





# High-Temperature High-Pressure pH and Reference Probes

# **Instruction Manual**

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### High Temperature and High Pressure Ag/AgCl Reference Probe

# WARNNING:

1. Extra CAUTION must be taken when dealing with pressurized systems. Probe or electrode components may fly out like projectiles to cause bodily harm or death, and/or property damage. Avoid exposure of head and body in potential paths of these objects. Use probe only in an access-controlled area or a closed case.

2. Do not rotate the components as shown in Figure. ANY ATTEMPT to rotate these components may compromise the safety integrity of the probe. It may also damage the electrode of the probe and void warranty.



Model:	RX-b-XXX-XXX
Electrode Type:	Ag-AgCl electrode, KCl solution
Insertion Tube:	3/8" OD (1/4" or <sup>1</sup> /2" OD available on request)
Insertion Tube Material:	Stainless steel 316L, Ti-2, or C-276
Fitting Material:	Stainless steel 316, Ti, or C-276
Sealing Material:	Corr Instruments Queon
Operating Temperature:	0 (°C) to 305°C (581 °F) for Probe;
	$\leq 120$ °C (248°F) for probe connection cable.
	Probe must be in water-based solution if heated above 90 °C
Operating Pressure:	0 to 2000 psig (136 bar) for standard probes (Sudden pressure
	change must be avoided to prevent damage to probe).
Calibration:	Probe should be calibrated against a standard reference electrode at room temperature before each use. Contact factory for correction formula to standard hydrogen electrode (SHE) scale at operating temperatures
Trouble Shooting:	Patent pending design avoids air bubble formation in liquid junction, which may occasionally happen and lead to unstable readings if probe has been placed upside down. Gently tapping or gently shaking the probe tip with probe in normal vertical position should remove the air bubbles from the junction.

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### **High Pressure Glass-Based pH Probe**

# WARNNING:

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1. Extra CAUTION must be taken when dealing with pressurized systems. Probe or electrode components may fly out like projectiles to cause bodily harm or death, and/or property damage. Avoid exposure of head and body in potential paths of these objects. Use probe only in an accesscontrolled area or a closed case.

2. Do not rotate the components as shown in Figure. ANY ATTEMPT to rotate these components may compromise the safety integrity of the probe. It may also damage the electrode of the probe and void

# Do not torque these components Fragile component inside. Avoid hard objects and avoid bending probe

warranty. Fragile glass bulb at probe tip. Handle with extreme care.

**Installation:** A high pressure reference electrode is required for the measurement of pH. Corr Instruments' silver/silver chloride high pressure probe can be used as the reference electrode. See separate sheets for recommended installation configurations.

**Measurement:** Measurement should be made only with high-input imped.  $(10^{13} \text{ ohm})$  meters.

**Calibration:** Calibrations with solutions of known pH (e.g., standard pH buffers,  $H_2SO_4$  or NaOH solutions) at operating temperature is required.

Model: Insertion Tube: Insertion Tube Material: Fitting Material: Sealing Material:	pH-G-xxx-xxx-xxxx 1/2" OD wall (3/8" or 5/8" OD availa Stainless steel 316L, Ti-2, or C-276 316 SS, Ti, or C276 Corr Instruments Qeuon	ıble)
Temperature:	20 to 120 °C (68 to 248 °F)	
	Probe must be in water-based so	olution if heated above
	<mark>90 °C</mark>	
Upper Pressure:	2000 psig (136 bar) for standard probes (	Sudden pressure
	change must be avoided to preve	ent damage to probe)
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### High Pressure ZrO<sub>2</sub>-Based pH Probe

# WARNNING:

1. Extra CAUTION must be taken when dealing with pressurized systems. Probe or electrode components may fly out like projectiles to cause bodily harm or death, and/or property damage. Avoid exposure of head and body in potential paths of these objects. Use probe only in an access-controlled area or a closed case.

2. Do not rotate the components as shown in Figure. ANY ATTEMPT to rotate these components may compromise the safety integrity of the probe. It may also damage the electrode of the probe and void warranty. Handle with extreme care, thin ZrO<sub>2</sub> tube is fragile.



**Installation:** A high pressure reference electrode is required for the measurement of pH. Corr Instruments' silver/silver chloride high pressure probe can be used as the reference

electrode. See separate sheets for recommended installation configurations.

**Measurement:** Measurement should be made only with high-input impedance voltmeter  $(>10^{13} \text{ ohm})$  such as the mV option of a pH meter.

**Calibration:** Calibrations curves obtained with solutions of known pH (e.g., standard pH buffers,  $H_2SO_4$  or NaOH solutions) at operating temperature is required.

Model:	pH-ZrO <sub>2</sub> -xxx-xxx-xxxx
Insertion Tube:	1/2" OD wall (3/8" or 5/8" OD available)
Insertion Tube Material:	Stainless steel 316L, Ti-2, or C-276
Fitting Material:	316 SS , Ti, or C276
Sealing Material:	Corr Instruments Qeuon
Temperature:	93 to 343 °C (200 to 650 °F)
Upper Pressure:	2000 psig (136 bar) for standard probes (Sudden pressure change must be avoided to prevent damage to probe)

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#### Installation of Probes in Autoclaves/Reactors or Mini Flow-Through Loops

Reference and glass-based probes must be vertical or at an angle greater than 10 degree with horizontal plane, except for curved probes. ZrO2-based pH probe can be at any orientation.

#### WARNNING:

Extra CAUTION must be taken when dealing with pressurized systems. Probe or electrode component may fly out like projectiles to cause bodily harm or death, and/or property damage. Avoid exposure of head and body in potential paths of these objects. Use probes only in an access-controlled area.





### pH Probe Cable Connections



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### **Storage for Reference and Glass-Based pH Probes**

Reference and glass-based pH probes must be filled with a solution (pH 4 buffer or 1 M KCl solution for pH probes, and 1 M KCl solution for reference probe) and sealed with a cap or a bottle when not in use. Exposure of probes internal components to air (without the cap or bottle) significantly shortens probe life or damage the probes.



Reference probe must be filled with a 1 M KCl solution

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### **Typical Calibration Curves for Glass -Based pH Probes at Different Temperatures Using Standard Buffer Solutions (1)**



Note: 1) Measurements were made at 1 bar pressure in pH 4, pH 7, and pH 10 buffer solutions; 2) Pressure effect on pH measurement can be neglected, and calibration curves obtained at 1 bar applies to high pressure conditions;

3) For buffer solutions for high temperature conditions see Appendix.
4) High input impedance (10<sup>13</sup> ohm) pH meter is required for the measurements.

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### **Typical Calibration Curves for Glass -Based pH Probes at Different Temperatures Using Standard Buffer Solutions (2)**





3) For buffer solutions for high temperature conditions see Appendix.
4) High input impedance (10<sup>13</sup> ohm) pH meter is required for the measurements.

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### **Typical Calibration Curve for a ZrO<sub>2</sub>-Based pH Probe** Using Standard pH Buffer Solutions at 95 °C

Note: 1) Measurements were made at 1 bar pressure in pH 4, pH 7, and pH 10 buffer solutions; 2) Pressure effect on pH measurement can be neglected, and calibration curves obtained at 1 bar applies to high pressure conditions;

- 3) For buffer solutions for high temperature conditions see Appendix.
  4) High input impedance (10<sup>13</sup> ohm) pH meter is required for the measurements.
- 5) Potential at pH 7 is not close to zero, depending on type of reference probe used.

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### Typical Calibration Curve for ZrO<sub>2</sub>-Based pH Probes Using a Glass-Based pH Probe at 97 °C

Note: Note: 1) Measurements were made at 1 bar pressure in solutions containing different amount of HCl or NaOH;

2) Pressure effect on pH measurement can be neglected, and calibration curves obtained at 1 bar applies to high pressure conditions;

3) For calibration solutions for high temperature conditions see Appendix.

4) High input impedance  $(10^{13} \text{ ohm})$  pH meter (with mV option) is required for the measurements.

5) Potential at pH 7 is not close to zero, depending on type of reference probe used.

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#### Appendix A

pH values of Commonly Used Standard Solutions for Calibrating pH Probes (Note: pH is not significantly affected by pressure up to 100 atm)

0			pH values		
C	HA	НВ	HC	HD	HE
25	1.67	3.57	4.01	6.86	9.16
60	1.72	3.57	4.09	6.83	8,93
90	1.80	3.67	4.21	6,90	8.83
100	1.82	3.69	4.24	6.92	8.81
125	1.90	3.79	4.37	6,96	8.73
150		3.92	4.50	7.08	8.66

Table A-1 Medium Temperature Calibration Solutions (25 to 150°C)\*:

Compositions:

HA c = 0.05 mol/L potassium tetroxalate;

HB potassium hydrogen citrate sat. at  $\theta = 25^{\circ}$ C;

HC c = 0.05 mol/L potassium hydrogen phthalate;

HD c = 0.025 mol/L potassium dihydrogen phosphate and c = 0.025 mol/L disodium hydrogen phosphate; HE c = 0.01 mol/L sodium tetraborate.

\*Helmuth Galster, "pH Measurement: Fundamentals, Methods, Applications, Instrumentation," John Wiley & Sons, 1991. Page 60.

θ °C				pH value			
C	HI	HK	HL	HM	HN	HO	HP
20	1.08	2.04	3.55	4.72	5.30	6.86	9.22
100	1.12	2.05	3.68	4.82	5.45	6.88	8.22
125	1.13	2.05	3.80	4.93	5.54	6.92	8.75
150	1.14	2.06	3.95	5.03	5.65	7.04	8.65
175	1.15	2.06		5.15	5.8	7.15	8.60
200	1.17	2.07		5.35	6.05	7.30	8.56
225	1.19	2.08		5.56	6.18	7.45	8.53
250	1.21	2.09		5.80	6.30	7.60	8.50

Table A-2 High Temperature Calibration Solutions (20 to 250°C)\*\*:

Compositions:

HI b = 0.1 mol/kg hydrochloric acid;

HK b = 0.01 mol/kg hydrochloric acid;

HL sat. potassium hydrogen tartrate;

HM b = 0.01 mol/kg acetic acid and b = 0.01 mol/kg sodium acetate;

HN 975 mL from b = 1/15 mol/kg potassium dihydrogen phosphate and 25 mL from 1/15 mol/kg disodium hydrogen phosphate;

HO b = 0.025 mol/kg potassium dihydrogen phosphate and b = 0.025 mol/kg disodium hydrogen phosphate;

HP b = 0.01 mol/kg disodium tetraborate.

\*\*Helmuth Galster, "pH Measurement: Fundamentals, Methods, Applications, Instrumentation," John Wiley & Sons, 1991, Page 262.

### **Appendix B**

T (°F) T (°C)		H <sub>2</sub> SO <sub>4</sub> Conc	H <sub>2</sub> SO <sub>4</sub> Concentration (m)			NaOH Concentration (m)		
- ( - )	1 ( 0)	5.00E-05	5.00E-04	5.00E-03	0.01	1.00E-03	1.00E-04	
68	20				12.07		10.11	
77	25	4.01	3.03	2.12	11.91	10.94	9.95	
86	30	4.01	3.04	2.13	11.75	10.78	9.79	
95	35	4.01	3.04	2.14	11.6	10.63	9.64	
104	40	4.01	3.04	2.15	11.46	10.49	9.5	
122	50	4.01	3.05	2.17	11.19	10.22	9.23	
140	60	4.01	3.06	2.19	10.95	9.98	8.99	
158	70	4.01	3.07	2.2	10.73	9.76	8.77	
176	80	4.02	3.08	2.22	10.52	9.56	8.57	
194	90	4.02	3.1	2.24	10.34	9.37	8.38	
203	95	4.02	3.1	2.25	10.25	9.29	8.3	
212	100	4.02	3.11	2.26	10.17	9.21	8.22	
221	105	4.03	3.12	2.27	10.09	9.13	8.14	
230	110	4.03	3.13	2.28	10.02	9.05	8.07	
248	120	4.04	3.15	2.29	9.88	8.92	7.93	
266	130	4.05	3.17	2.31	9.76	8.8	7.81	
284	140	4.06	3.2	2.32	9.65	8.69	7.7	
302	150	4.07	3.22	2.32	9.55	8.59	7.6	
320	160	4.09	3.23	2.33	9.46	8.5	7.51	
338	170	4.11	3.25	2.34	9.38	8.42	7.44	
356	180	4.13	3.27	2.34	9.31	8.36	7.37	
374	190	4.15	3.28	2.35	9.25	8.3	7.32	
392	200	4.18	3.29	2.35	9.2	8.25	7.27	
410	210	4.2	3.3	2.35	9.16	8.21	7.23	
428	220	4.22	3.3	2.36	9.13	8.18	7.2	
446	230	4.24	3.31	2.36	9.1	8.15	7.17	
464	240	4.25	3.31	2.36	9.08	8.13	7.15	
482	250	4.27	3.32	2.36	9.06	8.12	7.14	
500	260	4.28	3.32	2.37	9.06	8.12	7.14	
518	270	4.29	3.32	2.37	9.06	8.12	7.14	
536	280	4.29	3.32	2.37	9.06	8.13	7.15	
545	285	4.3	<mark>3.32*</mark>	2.37	9.07	<mark>8.13*</mark>	7.16	
554	290	4.3	3.33	2.38	9.07	8.14	7.16	
572	300	4.3	3.33	2.38	9.09	8.16	7.18	
590	310	4.3	3.33	2.38	9.11	8.18	7.21	

# Table A-3. pH values of H<sub>2</sub>SO<sub>4</sub> and NaOH of different concentrations (m) at elevated temperatures (Note: pH is not significantly affected by pressure up to 100 atm)

\* Note: The above results are close to the pH values published by L.W. Niedrach (J. of Electrochem. Soc., Vol 127, page 2126 (1980)) for the two solutions (3.32 and 8.22) at 285 oC. The small difference for 0.001m NaOH was probably due to the water dissociation constants used.

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