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1. Introduction

As a pioneer of process analyzers, Yokogawa has consistently been developing on-line analytical instruments with excellent operability and maintainability.

The P/H Cell pH Transmitter released in 1971 triggered the 2-wire analyzer market, changed the image of the conventional analyzers, and enabled simple and easy instrumentation.

The analyzer was also quick to employ an ultrasonic cleaning system that is now commonly used and well received by users.

Since then the application range of on-line pH measurement has expanded and today it covers from various processes, including water and sewage treatment to industrial wastewater and effluent treatment.

This document is intended for those who use a process pH analyzer for the first time and describes the principle of a pH analyzer and various types of pH sensors.

2. What is pH

pH is a measure of acidity and alkalinity and is expressed as the negative logarithm of the hydrogen ion concentration, or:

$$\text{pH} = -\log_{10} [\text{hydrogen ion concentration}] \text{ ----- (2.1)}$$

The “p” in pH comes from the word “power” in logarithmic calculation and the “H” represents hydrogen.

As shown in Table 2.1, the hydrogen ion concentration of a neutral solution is 10^{-7} mol/L, that of a 0.1 mol/L HCl solution is 10^{-1} mol/L, and that of a 0.1 mol/L NaOH solution is 10^{-13} mol/L, which are very small and not practical values. Thus, by changing exponential expressions to logarithmic expressions and adding a negative sign, simple numbers, 7, 1, and 13, can be obtained, respectively. This is how the pH value is expressed.

Table 2.1 Relationship between Hydrogen Ion Concentrations and pH Values

Solution	Hydrogen Ion Concentration (mol/L)	pH= $-\log_{10} [\text{H}^+]$
0.1 mol/L HCl	10^{-1}	1
0.01 mol/L HCl	10^{-2}	2
Neutral solution	10^{-7}	7
0.01 mol/L NaOH	10^{-12}	12
0.1 mol/L NaOH	10^{-13}	13

The definition of equation (2.1) is more precisely expressed as equation (2.2).

$$\text{pH} = -\log_{10} [\text{hydrogen ion activity}] \text{ ----- (2.2)}$$

The hydrogen ion activity is the product of the hydrogen ion concentration and the activity coefficient. The activity coefficient is a measure of how much the ions are involved in chemical reactions in a solution. When a solution has a small amount of ions and allows the activity of ions each other, such as dilute solutions, its activity coefficient is 1.0. When the ion concentration increases, ions interact with each other and thus the coefficient decreases below 1.0. Since ordinary solutions have the activity coefficient that approximates to 1.0, there are no big problems in considering equation (2.1) as the definition of pH.

3. Methods of pH Measurement

Several methods of pH measurement have been developed and upgraded. Major methods are as follows.

- (1) Indicator method
- (2) Hydrogen electrode method
- (3) Quinhydrone electrode method
- (4) Antimony electrode method
- (5) Glass electrode method.

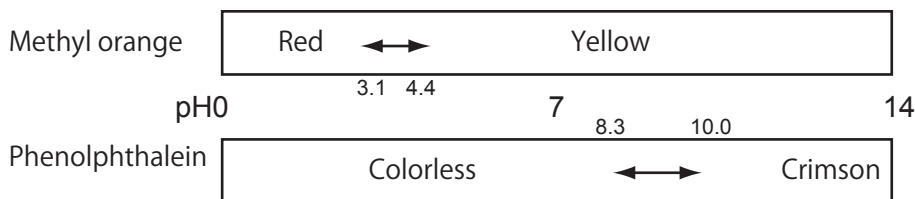
3.1 Indicator Method

The indicator method uses litmus papers or reagents such as methyl orange and phenolphthalein solutions. Indicator method is one of a traditional but a simple measuring method.

The simplest method is soaking litmus papers in a test solution. Blue litmus paper turns red in an acidic solution. Red litmus paper turns blue in a basic solution.

Methyl orange and phenolphthalein indicator solutions change color at different pH's.

Place a few drops of the indicator solution into a test solution. From the degree of color change, you will know an approximate pH value of the solution.



While this indicator method is easy in handling, it cannot provide accurate measurement. Another disadvantage is a measurement difficulty with a colored solution.

3.2 Hydrogen Electrode Method

A platinum electrode on which hydrogen gas is adequately adsorbed, is called a hydrogen electrode. Placing this electrode in a test solution generates a potential corresponding to the hydrogen ion concentration (to be precise, the hydrogen ion activity) of the solution, and thus the pH of the test solution can be determined.

This hydrogen electrode method is to directly measure the hydrogen ion activity and is used as one of the standard pH measurement methods today. However, it is not used as an industrial standard because it requires hydrogen gas that has an explosion risk, its operation is troublesome, and furthermore, it may involve a sodium ion error and other errors..

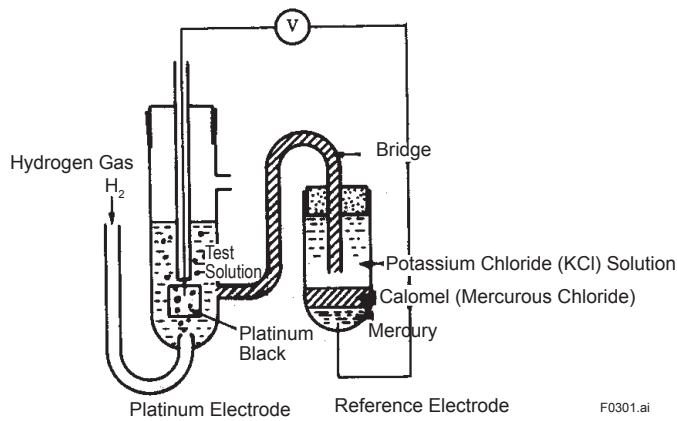


Figure 3.1 Example of Measurement Using Hydrogen Electrode

3.3 Quinhydrone Electrode Method

This method is to determine the pH from the potential difference between the two electrodes: a platinum electrode and a reference electrode. A small amount of quinhydrone ($C_6H_4O_2 \cdot C_6H_4(OH)_2$) is added to a test solution and after vigorous stirring, two electrodes are immersed in the solution to determine the potential difference. This method utilizes the fact that dissolving quinhydrone in a solution changes the ratio of benzoquinone to hydroquinone depending on the pH of the solution, thereby changing the potential difference. It is simple, but it can apply only to a test solution with pH 8 or less and cannot be used when a test solution contains oxidizing or reducing substances. Because of these application limitations, now this method is almost out of use.

3.4 Antimony Electrode Method

Antimony oxide is generated on a polished surface of antimony. When it is immersed in a solution, the oxide dissolves to form hydroxide. Depending on the pH of the solution, the ionization equilibrium of the antimony hydroxide varies. The antimony electrode method is based on this fact. It involves immersing an antimony rod (a commonly used rod has a diameter of approximately 10 mm) polished with a sand paper or cloth, together with a reference electrode, in a test solution. The pH is determined from the potential difference between the antimony rod and the reference electrode. (See Figure 3.2.)

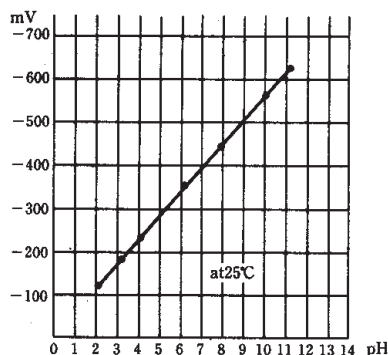


Figure 3.2 Characteristics of Antimony Electrode in Standard Solution

The antimony electrode is used when a test solution contains fluorine and glass electrode characteristics deteriorate in a short period of time or a glass membrane dissolves. Readings by the antimony electrode method vary significantly depending on the condition of the antimony surface and thus may be difficult to be reproducible.

When using the electrode, it is required to polish the antimony surface to always expose a fresh antimony metal.

If a test solution contains oxidizing or reducing agents, such as sulfide and peroxide, or strong complex compounds, such as tartaric acid, citric acid, and oxalic acid (borate standard solution cannot be used), this method is not applicable.

The pH measuring range of the antimony electrode method is from pH 2 to pH 12 and outside this range the linearity is not provided. Operating temperature should be at or around normal temperature because readings tend to be unstable at a temperature of 50°C or higher.

3.5 Glass Electrode Method

Measurement of pH using a glass electrode makes use of the potential difference developed between the two sides of a thin glass membrane that separates two solutions with different pH. The potential difference developed is proportional to the pH difference of the two solutions.

As shown in Figure 3.3, container G made of a thin glass membrane is filled with solution B with known pH and the container G is immersed in solution A.

Potentials are developed on the two sides of the glass membrane.

By immersing relevant electrodes, E_1 and E_2 , in solutions, A and B, respectively, the potential difference between the two electrodes can be determined with voltmeter V and thus a voltage developed on the glass membrane can be known.

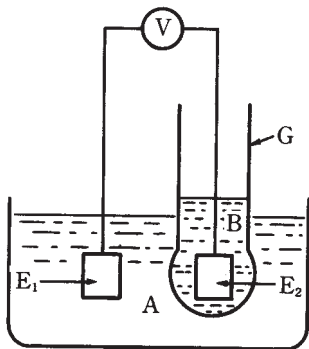
In comparison with other methods mentioned above, the glass electrode method has the following advantages.

- Wide measuring range: operates in a wide range of 0 to 14 pH without practical problems.
- Fast response: requires the shortest time for measurement.
- Easy operation and continuous measurement.
- Excellent reproducibility, free from operator error: achieves good measurement accuracy. Results obtained by the indicator or antimony electrode method may differ depending on the operator.
- Minimal errors such as a sodium error and protein error: Other methods may have such errors and many of them may not be applicable to a test solution containing oxidizing or reducing substances.

On the other hand, disadvantages of the glass electrode method are:

- Glass electrode is subject to breakage: an electrode with a thin glass membrane with a thickness of 0.01 to 0.5 mm, requires care in handling. Thanks to the improvement in glass materials, the latest glass membrane has at least 0.2 mm in thickness, making this disadvantage smaller.
- Electrode's internal resistance is high: a millivolt meter with specially high input resistance is required because the electric resistance of the glass membrane is high: some MΩ to some 100 MΩ. Also, the insulation resistance in the entire measurement circuit needs to be extremely high, requiring care in handling. In the hydrogen, quinhydrone or antimony electrode method, potential differences can be measured with a normal potentiometer or a moving coil type millivolt meter because the electrode's internal electric resistance is low.

These advantages or disadvantages show that the electrode method provides highly accurate measurement, has only a few measurement restrictions, and allows continuous measurement, making this method most suitable for the industrial purpose. The glass electrode method is so generalized these days that the pH measurement might mean the glass electrode method.



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- A: Test Solution
- B: Solution with Known pH
- E₁: Electrode
- E₂: Electrode
- G: Container Made of Thin Glass Membrane
- V: Voltmeter

Figure 3.3 pH Measurement Using Glass Electrode

4. pH Measurement Using a Glass Electrode

4.1 Measurement Principle

Figure 4.1 shows the diagram of glass electrode membrane. Both membrane surfaces in contact with solutions are hydrated and the hydrogen ion activity in these hydrated layers is constant. A boundary potential develops depending on the ratio of the hydrogen ion activity of the hydrated layer and that of the solution. This boundary potential, e.g. is expressed by the Nernst equation as follows.

$$e_i = - \frac{2.3026 R T}{F} \text{pH}_i + C_i \text{ (Internal Solution Side) } \dots\dots\dots (4.1)$$

$$e_s = - \frac{2.3026 R T}{F} \text{pH}_s + C_s \text{ (Sample Solution Side) } \dots\dots\dots (4.2)$$

Where: e_i : potential of internal solution
 e_s : potential of sample solution
 R : gas constant, 8.3144 [J/(mol·K)]
 T : absolute temperature, (t [°C]+273.15) [K]
 F : Faraday constant, 9.6485×10^4 [C/mol]
 C_i : potential at interface between glass and internal solution
 C_s : potential at interface between glass and sample solution
 pH_i : pH of internal solution
 pH_s : pH of sample solution

Given the potential of the internal solution is reference, the potential difference across the membrane, e_g , is expressed as follows:

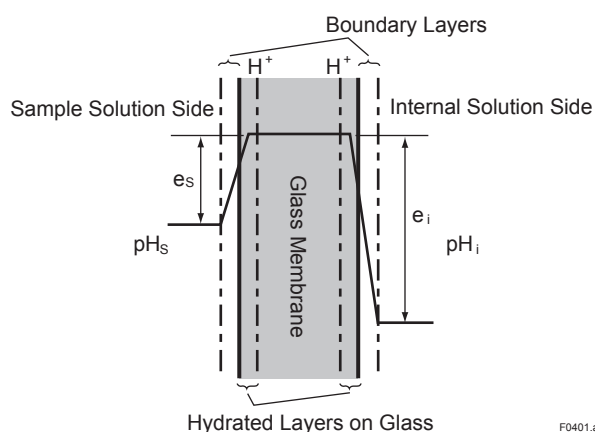
$$e_g = e_s - e_i = \frac{2.3026 R T}{F} (\text{pH}_i - \text{pH}_s) + (C_s - C_i) \dots\dots\dots (4.3)$$

To determine the difference of membrane potentials, two inner electrodes are incorporated in a glass electrode and a reference electrode, and the potential difference between the two electrodes is measured by a pH converter with high input impedance. This potential difference E_g is expressed as follows when the difference of single electrode potential of the two inner electrodes and $C_s - C_i$ in equation (4.3) are collectively represented by E_{AS} .

$$E_g = \frac{2.3026 R T}{F} (\text{pH}_i - \text{pH}_s) + E_{AS} \dots\dots\dots (4.4)$$

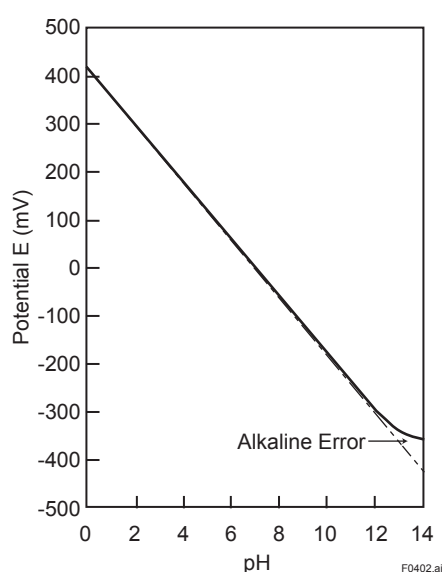
$$E_g = (54.20 + 0.1984 t) \times (\text{pH}_i - \text{pH}_s) + E_{AS} \dots\dots\dots (4.5)$$

A pH buffer solution with a constant pH is filled in the glass electrode of the internal solution and thus pH_i is constant. Using a solution (pH standard solution) with known pH as a sample solution, the relationship between millivolt and pH at a certain temperature can be determined, for example, as shown in Figure 4.2. Once the relationship is known, the pH can be directly obtained from the membrane potential difference.



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Figure 4.1 Glass Membrane



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Figure 4.2 Relationship between Glass Electrode Potential and pH

4.2 Temperature Compensation

In equation (4.3), $2.3026RT/F$ represents the electromotive force (emf) per pH unit and because it has a temperature factor, it varies with the temperature. For example, the emf per pH at 0°C is 54.199 mV, the one at 25°C is 59.159 mV, and the one at 60°C is 66.104 mV, as shown in Table 4.1. In order to compensate the slope of the emf depending on temperature on a pH converter, a resistance temperature sensor for temperature compensation is generally incorporated together with a glass electrode and a reference electrode.

Table 4.1 Electromotive force (emf) per pH ($2.3026RT/F$)

Temperature (°C)	$2.3026RT/F$ (mV)	Temperature (°C)	$2.3026RT/F$ (mV)	Temperature (°C)	$2.3026RT/F$ (mV)
0	54.199	35	61.144	70	68.088
5	55.191	40	62.136	75	69.081
10	56.183	45	63.128	80	70.073
15	57.175	50	64.120	85	71.065
20	58.167	55	65.112	90	72.057
25	59.159	60	66.104	95	73.049
30	60.152	65	67.096	100	74.039

4.3 The Asymmetry Potential

Theoretically when identical buffer solutions ($pH_i = pH_s$) are present on both sides of the membrane of a glass electrode, the emf should be 0 mV. In reality, some potentials ($C_s - C_i$) develop depending on the thickness of the glass membrane, heat treatment process, service history, or other factors. This is called the real asymmetry potential. In addition to this potential, the difference in single electrode potential between the inner electrodes, the glass electrode and the reference electrode, and a liquid junction potential* are collectively referred to as the apparent asymmetry potential or simply as the asymmetry potential. This asymmetry potential is E_{AS} in equation (4.4).

* Liquid junction potential occurs due to dirt or clogging of the liquid junction or to other factors.

4.4 Span Adjustment

Actually, the emf per pH of a glass electrode is not always equal to the value of $2.3026RT/F$ in the Nernst equation. Therefore, a pH analyzer requires compensation for small differences from the theoretical slope of potential, which can be done by adjustment using a pH 4 or pH 9 standard solution. This is called span adjustment.

4.5 The Alkaline Error

As shown in Figure 4.3, the emf of a glass electrode deviates from the linear value on the alkaline side. This is called the alkaline error. The magnitude of the alkaline error varies depending on the glass membrane compositions. The alkaline error is likely to occur with the presence of sodium and lithium and even with the same pH, it varies depending on the types and concentrations of cations and on the temperature. These conditions should be specified when the alkaline error is presented. Figures 4.4 and 4.5 show examples of the alkaline error.

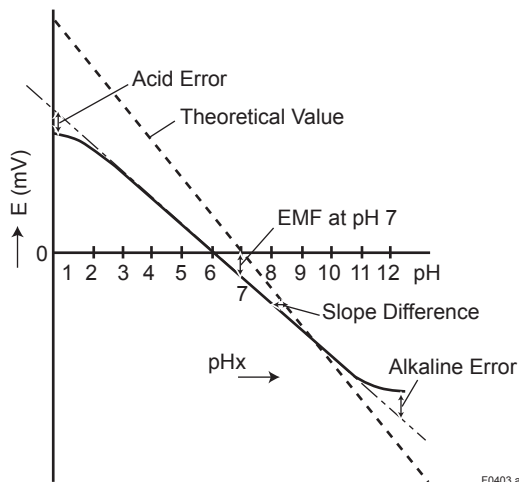


Figure 4.3 EMF Characteristics of Glass Electrode

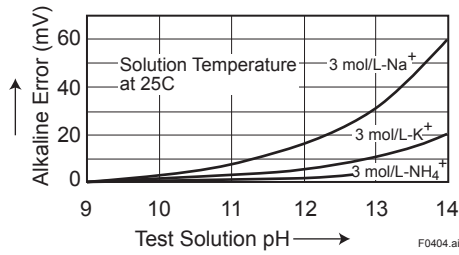


Figure 4.4 Ion Type vs Alkaline Error

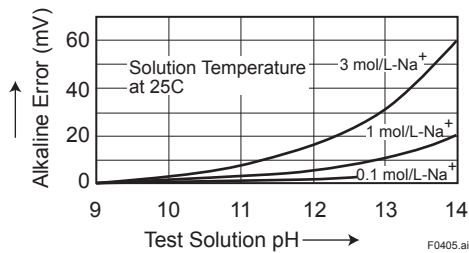


Figure 4.5 Ion Concentration vs Alkaline Error

4.6 The Acid Error

The acid error also varies depending on the glass membrane compositions and the types of acids. It increases gradually with immersion time and finally reaches equilibrium. Once a glass electrode has the acid error, it cannot recover soon even by being immersed in a neutral solution and needs considerable time for recovery. The acid error is small compared to the alkaline error so it hardly matters to practical use.

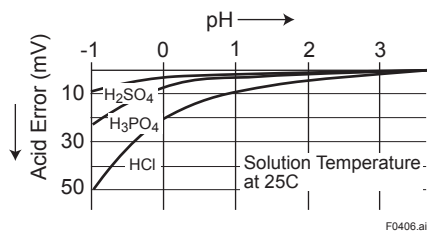


Figure 4.6 Acid Type vs Acid Error

5. Standard Solutions

5.1 Types of Standard Solutions

In pH measurement using a glass electrode, solutions listed in Table 5.1 are used as standard solutions.

Table 5.1 Standard Solutions and Their Composition (JIS Z8802)

Name	Composition
Oxalate standard solution	0.05 mol/kg potassium tetraoxalate dihydrate
Phthalate standard solution	0.05 mol/kg potassium hydrogen phthalate
Neutral phosphate standard solution	0.025 mol/kg potassium dihydrogen phosphate — 0.025 mol/kg disodium hydrogen phosphate ₄
Borate standard solution	0.01 mol/kg sodium tetraborate decahydrate
Carbonate standard solution	0.025 mol/kg sodium hydrogen carbonate — 0.025 ml/kg sodium carbonate

Practical pH values of these solutions at various temperatures are shown in Table 5.2. The pH value at a temperature not listed in Table 5.2 should be calculated by smooth interpolation.

Table 5.2 pH Variation with Temperature (JIS Z8802)

temperature (°C)	Standard Solution				
	Oxalate	Phthalate (pH 4)	Neutral Phosphate (pH 7)	Borate (pH 9)	Carbonate*
0	1.67	4.01	6.98	9.46	10.32
5	1.67	4.01	6.95	9.39	(10.25)
10	1.67	4.00	6.92	9.33	10.18
15	1.67	4.00	6.90	9.27	(10.12)
20	1.68	4.00	6.88	9.22	(10.07)
25	1.68	4.01	6.86	9.18	10.02
30	1.69	4.01	6.85	9.14	(9.97)
35	1.69	4.02	6.84	9.10	(9.93)
38	—	—	—	—	9.91
40	1.70	4.03	6.84	9.07	—
45	1.70	4.04	6.83	9.04	—
50	1.71	4.06	6.83	9.01	—
55	1.72	4.08	6.84	8.99	—
60	1.73	4.10	6.84	8.96	—
70	1.74	4.12	6.85	8.93	—
80	1.77	4.16	6.86	8.89	—
90	1.80	4.20	6.88	8.85	—
95	1.81	4.23	6.89	8.83	—

* Values in parentheses are ones calculated by quadratic interpolation.
Note that this table may not need to be used for special pH measurement.

5.2 Preparation of Standard Solutions

5.2.1 Chemicals and Deionized Water

The purity of chemicals and deionized water used for preparation of pH standard solutions, are specified in the relevant JIS standard as below.

- potassium tetraoxalate dihydrate: JIS K8474
- Potassium hydrogen phthalate: JIS K8809
- Potassium dihydrogen phosphate: JIS K9007
- Disodium hydrogen phosphate: JIS K9020
- Sodium tetraborate decahydrate: JIS K8866
- Sodium hydrogen carbonate: JIS K8622
- Sodium carbonate: JIS K8625
- Deionized water: conductivity of 2×10^{-6} S/cm or less at 25°C. For use for borate and carbonate standard solutions, special care must be taken to remove carbon dioxide from the deionized water.

5.2.2 Procedures

The following explains how to prepare standard solutions.

- Oxalate standard solution: Dissolve 12.606 g (254.19 mol/L) of potassium trihydrogen dioxalate dihydrate in deionized water and dilute to 1 liter.
- Phthalate standard solution: Dissolve 10.119 g (204.221 mol/L) of potassium hydrogen phthalate in deionized water and dilute to 1 liter.
- Neutral phosphate standard solution: Dissolve 3.390 g (163.09 mol/L) of potassium dihydrogen phosphate and 3.536 g (141.96 mol/L) of disodium hydrogen phosphate, and dilute to 1 liter.
- Borate standard solution: Dissolve 3.804 g (381.37 mol/L) of sodium tetraborate decahydrate in deionized water and dilute to 1 liter.

5.2.3 Precautions

Agents used for preparation of standard solutions should meet the specifications for pH measurement in the relevant JIS. Also, deionized water used for dissolving agents should have conductivity of 2×10^{-6} S/cm or less at 25°C. Although there are no sufficient grounds for the required purity and conductivity, they meet the requirements.

As deionized water, use distilled water prepared by cutoff by atmospheric air and a soda lime tube, distillation, and cooling, or deionized water prepared using an ion exchange resin. Since the soda lime is strong alkali, be careful not to allow it to contaminate the distilled water. It is said that a standard solution using deionized water prepared by an ion exchange resin is quick to become moldy. However, this may not affect the use in a short time.

The pH value of a standard solution hardly change with considerable changes of concentration. A standard solution should be prepared by dissolving a specified amount of crystals and dilute to a certain volume in a measuring flask. Strictly speaking the concentration varies depending on temperature. However, this does not substantially affect the measurement if the solution is prepared at room temperature.

When preparing oxalate, phthalate and borate standard solutions, weighing and drying methods

may not need to be strictly followed because only one type of crystal is used.

However, when preparing neutral phosphate and carbonate standard solutions that are prepared by mixing two types of crystals, care must be taken in weighing and drying to avoid improper mixing ratio.

5.3 Storage of Standard Solutions

- Prepared oxalate, phthalate, and phosphate standard solutions should be stored in hermetically sealed, high quality hard glass or polyethylene containers. The pH value of the standard solution may change after long term storage. Before using a standard solution that has been stored after the preparation or a standard solution that has been exposed to and left in the atmosphere, compare its pH with the one of a freshly prepared standard solution and ensure that they are the same.
- Borate and carbonate standard solutions may absorb CO_2 and others in the atmosphere and their pH values may decrease. For storage, they should be hermetically sealed in the absence of air, in hard glass or polyethylene containers, i.e., the container should be filled up with the solution. Furthermore, the carbonate standard solution needs to be stored in an atmosphere not containing CO_2 . Both solutions cannot be reused and the remaining solutions should also be discarded.

5.4 Buffer Action of Standard Solutions

Buffer action is the property of the solution to defend against addition of acid or base and minimize pH changes. A pH standard solution is also called a buffer solution. Table 5.3 shows the buffer action of various standard solutions in concrete numeric values. The buffering capacity, dB/dpH, is the number of moles of strong acid or base required to change the pH of a 1-liter standard solution by one unit. The greater the capacity is, the more difficult the pH is to change when a strong acid or base solution is added. The dilution, $\Delta\text{pH}_{1/2}$, is the pH change that occurs when a standard solution is diluted with the same quantity of distilled water at 25°C. It indicates how much the pH is affected when a solution is diluted with water.

Table 5.3 Buffer Action of pH Standard Solutions (25°C)

	Oxalate Standard Solution	Phthalate Standard Solution	Neutral Phosphate Standard Solution	Borate Standard Solution
Buffering Capacity dB/dpH (mol)	0.07	0.016	0.029	0.020
Dilution $\Delta\text{pH}_{1/2}$	+0.19	+0.05	+0.08	+0.01

As an example, take a borate standard solution. The pH of the borate standard solution is 9.18 at 25°C. Although the standard solution itself is a dilute solution, it requires as much as 0.02 mol of strong base, such as NaOH, to change the pH of a 1-liter solution by one unit; the pH changes to 10.18. In the case of a solution without buffer action, the pH changes to approximately 12.

When a borate standard solution is diluted twofold with water, the pH increases by 0.01 pH, but the pH increases by as much as 0.3 pH if the solution does not have buffer action.

The standard solutions listed in Table 5.1 have good buffer action as shown in Table 5.3. Be careful when using a saturated calcium hydroxide solution and 0.1 mol/kg sodium hydroxide solution since they do not have any buffer action. Also, they have the property of changing of the pH in a short period of time by absorption of carbon dioxide gas in the air, and of significant changing of the pH with temperature changes. These properties should be carefully considered when using.

6. pH Sensors

A pH meter comprises a pH sensor and a pH analyzer/converter. If necessary, a sensor is mounted to a holder.

The following are pH sensors used for Yokogawa's FLEXA/EXA PH Series analyzers. For details, please refer to General Specification, GS 12B07B02-E.

General Purpose Type

- KCl filling type pH sensor (PH8EFP)
- KCl refillable type pH sensor (PH8ERP)

Special Application Type

- pH sensor for high purity water (PH8EHP)
- Polymer Electrolyte pH sensor (PH4P/PH4PT)
- Hydrofluoric Acid-resistant pH sensor (PH4F/PH4FT)
- pH/ORP sensor for Chemical Process (PH4C/PH4CT)

6.1 General pH Sensors: PH8EFP and PH8ERP

There are two types: KCl filling and KCl refillable types. Since both types have the same shape and dimensions with the exception of the KCl filling hole, they can be mounted to the same holder.

Figure 6.1 shows the dimensions of the general pH sensors. The KCl filling type (a) has a KCl filling hole, while the KCl refillable type (b) has a liquid junction and a long lasting internal solution. The glass electrode and junction of both types can be easily replaced.

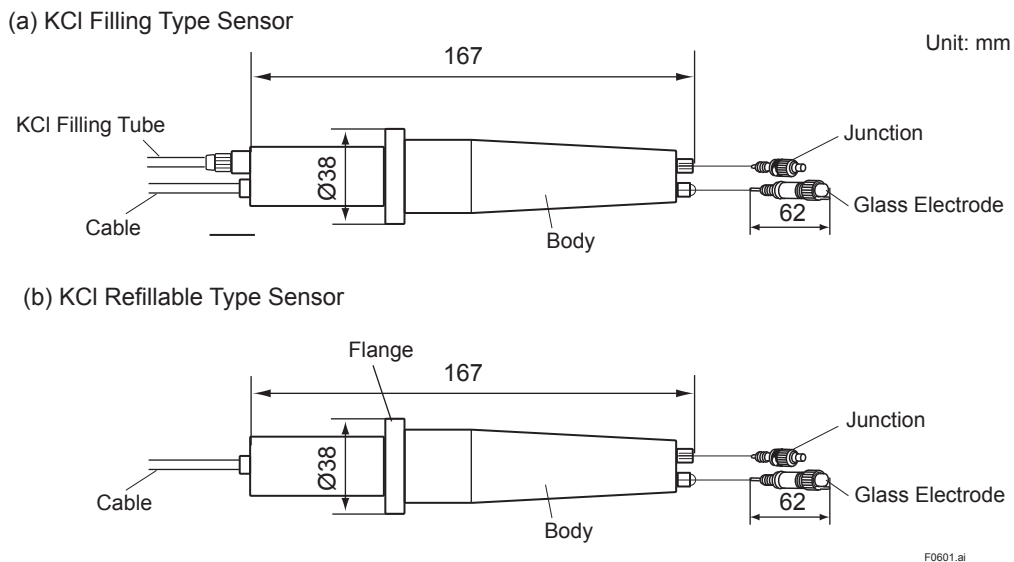


Figure 6.1 Dimensions of General pH Sensors

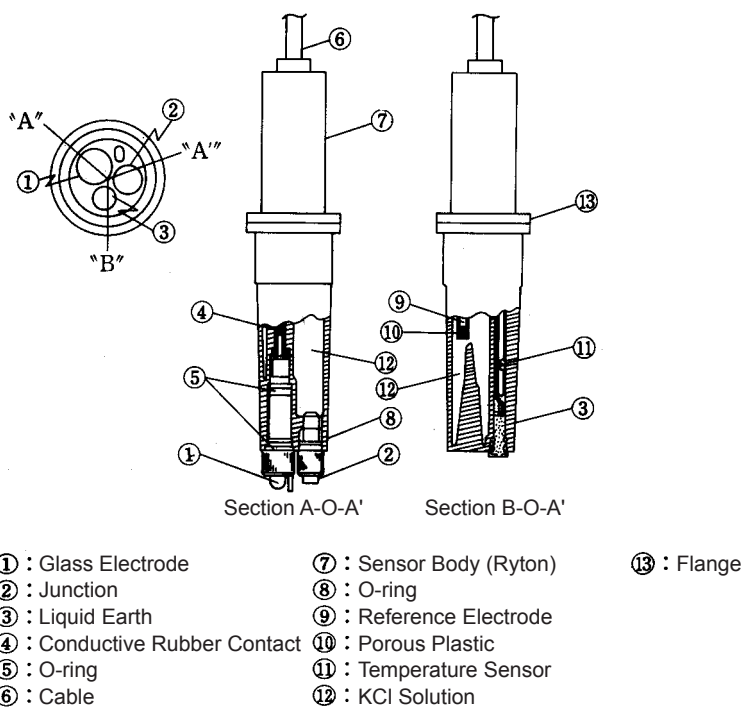


Figure 6.2 Internal View of the pH Sensor

Figure 6.2 shows the internal view of the KCl refillable type pH sensor. This sensor features the following.

- The junction and pH glass electrode are located at the tip of the sensor body so that the electrode can be fit in various cleaning systems — brush, jet, and ultrasonic cleaning. This construction also allows easy manual cleaning when the sensor is not equipped with a cleaning system.
- The flange has the same shape and dimensions as the one of the KCl refillable type, providing the interchangeability.
- The sealing ability is not compromised even if the sensor is entirely wet.
- The lightweight body allows easy buffer check.
- The sensor body can withstand temperatures of up to 260°C and tensile strength of 150 MPa.
- The sensor is designed so that the glass electrode and the reference electrode are isolated from each other. This construction prevents insulation deterioration from occurring.
- A conductive rubber is used as a contact at the electrical connection of the glass tip electrode. This prevents corrosion and thus insulation failure.

6.2 How to Select a pH Sensor: KCl Filling Type or KCl Refillable Type

KCl filling type — Sample temperature of -5 to $+105^{\circ}\text{C}$ and sample pH of 0 to 14 pH allow a wide range of applications. Best suited for applications where high measurement accuracy is required.

KCl refillable type — Easy maintenance. Although KCl replenishment intervals vary depending on the process conditions, KCl replenishment is required only once per 6 months to 2 years. Best suited for general effluent monitoring.

6.3 pH Sensors for Special Applications

6.3.1 Polymer Electrolyte pH Sensor PH4P, PH4PT

Developed as bioreactors to detect methane gas produced from methane fermentation, PH4P/PH4PT Polymer electrolyte pH sensor provide high performance in harsh environment, such as measuring pH of solutions containing a high concentration level of sulfate compounds, high-temperature alkali solutions or highly contaminated plant drain.

<Features and benefits>

Low maintenance ; Polymer electrolyte eliminates sensor clogging .Instead of applying ceramic to seal the liquid junction, the polymer electrolyte gel inside electrode (no refilling no pressurizing of electrolyte) helps prevent contamination of the liquid junction, while its large pore size (approx. 1.0 mm) provides the low junction potentials.

Durable with high pressure, high temperature.

PH4PT: A PH4P-type model with a resistance thermometer.

A model of TIIS Intrinsic safety compliance .

Can be used with FLXA[®]202 or FLXA[®]21 in explosion-proof classified zones.

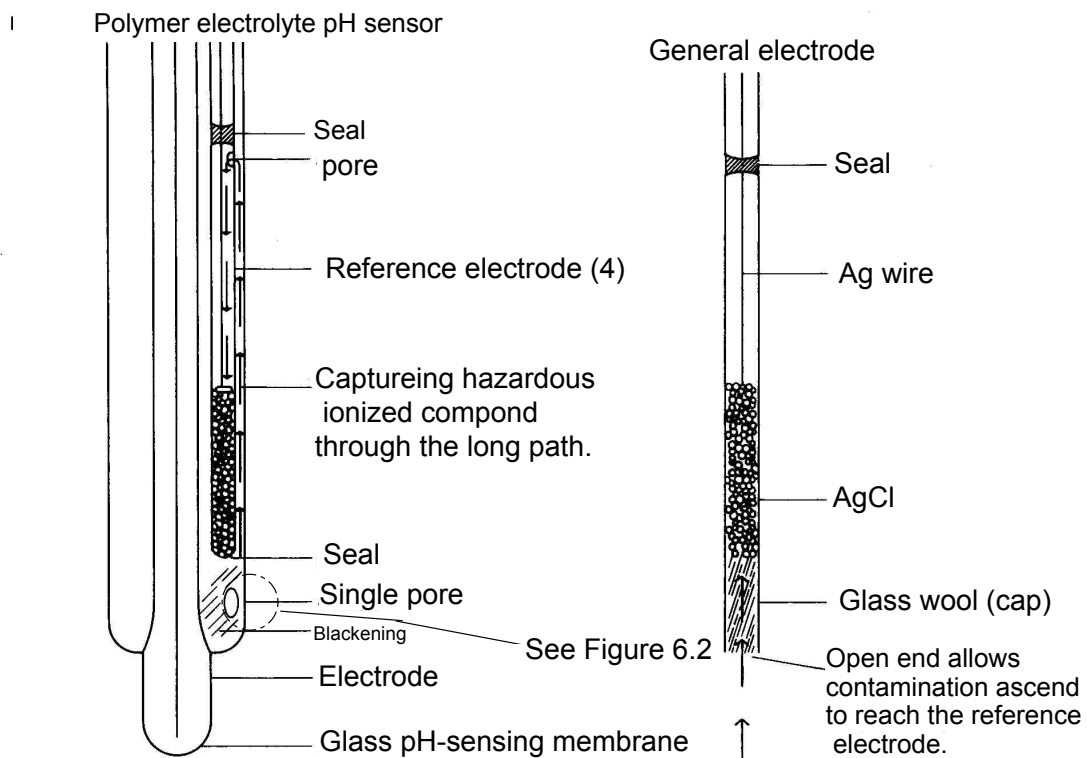


Figure 6.1 Sensor structure

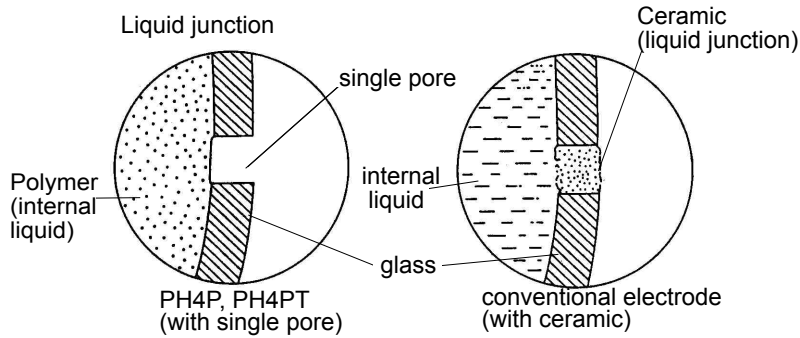


Figure 6.2 Liquid junctions

6.3.2 Hydrofluoric Acid-resistant pH sensor PH4F, PH4FT

Being different from a polymer electrolyte pH sensor, PH4F/PH4FT. PH4F/PH4FT employs hydrofluoric acid resistant glass in place of pH-sensing glass membrane incorporated with a polymer electrolyte pH sensor. For other features and benefits, read the article on the polymer electrolyte pH sensor.

Upper limit of HF concentration;

Max. 500 ppm at pH 2 to 3	Max. 1000 ppm at pH 3 to 4
Max. 10000 ppm at pH 4 to 5	No limit at pH 5 or greater

6.3.3 pH sensor for chemical process PH4C, PH4CT

Thanks to high viscosity gel being pressurized inside the electrode, a pressurized holder is not required.

PH4C, PH4CT features “Ag barrier” incorporated inside the reference electrode, which inhibits the movement of Ag ion from the reference electrode to the liquid junction. (Figure 6.3)

Ag barrier is effective even in a condition of high temperature.

<Features and benefits>

Easy installation:	No pressurized holder is required.
Clean liquid junction:	Pressurized internal electrode prevents the liquid junction from contamination. Less clogging with sulfate compounds due to the Ag barrier
Small alkaline error	Applying glass membranes for electrodes that are used to measure high alkaline values.
PH4CT	PC4C-type with resistant thermometer A model of TIIS Intrinsic safety compliance PH4CT can be used with FLXA202 or FLXA21 in explosion-proof classified zones.

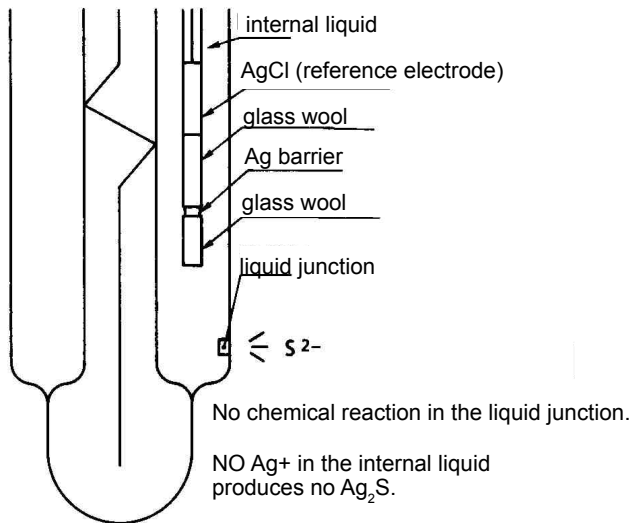


Figure 6.3 pH sensor for chemical process

6.3.4 pH sensor for high purity water PH8EHP

pH Sensor for High Purity Water: PH8EHP

Unlike normal pH measurement, there are various obstacles to pH measurement in high purity water. To remove the obstacles, the pH sensor and the holder (liquid chamber) are designed as shown in Figure 6.4. The pH sensor for high purity water has the same sensor body and glass electrode as the general KCl filling pH sensor has, but the different shape of junction.

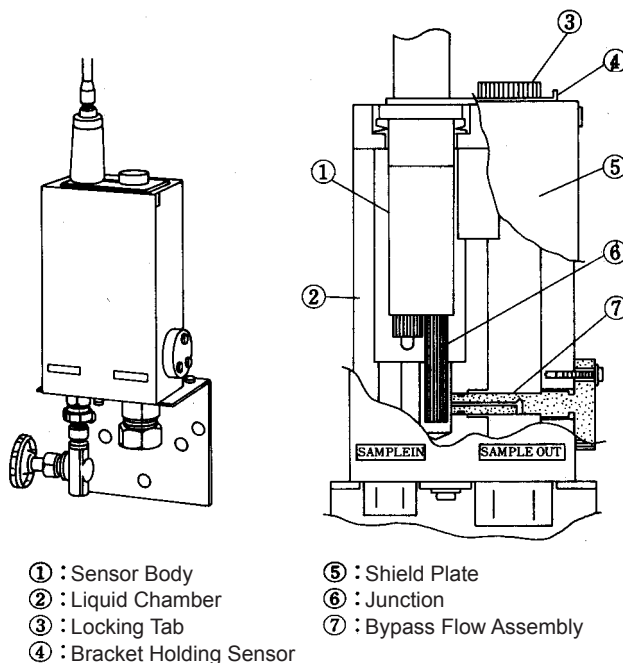


Figure 6.4 Structure of pH Sensor for High Purity Water and Holder

7. pH Sensor and Holder Selection Guide

Refer to pH/ORP Analyzer Selection Guide TI 12B07A03-03E.

8. Chemical Resistance Table

This table should be used only as a guide and no guarantee is given. The table shows the chemical resistance of material to individual chemicals. The result may differ if a sample contains more than one chemical.

Rating:

A = Recommended B = Applicable
C = Acceptable X = Not recommended

Model	General pH Sensor		Specialty pH Sensor
	PH8EFP	PH8ERP	PH8EHP
Type	KCl filling type	KCl refillable type	For high purity water
Specifications			
Normal measuring range	0 to 14 pH	2 to 12 pH	2 to 12 pH
Temperature range	-5 to 105°C	-5 to 80°C	0 to 50°C
Measuring pressure	Atmospheric pressure to 10 kPa (general purpose reserve tank) Atmospheric pressure to 500 kPa (medium pressure reserve tank)	Atmospheric pressure to 50 kPa	Atmospheric pressure
RTD	Pt1000 ohm	Pt1000 ohm	Pt1000 ohm
Applications			
Electrolysis process	X	X	X
General chemical process	B*1	X	X
Sulfide rich solution	C*2	X	X
High purity water (conductivity: 0.1 to 50 S/cm)	X	X	A
Solution containing organic compounds	B	X	X
Chemical process with chlorine or hydrogen gas	X	X	X
Solution containing fluorine (max conc is limited due to pH)	X	X	X
Highly alkaline process: >= 10 pH normally	A*1	X	X
Bioprocess with steam sterilization	X	X	X
Organic solvent rich solution	X	X	X
General wastewater/sewage	B*2	X	X
Human waste treatment	C*2	X	X
Plating process	B	X	X
Final effluent	A	B	X
Stack gas desulfurization facility*3	B	X	X
Converter Available			
PH400G 4-Wire pH Converter	B	B	B
PH202G/S 2-Wire Transmitter	B	B	B
PH100 Panel Mount pH Converter	C	C	X
Holder Available			
PH8HG Guide Pipe Holder	B	B	X
PH8HS/PH8HSF Immersion Holder (general/explosionproof)	B	B	X
PH8HF/PH8HFF Flow-through Holder (general/explosionproof)	B	B	X
PH8HH Holder for High Purity Water	X	X	A
HH350G Suspension Holder	B	B	X
PB350G Angled Floating Ball Holder	B	B	X
PB360G Vertical Floating Ball Holder	B	B	X
Related Parts	Highly alkaline electrode*1 Teflon junction*2		Junction for high purity water

Notes:

*1: For highly alkaline solutions, use an optional electrode for high alkali.

*2: Use an optional Teflon junction.

*3: Simultaneous measurement of pH and ORP is not available.

	Holder material			Ultrasonic transducer material Electrode solution ground tip				Seal O-ring material			Electrode body material			Remarks					
	Polypropylene			SUS 316			Hastelloy C		Titanium		Viton				Ryton				
	Concent'n	Temp	Judge	Concent'n	Temp	Judge	Concent'n	Temp	Judge	Concent'n	Temp	Judge	Concent'n	Temp	Judge	Concent'n	Temp	Judge	
Organic substances	Acetaldehyde	20	◎	100	30	◎	—	—	—	—	—	—	100	20	○				
	Acetone	100	20	○	50	25	◎	—	—	—	—	—	100	25	X	100	b	○	
	Aniline	100	20	◎	100	25	◎	—	—	—	—	—	—	—	—	100	90	○	
		100	70	○															
		100	100	△															
	Ether	100	20	△	100	25	◎	—	—	—	—	—	—	100	20	◎			
	Ethylene glycol	100	70	◎	100	25	◎	—	—	—	—	—	—	—	—	—	—	—	
		100	100	◎															
	Ethyl alcohol	96	70	◎	100	b	◎	—	—	—	—	—	—	100	90	◎			
	Methyl chloride	100	20	X	100	25	◎	—	—	—	—	—	—	—	—	—	—	—	
	Glacial acetic acid	100	70	◎	—	—	—	—	—	—	100	24	X	100	20	◎			
		100	100	○															
	Glycerin	100	70	◎	100	25	◎	—	—	—	—	—	—	—	—	—	—	—	
		100	100	◎															
	Chlorophenol	100	20	◎	—	—	—	—	—	—	—	—	—	100	20	◎			
		100	70	△															
		100	100	X															
	Xylene	100	20	X	—	—	—	—	—	—	—	—	—	100	20	◎			
	Chlorobezene	100	20	X	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
		100	100	X															
	Chloroform	100	20	X	100	b	◎	100	b	◎	100	b	◎	—	—	—	100	90	△
	Dioxane	100	20	◎	—	—	—	—	—	—	—	—	—	—	—	100	90	◎	
		100	70	△															
		100	100	X															
	Dichloroethare	100	70	X	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
	Ethyl nitrate	100	20	◎	100	105	◎	—	—	—	—	—	—	100	90	○			
		100	100	△															
	Carbon tetrachloride	100	20	X	90	b	△	—	—	90	b	◎	100	24	X	—	—	—	
	Trichloroethylene	100	20	X	100	b	○	100	b	◎	100	b	◎	—	—	100	90	X	
	Toluene	100	20	X	—	—	—	—	—	145	◎	—	—	100	90	◎			
	Benzophenone	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
	Benzaldehyde	100	20	◎	—	—	—	—	—	—	—	—	—	100	20	△			
		100	70	○										100	90	X			
		100	100	X															
	Benzyl alcohol benzene	100	20	◎	100	30	△	—	—	100	30	○	100	25	○	100	90	◎	
	Fomaldehyde	10	70	◎	37	b	◎	37	b	◎	37	b	◎	—	—	—	—	—	
		10	100	◎															
	Methylnaphthelen	—	—	◎	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
	Methyl ethyl ketone	100	20	○	—	—	—	—	—	—	—	—	—	—	—	100	90	◎	
		70	△																
Methyl alcohol	100	20	◎	100	25	◎	—	—	—	—	—	—	100	25	◎				
	100	20	◎																
Nitrobenzene	100	70	○	—	—	—	—	—	—	—	—	—	—	—	—	—	—		
	100	100	X																
Acetic acid	100	20	◎	10	b	◎	—	—	10	b	◎	—	—	—	—	—	—		
	100	70	△																
	100	100	X																
Phenol	100	20	◎	95	30	◎	95	30	○	95	30	◎	—	—	100	90	△		
	100	100	○																
Benzonic acid	100	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—		
Motor oil	100	20	◎	—	—	—	—	—	—	—	—	—	—	—	100	20	◎		
	100	70	○																
	100	100	△																
Petroleum ether	100	20	◎	—	—	—	—	—	—	—	—	—	—	—	100	20	○		
Kerosene	100	20	○	—	—	—	—	—	101	◎	—	—	—	—	100	20	○		
	100	70	X																
Tartaric acid	10	40	◎	50	100	△	50	100	△	50	100	◎	—	—	—	—	—		
	10	60	○																
	10	80	△																
Oil and fats	100	70	◎	100	25	◎	100	180	◎	100	180	◎	—	—	—	—	—		
Carbon sulfide	100	20	X	100	25	◎	—	—	—	—	—	—	100	25	◎	—	—		

Note: "b" refers to the boiling point.

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