



Level



Pressure



Flow



Temperature



Liquid  
Analysis



Registration



Systems  
Components



Services



Solutions

# יום עיון: מדידות אנליטיות

## התפתחות במדידות PH + ORP בעשור האחרון

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INTERNAL

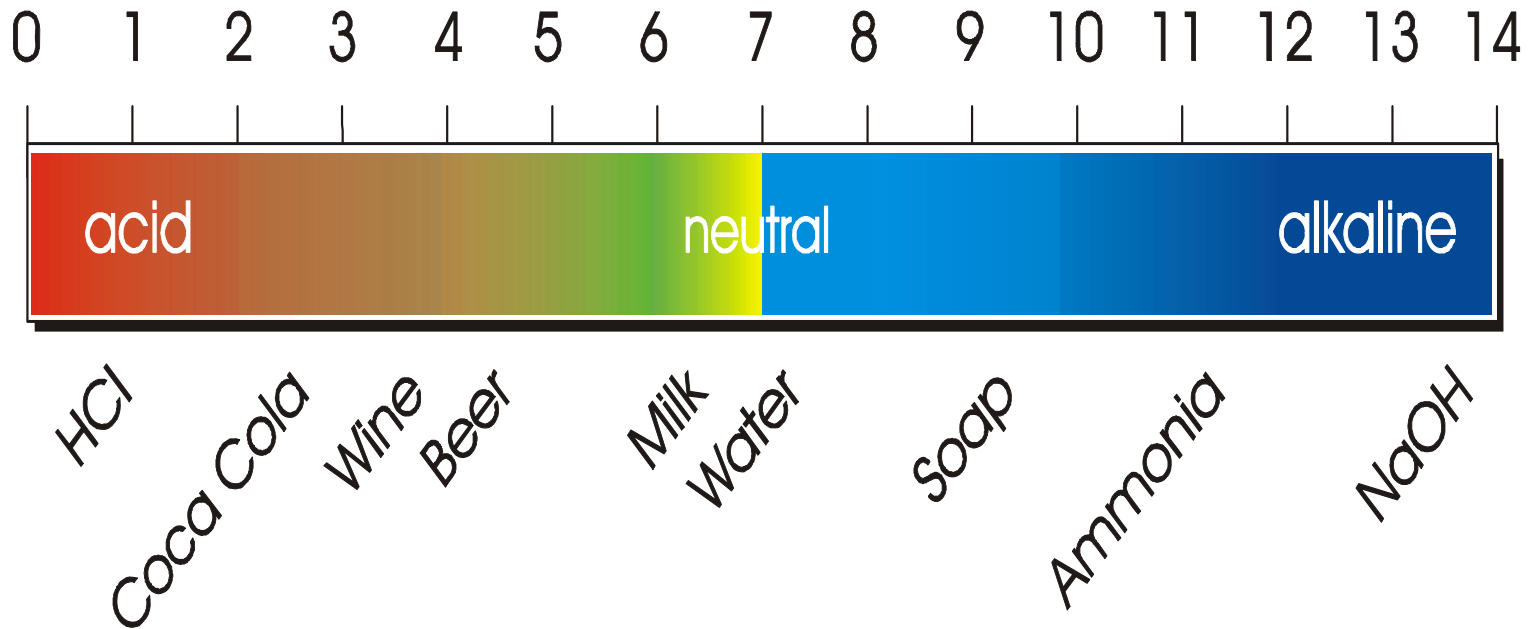
ליאון פורר

מרצה: מר ליאון פורר, B.Sc Technion

Endress+Hauser 

People for Process Automation

# pH scale



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## pH range

| pH | range    | H <sup>+</sup> concentration (mol/l) |
|----|----------|--------------------------------------|
| 0  | acidic   | 1                                    |
| 1  |          | 0.1                                  |
| 2  |          | 0.01                                 |
| 3  |          | 0.001                                |
| 4  |          | 0.0001                               |
| 5  |          | 0.00001                              |
| 6  | 0.000001 | 0.0000001                            |
| 7  | neutral  | 0.00000001                           |
| 8  | alkaline | 0.000000001                          |
| 9  |          | 0.0000000001                         |
| 10 |          | 0.00000000001                        |
| 11 |          | 0.000000000001                       |
| 12 |          | 0.0000000000001                      |
| 13 |          | 0.00000000000001                     |
| 14 |          | 0.000000000000001                    |

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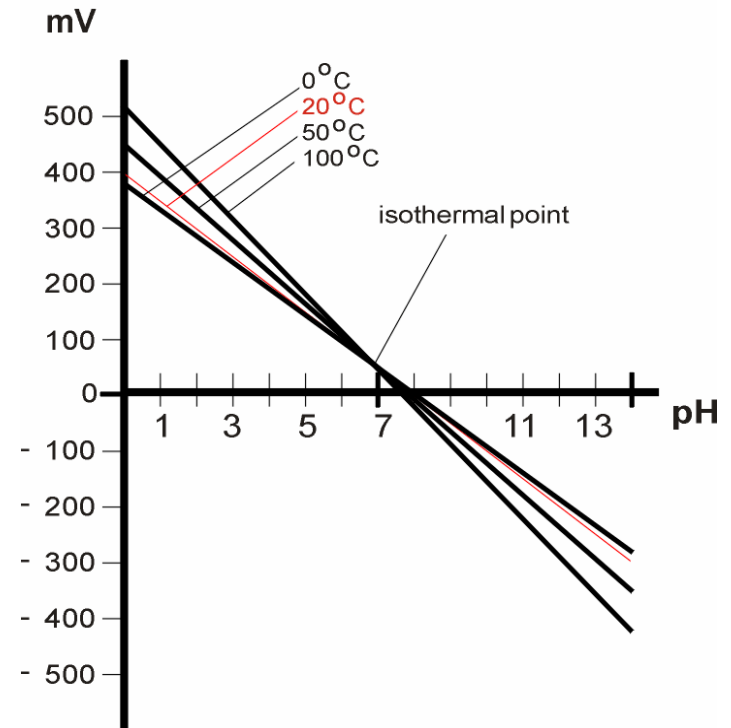
# Nernst Equation

$$U = U_0 + \frac{RT}{nF} \cdot \ln ( H^+ )$$

Slope

59,16 mV at 25 °C

U ... sensor voltage  
 U<sub>0</sub> ... voltage at pH 7  
 R ... gas constant  
 T ... absolute temperature  
 F ... Faraday constant  
 H<sup>+</sup> ... activity of H<sup>+</sup>-ions  
 n ... load of the ion (H<sup>+</sup>=1)

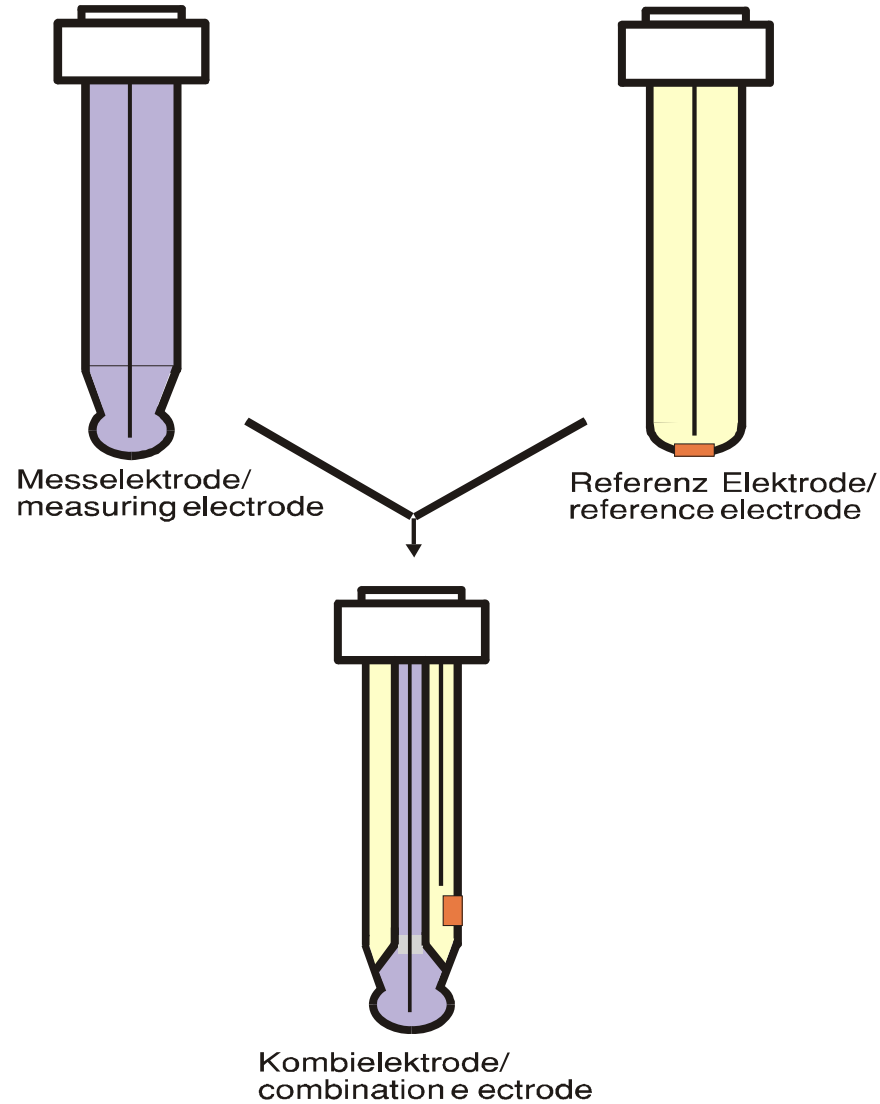


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# Glass combine electrode



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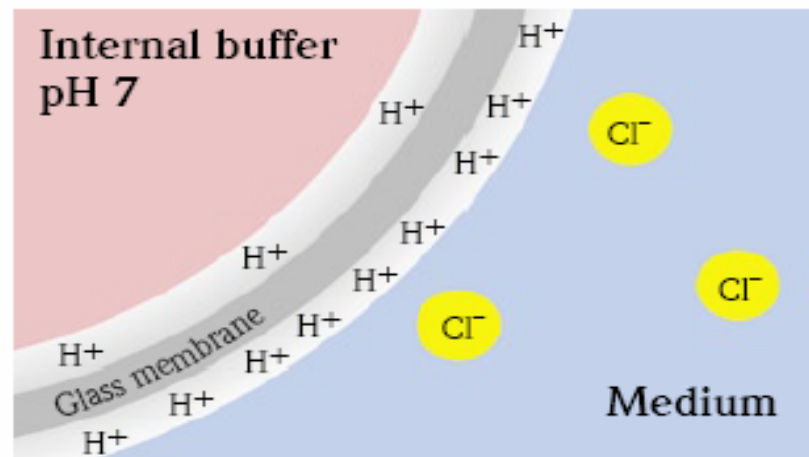
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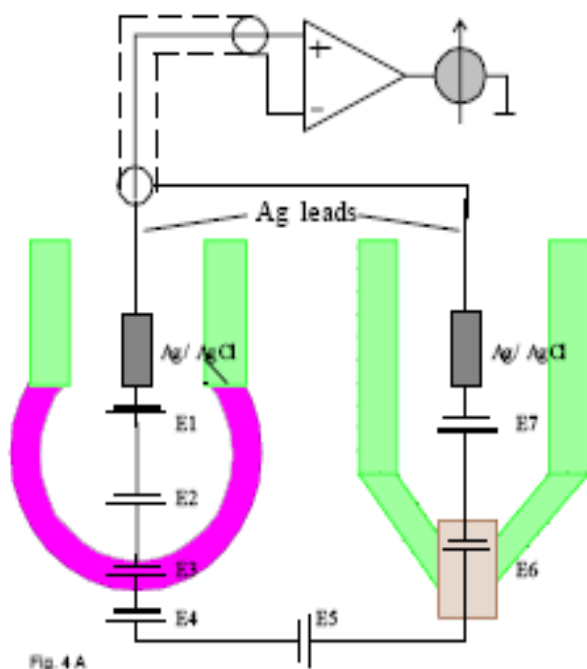
## Measuring principle glass electrode

- pH is a **potentiometric measurement** method.
- The measuring effect is based on a pH sensitive glass membrane whose surface reacts to the acid content with a specific voltage.
- This voltage is then measured relative to a reference element.
- pH is calculated according the Nernst law equation



**Voltage occurrence with  
pH measurement with glass electrodes**

## Individual electrode potential



- E 1 -** Half-cell voltage  $\text{Ag}/\text{AgCl} \parallel \text{KCl}$  (pH electrode), voltage depends on electrolyte concentration
- E 2 -** Potential of internal buffer  
--- inside glass membrane
- E 3 -** Asymmetry voltage across glass membrane
- E 4 -** Variable potential on the outside of the membrane (depends on pH value)
- E 5 -** Flow diffusion potential
- E 6 -** Diaphragm diffusion potential
- E 7 -** Half-cell voltage  $\text{Ag}/\text{AgCl} \parallel \text{KCl}$  (reference electrode), voltage depends on electrolyte concentration

# Reference system

## Diffusion potentials at phase boundaries

|                      | 0.1 mol/l KCl |       | 3.5 mol/l KCl |       |
|----------------------|---------------|-------|---------------|-------|
|                      | mV            | pH    | mV            | pH    |
| 1 N NaCl             | -11.2         | -0.19 | - 1.9         | -0.03 |
| 0.1 N NaCl           | - 6.4         | -0.11 | - 0.2         | -0.00 |
| 1 N HCl (pH = 0)     | 56.2          | 0.94  | 16.6          | 0.28  |
| 0.01 N HCl (pH = 3)  | 9.3           | 0.16  | 1.4           | 0.02  |
| 1 N NaOH (pH = 14)   | -45.0         | -0.75 | -10.5         | 0.13  |
| 0.1 N NaOH (pH = 13) | -18.9         | -0.32 | - 2.1         | -0.04 |

## Summary of variations in ion movement "u" in water at 25 °C

| ION                          |       | u = (movement in $\text{cm}^2 \cdot \text{ohm}^{-1} \cdot \text{mol}^{-1} / 25^\circ\text{C}$ ) |       |
|------------------------------|-------|-------------------------------------------------------------------------------------------------|-------|
| <u>Cations</u>               |       | <u>Anions</u>                                                                                   |       |
| H <sup>+</sup>               | 349.8 | OH <sup>-</sup>                                                                                 | 199.1 |
| Li <sup>+</sup>              | 38.6  | Cl <sup>-</sup>                                                                                 | 76.35 |
| Na <sup>+</sup>              | 50.1  | Br <sup>-</sup>                                                                                 | 78.14 |
| K <sup>+</sup>               | 73.5  | NO <sub>3</sub> <sup>-</sup>                                                                    | 71.46 |
| Ag <sup>+</sup>              | 61.9  | SO <sub>4</sub> <sup>-</sup>                                                                    | 74.1  |
| NH <sub>4</sub> <sup>+</sup> | 73.5  | Fe(CN) <sub>6</sub> <sup>3-</sup>                                                               | 100.9 |
|                              |       | Acetate                                                                                         | 40.9  |

The reference electrode is the most vulnerable and complicated part of a pH measuring chain regarding potential stability. Unlike the pH-sensitive electrode, it is not closed up but is in direct contact with the medium to be measured via a port – a diaphragm, gap or hole. Unfortunately, this port is not a one-way passage from the inside towards the outside. Therefore the ions can also diffuse from the outside towards the inside.

## Type of reference system

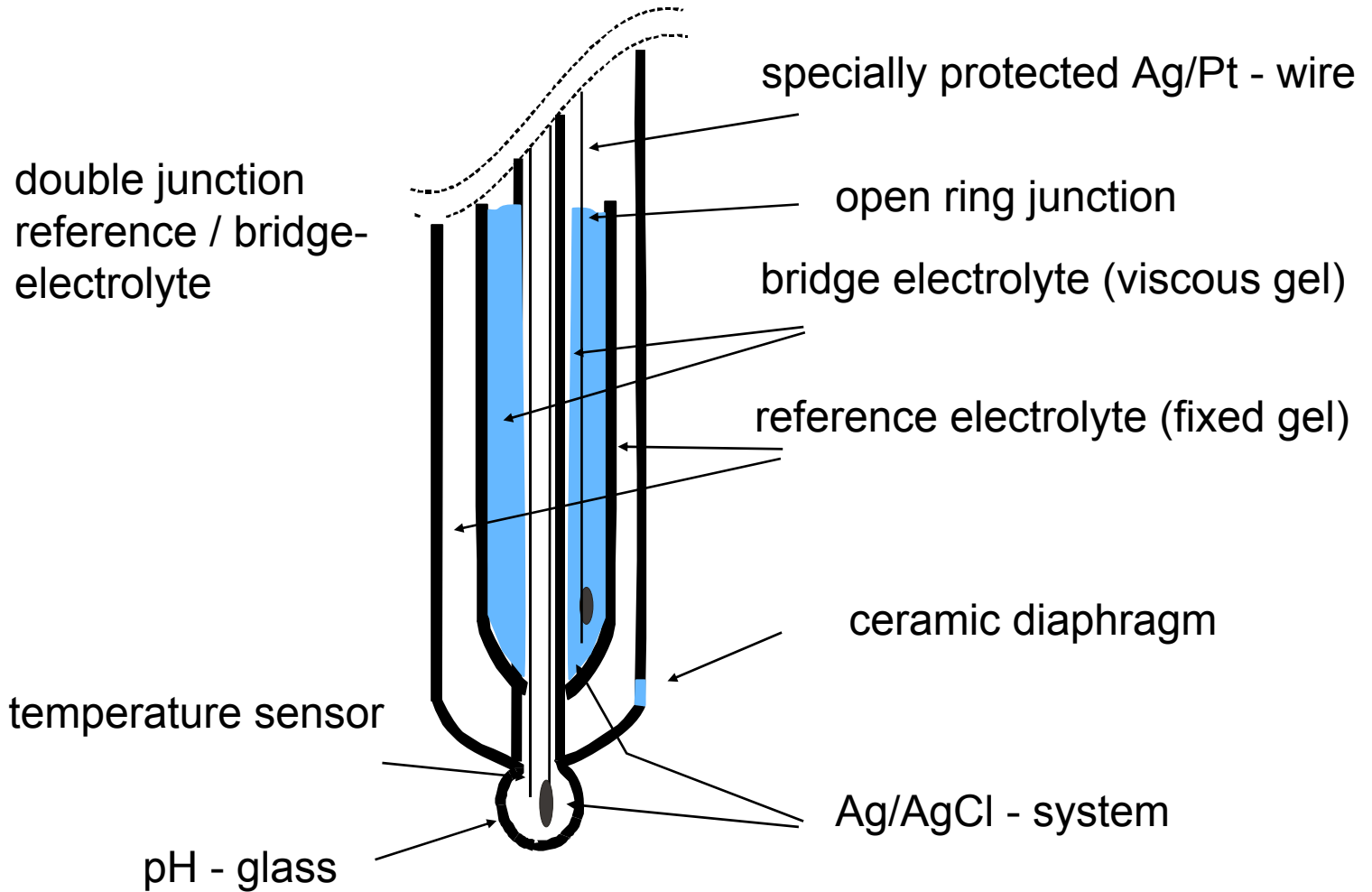
- Liquid pressurized (KCl based system)
- Gel
- Polymer non-diaphragm( open channel)

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# Double junction reference



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# IsFET-schematic view

**1 gate insulator with semiconductor phase**

**2 ceramic board**

**3 special flat sealing**

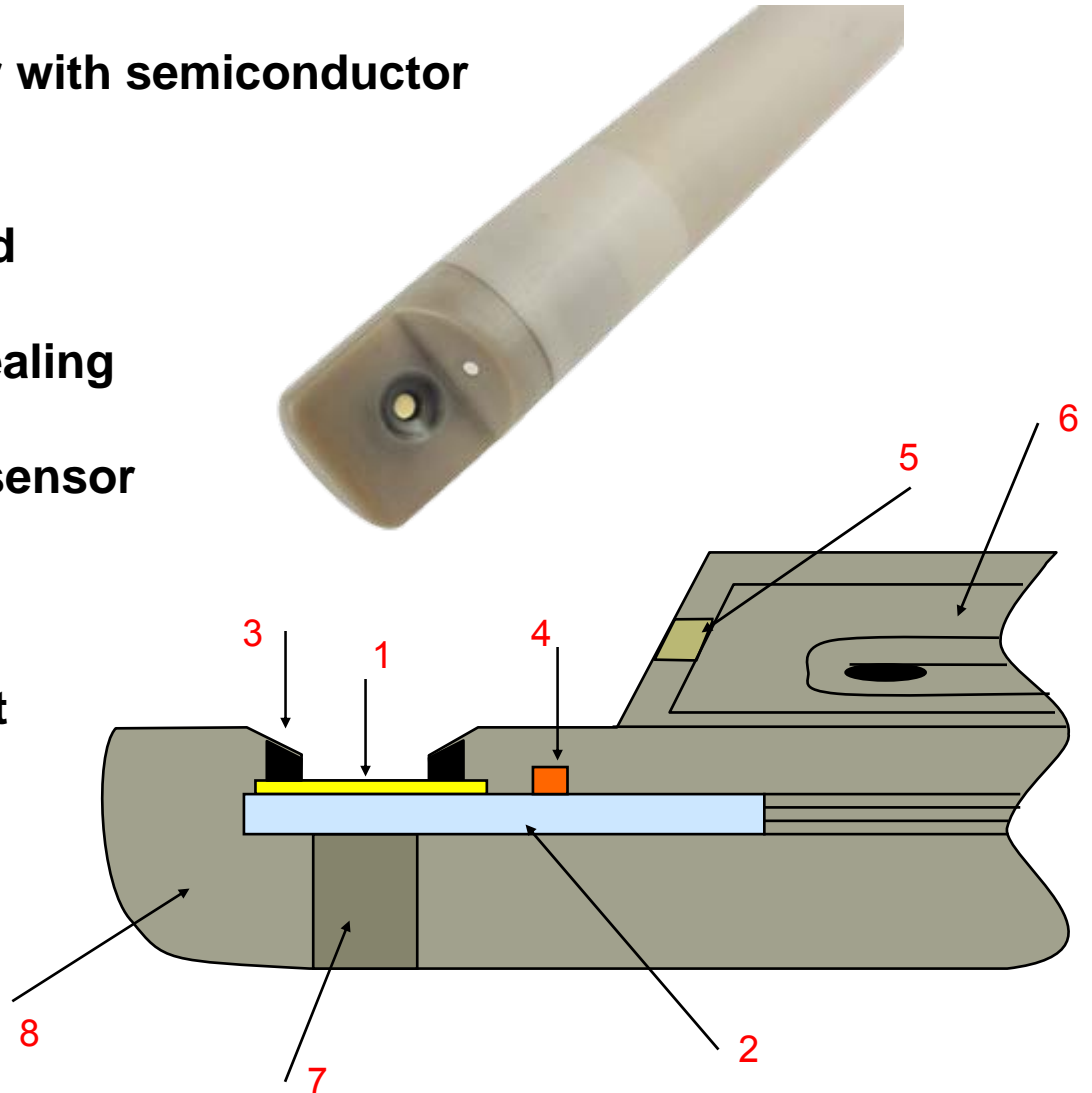
**4 temperature sensor**

**5 diaphragm**

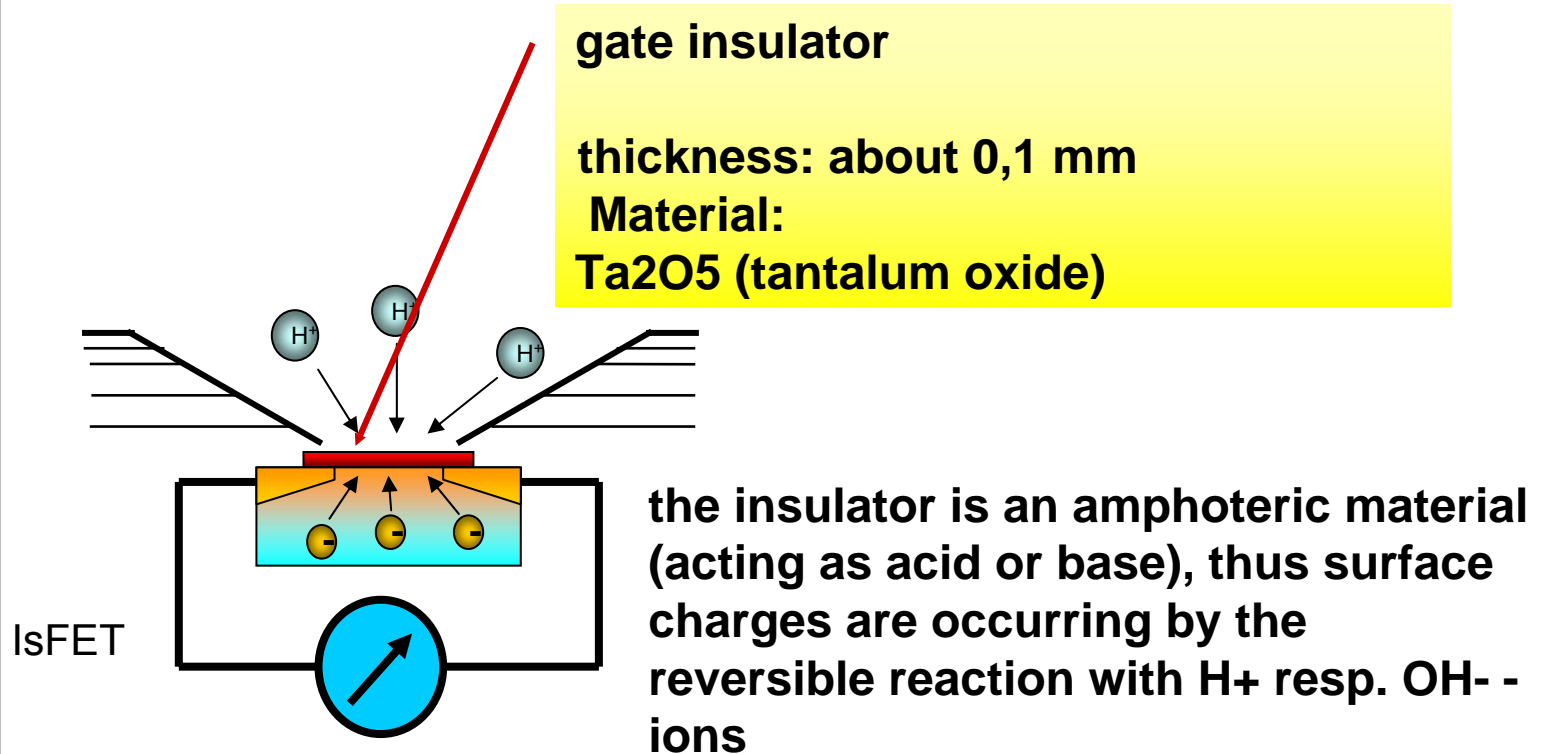
**6 reference part**

**7 elastic fixing**

**8 PEEK body**



# Measuring principle IsFET



**Contrary to the glass electrode no charges are transported through the insulator, the effect is purely **electrostatic****

## Redox measurement

What does it mean ORP or Redox

REDuction and OXidation

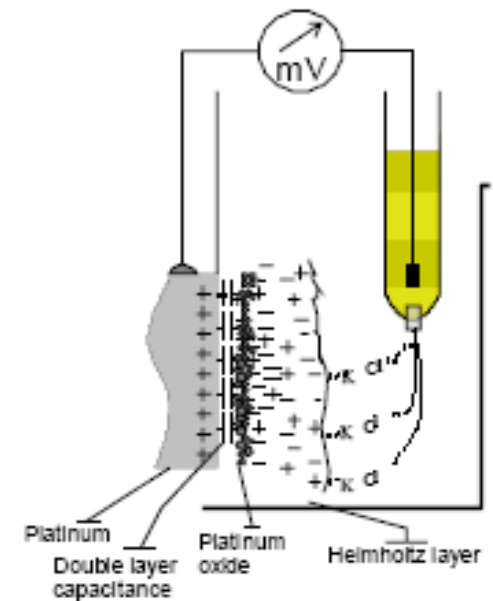
or

Oxidation Reduction Potential

- Redox is an activity of electrons.
- The substance receives electrons is reduced.
- The substance that release electrons oxidized.

$$\text{ORP} = \text{Log } C_{\text{ox}}/C_{\text{red}}$$

- The substance with the higher/more negative potential is capable of transferring electrons to the substance with more positive potential.



# Memosense

....is the revolution of pH-technology

....is the big step to the next generation of sensors.



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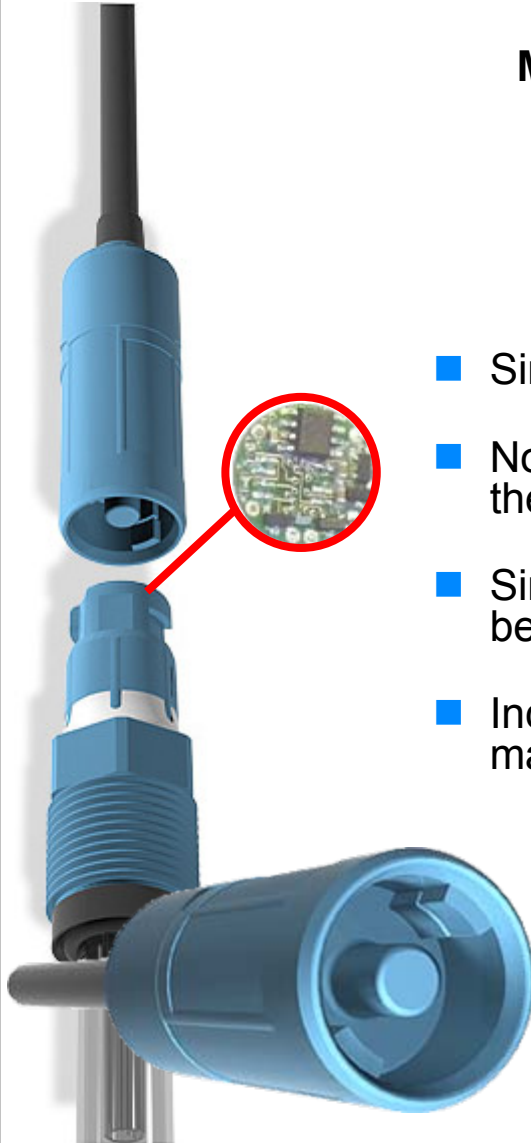
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# Convenient digital sensor

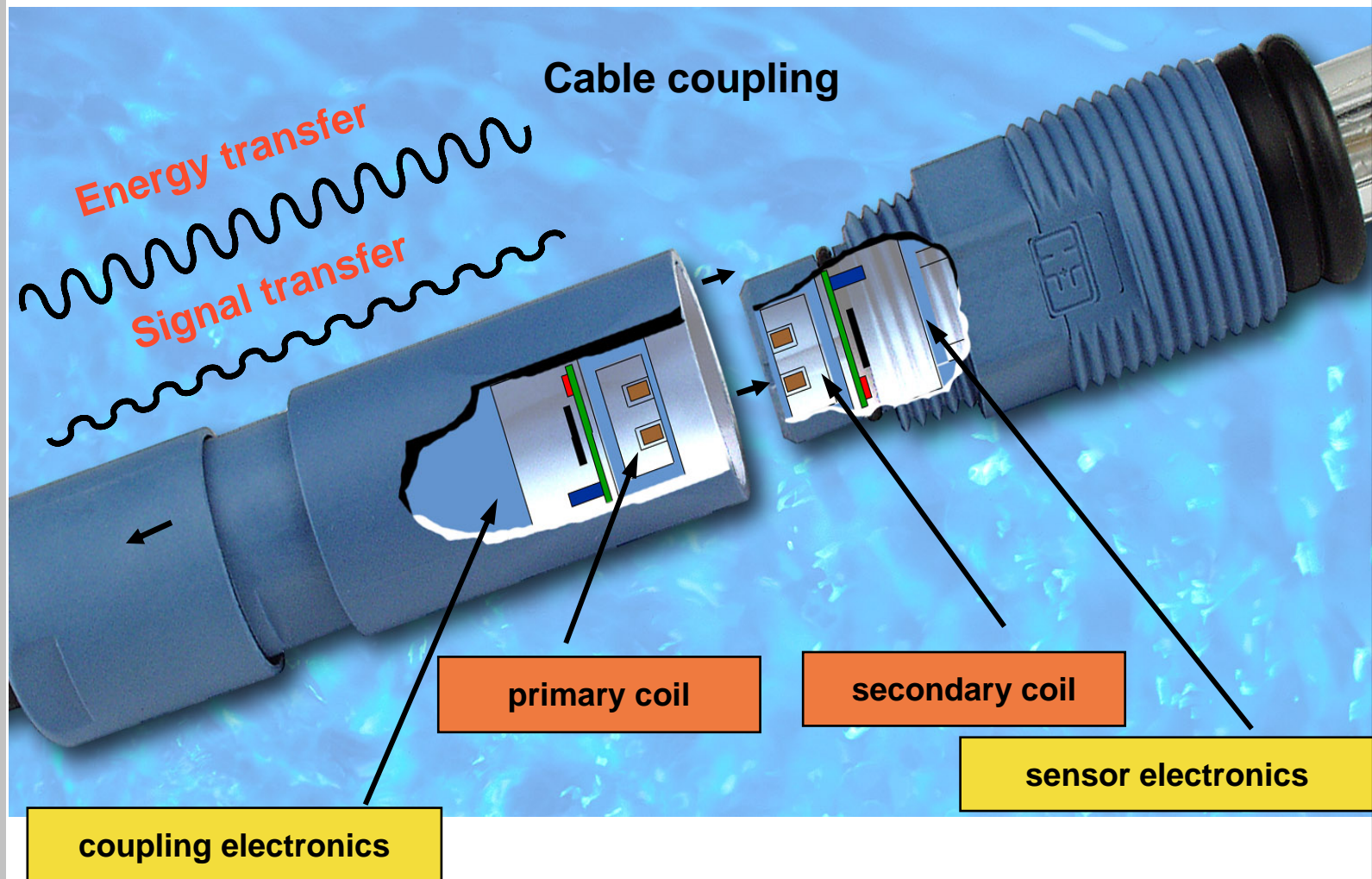
**Memosens converts the glass electrode into a**

**Digital sensor with integrated memory:**

- Simple sensor exchange with pre calibrated sensors.
- No calibration in the field, but high quality calibration in the laboratory.
- Simplified installation through increased distance between sensor and transmitter.
- Increased availability of measuring loop by predictive maintenance through stored sensor data.



# Signal transmission: Memosens



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## Memosens electrical advantage

- Cable design and attribute does not affect the measurement.
- Semiconductor coated cables are not anymore necessary, cable length is not any more important.
- Cable design and attribute does not affect the measurement.
- The pH electrode is a well-defined and complete sensor.
- The sensor is self-checking, cable attributes do not affect the sensor checks.





# Benefits at a glance

## Features

**Data stored in sensor**

**Head of electrode  
hermetically sealed**

**Digital signal is  
galvanic isolated**

## Advantages

- Calibration in laboratory possible
- Precalibrated sensors on stock

- Immersion possible
- Stable against pressure
- No influence of environment

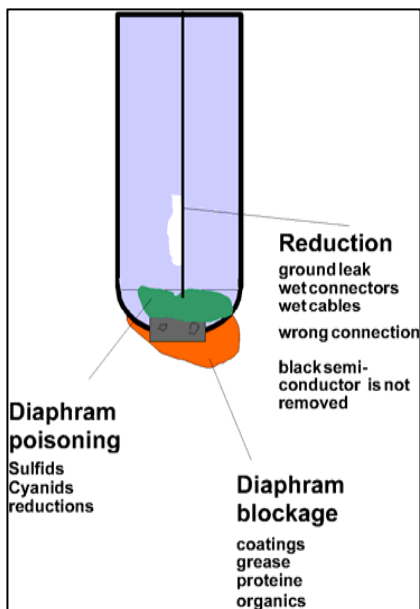
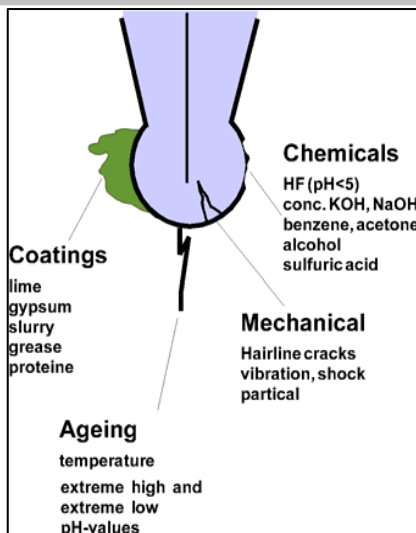
- No interference alarm with data transmission error
- Galvanic separation

## Benefits

- High availability
- No calibration outside
- Maintenance may be made by non skilled coworkers (e.g. at night)
- Safety in process
- Easy handling
- Quick installation or exchange of sensors

- Simple control of measuring chain
- Reliable values

pH / Maintenance



1. Rinse with tap water, if crystallization occurs with hot tap water (> 70°C)

2. Soak in cleaning agent for removal of:

|                      |                   |
|----------------------|-------------------|
| Oil, fat:            | Alkaline, Alcohol |
| Lime:                | HCL (4%)          |
| Metal hydroxide:     | HCL (4%)          |
| Cyanide:             | HCL (4%)          |
| Sulfide:             | HCL (4%)+         |
| thiourea (sat.)      |                   |
| Protein:             | HCL (4%)+ pepsin  |
| (sat.)               |                   |
| Heavy biol. deposit: | HCL (4%)          |
| Silicon:             | Acetone           |

3. Wipe with paper tissue, Rinse with tap water

4. Calibration with pH buffers



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# Any Questions?

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