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Construction and Testing of a Variable Temperature Potentiometry Cell for Student Use

Lee Kresge and Kenneth E. Hyde

State University of New York, College at Oswego, NY 13126

Donald A. Palmer

Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Building 4500S
Oak Ridge, TN 37831-6110

Potentiometric measurements are common to the undergraduate laboratory experience. Normally, experiments are carried out near room temperature and use an open or loosely capped cell (1) whose temperature is maintained by a circulating water bath. At temperatures above 50 °C, loss of water solvent from the cell becomes an increasing problem. If commercial electrodes are used at these higher temperatures for prolonged periods, evaporation affects the internal filling solutions, possibly resulting in variations in liquid-junction potential and electrode malfunction.

We report here the design and construction of two versatile submersible potentiometric cells for student use in the temperature range 0 to 100 °C. The poly(tetrafluoroethylene) (PTFE) version of the cell can be constructed from standard parts without the need for professional assistance. All components for the glass cell are commercially available, but construction requires glass work and some additional machining of commercial PTFE parts.

In the present article we test the cells configured as chloride concentration cells with fabricated Ag–AgCl electrodes. We also evaluate a chloride specific-ion electrode and double-junction reference electrode in a commercial (Metrohm) cell up to 50 °C. The experiments verify Nernstian behavior for all electrode–cell combinations over the temperature ranges investigated. The determination of the Nernst slope over a wide temperature range is an appropriate experiment for the undergraduate laboratory. Because these cells may be fitted with different fabricated or commercial electrodes, a variety of electrochemistry experiments (2–4) may be converted to variable temperature studies.

Cell Construction

Glass Cell

The cell shown in Figure 1 consists of two, concentric, threaded glass vessels. Each cylindrical threaded tube must first be sealed by welding glass flats over the open nonthreaded end. The outer vessel or test compartment (Ace Glass 7644-25) has a 50-mm i.d. and a depth of 130 mm. The threaded end is sealed with a PTFE plug and O-ring (Ace 5845-51). Three pipe-threaded fittings must be machined into the plug to accommodate two 1/8-in. Cole Parmer 06374-01 and one 1/16-in. CP 06391-85 to provide access for the two PTFE-clad electrodes and 1/16-in.-o.d. PTFE titrant line.

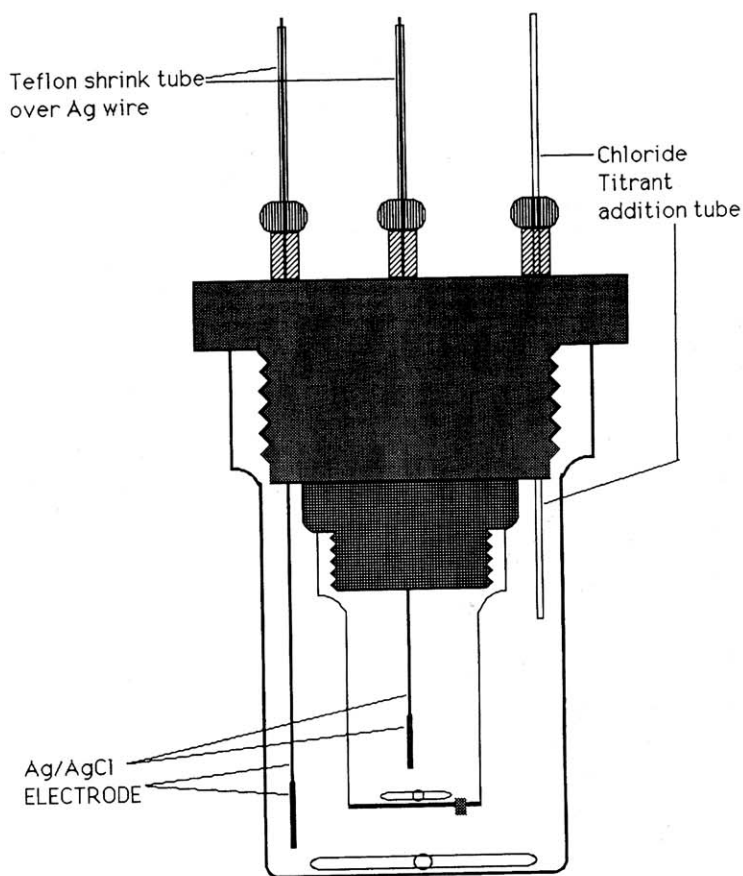


Figure 1. Submersible, glass, concentration cell configured as a chloride ion concentration cell with Ag–AgCl electrodes.

The line is connected through a PTFE miniature valve (CP 06473-10) and a Luer adapter that allows the titrant to be added via syringe. A double-threaded PTFE coupling (Ace 5841-51) suspends an inner reference vessel (25-mm-i.d., 70-mm depth Ace 7644-20) from the underside of the plug. A centered electrode passes through the coupling into the solution in the inner vessel, while the second electrode and titrant line access only the outer compartment.

The electrical contact, or salt bridge, is maintained by cementing a porous glass plug into a hole drilled at the bottom of the inner compartment. The entire cell is immersed in a water–ethylene glycol bath maintained at ± 0.1 °C. Circular magnets (Bell Art Products 3/4 and 1 1/4 diameter spinrings F-37140) are used in both compartments. The solutions are agitated by magnetic stirring via an immersible stirrer.

PTFE Cell

The design is similar to that of the glass cell above. The cell compartments are 1-oz and 8-oz capped wide-mouth PTFE sample bottles (CP 06103-30 and 06103-60). A straight bulk-head union (CP 06482-32) connects the caps for the inner and outer containers and provides the path for the inner PTFE-clad Ag–AgCl electrode. A compression fitting (CP 06374-01) allows the second PTFE-clad electrode to reach the outer compartment. Titrant-line entrance is provided by a mini-compression fitting (CP 06391-85).

Electrodes

Fabricated Ag–AgCl Electrodes

The electrodes are made in pairs by electrochemically oxidizing the bottom inch of two lengths of 2.0-mm-o.d. silver wire. This method produces electrodes with asymmetry potentials between paired electrodes of 0.5 mV or less. The ends of the silver wires are polished with fine emery cloth, washed repeatedly with deionized water, and anodized in 0.1 M HCl using a cathode of platinum wire or foil.

The power supply is adjusted to provide a 20-mA current. After 1 h, the electrodes are removed and rinsed with deionized water. Heat-shrinkable PTFE tubing is used to clad the upper unoxidized length of the wires. The pair is shorted together for several hours in an appropriate stirred solution (e.g., 0.01 M HCl) heated to 60 °C, whereupon the electrode pair is ready for use. A rapid nonelectrochemical method (3) for preparing Ag–AgCl electrodes for student use involves oxidation of silver wire in a mixed HCl/HNO₃ solution, but we have not tested these electrodes.

Commercial Electrodes

An Orion model 94-17B chloride ion electrode is used with an Orion model 90-02 double-junction reference electrode in the cell. The reference electrode is supplied with an outer-chamber filling solution that contains 10% KNO₃. Because the cell reference solution contains perchlorate ion, this must be replaced with NaNO₃ to prevent KClO₄ from precipitating at the solution–electrode interface.

Potentiometric Measurements

Electrodes are connected to either a pH meter in the millivolt mode or a digital multimeter (Keithley model 197).

Voltage readings may be displayed on a strip chart recorder or directed to a computer. Our data acquisition program uses the multimeter's IEEE-488 interface and simply prints voltage–time data.

Working Solutions Preparation

Titration and reference solutions are prepared by weight at the same ionic strength and acid concentration from stock solutions whose concentrations are precisely known and expressed in terms of unit mass of solution. Ramette (5) has promoted the term molality for the concentration units of millimoles solute per gram solution. Typical stock solutions are 5 molal NaClO₄, 5 molal HClO₄, and 1 molal HCl.

An example set of working solutions at *I* = 0.1 m (molal) is

- titrant: 0.01001 m HCl, 0.0900 m NaCl
- reference solution: 0.01000 M HClO₄, 0.000999 m NaCl, 0.0890 m NaClO₄

Titration in Fabricated Concentration Cells with Ag–AgCl Electrodes

The simplified notation for our concentration cell with Ag–AgCl electrodes is



The cell potential is given by

$$\Delta E = \frac{-2.303RT}{F} \log \left(\frac{a_{\text{Cl}^-(\text{test})}}{a_{\text{Cl}^-(\text{ref})}} \right) + E_j \quad (2)$$

where *E_j* is the junction potential, which depends on the nature of the ions *j* and their relative concentrations in the two compartments.

Therefore, *E_j* will be zero when the Nernst titration is initiated because the two solutions are identical. It remains small and negligible under the conditions of our titration where there is an excess of swamping electrolyte, and both the ionic strength and [H⁺] remain constant during the titration. The activity coefficients for chloride in the test and reference compartments are approximately equal due to the presence of a swamping electrolyte and the maintenance of a constant, matching ionic strength in both compartments. Thus, the above equation may be simplified,

A	A	B	C	D	E	F	G
1							
2	molality	molality	molality	mass	mass	molality	molality
3	HClO ₄ in	NaClO ₄	NaCl	OUTER	INNER	NaCl	HCl
4	ref. solution	ref. solution	ref. solution	ref. solution	ref. solution	titr. solution	titr. solution
5	0.099987	0.89019	0.009999	60.81	10.0441	0.90000	0.10000
6							
7	mass	E	E		calc. fraction	calc. molality	calc. ionic
8	titrant	actually	bias		H ₂ O	Cl	strength
9	solution	measured	corrected	temperature	after addition	after addition	after addition
10	0.0000	-0.04	0.00	75	0.8932	0.0099993	1.000
11	0.3408	-12.88	-12.84		0.8935	0.0158458	1.000
12	0.7210	-21.95	-21.91		0.8938	0.0222872	1.000
13	1.2475	-31.90	-31.86		0.8942	0.0310693	1.000
14	2.0550	-42.22	-42.18		0.8949	0.0442361	1.000
15	3.2867	-53.30	-53.26		0.8959	0.0636445	1.000
16	5.0180	-64.54	-64.50		0.8972	0.0896297	1.000
17	7.2188	-72.98	-72.94		0.8988	0.1206506	1.000
18	10.3991	-82.07	-82.03		0.9010	0.1619183	1.000

Figure 2. A spreadsheet for student use with potentiometric titrations.

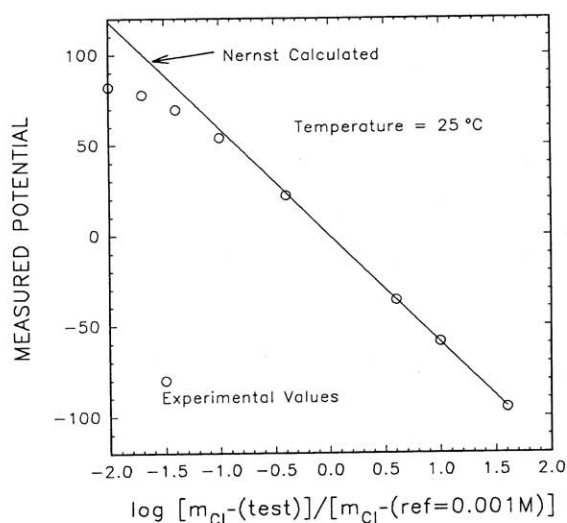


Figure 3. Deviations from Nernstian behavior at low chloride in a concentration cell with Ag–AgCl electrodes.

$$\Delta E = \frac{-2.203RT}{F} \log \left(\frac{m_{\text{Cl}^-}(\text{test})}{m_{\text{Cl}^-}(\text{ref})} \right) \quad (3)$$

so that the cell potential is proportional to the logarithm of the variable chloride concentration of the test compartment.

Preparation of the Titration Cell

Starting with a clean, dry concentration cell, a measured mass of reference solution is transferred into each cell compartment. The amount of solution added to the outer compartment should bring its level to that of the inner compartment, thereby minimizing the hydrostatic pressure difference across the liquid junction. In our glass cell, the inner compartment contains about 12 g of reference solution, whereas the outer compartment requires about 55 g of this solution. The cell is immersed in the constant-temperature bath with the electrode leads shorted. After allowing approximately 1 h for thermal equilibration, the short is removed.

Nernst Titration

The titration is initiated when the cell voltage stabilizes, that is, when a voltage drift is less than 0.5 mV in 10 min. Because a Nernst titration starts with identical solutions in both compartments of the concentration cell, the initial potential should be zero. Any deviation from this value may be associated with an asymmetry potential for the electrode pair and is subtracted from the titration potentials before additional data treatment.

All titrations are carried out on a basis of weight (6–8) with titrant being added from a 10-mL glass gas-tight Luer syringe (Hamilton 1010). Enough titrant is added to cause about a 10-mV change in potential. The excess titrant in the delivery tube is blown through the tube with air from the titrant syringe or drawn back into the syringe. Because the titrant solution is added gravimetrically, a dilution factor must be applied to calculate the concentration of chloride in the test solution after each titrant addition. Use of the spreadsheet shown in Figure 2 proved convenient for this purpose.

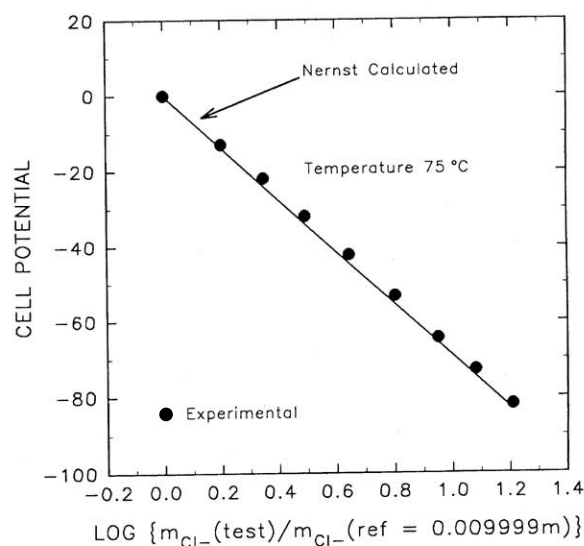


Figure 4. Student Nernst titration at 75 °C in a fabricated glass cell with Ag–AgCl electrodes.

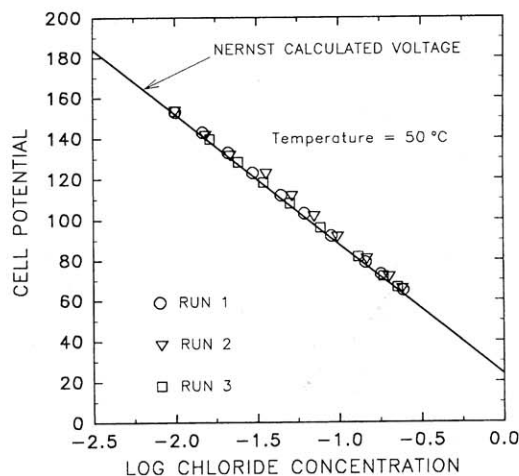


Figure 5. Student Nernst titrations at 50 °C in a commercial cell with commercial electrodes.

Calculations

A linear Nernst slope of 0.1985 $T(\text{K})$ mV per decade should be obtained when the logarithm of the chloride concentration in the test compartment is plotted against the cell potential (9) (see Fig. 3). Significant deviations from this behavior may be associated with defective electrodes, incorrect solution compositions, improper cell design, or significant drift of cell potential during the titration. The concentration-cell approach should be applicable down to chloride concentrations of approximately 0.0001 m. Deviations from Nernstian behavior associated with the spontaneous dissolution of AgCl from an electrode have been reported (10) at low chloride concentrations and are illustrated in Figure 3.

The spreadsheet's linear regression capabilities are used to calculate the slopes, intercepts, and correlation coefficients for the data,

$$\text{voltage vs. } \log \left(\frac{m_{\text{Cl}^-}(\text{test})}{m_{\text{Cl}^-}(\text{ref})} \right)$$

Summary of Student Nernst Titration Results

Run No.	Commercial Chloride Electrode and Cell		Ag-AgCl Electrodes with Fabricated Cell			
			Temperature			
	25 °C	50 °C	25 °C	50 °C	75 °C	100 °C
1	56.0	64.0	58.4	64.9	68.3	74.9
2	56.7	63.2	57.5	62.5	68.3	75.3
3	58.1	64.2	56.9	64.2		75.3
4	58.1	63.8				76.5
Average	57.2	63.8	57.6	63.9	68.3	75.5
Nernst	59.2	64.1	59.2	64.1	69.1	74.0

Figure 4 presents the results of a student Nernst titration at 75 °C.

Titration with Commercial Electrodes in a Commercial Cell

The cell is equipped with a loose cover that positions the electrodes and a thermometer, and allows for the addition of the titrant. The cell potential is related to the chloride concentration of the cell solution by the Nernst equation.

$$E = E_o + S \log(a_{\text{Cl}^-}) = E_o + S \log(\gamma_{\text{Cl}^-} m_{\text{Cl}^-}) \quad (4)$$

where E_o is a constant reference potential, and S is the Nernst slope, $2.303RT/F$.

Because the ionic strength is high and constant relative to the chloride concentration, the activity coefficient (γ) remains constant, and the activity (a) is directly proportional to the chloride ion concentration. The Nernst slope is obtained from a plot of cell potential vs. log chloride molality.

To begin the titration, about 40 g of reference solution is added to the cell and allowed to equilibrate to constant temperature and cell potential. A titrant aliquot is added from a weighed transfer pipet (e.g., BIO-RAD polyethylene disposable pipets, fine-tipped, Style G) to cause about a 10-mV change. Titrant additions continue until the chloride ion concentration in the cell approaches 10% of the ionic strength of the solution. The data (cell potential in millivolt and grams of titrant added) are entered into a spreadsheet for treatment similar to that used with the data obtained with the fabricated cells. Figure 5 shows the results of three student Nernst titrations at 50 °C.

At temperatures above ambient, condensation occurs on the underside of the adapter-cover. Water condensation and evaporation made titrations above 50 °C impossible with this cell type because constant refluxing action (evaporating solution condensing on the cap and dripping

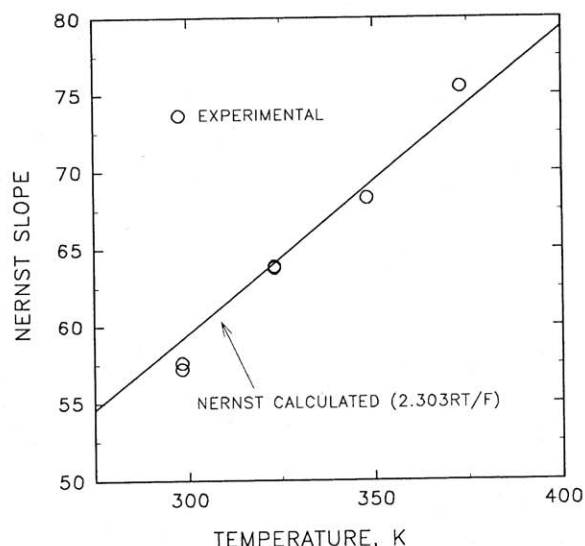


Figure 6. Summary of Nernst titrations at various temperatures.

back into the reference solution) made accurate data acquisition difficult.

Summary

Student slopes from the Nernst titrations in both the commercial and fabricated cells at different temperatures are summarized in the table. The average Nernst slopes for each electrode type (commercial vs. fabricated Ag/AgCl) agree well at temperatures where measurements overlap. Thus, the performance of the cells is comparable, but only the fabricated cell design is useful at the higher temperatures. Figure 6 is a plot of Nernst slopes vs. temperature and indicates reasonable agreement with the calculated slopes.

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