pH Meters and pH Titration

prepared by R. F. Schneider (Rev 10/08)

The pH meter is one of a class of devices that use electrochemical properties to measure the concentrations of species in solution. Such devices make use of the voltage difference between electrodes that depend on the concentration of one or more constituents of the solution. They can be constructed for solutions in solvents other than water but, the basic electrochemical properties with which the beginning student is familiar tend to be limited to those in water solution. We assume that all reactions are conducted in water.

Concepts: Nernst equation, oxidation, reduction, reaction quotient, standard states, electrodes, electrochemical cells, buffers, homogeneous solution,

Background Information:

The basis for the measurement of voltages that depend on the concentration of ions in aqueous solution lies in the thermodynamic relationship called the **Nernst equation**. This principle is expressed in general by the following:

Given the oxidation-reduction reaction involving n electrons transferred,

(1) $$aA(aq) + bB(aq) + \ldots \rightarrow cC(aq) + dD(aq) + \ldots..$$

(2) $$E = E^0 - \frac{\mathbf{R}T}{n\boldsymbol{F}} \ln \left\{ \frac{[C]^c [D]^d \ldots}{[A]^a [B]^b \ldots} \right\}$$ **, or**

(3) $$E = E^0 - \frac{\mathbf{R}T}{n\boldsymbol{F}} \ln \mathbf{Q}$$

where:

- **R** is the gas constant
- T is the Absolute Temperature
- ***F*** is the value of the **Faraday**, a combination of fundamental constants, namely, the charge on one mole of electrons
- E^0 is a voltage that depends on the identity of the reactants and products in the reaction
- n is the number of electrons involved in the oxidation half reaction, and

the expression in braces in Equation 2 is the **reaction quotient**, **Q**

The **reaction quotient** is the quotient of the *[product of the concentrations (or partial pressures if gases are involved) of the products of the reaction each raised to the power corresponding to their coefficients in the balanced chemical reaction]* to the (*product of the* *concentrations of the reactants raised to the appropriate powers as they appear in the chemical reaction).* By convention, substances in their **standard states** (e.g., solids) are excluded from the expression.

For a one electron oxidation-reduction reaction involving H^+ as a product, if the other substances are all in their standard states,

(4) $$E = E^0 - \frac{\mathbf{R}T}{\boldsymbol{F}} \ln [H^+]$$

or, noting that $\ln [H^+] = 2.303 * \log [H^+]$ (ln 10 = 2.30258509…..)

(5) $$E = E^0 + \frac{2.303\ \mathbf{R}T}{\boldsymbol{F}} \text{pH}$$ (where E^0 depends on the specific reaction)

I.e., *the voltage characteristic of such a reaction depends linearly on the pH.* This relationship is exhibited in the graph below. The solid line represents the linear relationship at 25°C. The dotted line shows how the slope decreases when the temperature is reduced to 0°C.

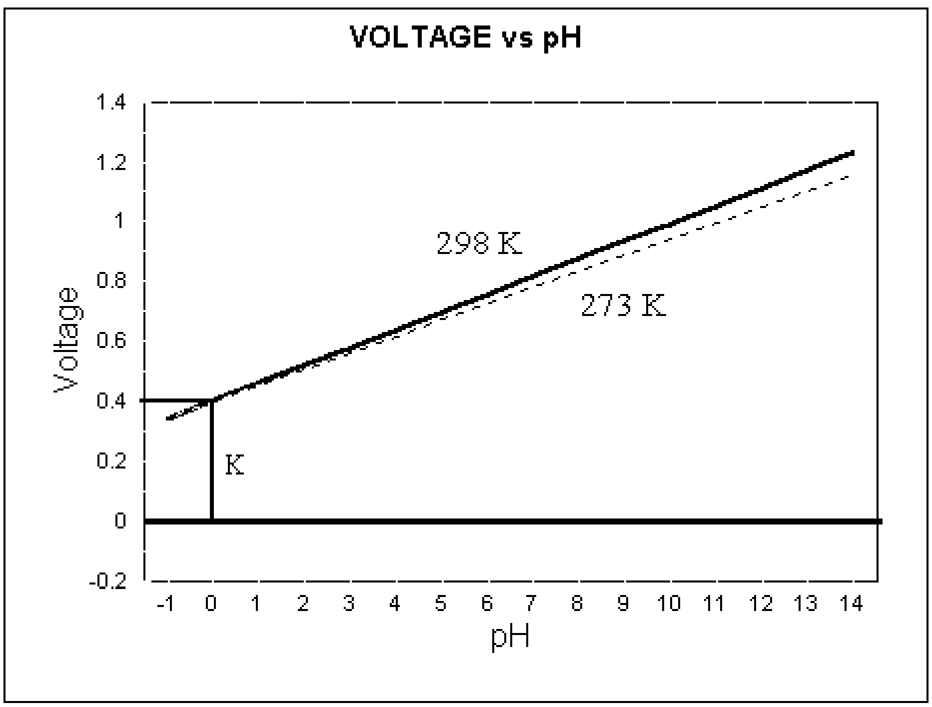


FIGURE 1

It has been found experimentally that a device can be constructed which makes use of this simple relationship between voltage and pH. The device includes a **glass electrode**, an object whose voltage responds to concentration differences on two sides of a very thin glass membrane. In the glass electrode, a reference electrode (often silver-silver chloride) establishes a reference against which the voltage of a glass membrane is measured. The outside surface of the glass membrane is immersed in a solution whose pH we wish to determine. The voltage difference between the glass electrode and the reference electrode has the linear relationship expressed in equation (4).

The glass electrode can be thought of as a complete electrochemical cell one half of which responds to the [H^+] in an aqueous solution with which it comes into contact. The details of the operation of the glass electrode are complex, and we do not address them at this time. While the glass electrode is normally used for pH measurements, other materials (including special glass formulations) are found to respond in a similar way to the concentration of other ions. Such electrodes are called ion-selective electrodes and they exist for a considerable range of ions.

Note that the **slope** of the linear relationship in equation (4) depends on, and *only* on, the (Absolute) temperature. Its value at 25°C (298 K) is .0592. The value of the constant K, i.e., the **intercept** of the linear equation when pH = 0 (i.e., [H^+] = 1.000) is a complex combination of constants. Do we need to concern ourselves with these constants? Not if we are willing to adopt the practice of calibrating the glass electrode.

Standard Buffers

If we know the (Absolute) temperature and we have a solution with a precisely known pH at that temperature, we can use the solution to establish the intercept of equation (5). Such solutions are called **standard buffers**. They are prepared in such a way as to resist changes in pH that may result from small additions of other substances (e.g., the carbon dioxide in the air) or even small amounts of water that may adhere to the electrode when it is placed in the buffer. ***Note that a single standard buffer suffices to fix the entire pH range***. For very precise pH measurements, a second buffer at a different pH can be used to verify the calibration.

Standard buffers are available commercially. These buffers are prepared under careful laboratory conditions and their variation in pH with temperature is known and displayed on their containers. One such standard buffer is made by preparing a solution of 0.05 mol of potassium hydrogen phthalate in 1 kg of water (0.05 **molal** rather than **molar**). The solution is prepared by using a known **weight** of water, not a known **volume**. This assures that differences in the density of water at different temperatures does not affect the composition of the solution. The pH of such a solution has been compared with primary standard electrochemical cells at a variety of temperatures. Over the typical laboratory temperature range (0 °C to 30 °C), the pH of such a solution varies by less than 0.3%. For work requiring greater precision, the values of the pH as a function of temperature are tabulated in standard reference works.

You may recall that potassium hydrogen phthalate has been used as a primary standard in other exercises involving the determination of the concentration of solutions of sodium hydroxide.

The pH Meter

What about the device that measures the voltage, i.e., the voltmeter - or pH meter - as it is called when it is used to measure pH? Such devices are sophisticated instruments that must have certain properties to insure the accuracy and precision of a measurement.

1.) The device must be able to measure the voltage with a minimal flow of current.

The flow of current would indicate that a reaction is occurring. If a reaction occurred, the concentrations of the species would change with time. In addition, the solution would heat up due to the flow of current through the solution.

2.) The device must be able to measure small voltage differences with adequate precision and accuracy.

At 25^oC, a change in pH of 1 unit (a ten-fold change in [H^+]) corresponds to a voltage change of only 0.0592 V, i.e., ~ 60 mV. In a typical home, or laboratory, environment, very large voltages (many kV) can develop due to static charges. The device needs to be shielded from the influence of such extraneous voltages.

3.) The device should be able to accommodate significant changes in temperature.

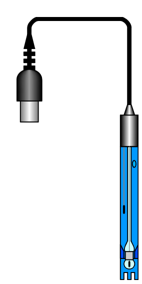
If the temperature changes significantly during the course of a series of pH measurements, an adjustment must be made, either manually or automatically.

Solid state devices provide a convenient way to implement all of the above concerns. With a combination of *hardware* and *software* features, a modern pH meter can measure voltages with a reproducibility of 0.1 mV. Temperature compensation can be incorporated by the inclusion of temperature measuring components (thermistors) in the device. These devices automatically compensate for changes in the ambient (laboratory) temperature. For very precise pH determinations, they accommodate a probe that can measure, and adjust for, changes in the temperature of the solution whose pH is being measured. In older pH meters, a manual control is provided to adjust the voltage reading for the temperature of the sample.

Modern pH meters also have the ability to convert voltage readings directly into pH readings (once a calibration at a known temperature has been conducted). This is accomplished through built-in programs.

Electronic circuits are sometimes unstable immediately after being activated (turned on). For that reason, the pH meter should be turned on for a few minutes before any measurements are made. Since some (albeit, extremely small) current flows during pH measurement, the meters are generally equipped with a STANDBY switch which permits the electronic circuits to maintain stability, but prevents current flow through the electrode.

Care and use of the Glass Electrode



The glass electrode is a delicate device. The glass membrane that makes it work is very thin and fragile. The electrode assembly is usually encased in a protective sheath to minimize the impact of mechanical jarring. The internal assembly may contain an additional reference electrode. Such electrodes are called combination glass electrodes.
The electrode must be conditioned for it to operate reliably. Conditioning means keeping the outer surface of the membrane in contact with water at all times. For that reason, the

electrode is usually kept in a beaker of water except during the time of measurement or during calibration.

The glass electrode can measure the pH only in that part of the solution with which it comes into direct contact. This suggests several practical concerns and consequent actions. The solution whose pH is desired must be **homogeneous**, i.e., it must have a uniform composition. Since a layer of liquid will adhere to the glass membrane surface after removal from a solution, it must be rinsed clean (but not dry) between use in different solutions. *The distilled water stream from a wash bottle usually suffices to rinse any remaining sample away*. However, if a drop of the rinse water adheres to the membrane surface, or to the protective sheath around the electrode, this can change the [H^+] in the vicinity of the electrode when it is next immersed. Therefore, the container with the solution whose pH is to be measured should be swirled to insure that the concentration in the vicinity of the electrode is the same as in the rest of the solution. The swirling is particularly important when continuous pH measurements are being made over a period of time, such as during a titration.

When pH measurements are finished, the glass electrode should be rinsed with distilled water and replaced in the water-filled storage beaker. The pH meter itself should be set to STANDBY.

Procedures:

The following constitute the steps that should be carried out in the use of the pH meter with a glass electrode.

Calibration:

1. Be sure that the glass electrode is immersed in water in the storage container.

2. If it is not already on, turn on the pH meter and be sure that it is in STANDBY mode.

3. Examine the assembly that adjusts the position of the electrode to determine the way it functions.

4. Obtain a beaker with standard buffer. Place it in a position that will permit the electrode to be conveniently placed in the buffer solution.

5. Raise the electrode out of the storage water. Rinse it with a stream from a wash bottle containing distilled water. If a significant amount of water adheres to the electrode casing, carefully, without wiping, wick the water away with a paper towel. **Do not wipe the glass membrane**.

6. Remove the storage beaker and replace it with the beaker containing the buffer. Lower the electrode into the buffer making sure that the lower section is fully immersed
7. Turn the pH meter control to the "pH" position.

For older type meters, adjust the temperature control knob to reflect the laboratory temperature. (It is assumed that the buffer solution is at room temperature.) Adjust the calibration knob until the pH reading is equal to the pH of the buffer solution at the appropriate temperature.

For newer meters, press the standardization key. A menu of options will be displayed. Choose the appropriate option depending on whether this is a new standardization or an update.

8. Swirl the beaker gently to be sure that the buffer solution is homogeneous and that the glass electrode comes into contact with a portion of the homogeneous solution.

9. Raise the electrode out of the buffer solution. Replace the beaker containing the buffer with the storage beaker. Rinse the electrode with a wash bottle and immerse the electrode in the storage beaker liquid.

10. Restore the pH meter status to STANDBY

Making a single pH determination

Follow the same steps as in the standardization with the exception that the beaker now contains the solution to be measured and that in Step 7, no adjustment should be made. If you are using an older type pH meter, be sure to note if the temperature has changed significantly since the standardization. If so, the temperature knob may need adjustment. For the newer meters, press the MEASURE/MONITOR key until the meter is in the MEASURE mode and the "key" icon is on. Wait until the measurement is complete (an S appears in the lower right hand corner of the display). You may wish to verify the reading by pressing the pH key to obtain another reading.

Monitoring pH - Titration Curves

The pH meter can be used to monitor the change in pH when a reaction occurs. In a pH titration, the independent variable is the quantity of a reagent added to the reaction container. Again, the procedure is identical to that in the standardization or a single measurement, with the following exceptions. The electrode is placed in the container into which the titrant is being delivered and remains there for the entire titration. The importance of swirling the reaction container cannot be overemphasized. The pH meter can only see that part of the solution with which it is in contact. If reagent is being added at a remote place in the solution, **the pH can vary by several units** at that location until the reaction solution is stirred to insure uniform concentrations of all species. For the new pH meters, in step 7, be sure the meter is in the MONITOR mode rather than the MEASURE mode (the "key" icon is off). In every instance of use of a pH meter, be sure that the meter and electrode are restored to the proper status and condition when you have completed the measurements.

SUPL-006 Pre-Laboratory Assignment

Name ______________________________ Section ______ Date ______

1. From the Nernst equation as it applies to the pH electrode, Equation (4), calculate the difference in pH corresponding to a difference in voltage of 0.1 mV (0.0001 V) at 20^{o}C.

2. From the same equation, calculate the error in a pH measurement caused by an error of 10 C^o in the temperature at 20^{o}C. E.g., if the pH meter is set at 30^{o}C with an actual temperature of 20^{o}C.

3. How must the glass electrode be stored between uses of the pH meter?

4. Why must the pH meter be left on standby when it is not being used to measure pH?

5. The voltage measured by a pH meter is linear with pH. The linear relationship is characterized by a *slope* and *intercept*. In the calibration of a pH meter with a glass electrode, which characteristic, slope or intercept, is affected by an adjustment of temperature?

6. What feature of buffers makes them appropriate for use in standardization of pH meters?