Physical properties of chemical compounds: determination of melting point, refractive index and pH

Determination of physical properties of organic compounds

To characterize a compound, its physical properties should be determined, e.g. density, refractive index, melting point, boiling point. These physical constants may also serve as purity indicators. A compound can be considered chemically pure if its physical properties do not change after multiple purifying operations (distillation, crystallisation, sublimation).

1. Melting Point

The melting point of a substance is the temperature at which the material changes from a solid to a liquid state. Pure crystalline substances have a clear, sharply defined melting point. Any contingent impurity always DECREASES the melting point temperature no matter if the impurity itself exhibits higher melting point.

Melting Point Determination

The pharmacopeias regard the capillary method as the standard technique for melting point determination. In this methodology, a thin glass capillary tube containing a compact column of the substance to be determined is introduced into a heated stand (liquid bath or metal block) in close proximity to a high accuracy thermometer. The temperature in the heating stand is ramped at a user-programmable fixed rate until the sample in the tube transitions into the liquid state. While determining a melting point, several observations and the temperatures are recorded.

Melting Point Determination with SMP11 (Stuart, Irsko)

Introduce a dry substance into a capillary with one sealed end. The length of the compound should be 2 - 4 mm. Insert both the thermometer and the capillary with a sample into the metal block beneath the observation lense. Neither the thermometer nor capillary ends should touch the metal block.

When heating up, follow the directions on the instrument – start with a gradient 10-20 °C/min, then decrease. When the smallest crystalls start to melt, interrupt the heating and read out the temperature when the crystalls are liquefied.

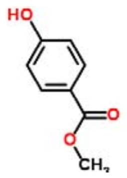
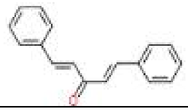
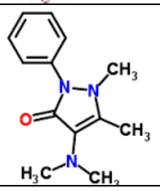
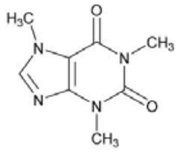
Fig. 1 Melting point device used in laboratory exercise

Cooling the device prior to the next measurement

To start the next measurement soon, the metal block may be cooled back to the room temperature. It is done by a cold bronze metal piece which has been kept in an ice-bath. The ice-bath is intended only for the bronze piece, DO NOT PUT GLASS THERMOMETER INTO THE ICE-BATH, otherwise it breaks!

Task

Learn to operate the melting point device by checking melting points of several standards. If your values are in a good agreement, measure the melting point of an uknown and identify it.

Name	*formula*	*Melting point*
Methylparabene		127°C
Propylparabene		96°C
Butylparabene		68°C
Dibenzylacetone		112°C
Aminophenazone		107°C
Caffein		234°C

Melting points of standards

2. Index of refraction

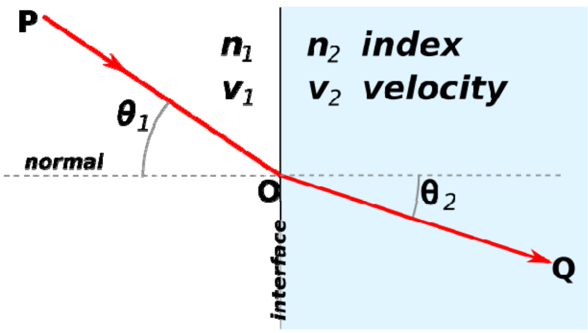
The **refractive index** or **index of refraction** of a substance is a measure of the speed of light in that substance. It is expressed as a ratio of the speed of light in vacuum relative to that in the considered medium. The velocity at which light travels in vacuum is a physical constant, and the fastest speed at which energy or information can be transferred. However, light travels slower through any given material, or medium, that is not vacuum. A simplified, mathematical description of refractive index is as follows:

$$n = \frac{\text{velocity of light in a vacuum}}{\text{velocity of light in medium}}$$

Hence, the refractive index of water is 1.33, meaning that light travels 1.33 times as fast in a vacuum than it does in water. A practical definition of refractive index comes from Willebrord Snel van Royen (W. Snellius) as a ratio of sinuses of measured angles of the passing light. The Snell´s law can be written as

$$n = \frac{c_1}{c_2} = \frac{\sin\alpha}{\sin\beta}$$

n = index of refraction (indirectly dependent on temperature: if the temperature increases by 1 °C, r.i. drops by 3 - 8.10^{-4} units. Such a change is more pronounced at liquids than solids)
c_1, c_2 = speed of light in media 1,2
α = angle of incidence
β = angle of refraction



Standard wavelength and temperature are usually given as subscripts (e.g. n_{D20}: D = spectral line D of a spectrum of sodium, 585 nm, temperature 20°C).

#

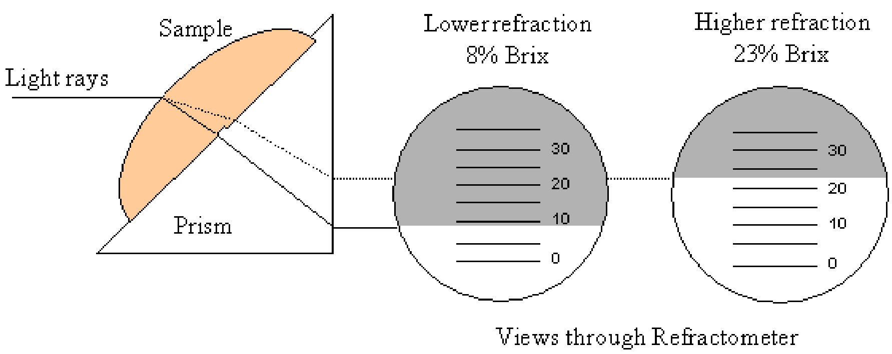


Fig. 2
Principle of refractive index measurement

Refractive index determination

A method of r.i. determination is based on measurement of critical angle when light comes out from a glass refractive prism.
With a common Abbe´s refractometer we can measure with daylight (polychromatic light) and the read-out value is corrrected to sodium line D. Precision of the measurement is ± 0,0001, range 1,300 - 1,700. If neccessary, temperature can be set as precise as ± 0,2 °C (a connection to an external thermostate).

Fig.3 Abbe´s refractometers

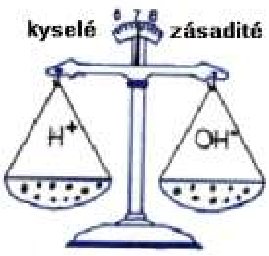
Task

Learn to operate Abbe´s refractometer by checking refractive indices of several standards. If your values are in a good agreement, measure refractive index of an uknown and identify it.

	n
water	1.3330
methanol	1.3284
toluene	1.4969
1-butanol	1.3993
2-propanol	1.3856
acetone	1.3586
chloroform	1.4458

Refractive indices of standards

3. Measurement of pH of aqueous solutions

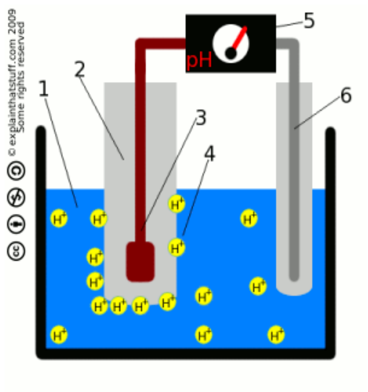


In chemistry, **pH** is a measure of the acidity or basicity of a solution. Pure water is said to be neutral, with a pH close to 7.0 at 25 °C (77 °F). Solutions with a pH less than 7 are said to be acidic and solutions with a pH greater than 7 are said to be basic or alkaline.
Measuremen of pH is one of the most importantoperation in an anlytical operation

pH measurements

A typical pH meter has two basic components: the meter itself, which can be a moving-coil meter or a digital meter (one with a numeric display), and either one or two probes that you insert into the solution your testing. If you have two probes, each one is an electrode (you always need two electrodes to make a complete electrical circuit); if you have only one probe, both of the two electrodes are built inside it in one handy unit. The electrodes aren't like normal electrodes (simple pieces of metal wire); each one is a mini chemical set in its own right. The electrode that does the most important job, which is called the **glass electrode**, has a silver-based electrical wire suspended in a solution of potassium chloride, contained inside a bulb made from a very special glass coated with silica and metal salts. The other electrode is called the **reference electrode** and has a potassium chloride wire suspended in a solution of potassium chloride.

Photo: How a pH meter works: 1 = Solution being tested; 2 = Glass electrode, coated with special silica glass, and containing potassium hydroxide; 3 = Silver electrode; 4 = Hydrogen ions interact with silica glass bulb; 5 = pH meter converts voltage (potential difference) into pH reading; 6 = Reference electrode.



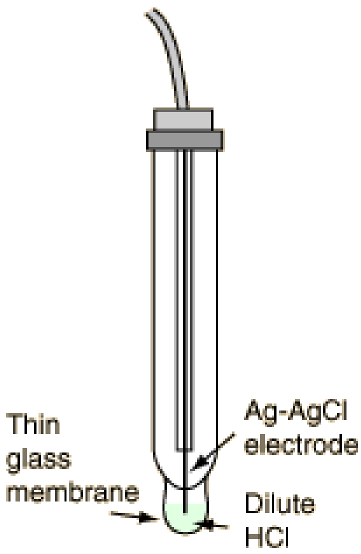
Operation

How does it work? When you dip the two electrodes (or one probe containing the two electrodes) into your solution, some of the hydrogen ions in the solution move toward the glass electrode and replace some of the metal ions in its special glass coating. This creates a tiny voltage across the glass that the silver electrode picks up and passes to the voltmeter. Broadly speaking, the other (reference) electrode acts as a baseline or reference for the measurement—or you can think of it as simply completing the circuit. The voltmeter measures the voltage generated by the solution and displays it as a pH measurement. An increase in voltage means more hydrogen ions and an increase in acidity, so the meter shows it as a decrease in pH; in the same way, a decrease in voltage means fewer hydrogen ions, more hydroxide ions, a decrease in acidity, an increase in alkalinity, and an increase in pH.

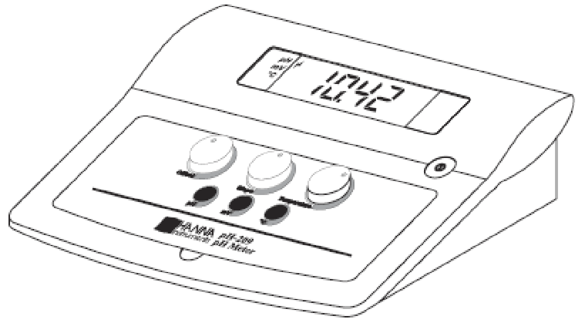
Making accurate pH measurements

For pH meters to be accurate, they have to be properly **calibrated** (the meter is accurately translating voltage measurements into pH measurements), so they usually need testing and adjusting before you start to use them. You calibrate a pH meter by dipping it into **buffers** (test solutions of known pH) and adjust the meter accordingly. Another important consideration is that pH measurements made this way depend on temperature. Some meters have built-in thermometers and automatically correct their own pH measurements as the temperature changes; those are best if fluctuations in temperature are likely to occur while you're making a number of different measurements. Alternatively, you can correct the pH measurement yourself, or allow for it by calibrating your instrument and making pH measurements at broadly the same temperature.

Glass electrode (combined – it consist of both measuring glass electrode and reference Ag-AgCl electrode)



pH meter Hanna109

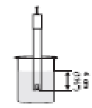


TAKING pH MEASUREMENTS

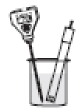
Make sure that the instrument has been calibrated for pH before taking pH measurements.

- Switch the instrument on by pressing the ON/OFF switch.

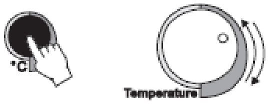
- Immerse the electrode tip (4 cm/1½") into the sample and shake briefly.



- Take the temperature of the solution with a ChecktempC or a glass thermometer (e.g.25°C).



- Press the °C key to display temperature setting on the LCD and adjust the temperature knob to display the temperature of the sample.



- Press the pH key to display the pH measurement.

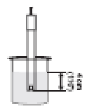
- The display shows the pH value of the test solution compensated for temperature.

If measurements are taken in different samples successively, it is recommended that the electrode be rinsed thoroughly for better conditioning and to eliminate cross-contamination of the sample.
For the rinsing process, it is recommended to use a liberal amount of the next solution to be measured.

TAKING ORP MEASUREMENTS

pH 209 has the capability to take ORP measurements, using an ORP electrode. Hanna Instruments offers a variety of ORP electrodes for this purpose (see accessories). Contact your Dealer for more information.

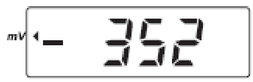
- Connect the ORP electrode to the meter and submerge the tip (4 cm / 1½") into the sample to be tested.



Note: ORP measurements are taken without temperature compensation.

- Press the mV key to enter the mV mode. Allow a few minutes for the reading to stabilize.

- The display will indicate the mV value (positive or negative).



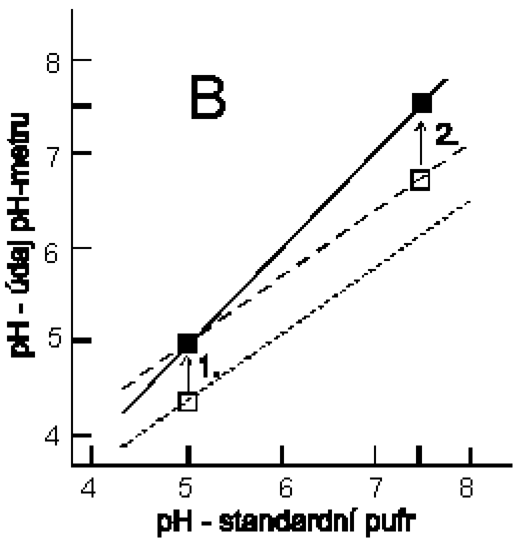
AFTER MEASUREMENTS

- Press the ON/OFF switch again to switch the instrument off.

In order to calibrate correctly, we need at least 2 calibration solutions – buffers. We select buffers range according to the samples we intend to measure later on., e.g.:
Measuring acidic solution requiers calibration with buffers pH 4.0 and pH 7.0
Measuring basic solutions requires buffers pH 7.0 and pH 10.0.

Measuring pH you must not:
Break the glass of the electrode which would deteriorate the electrode.

Explanation of the calibration procedure



pH VALUES AT VARIOUS TEMPERATURES

Temperature has an effect on pH. The calibration buffer solutions are affected by temperature changes to a lesser degree than normal solutions.

For manual temperature calibration please refer to the following chart.

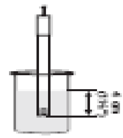
TEMP		pH VALUES				
°C	°F	**4.01**	**6.86**	**7.01**	**9.18**	**10.01**
0	32	4.01	6.98	7.13	9.46	10.32
5	41	4.00	6.95	7.10	9.39	10.24
10	50	4.00	6.92	7.07	9.33	10.18
15	59	4.00	6.90	7.04	9.27	10.12
20	68	4.00	6.88	7.03	9.22	10.06
25	77	4.01	6.86	7.01	9.18	10.01
30	86	4.02	6.85	7.00	9.14	9.96
35	95	4.03	6.84	6.99	9.10	9.92
40	104	4.04	6.84	6.98	9.07	9.88
45	113	4.05	6.83	6.98	9.04	9.85
50	122	4.06	6.83	6.98	9.01	9.82
55	131	4.07	6.84	6.98	8.99	9.79
60	140	4.09	6.84	6.98	8.97	9.77
65	149	4.11	6.85	6.99	8.95	9.76
70	158	4.12	6.85	6.99	8.93	9.75

pH CALIBRATION

PROCEDURE

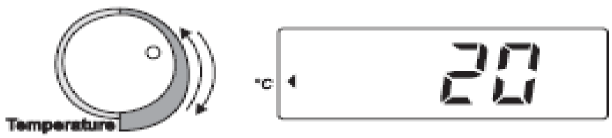
- Switch the instrument on by pressing the ON/OFF button.

- Rinse and immerse the pH electrode into pH 7.01 buffer and shake briefly. Wait for the reading to stabilize.

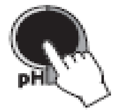


- Press the °C key to select temperature setting.

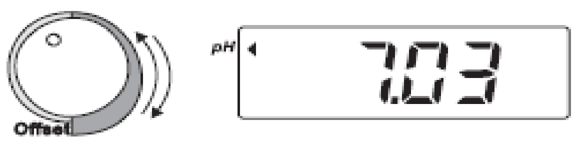
- Adjust the Temperature knob until the LCD shows the noted temperature.



- Press the pH key to select pH measurement.



- Wait a couple of minutes and adjust the OFFSET knob until display shows the pH value at the noted temperature (see the pH versus temperature chart).



- Rinse and immerse the pH electrode in pH 4.01/pH 10.01 buffer and shake briefly.
- Wait a couple of minutes and adjust the SLOPE knob until display shows the pH value at the noted temperature (see the pH versus temperature chart).

Task

- Calibrate pH meter

- Measure pH of a solution of acetic acid (aqueous solution)

- Knowing pH, calculate analytical (total) molar concentration of acetic acid in the solution. The calculation is based on definition of the dissociation constant of acetic acid (a weak acid) $K_a = 10^{-4.75}$ mol/l. The following shows a reverse example how to calculate pH of 0.10 M acetic acid.

$$K_a = \frac{[H^+][Ac^-]}{[HAc]} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10} = 1.76 \times 10^{-5}$$

$$x = [H^+] = 0.00133\ M \qquad pH = -\log[H^+] = 2.87$$