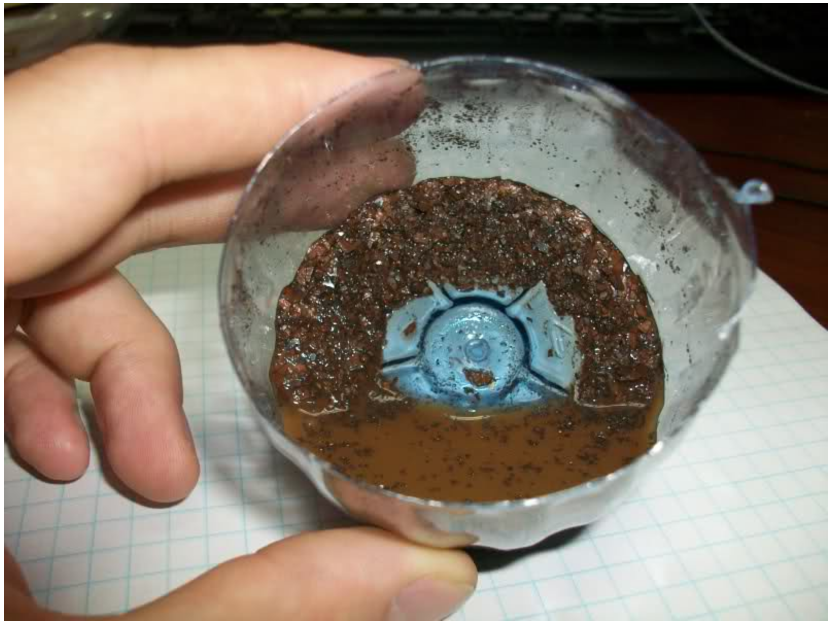
- $CaCO_3$ formed upon boiling water with temporary hardness, is NOT soluble in water.
- This calcium carbonate precipitates out, coating the insides of boilers, kettles, pipes etc.

It reduces the efficiency of any heating element, using more energy.
It can block pipes and damage equipment. Expensive to remove.

Disadvantages of Hard Water

Sludge Formation

- Salts such as $MgCl_2$, $CaCl_2$, $MgCO_3$, $MgSO_4$ etc. have higher solubility in hot water than cold water.
- Get deposited in the "cold" part of boilers.
- Soft and loose precipitates.



Poor conductor of heat. Can combine with scale formation.
Removed by wire brush.

Disadvantages of Hard Water

Soap Scum Formation

- Calcium and magnesium ions react with soap to make calcium and magnesium stearate.

$$2\ C_{17}H_{35}COONa + CaCl_2 \rightarrow (C_{17}H_{35}COO)_2Ca + 2\ NaCl$$

(Sodium stearate) (calcium stearate)

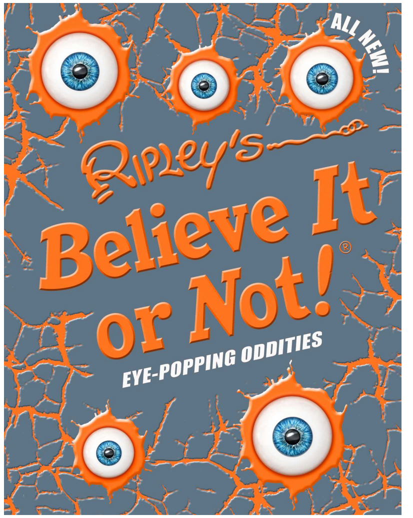
$$2\ C_{17}H_{35}COONa + MgSO_4 \rightarrow (C_{17}H_{35}COO)_2Mg + Na_2SO_4$$

(Magnesium stearate)

Lather is only formed once all the Ca_2^+ /Mg_2^+ ions have been precipitated.

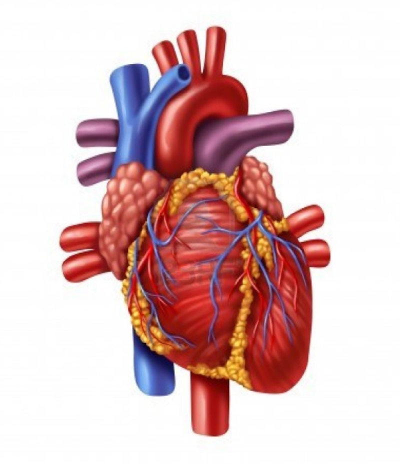
Less bubbles, more soap!!!

Advantages of Hard Water

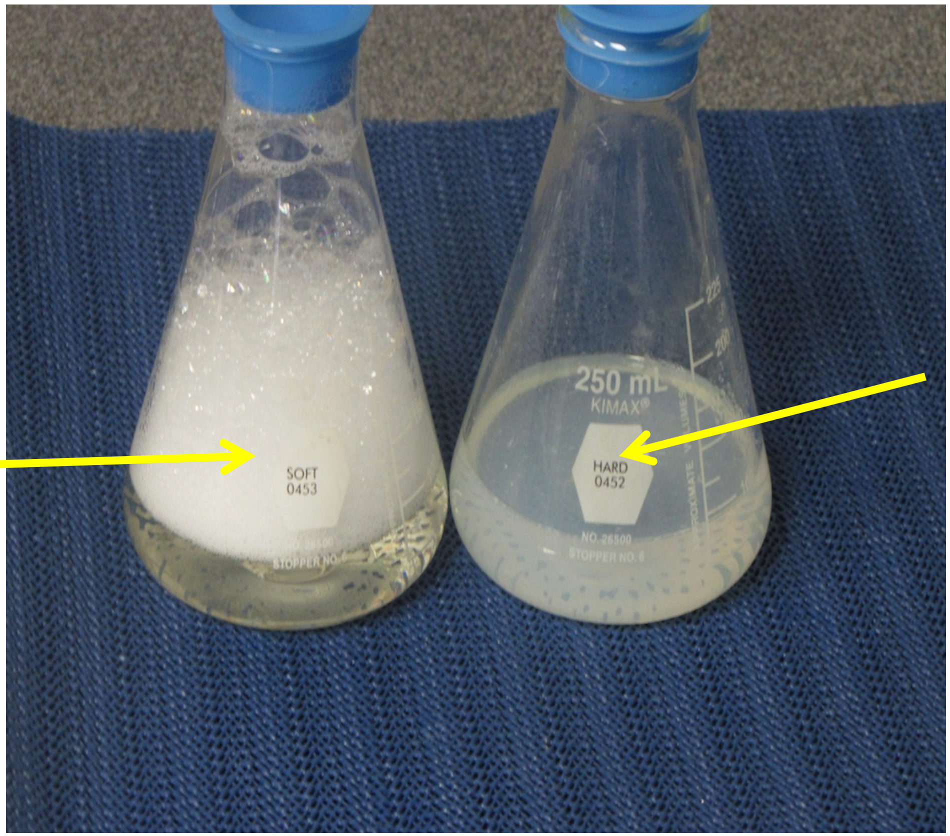


Some people still prefer it! Can you think of any reasons why?

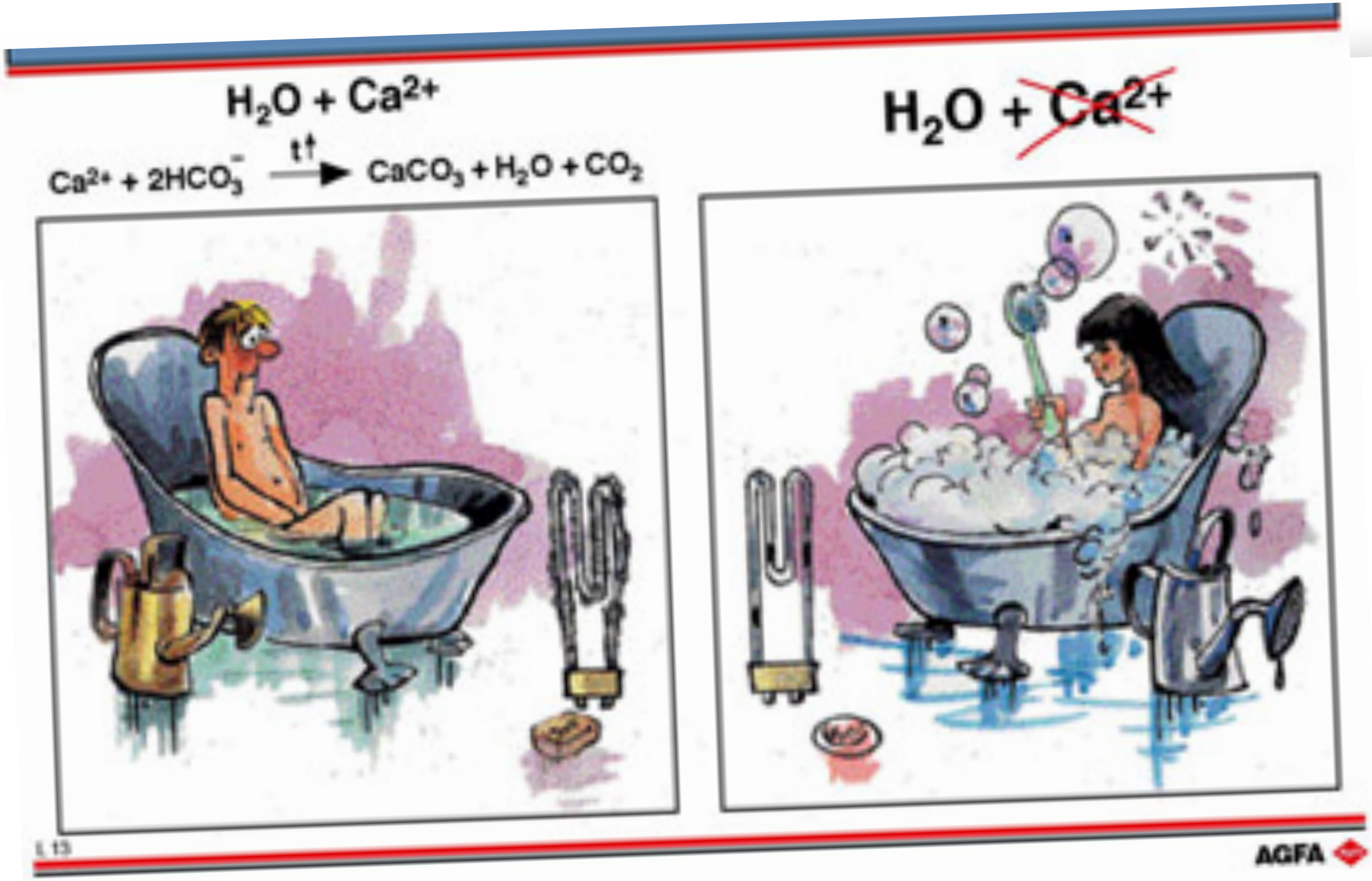
- Taste: some people prefer it
- It's good for your teeth and bones (Calcium ions)
- It can protect against heart problems
- It prevents the poisonous lead dissolved in drinking water.



Soft



Hard



REMEMBER: While other metal ions can be in water, only Ca^{2+} and Mg^{2+} cause hardness.

Where do the ions in our drinking water come from?

Water runs over rocks and dissolves ions

Which 2 ions cause hard water?

Calcium and Magnesium

Which rock gives you temporary hard water?

Limestone

What is the chemical name for limestone?

Calcium carbonate

Why does this normally insoluble chemical dissolve?

Acid rain

What ions are produced when limestone reacts with acid rain?

Ca^{2+} and HCO_3^-

What happens to HCO_3^- ions if you heat them?

They break down to CO_3^{2-} ions

If you have CO_3^{2-} ions and Calcium ions in the same water, what happens?

They precipitate as $CaCO_3$

What problem arises in heating systems and temporary hard water?

scale

Why do we care about limescale?

Reduces efficiency/ blocks pipes

What rock gives you permanently hard water?


Calcium Sulphate

What effect does boiling have on permanently hard water?

None

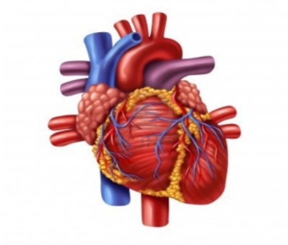
What do calcium and magnesium ions form with soap?

Scum

What does this mean for the amount of soap needed?

More soap for the same lather

What are the positives to hard water



Taste/ bones and teeth/ heart

After class

- List out different water sources in the campus and comment on their hardness level.

- Check water hardness level in your city:

http://www.ionicsystems.com/water-hardness-maps/india-hardness-map/

Degree of Hardness

Hardness is expressed in terms of equivalence of $CaCO_3$: highly insoluble (easy for precipitation) and molecular weight of 100 (easier calculation).

For a particular hardness producing substance, say **X**,

$$CaCO_3 \text{ Equivalent } = \frac{\text{Strength of } \mathbf{X} \text{ (mg/L) x 50}}{\text{Chemical equivalent of } \mathbf{X}}$$

NOTE: There may be no Calcium carbonate in the sample at all!!! But we are expressing it as an equivalence.

Example: Find multiplication factor for converting into $CaCO_3$ equivalents for following salts and ions?

$Ca(HCO_3)_2$		CO_2	
$Mg(HCO_3)_2$		HCO_3^-	
$CaSO_4$		OH^-	
$CaCl_2$		CO_3^{2-}	
$MgSO_4$		H^+	
$MgCl_2$		$Mg(NO_3)_2$	
$CaCO_3$		$NaAlO_2$	
$MgCO_3$		$FeSO_4$	

Na = 23, Mg = 24, Al = 27. S = 32, Ca = 40, Fe = 56

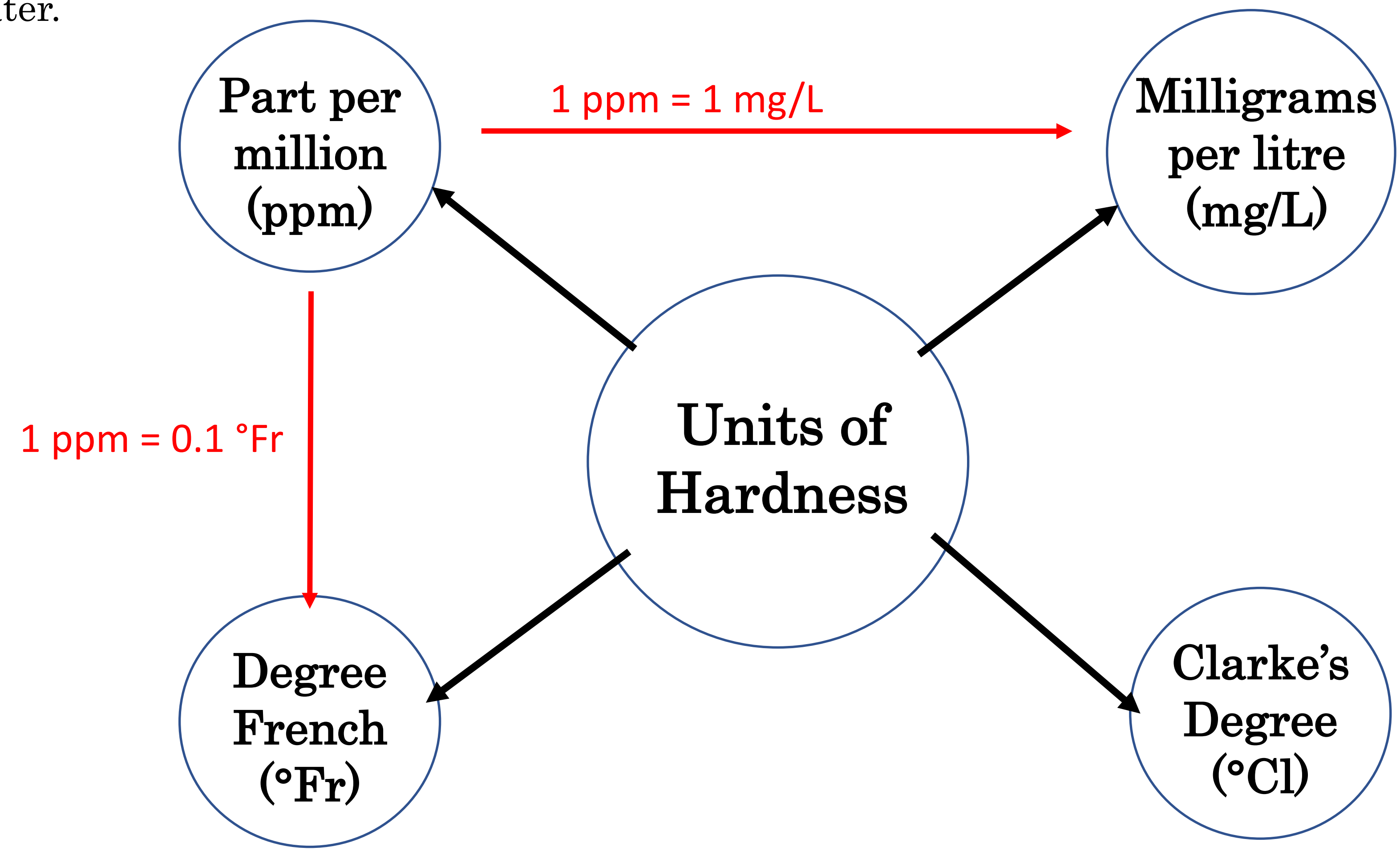
Example: Find multiplication factor for converting into $CaCO_3$ equivalents for following salts and ions?

$Ca(HCO_3)_2$	50/81	CO_2	50/22
$Mg(HCO_3)_2$	50/73	HCO_3^-	50/61
$CaSO_4$	50/68	OH^-	50/17
$CaCl_2$	50/55.5	CO_3^{2-}	50/30
$MgSO_4$	50/60	H^+	50/1
$MgCl_2$	50/47.5	$Mg(NO_3)_2$	50/74
$CaCO_3$	50/50	$NaAlO_2$	50/82
$MgCO_3$	50/42	$FeSO_4$	50/76

Units of Hardness

1 ppm = 1 part by weight of $CaCO_3$ equivalent in 10^6 parts by weight of water.

1 mg/L = 1 mg of $CaCO_3$ equivalent in one litre of water.



1 °Fr =1 part of $CaCO_3$ equivalent in 10^5 parts of water.

1 °Cl = 1 part of $CaCO_3$ equivalent in 70, 000 parts of water.

Degree of Hardness

Hardness Level	ppm
Soft	0 - 17
Slightly Hard	17 - 60
Moderately Hard	60 - 120
Hard	120 - 180
Very Hard	180 and above

Source: Water Quality Association (WQA)

Example: A water sample contains 150 mg of $CaSO_4$ per litre. Calculate the hardness?

Answer:

Chemical equivalent of $CaSO_4$ = 68

$$CaCO_3 \text{ equivalent} = \frac{150 \text{ x } 50}{68} \text{ mg/L} = 110.29 \text{ mg/L}$$

AAS analysis of a water sample determined the Ca^{2+} hardness to be 36 mg/L and the Mg^{2+} hardness to be 16 mg/L. What is the total hardness expressed as $CaCO_3$ equivalents?

$$\frac{36 \text{ mg } Ca^{2+}}{} * \frac{50 \text{ g } CaCO_3}{20.05 \text{ g } Ca^{2+}} = 90 \text{ mg/L as } CaCO_3$$

$$\frac{16 \text{ mg } Ca^{2+}}{} * \frac{50 \text{ g } CaCO_3}{12.15 \text{ g } Mg^{2+}} = 66 \text{ mg/L as } CaCO_3$$

Total hardness = 90 + 66 = 156 mg/L as $CaCO_3$

Calculate hardness of all salts/ions → Type of substance → Type of hardness

How many grams of $MgCO_3$ dissolved per litre gives 124 ppm of hardness?

$$\text{Hardness} = \frac{\text{Strength of } \mathbf{MgCO_3} \text{ (mg/L) x 50}}{\text{Chemical equivalent of } \mathbf{MgCO_3}}$$

$$\text{Strength of } \mathbf{MgCO_3} = 124 \text{ x } \frac{(\mathbf{MgCO_3} \text{ equivalence})}{CaCO_3 \text{ equivalence}} \quad \text{ppm}$$

$$= 124 \text{ x } (42/50) \text{ ppm} = 104.16 \text{ ppm}$$

$$= 104.16 \text{ mg/L}$$

A water sample was found to contain the following impurities:

Impurity	Quantity (g/L)
$Ca(HCO_3)_2$	0.004
$Mg(HCO_3)_2$	0.006
$CaSO_4$	0.012
$MgSO_4$	0.008
$CaCl_2$	0.002

Calculate the temporary, permanent and total hardness in ppm and °Fr.

Hardness Measurement

- Useful test that provides a measure of the water quality to be used for household and industrial purposes.

- Measure before having to deal with scale formation.

- EDTA Method
- O. Hehner's Method
- Soap Titration Method
- Warta-Pfeifer Method

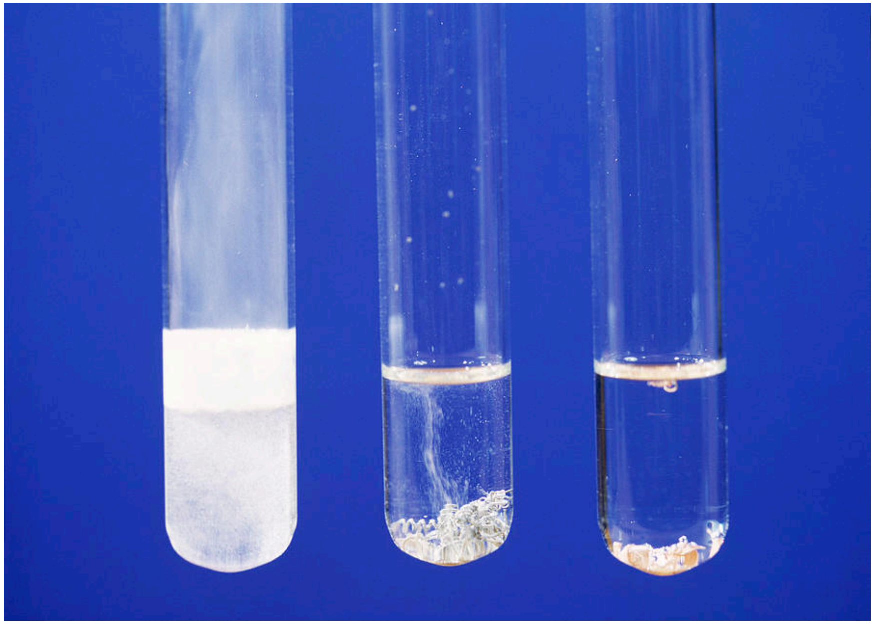
Strategy

- If you are looking for "hardness", what are you actually searching for…?

Metal ions!

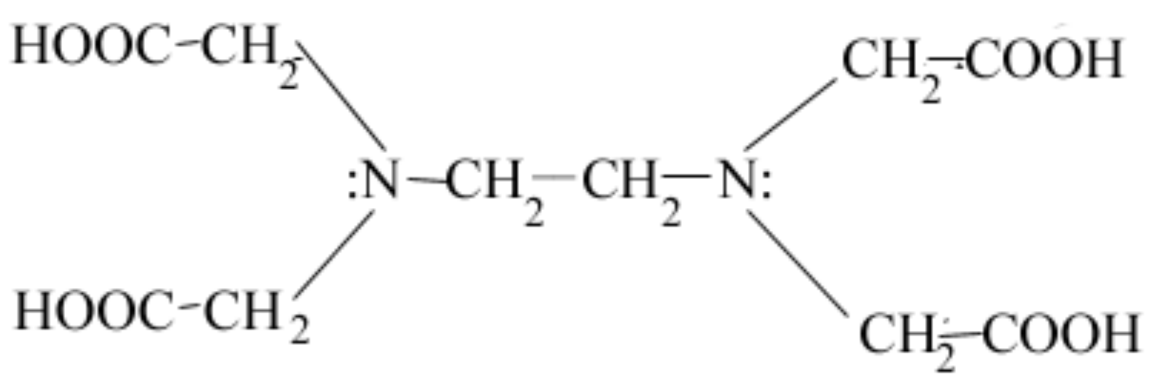
- What's the easiest way to quantify the amount of metal ions?

Precipitate them!

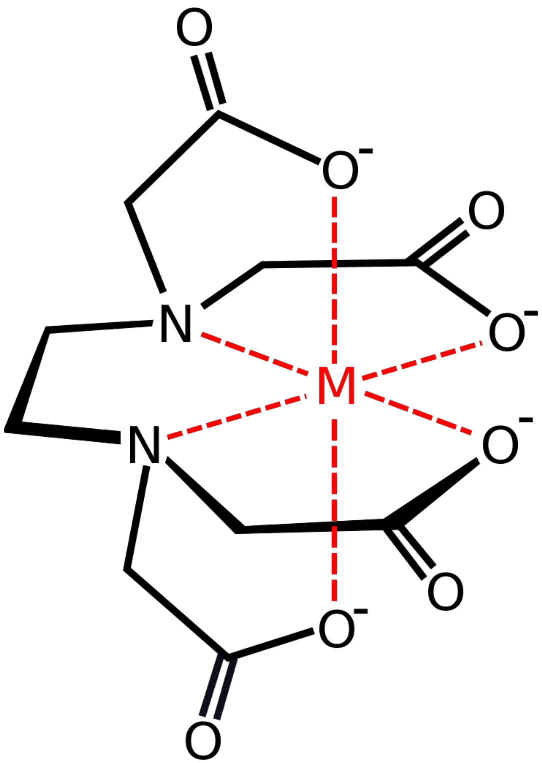


EDTA Method

- Complex formation titrations
- Chelating or complexing agent in metal ion titrations is **EDTA,** (ethylenediaminetetracetic acid).
- Tetraprotic acid
- Sodium salt of EDTA is used because of its high solubility.
- This causes the water to become softened, but the metal ions are not removed from the water.



$$M^{2+} + EDTA^{4-} \rightarrow [\ M\text{-}EDTA\ ]^{2-} + 2H^{+}$$



EDTA, M^{2+}, and M-EDTA are all soluble and colorless. No visible change…

Need a secondary indicator – some visible change.

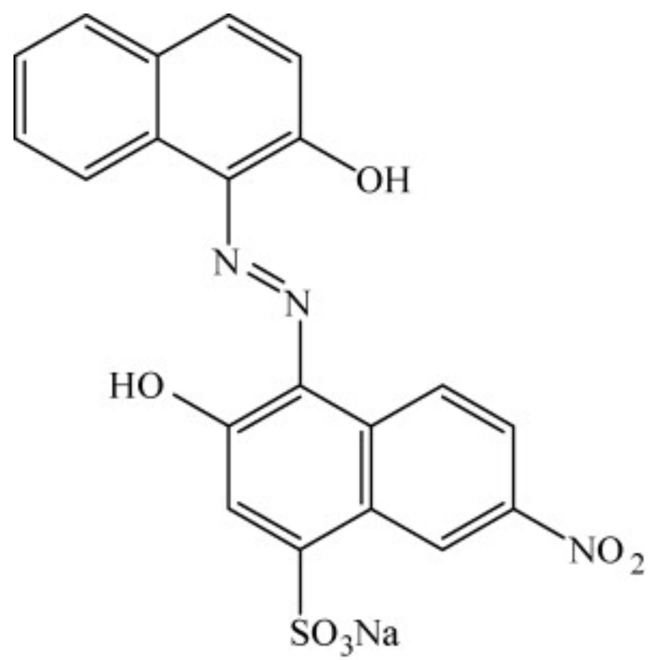
Indicator:

Erichrome Black T (EBT)

- EBT is a blue colored dye when alone in water and turns red when complexed with a Metal ion.
- Works at pH 10
- Excess EDTA causes a red to blue color change at near neutral pH.

M-EBT + EDTA → M-EDTA + EBT

(red) *(colorless)* *(blue)*



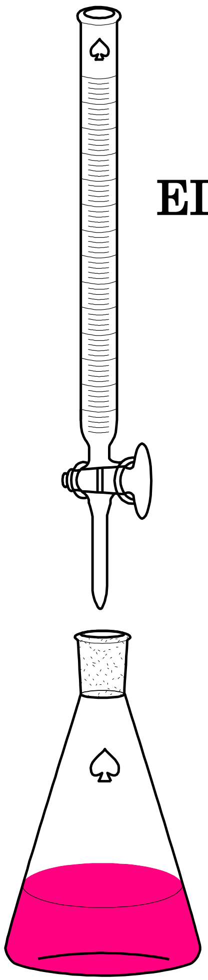
Eriochrome black T

1st Step: The calcium ion coordinates with the indicator (*Eriochrome Black T*).

$$\mathbf{H_2In^-} + \mathbf{Ca^{2+}} \leftrightarrow \mathbf{CaIn^-} + \mathbf{2H^+}$$

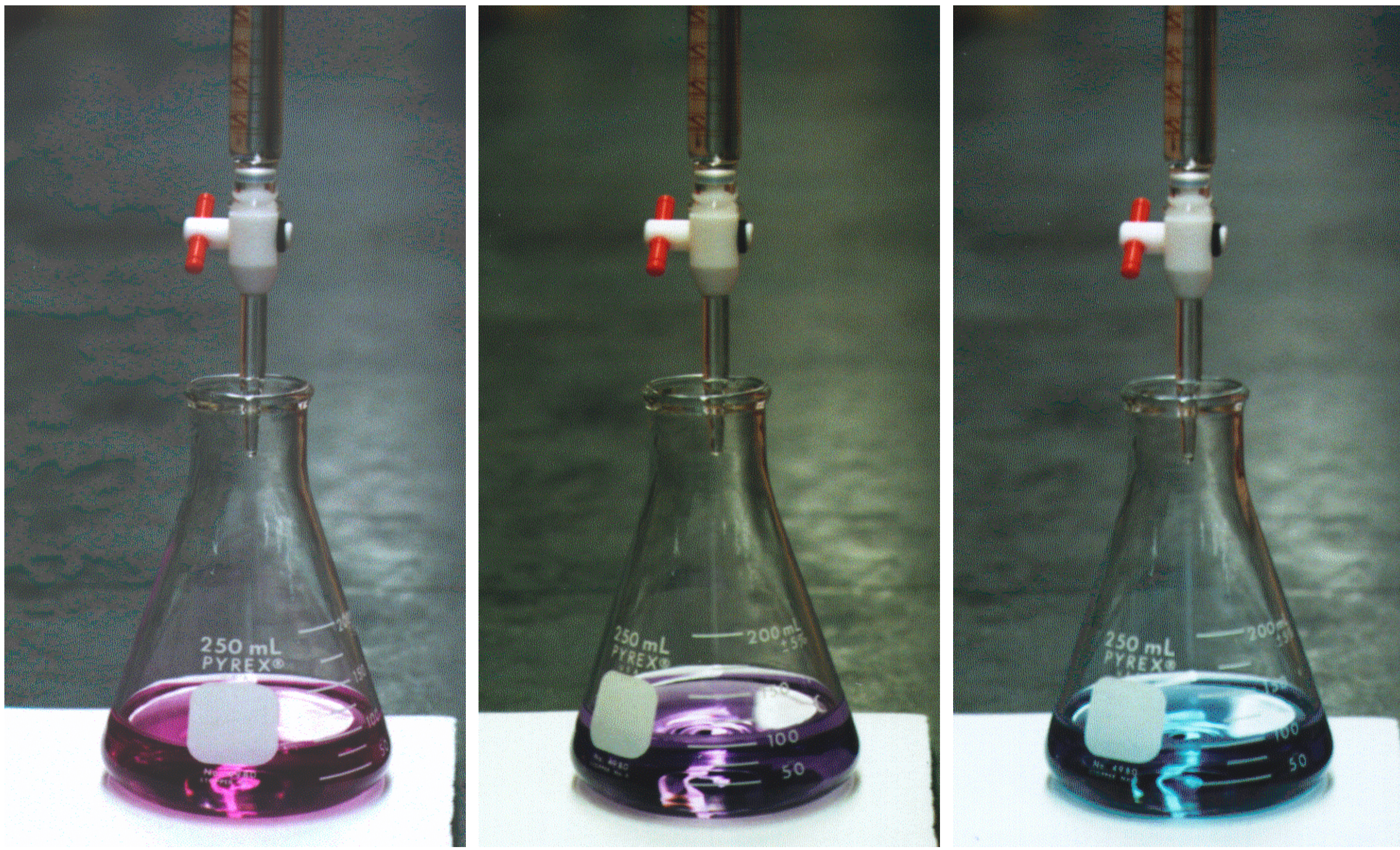
2nd Step: The EDTA chelates the calcium ion and releases the indicator.

$$\text{EDTA}\ (aq) + \mathbf{CaIn^-(aq)} \rightarrow \mathbf{HIn^{2-}}(aq) + CaEDTA\ (aq)$$



EDTA

Water + EBT



Experiment:

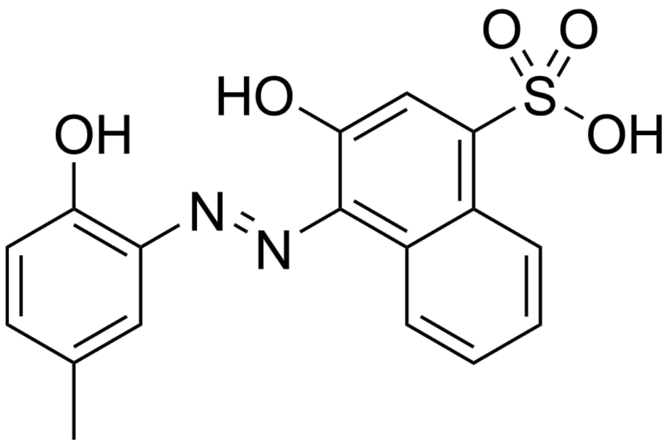
- The hard water is buffered to a pH value of approx. 10 using ammonia buffer and a few drops of EBT are added, thus formed weak complex of metal ion and EBT has wine-red colour.

- Add EDTA, which first combines with free metal ions and form colorless metal-EDTA complex. After all ions have been consumed, next EDTA drops displaces EBT from the metal-indicator complex. Thus freed EBT changes the solution colour to blue.

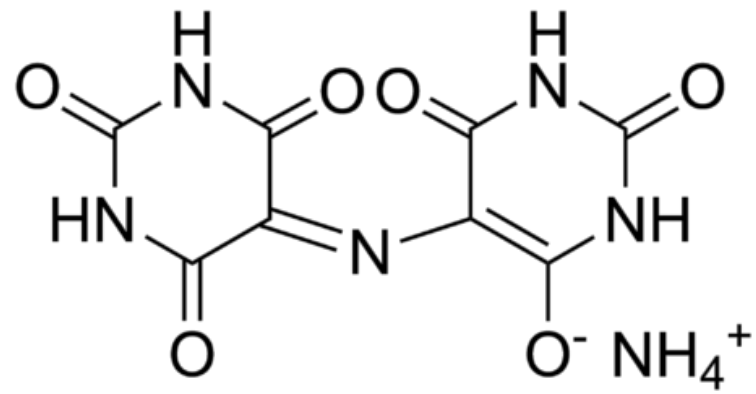
- Total hardness is thus determined:

    - $M_{EDTA} \times V_{EDTA} = M_{UHW} \times V_{UHW}$
    - Strength (gms/L) = M_{UHW} x Molar mass of $CaCO_3$
    - Total hardness.

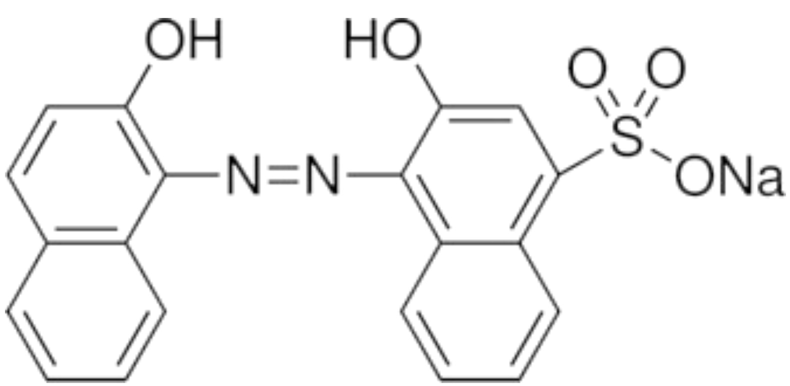
Couple of Other Indicators



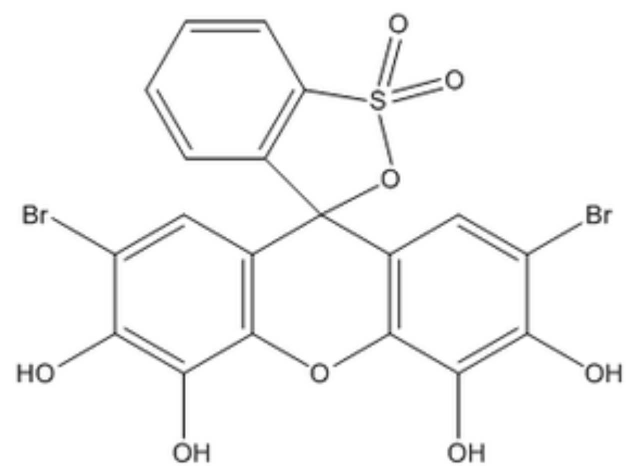
Calmagite



Murexide



Solochrome Dark Blue



Bromopyrogallol Red

EDTA

- Certain enzymes are responsible for food spoilage. EDTA is used to remove metal ions from these enzymes.
- Used to promote colour retention, and to improve flavour retention in foods.
- Mercury and lead poisoning treatment.

0.28 g of $CaCO_3$ was dissolved in HCl and the solution was made to one litre with distilled water. 100 ml of the above solution required 28 ml of EDTA solution on titration. 100 ml of the hard water sample required 35 ml of the same solution on titration. After boiling 100 ml of this water, cooling and filtering and then 10 ml EDTA solution was used on titration. Calculate the temporary and permanent hardness of water.

Step 1: standardization of EDTA solution:

1 L of standard hard water contains 0.28 gm $CaCO_3$.

$$(0.28 / 100) \text{ X } 100 = M_{EDTA} \text{ X } 28$$

Step 2: Total hardness:

$$M_{UHW} \text{ X } 100 = M_{EDTA} \text{ X } 35$$

$$w \text{ (g/L)} = M_{UHW} \text{ x } 100$$

A standard hard water contains 1000 mg of $CaCl_2$ per liter. 50 ml of this required 50 ml of EDTA solution, 50 ml of sample water required 40 ml of EDTA solution. The sample after boiling required 20 ml EDTA solution. Calculate the temporary and permanent hardness of the given water sample.

Total hardness = 800 ppm
Permanent hardness = 400 ppm
Temporary hardness = 400 ppm

20 ml of $CaCl_2$ solution, whose strength is equivalent 1.5 g of $CaCO_3$ per litre, required 30 ml of EDTA solution. Calculate the hardness of a water sample, whose 10 ml required 10 ml of this EDTA solution.

Total hardness = 1000 ppm

200 mL of water sample has hardness equivalent to 25 mL of 0.08 N $MgSO_4$. Find the hardness?

Normality = number of gram equivalents per L of solution

Number of gm. equivalents of $MgSO_4$ = V_{MgSO4} x Normality

= 25 * 0.08 / 1000

Number of gm. equivalents = weight (gm) / Equivalent weight

Weight of $MgSO_4$ in grams in sample = 25 * 0.08 * Eq. wt. $MgSO_4$ / 1000

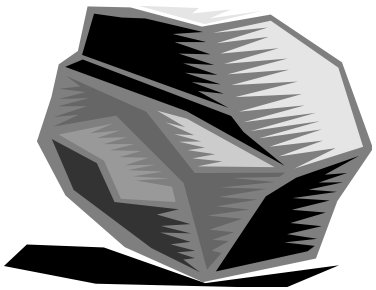
Weight of $MgSO_4$ in 1L water = (25 * 0.08 * Eq. wt. $MgSO_4$ / 1000) x (1000/200)

Hardness = Weight of $MgSO_4$ x 50/Eq. $MgSO_4$

500 ppm

Alkalinity of water

- Hard water is generally associated with high alkalinity.



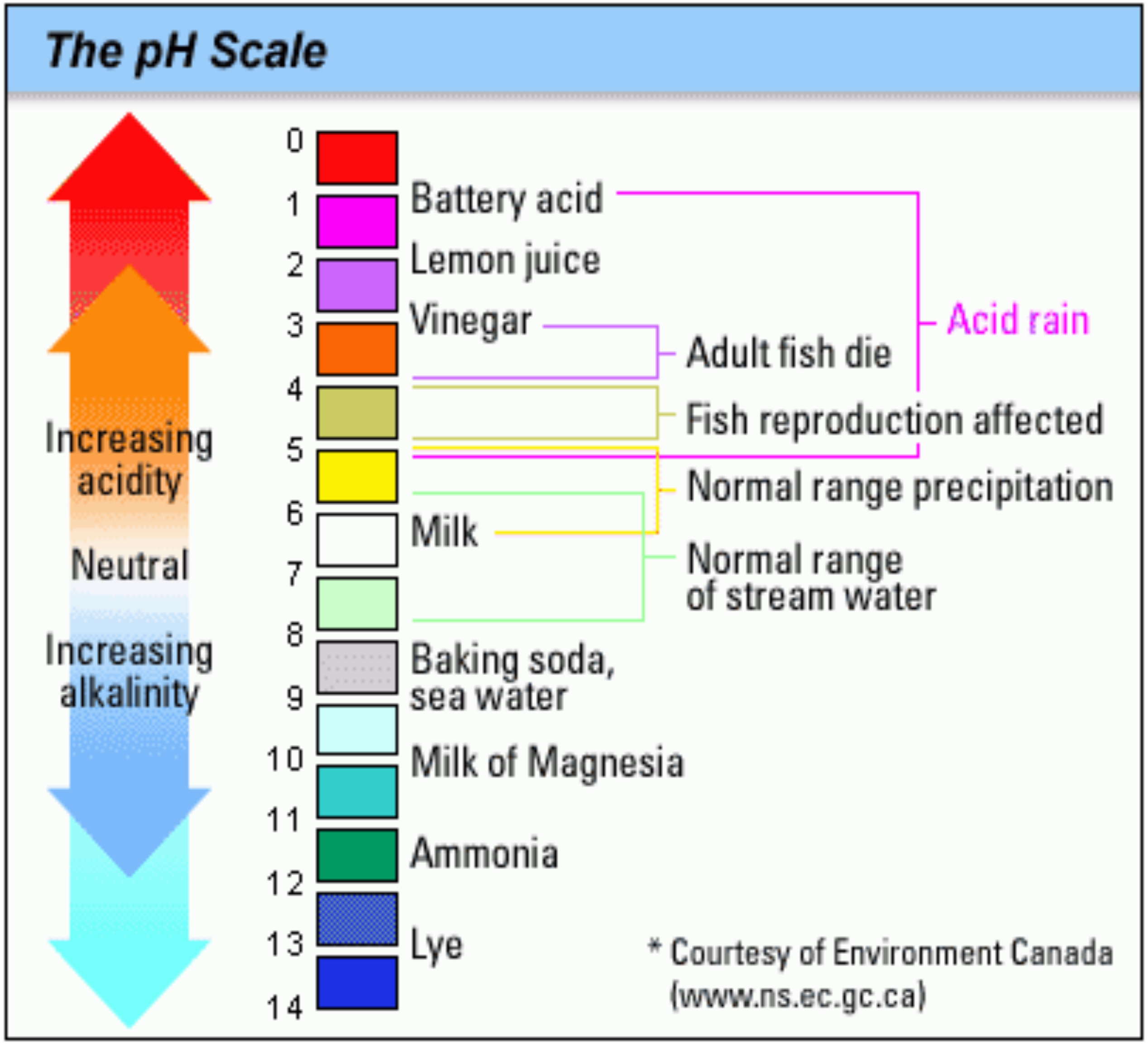
$CaMg(CO_3)_2 \longrightarrow Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$

Alkalinity

Hardness

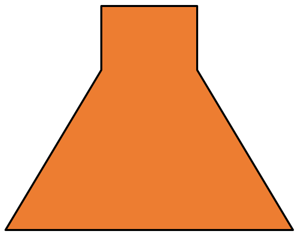
Dolomitic limestone

Hardness and alkalinity generally go hand-in-hand but they are NOT one and the same.


The pH Scale
Increasing acidity
Neutral
Increasing alkalinity
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Battery acid
Lemon juice
Vinegar
Milk
Baking soda, sea water
Milk of Magnesia
Ammonia
Lye
Acid rain
Adult fish die
Fish reproduction affected
Normal range precipitation
Normal range of stream water
* Courtesy of Environment Canada (www.ns.ec.gc.ca)

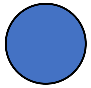
The Effect of Water Alkalinity on Acid Requirement

Sample A



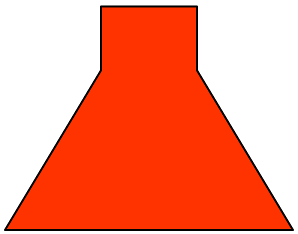
pH = 9

Alk = 50 ppm



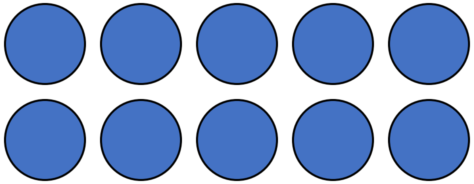
One drop of acid to get pH 6

Sample B



pH = 7

Alk = 300 ppm



Ten drops of acid to get pH 6

Alkalinity of water

- Alkalinity is defined as the ability to neutralize acids.

- Alkalinity of water is due to the presence of any of the ions $\boldsymbol{OH^-, CO_3^{-2}}$ and $\boldsymbol{HCO_3^-}$ or mixture of OH^- and CO_3^{-2} or mixture of CO_3^{-2} and HCO_3^-.

- OH^- and HCO_3^- ions cannot be present together because they combine by reaction

$$OH^- + HCO_3^- \rightarrow CO_3^{-2} + H_2O$$

- No more than two of the three ions (OH^-, CO_3^{-2} and HCO_3^-) can exist in the solution.

Determination of Alkalinity

- Acid-base Titration
- Concentration of ions responsible for alkalinity can be determined by titration of a known volume of a sample of water with a standard acid solution (HCl) to phenolphthalein end point and methyl orange end point.
- Also expressed in terms of an equivalent amount of calcium carbonate in ppm or mg/L.
- Irrigation water should have an alkalinity of less than 100ppm; if higher than 150 ppm, acidification is needed.

Acid-base Titration

At the start of titration, phenolphthalein end point (where pink colour just disappeared) OH^- is completely neutralized and CO_3^{-2} is half neutralized but HCO_3^- has not reacted at all.

The neutralization reactions up to phenolphthalein end point are

$$OH^- + H^+ \rightarrow H_2O$$
$$CO_3^{-2} + H^+ \rightarrow HCO_3^-$$

After phenolphthalein end point, methyl orange indicator is added and titration is continued. At methyl orange end point, colour of the solution changes from light yellow to pale pink. From phenolphthalein end point to methyl orange end point, HCO_3^- is being neutralized.

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O$$

Acid-base Titration

- If V_1 is the volume of acid used from the start of the titration to the phenolphthalein end point and V_2 is the volume from the phenolphthalein end point to the methyl orange end point, then the relation between V_1 and V_2 for a single component and mixture are listed in the table below.

Relative Titrant Volume	Constituent(s) in the sample
• $V_2 = 0$	OH^-
• $V_1 = V_2$	CO_3^{2-}
• $V_1 = 0$	$HCO3^-$
• $V_1 > V_2$	OH^- and CO_3^{2-}
• $V_1 < V_2$	CO_3^{2-} and $HCO3^-$

- Thus from the relative volumes of V_1 and V_2 the composition of the water sample can be obtained. After knowing the composition, the volume can be used to find out the concentration of each component in the solution.

Calculation

Standardization of HCl solution by standard Na_2CO_3 solution

- Strength of Na_2CO_3 solution = S_B
- Volume of Na_2CO_3 solution taken = V_B = 25 ml
- We have $V_BS_B = V_AS_A$, $S_A = (V_BS_B)/V_A$
- Hence the strength of the HCl solution is = ________(N)

Estimation of Alkalinity

Phenolphthalein Alkalinity, P

- $N_{HCl}\, V_{HCl} = N_p\, V_p \quad \rightarrow \quad N_p = N_{HCl}\, V_{HCl} / V_p$

- $N_p = \dfrac{\text{gm.}}{\text{Equiv.Wt. X V}} = \dfrac{\text{w (gm/L)}}{\text{Equiv.Wt.}} \rightarrow \quad w = N_p \text{ x Equiv. Wt.}$

- $\text{Alkalinity} = w \text{ x } \dfrac{50}{\text{Equiv.Wt.}} = N_p \text{ x } \cancel{\text{Equiv. Wt.}} \text{ x } \dfrac{50}{\cancel{\text{Equiv.Wt.}}} \text{ equiv. } CaCO_3$

$$= N_p \text{ x } 50 \text{ gm/L} = Np \text{ x } 50 \text{ x } 1000 \text{ mg/L (ppm)}$$

$$P = \frac{N_{HCl}\, VHCl \text{ x } 50 \text{ x } 1000}{V_p} \text{ ppm}$$

Estimation of Alkalinity

Phenolphthalein + Methyl Orange Alkalinity, M

- $N_{HCl}\ V_{HCl} = N_p\ V_p \quad \rightarrow \quad N_p = N_{HCl}\ V_{HCl}\ /\ V_p$

- $N_p = \dfrac{\text{gm.}}{\text{Equiv.Wt. X V}} = \dfrac{\text{w (gm/L)}}{\text{Equiv.Wt.}} \rightarrow \quad w = N_p \text{ x Equiv. Wt.}$

- $\text{Alkalinity} = \text{w x } \dfrac{50}{\text{Equiv.Wt.}} = N_p \text{ x } \cancel{\text{Equiv. Wt.}} \text{ x } \dfrac{50}{\cancel{\text{Equiv.Wt.}}} \text{ equiv. } CaCO_3$

$$= N_p \text{ x 50 gm/L} = \text{Np x 50 x 1000 mg/L (ppm)}$$

$$M = \frac{N_{HCl}\ \text{VHCl x 50 x 1000}}{V_p} \text{ ppm}$$

Here, $V_{HCl} = V_1 + V_2$

Estimation of Alkalinity

Case 1

- If $V_2 = 0$, then alkalinity is due to $\boldsymbol{OH^-}$ ion only.

- $N_{HCl}\ V_{HCl} = N_p\ V_p \rightarrow N_p = N_{HCl}\ V_{HCl} / V_p$

- Alkalinity $= w \times \frac{50}{\text{Equiv.Wt.}} = N_p \times \cancel{\text{Equiv. Wt.}} \times \frac{50}{\cancel{\text{Equiv.Wt.}}}$ equiv. $CaCO_3$

$$= N_p \times 50 \text{ gm/L} = Np \times 50 \times 1000 \text{ mg/L (ppm)}$$

$$= \frac{\mathbf{N_{HCl}\ VHCl \times 50 \times 1000}}{\mathbf{V_p}} \textbf{ ppm} = \mathbf{P}$$

Case 2

- If $V_1 = V_2$, then alkalinity is due to CO_3^{-2} only.

$$P = \frac{N_{HCl}\, V_1 \times 50 \times 1000}{V_p} \text{ ppm}$$

$$M = \frac{N_{HCl}\,(V_1 + V_2) \times 50 \times 1000}{V_p} \text{ ppm} = 2P$$

- Alkalinity = M or 2 P

Case 3

- If $V_1 = 0$, then alkalinity is due to HCO_3^{2-} only

$$M = \frac{N_{HCl}\,(V_1 + V_2)\ \text{x}\ 50\ \text{x}\ 1000}{V_p}\ \text{ppm}$$

Alkalinity = M

Case 4

- If $V_1 > V_2$, then alkalinity is due to OH^- and CO_3^{-2} ions.
- Total volume of HCl required for titration is $(V_1 + V_2)$.
- Volume of HCl required for CO_3^{-2} ion titration = $2\,V_2$
- Volume of HCl required for OH^- ion titration = $(V_1+V_2) - 2V_2$

$$P = \frac{N_{HCl}\,V_1 \times 50 \times 1000}{V_p}\ \text{ppm}$$

$$M = \frac{N_{HCl}\,(V_1 + V_2) \times 50 \times 1000}{V_p}\ \text{ppm}$$

$P = V_1$
$M = V_1 + V_2$

Alkalinity by $CO_3^{2-} = 2V_2 = 2M - 2P$

$V_1 + V_2 - 2V_2 = V_1 - V_2 = 2P - M$

Case 5

- If $V_1 < V_2$, then alkalinity is due to $\boldsymbol{CO_3^{-2}}$ and $\boldsymbol{HCO_3^{-}}$ ions.
- Total volume of HCl required for titration is $(V_1 + V_2)$.
- Volume of HCl required for CO_3^{-2} ion titration = $2\,V_1$
- Volume of HCl required for HCO_3^{-} ion titration = $(V_1+V_2) - 2V_1$

$$\mathbf{P} = \frac{\mathbf{N_{HCl}\,V_1 \times 50 \times 1000}}{\mathbf{V_p}}\ \mathbf{ppm}$$

$$\mathbf{M} = \frac{\mathbf{N_{HCl}\,(V_1 + V_2) \times 50 \times 1000}}{\mathbf{V_p}}\ \mathbf{ppm}$$

$P = V_1$
$M = V_1 + V_2$

Alkalinity by $CO_3^{2-} = 2V_1 = 2\mathbf{P}$

Alkalinity by $HCO_3^{-} = V_1 + V_2 - 2V_1 = V_2 - V_1 = \mathbf{M - 2P}$

I titrate a 25.00 mL water sample with 0.1250 M HCl. I achieve the first endpoint at 22.5 mL of HCl and the second after addition of another 27.6 mL of HCl.

What can we comment about alkalinity of this water sample?

50 mL of a water sample required 10 mL of N/50 HCl using methyl orange indicator but did not give any colouration with phenolphthalein. What is the type and extent of alkalinity present in the solution?

$V_1 = 0$ mL, $V_2 = 10$ mL

HCO_3^- only.

$$\textbf{Alkalinity} = \textbf{M} = \frac{N_{HCl}\,(V_1 + V_2) \times 50 \times 1000}{V_p}\ \textbf{ppm}$$

$= 200$ ppm