Chapter 14: Potentiometry

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Converting Voltages from one Reference Scale to Another

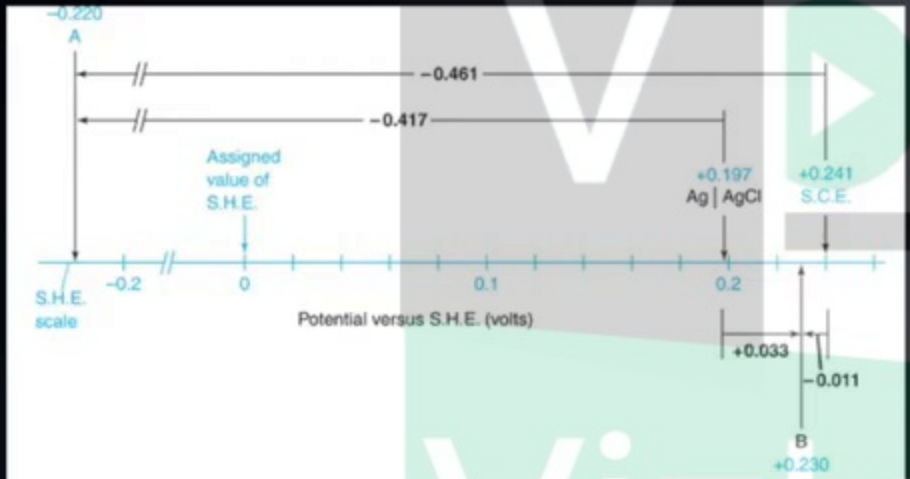

FIGURE 14-6 A diagram that helps us convert electrode potential between different reference scales.

Harris, *Quantitative Chemical Analysis*, 8e

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Steps:

1. Identify reference values
2. Convert to S.H.E.
3. Convert to desired scale

Example:

A sample reading -0.047V vs Ag|AgCl

Vs S.H.E. E= -.244V

Vs S.C.E. E= -0.003V

Using a Silver Electrode

To measure a halide:

- K_{sp} relates $[Ag^+]$ to the halide concentration if there is a solid silver halide in solution

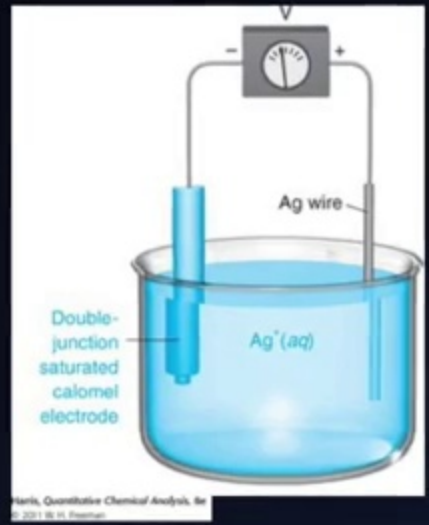
Example:

AgBr

$[Ag^+]=K_{sp}\backslash[Br^-]$

$E=0.558+0.05916*\log\ [Ag^+]$

$$E=0.558+0.05916*\log\left(\frac{K_{sp}}{[Br^-]}\right)$$



Advantages and Disadvantages of I.S.E..

ADVANTAGES

- Wide range with linear response to log $\mathcal{A}$
- Nondestructive
- Non-contaminating
- Short response time
- Unaffected by color or turbidity

DISADVANTAGES

- Precision$\leq$ 1%
- Electrodes can be fouled by organic solutes
- Certain ions interfere with or poison certain electrodes
- Some have limited life and/or are fragile

Glass pH electrode

How does it work?

- The pH sensitive glass surfaces form a hydrated gel in water in which metal diffuses out and H^+ diffuses in
- An ion-exchange equilibrium occurs
- The porous plug serves as the salt bridge
- The ideal pH electrode potential changes by 59.16 mV for every pH unit change of analyte activity at 25°C.

What is being calibrated during calibration?

- The voltage measurement with the electrode in each buffer is tested to make a calibration line
  - Using $\geq$ 2 buffers is essential as a result

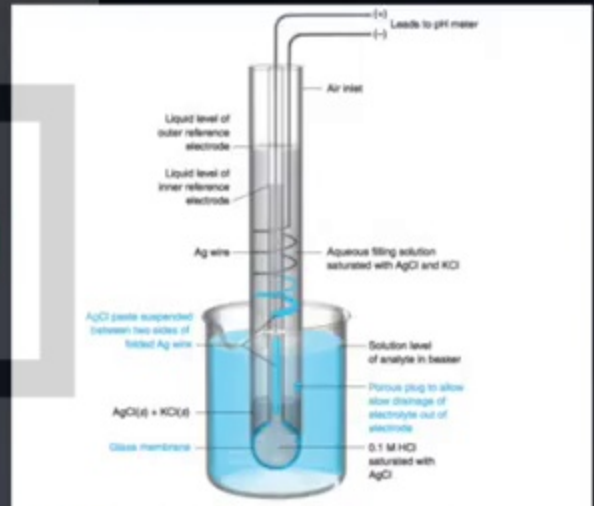


FIGURE 14-11 Diagram of a glass combination electrode with a silver-silver chloride reference electrode. The glass electrode is immersed in a solution of unknown pH so that the porous plug on the lower right is below the surface of the liquid. The two Ag | AgCl electrodes measure the voltage across the glass membrane.

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