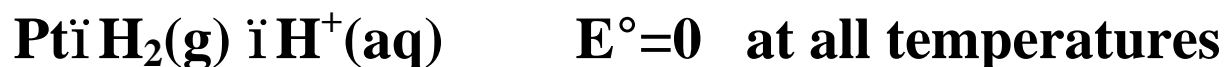

Electrochemistry

Special Electrode Applications

Reduction Potentials

- A. It is only possible to measure the overall potential of a cell, not an individual contribution from an electrode. It is convenient to define one electrode as having a zero potential so that values can be tabulated for all others.
- B. The standard hydrogen electrode (SHE) is defined as having a zero potential for either ox or reduction.



C. The total cell potential is then defined as

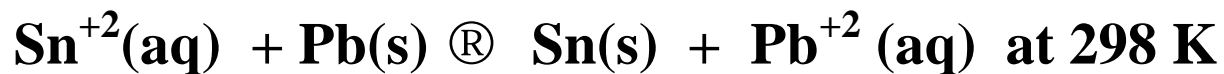
$$\text{red potential} + \text{ox potential} = \text{cell potential}$$

- 1. It is possible to use the SHE as 1 electrode and any other half cell rxn as the other electrode. By observing polarity and measuring the voltage of the system, ox or red potentials for all half-cells can be measured.**
- 2. Since the reduction potential is equal but of opposite sign to the oxidation potential a chart of either ox or red potentials can be constructed. It is now customary to report cell potentials as reduction potentials. This table can be used to predict the E° of any combination of half-cells.**
- 3. If the sum of the ox and red potentials is positive the rxn is spontaneous.**

Examples

a. Can Zn displace Cu from solution when the ions are of unit activity?

b. What is the equil constant for



D. The electrochemical series

By ranking the reduction potentials in decreasing order we can predict whether a given rxn will occur. Since a rxn is spontaneous if $E^\circ > 0$ then a rxn underneath (or lower E°) will reduce a rxn above.

E. Solubility

We can predict the solubility based on the value of E° .

Example : What is the K_{sp} of Hg_2Cl_2 at 298 K?

Special Electrode Applications

A. pH and the hydrogen electrode

$$E_{(\text{H}^+ \text{® H}_2)} = E^\circ_{(\text{H}^+ \text{® H}_2)} - \frac{RT}{nF} (\ln Q)$$

$$\text{Since } E^\circ = 0 \text{ then } E_{(\text{H}^+ \text{® H}_2)} = -\frac{RT}{2F} (\ln a_{\text{H}_2}/a_{\text{H}^+}^2)$$

$$\text{or } E_{(\text{H}^+ \text{® H}_2)} = +\frac{RT}{F} (\ln a_{\text{H}^+} / a_{\text{H}_2}^{1/2})$$

$$\text{Also } \ln a_{\text{H}^+} = 2.303 \log_{10} a_{\text{H}^+} = -2.303 \text{ pH}$$

$$\text{This gives } E_{(\text{H}^+ \text{® H}_2)} = -2.303 \frac{RT}{F} (\text{pH})$$

$$\text{At } 25^\circ \text{ C} \quad \frac{RT}{F} = 0.02569 \text{ V so finally}$$

$$E_{(\text{H}^+ \text{® H}_2)} = -0.05916 \text{ V (pH)}$$

Each change in pH changes the potential by 59.16 mV.

B. Measuring pH

- 1. Typically a saturated calomel (Hg_2Cl_2) electrode is used opposite a hydrogen electrode. At the hydrogen electrode**

$$\mathbf{E (\text{H}^+/\text{H}_2) = -0.05916 \text{ pH}}$$

$$\mathbf{\text{so } E = -0.05916 \text{ pH} + E_{\text{ox}} (\text{calomel})}$$

This allows the calculation of pH.

- 2. The hydrogen electrode is difficult to assemble and is usually replaced by the glass electrode - an electrode filled with a phosphate buffer and saturated AgCl. It has a convenient $E = 0$ at $\text{pH} = 7$. This glass electrode is sensitive to H ion activity by way of the action of Na and Li ions in the glass. The glass itself is not permeable to H ions.**

C. Electrochemical titrations

1. Potentiometric

A redox rxn can be monitored by using a platinum electrode in the mixture opposite another reference electrode. As in pH titrations there is a sharp change of cell potential at the equiv. pt.

2. Coulometric

A constant current is used to produce a specific substance at an electrode by electrolysis. This substance then reacts chemically in solution to produce some measurable change.

3. Conductometric

The conductance of a solution is monitored as a rxn progresses. The equiv. pt can be determined from the change in slope.