

Electrochemistry, Oxidation Reduction, Metal corrosion and corrosion protection

1、 Purpose

- (1) Know the original battery and the electrode potential;
- (2) Apply electrode potential to determine the relative strength of the material redox capacity;
- (3) Understand the method of determining the potential of the galvanic potential and the potential of the electrode and the factors that affect the electrode potential.
- (4) Know the basic principles of metal corrosion
- (5) Understand the basic principles and methods of preventing metal corrosion

2、 Principle

(1) The relative magnitude of the electrode potential can be a quantitative measure of the relative strength of the oxidized or reductant species in the aqueous solution. The higher the potential value of the electrode pair is, the stronger the oxidation ability of the oxidized material, and the weaker the reduction ability of the corresponding reducing substance; and vice versa.

The Nernst equation reflects the relationship between the ion concentration in the electrode reaction and the electrode potential:

$$E_{(electrode)} = E^{\theta}_{(electrode)} + \frac{RT}{ZF} \ln \frac{\frac{c(ox)}{c^{\theta}}}{\frac{c(re)}{c^{\theta}}}$$

When $T = 298.15K$, the R , F value into the above equation, Nernst formula can be written:

$$E_{(electrode)} = E^{\theta}_{(electrode)} + \frac{0.0592V}{z} \lg \frac{\frac{c(ox)}{c^{\theta}}}{\frac{c(re)}{c^{\theta}}}$$

The effect of pH on the electrode potential and oxidation-reduction reaction must also be considered for an H^+ or OH^- electrode pair reaction. For example, $K_2Cr_2O_7$ exhibits strong oxidizing properties in an acidic medium and can be reduced to Cr^{3+} , but it is difficult to exhibit strong oxidizing properties in a neutral solution.

The original battery consists of positive and negative electrodes, the size of its electromotive E value and the composition of the positive electrode positive electrode potential E_+ and negative electrode potential E_- value of the size: $E = E_+ - E_-$.

The primary cell electromotive force E can be measured experimentally. In this experiment, the electromotive force of primary cell was measured by pH meter. (Since the internal resistance of the acidity meter is extremely large, the current intensity in the loop is extremely small when measuring, the internal voltage drop of the primary battery is approximately zero, and the measured external voltage drop can be approximated as the electromotive force of the primary battery.)

(2) When the metal is in contact with the surrounding medium, the damage caused by the chemical action or the electrochemical action is called corrosion of the metal. In a corroded battery, usually the more active metal is the anode, and the oxidation reaction is corroded; the less active metal or other substance is the cathode, and the oxidizing ions or molecules in the medium acquire electrons on the surface to undergo reduction reaction. It is not corroded by itself.

3、Materials and Apparatus

3.1 Apparatus: Acidity meter, zinc electrode, copper electrode, calomel electrode, carbon rod, salt bridge, 2 beaker (100 mL), 1 beaker (50 mL), glass rod, surface dish, filter paper.

Materials:

H_2SO_4 (1 mol L^{-1} , 3 mol L^{-1}),

NaOH (6 mol L^{-1}),

FeCl_3 (0.1 mol L^{-1}),

KBr (0.1 mol L^{-1}),

KI (0.1 mol L^{-1}),

CuSO_4 (0.1000 mol L^{-1}),

I_2 H_2O ,

Cl_2 H_2O ,

Na_2SO_3 (0.1 mol L^{-1})

$\text{NH}_3 \cdot \text{H}_2\text{O}$ (6 mol L^{-1}),

FeSO_4 (0.1 mol L^{-1}),

KMnO_4 (0.1 mol L^{-1}),

KCl (saturation),

ZnSO_4 (0.1 mol L^{-1}),

Starch solution,

$\text{Br} \text{H}_2\text{O}$,

CCl_4 ,

3.2 Apparatus: Test tube, surface dish, beaker, salt bridge, milliamperemeter (or voltmeter), iron electrode, copper electrode, dropper, filter paper

Materials: HCl (0.1 mol L^{-1} , 2 mol L^{-1}), HNO_3 (6 mol L^{-1}), $\text{K}_3[\text{Fe}(\text{CN})_6]$ (0.1 mol L^{-1}), NaCl (5%), O-phenanthroline solution (0.1%), phenolphthalein (1%), dithizone solution, hexamethylenetetramine solution, zinc sheet, copper wire, iron sheet, nail

4、Procedure

(1) The relative strength of the oxidant or reducing agent is compared using the electrode potential

① According to laboratory prepared reagents: H_2SO_4 (1 mol L^{-1}), CCl_4 (as an extractant), KBr (0.1 mol L^{-1}), KI (0.1 mol L^{-1}), FeCl_3 (0.1 mol L^{-1}), KMnO_4 (0.1 mol L^{-1}). Design of experimental proof the reducing power of I^- is greater than the reducing ability of Br^- .

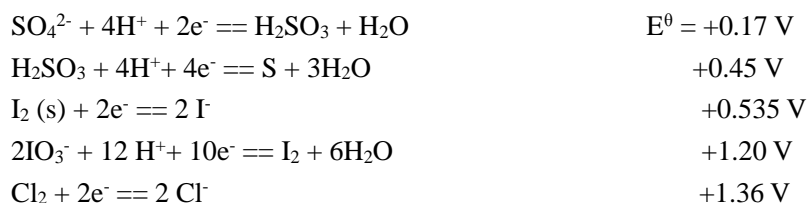
② According to laboratory prepared reagents: I_2 H_2O , $\text{Br} \text{H}_2\text{O}$, CCl_4 , FeSO_4 (0.1 mol L^{-1}), SnCl_2 (0.1 mol L^{-1}). Design of experimental proof the oxidation capacity of Br_2 is greater than that of I_2 .

Write the above reaction phenomenon and related reaction formula, and summarize the relationship between the strength of oxidant and reducing agent and $E^\theta_{(\text{electrode})}$.

(2) The electrode potential is used to explain the following phenomena

Add 2 drops of KI (0.1 mol L^{-1}) solution to the tube then add 2 mL H_2O , 2 drops starch solution, a few drops Cl_2 H_2O , observed after the phenomenon of shock. The solution was divided into two parts, one by adding Cl_2 H_2O until the color of the solution changed; the other by adding Na_2SO_3 solution, observe and record the phenomenon.

Explain the phenomenon according to the following electrode potential, and write the reaction equation. Describe the role of I_2 in both reactions.



(3) Primary battery

Take two 50 mL beakers, add 30 mL of $ZnSO_4$ to a beaker, insert the zinc piece with copper wire, insert 30 mL $CuSO_4$ solution into another beaker, insert the copper sheet with copper wire, The two beakers in the solution connected to form the original battery.

Take a piece of filter paper on the surface of the dish and add NaCl solution, then add 1 drop of phenolphthalein indicator. The two ends of the copper wire on the two poles of the primary battery are separated by a distance and are in contact with the filter paper. After a few minutes, observe the change in color near the wire contact points on the filter paper.

Try to write out the reaction on the two electrodes of the electrolytic cell and explain the reason for the color change near the contact point of the wire.

(4) Determination of primary cell electromotive force

Install the primary battery as shown below:

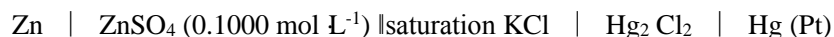


The electromotive force was measured twice with a pH meter, and the data were recorded separately, and the average value is the electromotive force value of the Cu-Zn galvanic cell.

(5) Determination of Electrode Potential and Factors Influencing Electrode Potential

① Determination of Zn^{2+} / Zn Electrode Potential

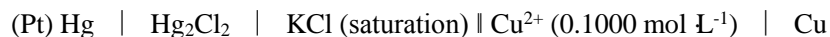
Install the primary battery as shown below:



The Zn sheet and saturated calomel electrode were inserted into the $ZnSO_4$ ($0.1000 \text{ mol L}^{-1}$) solution to form a Zn - Hg primary cell. The electromotive force was measured, the measured value and the room temperature t were recorded. The electrode potential of Zn^{2+} / Zn was then calculated. Electrode potential of saturated calomel electrode: $E_{\text{Calomel}} = 0.2410 \text{ V} - 0.00065 (t - 25) \text{ V}$

② Determination of Cu^{2+} / Cu Electrode Potential

Install the primary battery as shown below:



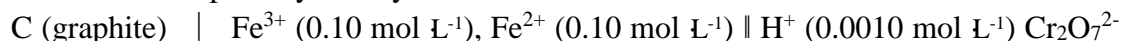
The Cu sheet and saturated calomel electrode were inserted into $CuSO_4$ ($0.1000 \text{ mol L}^{-1}$) solution to form an Hg-Cu primary cell. The electromotive force was measured, the measured value and the room temperature t were recorded. The electrode potential of Cu^{2+} / Cu was then calculated.

③ Influences of concentration on the electrode potential

The calomel electrode was removed and $NH_3 \cdot H_2O$ (6 mol L^{-1}) was slowly added to the $CuSO_4$ solution and stirred until the precipitate formed and dissolved. (Generate a dark blue solution: $Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$) The electromotive force at this time was measured, and the electrode potential of Cu^{2+} / Cu was calculated.

④ Effect of solution pH on electrode potential

Install the primary battery as shown below:



(0.10 mol L⁻¹), Cr³⁺ (0.10 mol L⁻¹) | C (graphite)

The electromotive force of the primary battery was measured by using the filter paper after soaking in saturated KCl solution. Then, the pH value of Cr₂O₇²⁻ solution was adjusted to 1 with 3 mol L⁻¹ H₂SO₄ solution. And the pH value of Cr₂O₇²⁻ solution was adjusted to 7 by 6 mol L⁻¹ NaOH solution, and the electromotive force of galvanic cell was measured.

According to the measured results, the electrode potential values of Cr₂O₇²⁻ / Cr³⁺ in different media were calculated in different media.

- (6) Corrosion of primary battery formation: Take a small piece of pure zinc and place it in a test tube containing 2-3 mL of 0.1 HCl (0.1 mol L⁻¹) solution to observe the phenomenon. Then take a copper wire into the test tube and contact the zinc plate to observe the phenomenon (note where the bubble occurs). Write the reaction formula and explain it.
- (7) Differential gas corrosion: Drop 1-2 drops of the solution (1 mL NaCl + 2 drops of K₃ [Fe(CN)₆] + 2 drops of 1% phenolphthalein solution) onto the iron piece polished with sandpaper, observe the phenomenon, let stand for 3-5 min, then carefully observe the color produced by the contact area of the droplet. Why are these phenomena happening? Write about the reaction formula.
- (8) Cathodic protection: Place a piece of filter paper on the surface dish and wet it with your own prepared etching solution. The two nails were placed on the wet filter paper at a distance and connected to the positive and negative electrodes of the Cu-Zn primary battery. After standing for a while, observe what is happening and explain it.

5、Question

- (1) How to compare the oxidative or reductive strength of the following substances by experiment?

I₂, Br₂, Cl₂ and Fe³⁺; Cl⁻, Br⁻, I⁻ and Fe²⁺

- (2) How to determine the positive and negative of the original battery? When measuring the electromotive force of the primary battery, what happens if the positive and negative terminals are reversed? How to deal with?
- (3) What is the effect of the acidity of the medium on the electrode potential of Cr₂O₇²⁻ / Cr³⁺?
- (4) Why are metals containing impurities more susceptible to corrosion than pure metals?
- (5) Briefly describe the general principles of preventing metal corrosion.
- (6) When OH⁻, S²⁻ or NH₃ • H₂O are added to the positive or negative electrode respectively in the copper and zinc galvanic cell, how will the electromotive force of the galvanic cell change?