

第九章 可逆电池的电动势及其应用

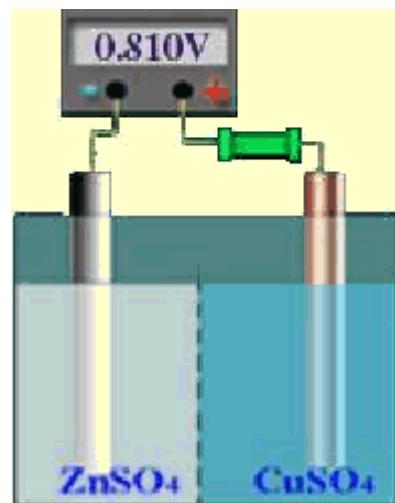
9.1 可逆电池和可逆电极

一、可逆电池

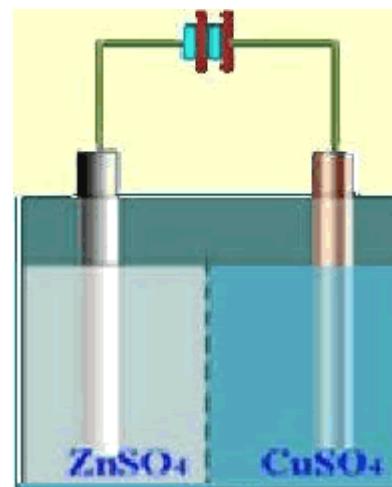
原电池



电解池



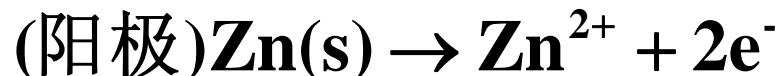
化学反应可逆



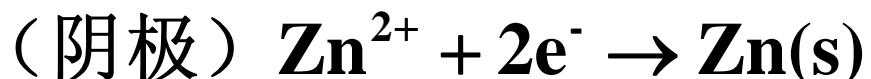
能量变化可逆



作为原电池



作为电解池



二、可逆电极和电极反应

1、第一类电极

金属与其阳离子组成的电极

氢电极

氧电极

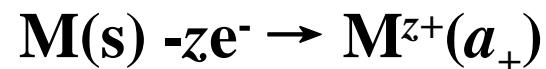
卤素电极

汞齐电极

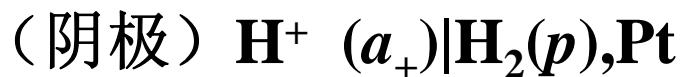
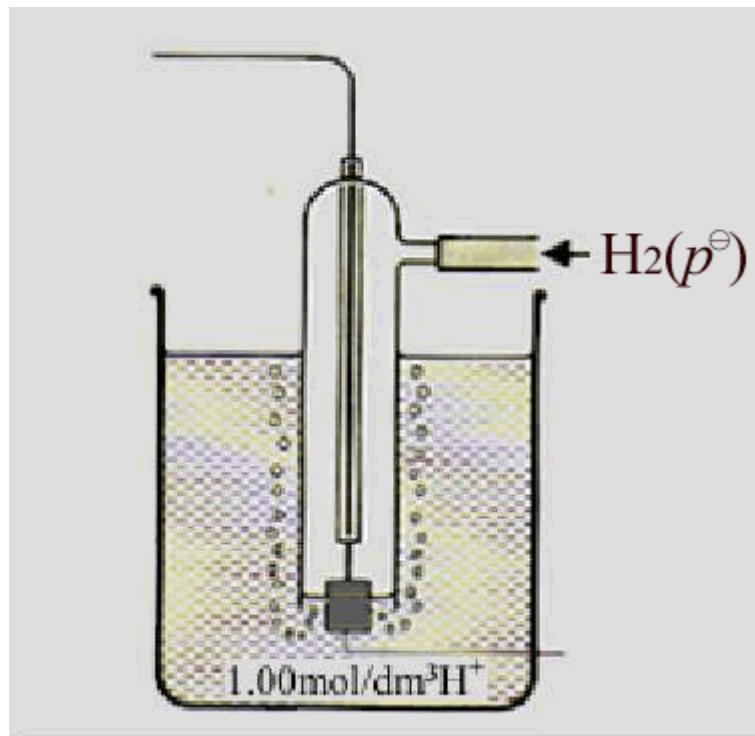
- 金属与其阳离子组成的电极

(阴极) $M^{z+}(a_+) | M(s)$

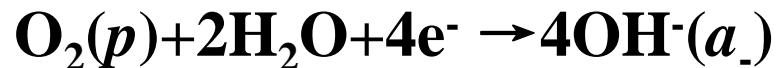
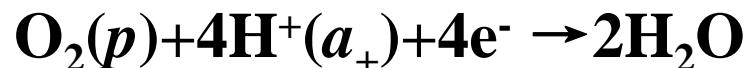
(阳极) $M(s) | M^{z+}(a_+)$



- 氢电极



- 阳电极



- 卤素电极



- 汞齐电极



2、第二类电极

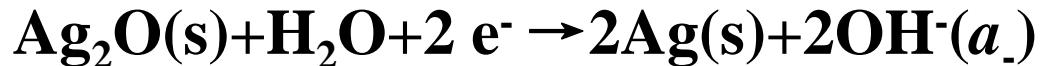
金属-难溶盐及其阴离子组成的电极

金属-氧化物电极

- 金属-难溶盐及其阴离子组成的电极



- 金属-氧化物电极



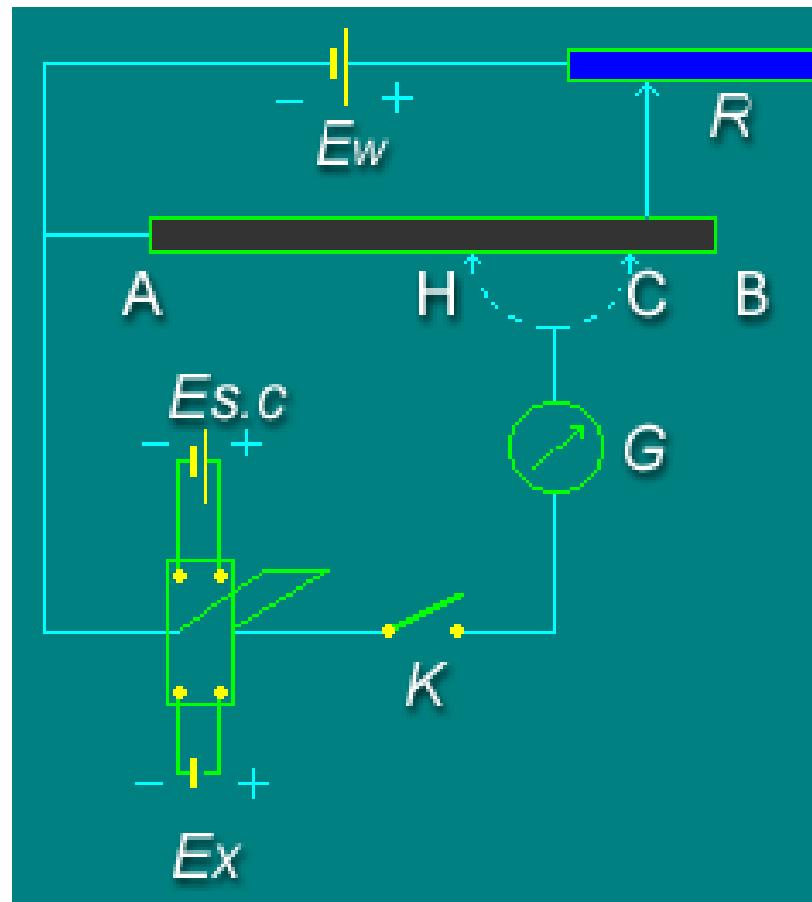
3、第三类电极

氧化-还原电极



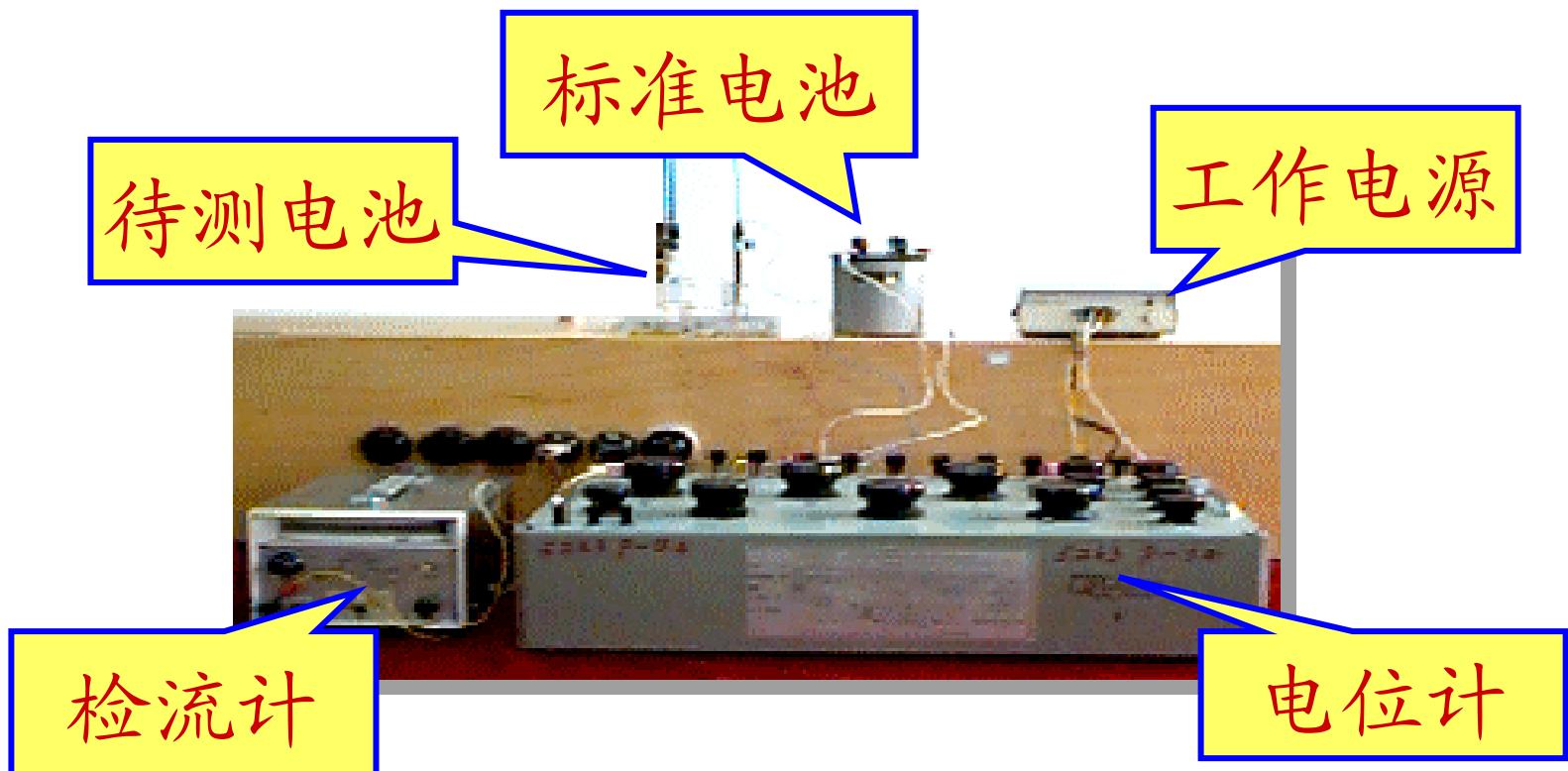
9.2电动势的测定

一、对消法测电动势 1、原理

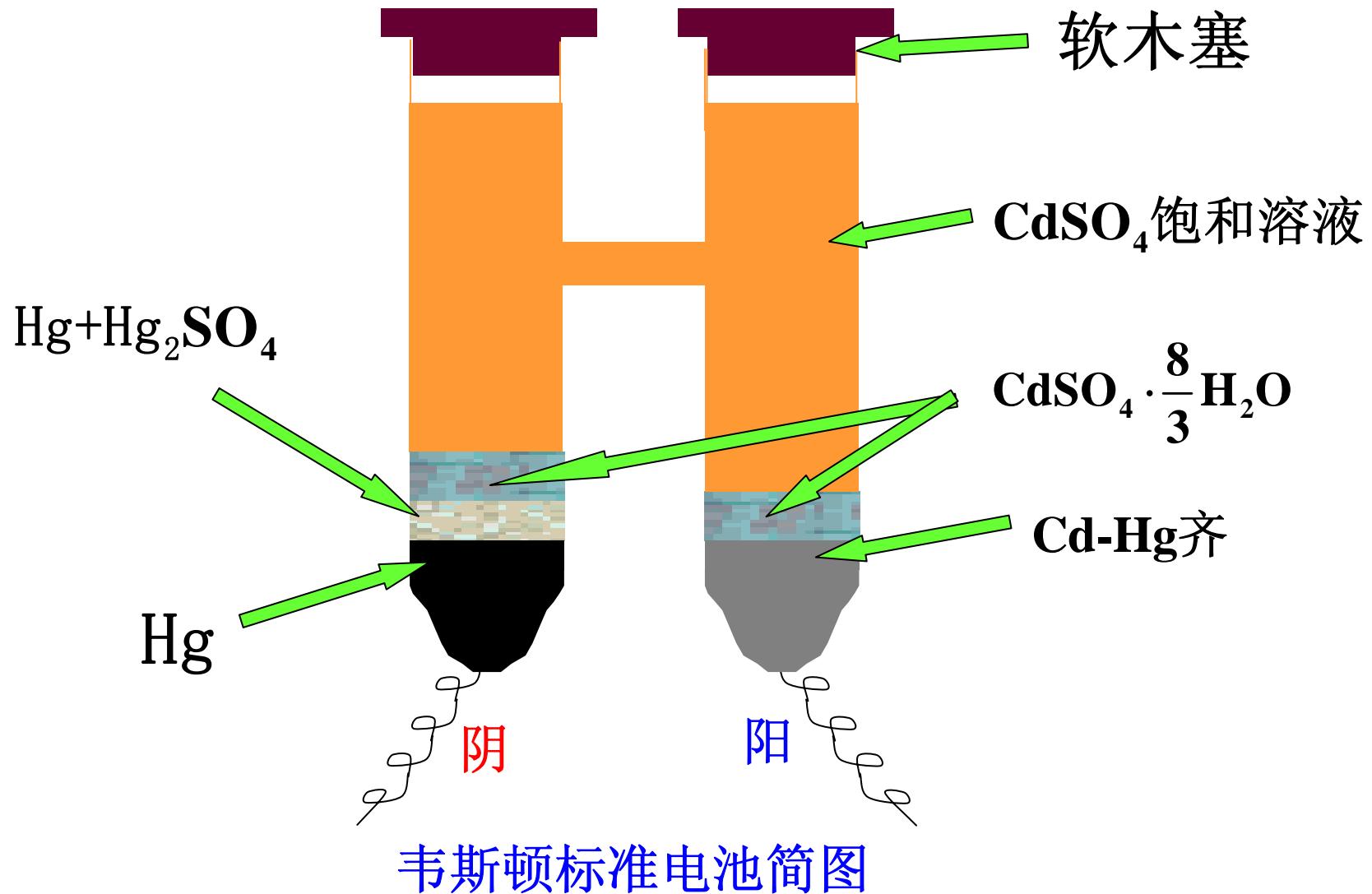


$$E_x = E_{s.c.} \cdot \frac{AC}{AH}$$

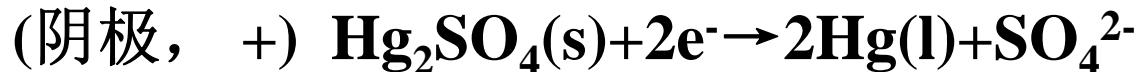
2、实验装置图



3、标准电池



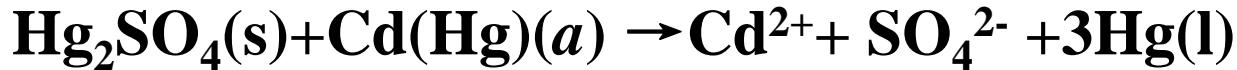
电池反应:



净反应:



或



标准电池电动势与温度的关系

$$E_T/\text{V} = 1.01845 - 4.05 \times 10^{-5}(T/\text{K} - 293.15) - 9.5 \times 10^{-7}(T/\text{K} - 293.15)^2 + 1 \times 10^{-8}(T/\text{K} - 293.15)^3$$

通常要把标准电池恒温、恒湿存放，使电动势稳定

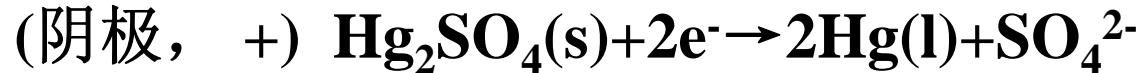
9.3 可逆电池的书写方法及电动势的取号

一、可逆电池的书写方法

- 1、左边的电极为负极，起氧化作用；
右边的电极为正极，起还原作用。
- 2、“|”表示不同物相界面，有界面电势存在
- 3、“||”表示盐桥，表示溶液与溶液之间的接界电势降到可以忽略不计
- 4、要注明温度和压力，（不注明一般指298.15 K和标准压力）；要标明电极的物态，气体要注明压力；
电解质溶液要注明活度或浓度
- 5、电池电动势用右边正极的还原电极电势减右边负极的还原电极电势



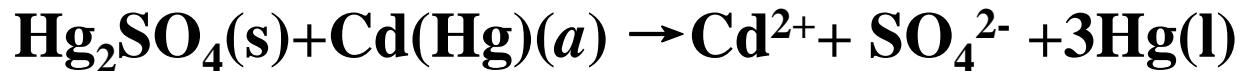
电池反应：



净反应：



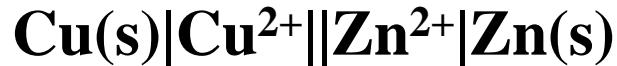
或



二、可逆电池电动势的取号

自发电池 $E > 0$

非自发电池 $E < 0$



9.4 可逆电池的热力学

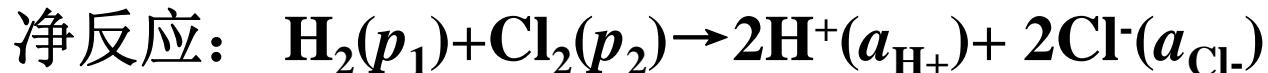
- 电化学与热力学联系的桥梁



$$(\Delta_r G)_{T,p,R} = W_{f,\max} = -nEF$$

$$(\Delta_r G_m)_{T,p,R} = -\frac{nEF}{\xi} = -zEF$$

一、Nernst方程



$$\Delta_r G_m = \Delta_r G_m^\ominus + RT \ln \frac{a_{\text{H}^+}^2 a_{\text{Cl}^-}^2}{a_{\text{H}_2} a_{\text{Cl}_2}}$$

$$E_1 = E^\ominus - \frac{RT}{zF} \ln \frac{a_{\text{H}^+}^2 a_{\text{Cl}^-}^2}{a_{\text{H}_2} a_{\text{Cl}_2}}$$

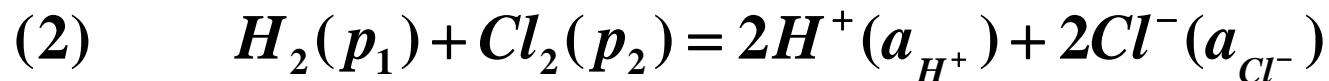
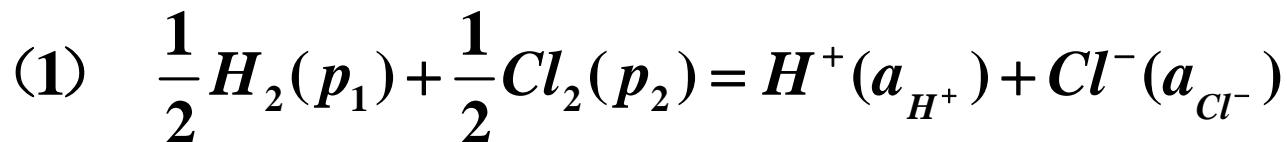
二、由标准电动势 E^\ominus 求电池反应的平衡常数

$$\Delta_r G_m^\ominus = -RT \ln K^\ominus$$

$$E^\ominus = \frac{RT}{zF} \ln K^\ominus$$

$$\Delta_r G_m^\ominus = -zE^\ominus F$$

某电池的电池反应可用如下两个方程表示，分别写出其对应的 $\Delta_r G_m^\ominus$ ， K_a^θ 和 E 的表示式，并找出两组物理量之间的关系



$$\text{解: } \Delta_r G_m(1) = \Delta_r G^\ominus(1) + RT \ln \frac{a_{H^+} a_{Cl^-}}{a_{H_2}^{1/2} a_{Cl_2}^{1/2}}$$

$$E_1 = E_1^\ominus - \frac{RT}{F} \ln \frac{a_{H^+} a_{Cl^-}}{a_{H_2}^{1/2} a_{Cl_2}^{1/2}}$$

$$\Delta_r G_m(2) = \Delta_r G^\ominus(2) + RT \ln \frac{a_{H^+}^2 a_{Cl^-}^2}{a_{H_2} a_{Cl_2}}$$

$$E_2 = E_2^\ominus - \frac{RT}{2F} \ln \frac{a_{H^+}^2 a_{Cl^-}^2}{a_{H_2} a_{Cl_2}}$$

$$\Delta_r G_m(1) = \frac{1}{2} \Delta_r G_m(2)$$

$$\Delta_r G^\ominus(1) = \frac{1}{2} \Delta_r G^\ominus(2)$$

$$E_1^\ominus = E_2^\ominus, E_1 = E_2$$

$$\Delta_r G^\ominus(1) = -RT \ln K_a^\ominus(1)$$

$$\Delta_r G^\ominus(2) = -RT \ln K_a^\ominus(2)$$

$$K_a^\ominus(1) = \sqrt{K_a^\ominus(2)}$$

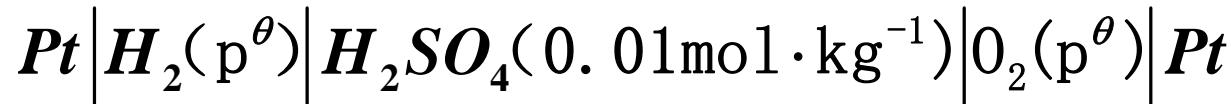
三、由电动势E及其温度系数求反应的 Δ_rH_m 和 Δ_rS_m

$$\Delta_r S_m = zF \left(\frac{\partial E}{\partial T} \right)_p$$

$$\Delta_r H_m = \Delta_r G_m + T \Delta_r S_m = -zEF + zFT \left(\frac{\partial E}{\partial T} \right)_p$$

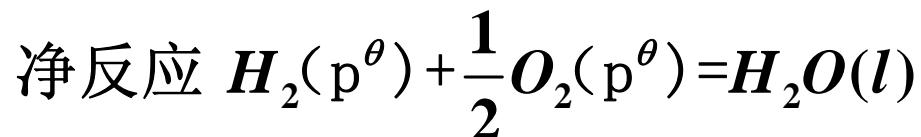
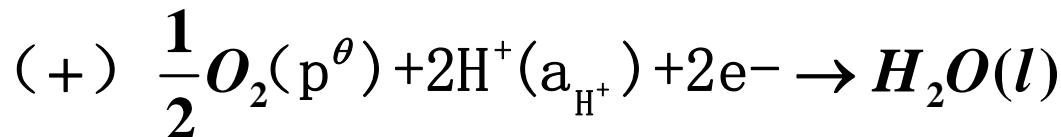
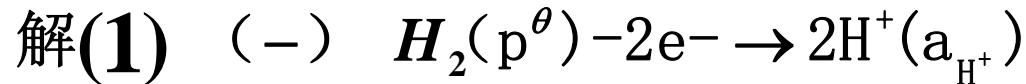
$$Q_R = T \Delta_r S_m = zFT \left(\frac{\partial E}{\partial T} \right)_p$$

(1) 求298K时，下列电池的温度系数：



已知该电池的电动势 $E = 1.228V$, $H_2O(l)$ 的标准摩尔生成焓 $\Delta_f H_m^\theta = -285.83\text{kJ}\cdot\text{mol}^{-1}$

(2) 求273K时该电池的电动势 E , 设在273 ~ 298K之间, $H_2O(l)$ 的生成焓不随温度而改变, 电动势随温度的变化率是均匀的。



$$\Delta_r G_m = -zEF = -2 \times 1.228 \times 96500 = -237.0 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r G_m = \Delta_r H_m - T\Delta_r S_m = \Delta_r H_m - zFT\left(\frac{\partial E}{\partial T}\right)_p$$

$$\left(\frac{\partial E}{\partial T}\right)_p = \frac{\Delta_r H_m - \Delta_r G_m}{zFT} = \frac{(-285.83 + 237.0) \times 10^3}{2 \times 96500 \times 298} = -8.49 \times 10^{-4} V \cdot k^{-1}$$

$$(2) \left(\frac{\partial E}{\partial T}\right)_p \approx \frac{\Delta E}{\Delta T} = \frac{E_{(298)} - E_{(273)}}{298 - 273} = -8.49 \times 10^{-4} V \cdot k^{-1}$$

$$E_{(273)} = 1.249 V$$

8.5 电动势产生的机理

电极与溶液间的电位差

电动势的值

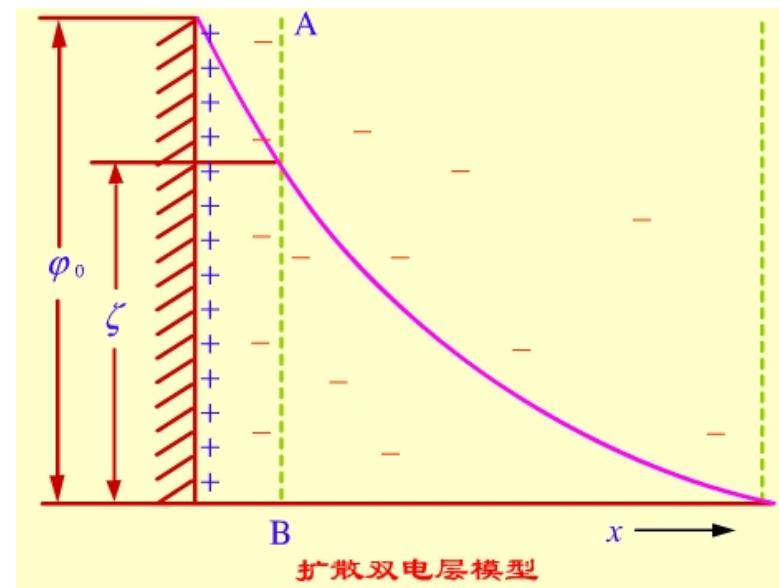
准确断路

电动势产生的机理

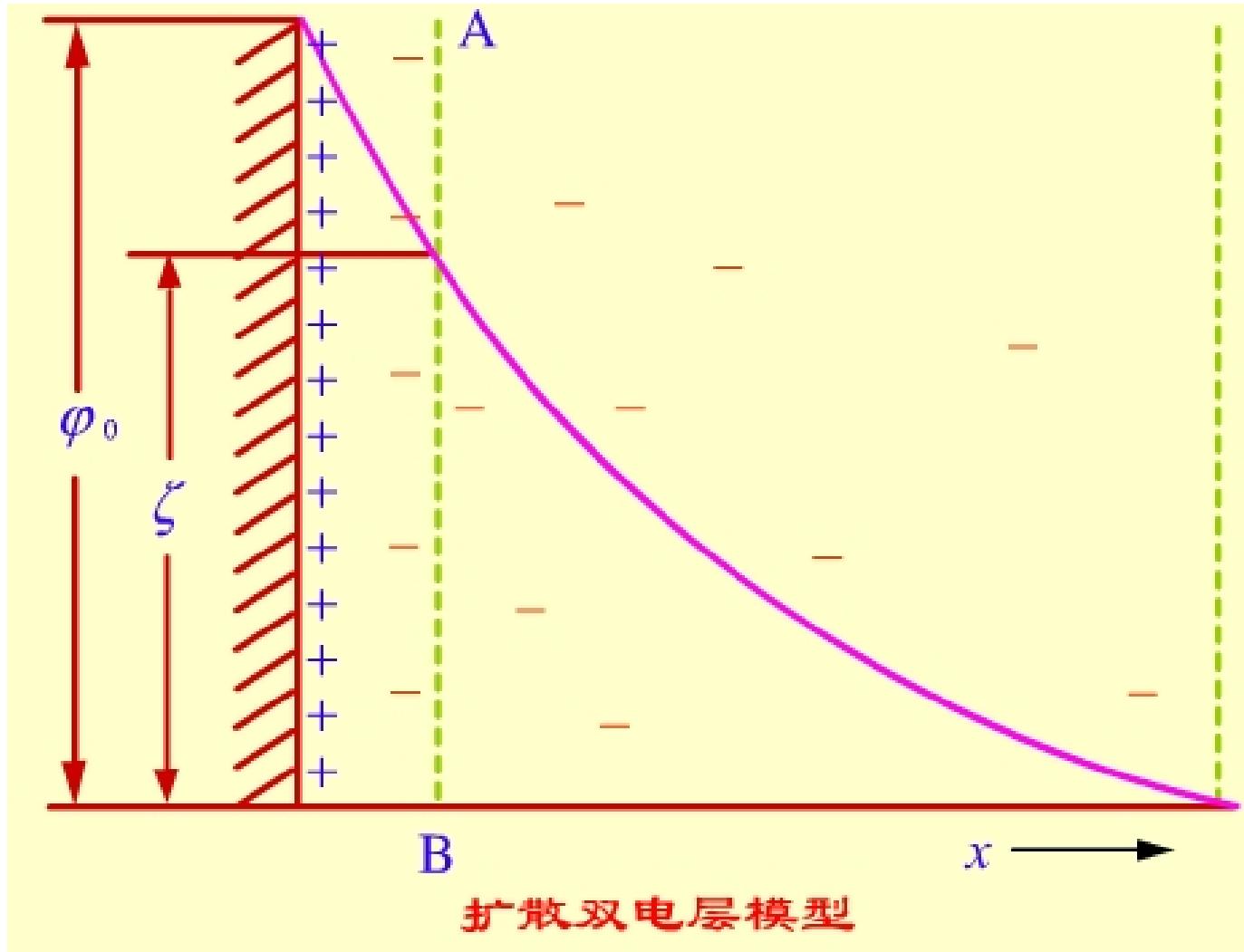
界面电势差

在金属与溶液的界面上，由于正、负离子静电吸引和热运动两种效应的结果，溶液中的反离子只有一部分紧密地排在固体表面附近，相距约一、二个离子厚度称为**紧密层**；

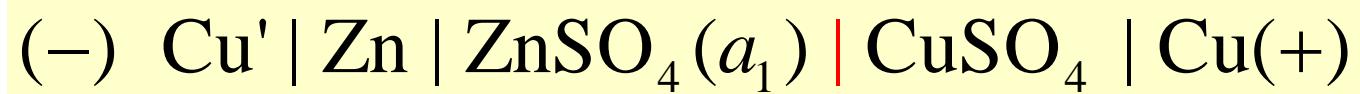
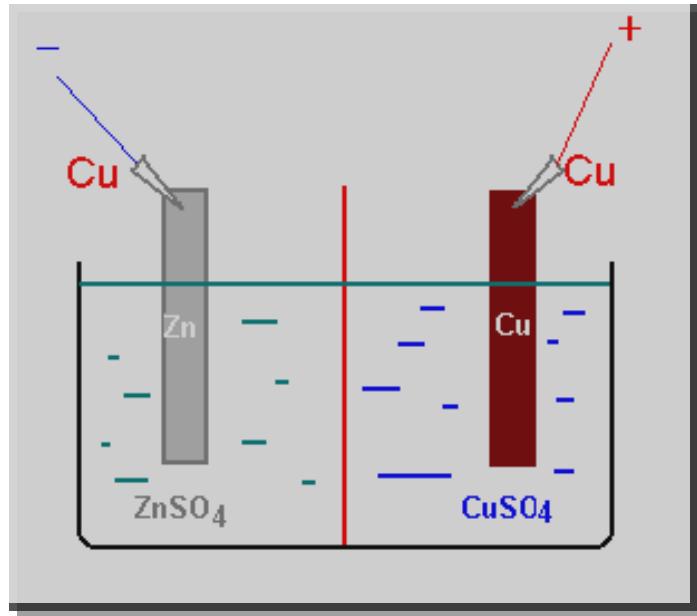
另一部分离子按一定的浓度梯度扩散到本体溶液中，称为**扩散层**。紧密层和扩散层构成了**双电层**。金属表面与溶液本体之间的电势差即为界面电势差。



电动势产生的机理



电动势的值



$$\Phi_{\text{接触}} \quad \Phi_- \quad \Phi_{\text{扩散}} \quad \Phi_+$$

$$E = \Phi_{\text{接触}} + \Phi_- + \Phi_{\text{扩散}} + \Phi_+$$

使用盐桥， $\Phi_{\text{扩散}} \rightarrow 0$ 而 $\Phi_{\text{接触}} \rightarrow 0$ $E = \Phi_- + \Phi_+$

正确断路

当电池的两个终端相为同一物质时，称为正确断路。
例如下述电池：

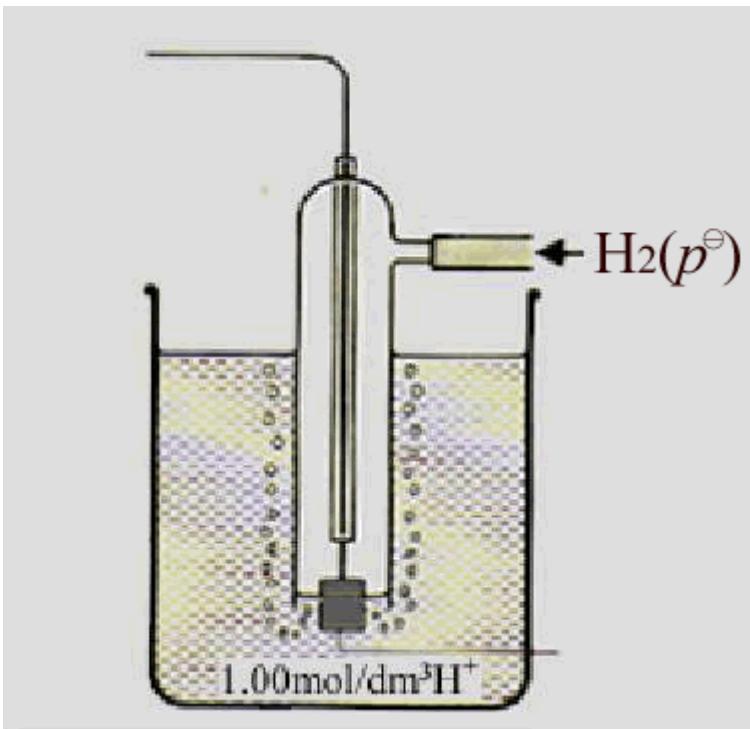


测定电动势时必须正确断路，才能使电动势等于两个相同金属的外电位之差，可以测量。

9.6 电极电势和电池的电动势

一、 标准电极电势

1、标准氢电极



$$\varphi^\ominus(\text{H}^+|\text{H}_2) = 0$$

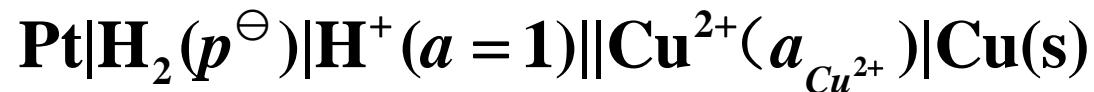
标准氢电极 || 给定标准电极

电动势 E = 标准电极电势
(标准还原电极电势)

2、电极电势

标准氢电极 || 给定电极

电动势 $E = \text{电极电势}$
(还原电极电势)



$$a_{\text{Cu}^{2+}} = 1, \quad E = E^\ominus = \varphi_{\text{Cu}^{2+}/\text{Cu}}^\ominus$$

$$a_{\text{Cu}^{2+}} \neq 1, \quad E = \varphi_{\text{Cu}^{2+}/\text{Cu}}$$

3、电极电势的Nerst方程



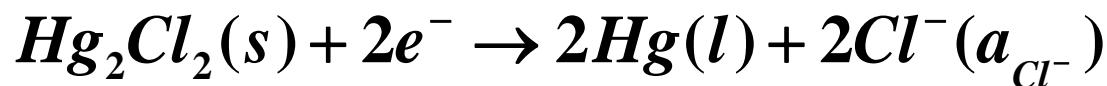
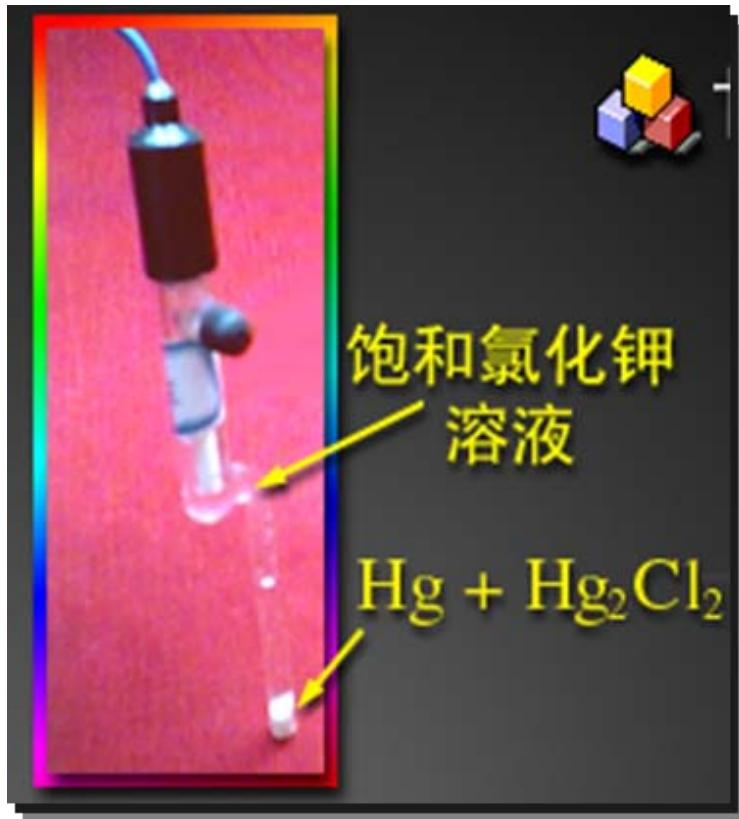
$$\varphi_{Cu^{2+}/Cu} = \varphi_{Cu^{2+}/Cu}^\theta - \frac{RT}{2F} \ln \frac{a_{Cu}}{a_{Cu^{2+}}}$$

$$= \varphi_{Cu^{2+}/Cu}^\theta - \frac{RT}{2F} \ln \frac{1}{a_{Cu^{2+}}}$$



$$\varphi_{Ox/Red} = \varphi_{Ox/Red}^\theta - \frac{RT}{zF} \ln \frac{a_{Red}}{a_{Ox}}$$

4、二级标准电极——甘汞电极



$$\begin{aligned}\varphi_{Hg_2Cl_2/Hg} &= \varphi_{Hg_2Cl_2/Hg}^\theta - \frac{RT}{2F} \ln \frac{a_{Cl^-}^2 a_{Hg}^2}{a_{Hg_2Cl_2}} \\ &= \varphi_{Hg_2Cl_2/Hg}^\theta - \frac{RT}{2F} \ln a_{Cl^-}^2 \\ &= \varphi_{Hg_2Cl_2/Hg}^\theta - \frac{RT}{F} \ln a_{Cl^-}\end{aligned}$$

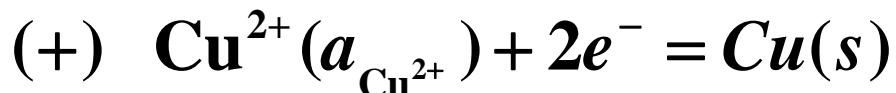
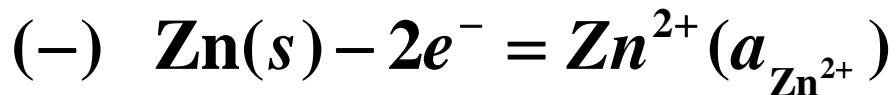
二、电池电动势的计算

1、从电极电势计算电池的电动势

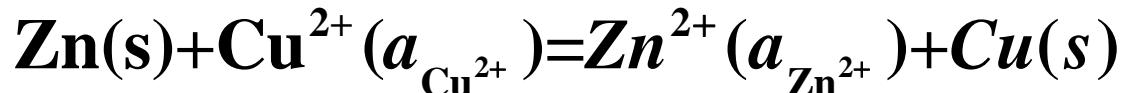


$$\begin{aligned} E &= \varphi_{\text{Cu}^{2+}/\text{Cu}} - \varphi_{\text{Zn}^{2+}/\text{Zn}} \\ &= (\varphi_{\text{Cu}^{2+}/\text{Cu}}^\theta - \frac{RT}{2F} \ln \frac{a_{\text{Cu}}}{a_{\text{Cu}^{2+}}}) - (\varphi_{\text{Zn}^{2+}/\text{Zn}}^\theta - \frac{RT}{2F} \ln \frac{a_{\text{Zn}}}{a_{\text{Zn}^{2+}}}) \\ &= (\varphi_{\text{Cu}^{2+}/\text{Cu}}^\theta - \varphi_{\text{Zn}^{2+}/\text{Zn}}^\theta) - \frac{RT}{2F} \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} \end{aligned}$$

2、从电池的总反应式用Nernst方程计算电池的电动势



电池反应



$$E = E^\theta - \frac{RT}{2F} \ln \frac{a_{\text{Zn}^{2+}} a_{\text{Cu}}}{a_{\text{Cu}^{2+}} a_{\text{Zn}}} = E^\theta - \frac{RT}{2F} \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}}$$

$$E^\theta = \varphi_{\text{Cu}^{2+}/\text{Cu}}^\theta - \varphi_{\text{Zn}^{2+}/\text{Zn}}^\theta$$

9.7 浓差电池和液接电势

① 浓差电池

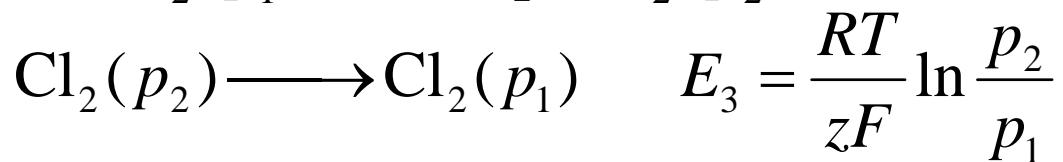
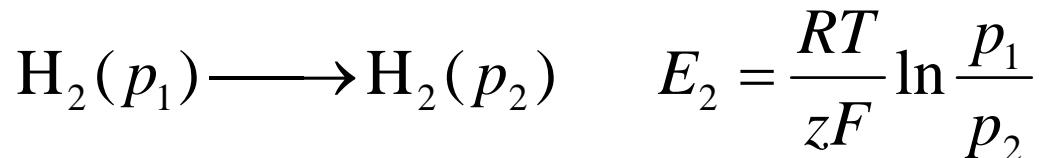
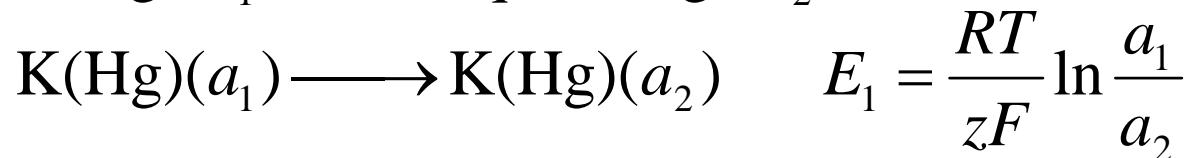
② 液体接界电势

③ 对盐桥作用的说明

④ 总电动势 E 与 E_c , E_j 的关系

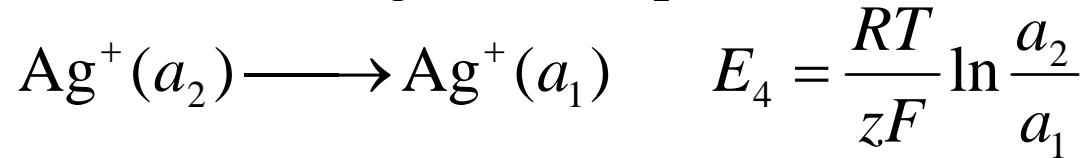
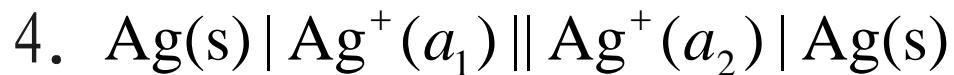
(1) 浓差电池(Concentration Cell)

A. 电极浓差电池

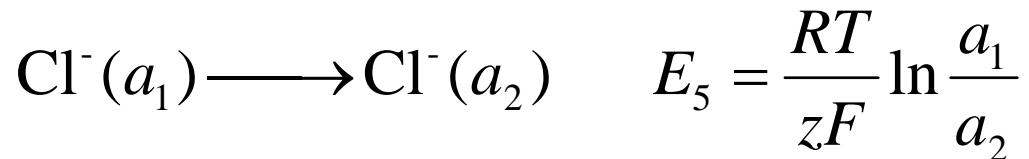
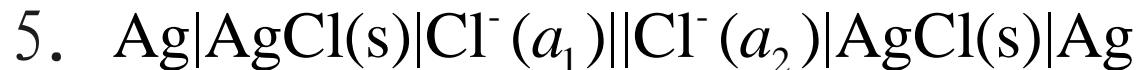


B. 电解质相同而活度不同

阳离子转移



阴离子转移



浓差电池的特点：

- 电池标准电动势 $E^\ominus = 0$
- 电池净反应不是化学反应，仅仅是某物质从高压到低压或从高浓度向低浓度的迁移。

(2) 液体接界电势 E_j 或 E_l

液接电势 (Liquid Junction Potential)

1. 液体界面间的电迁移 (设通过1mol电量)



整个变化的 $\Delta G_j = t_+ RT \ln \frac{a'_+}{a_+} + t_- RT \ln \frac{a'_-}{a_-}$

2. 液接电势的计算

$$\Delta G_j = -zE_j F$$

$$E_j = \frac{t_+ RT}{zF} \ln \frac{a_{H^+}}{a_{H^+}'} - \frac{t_- RT}{zF} \ln \frac{a_{Cl^-}}{a_{Cl^-}'}$$

对1-1价电解质，设： $a_{H^+} = a_{Cl^-} = \frac{m}{m^\ominus}$ $a'_{H^+} = a'_{Cl^-} = \frac{m'}{m^\ominus}$

$$E_j = (t_+ - t_-) \frac{RT}{F} \ln \frac{m}{m'}$$

$$t_+ - t_- = 2t_+ - 1$$

测定液接电势，可
计算离子迁移数。

(3) 对盐桥作用的说明

- 盐桥中离子的 $r_+ \approx r_-$, $t_+ \approx t_-$, 使 $E_j \approx 0$ 。
- 常用饱和KCl盐桥, 因为 K^+ 与 Cl^- 的迁移数相近, 当有 Ag^+ 时用 KNO_3 或 NH_4NO_3 。
- 盐桥中盐的浓度要很高, 常用饱和溶液。
- 盐桥只能降低液接电势, 但不能完全消除, 只有电池反串联才能完全消除 E_j , 但化学反应和电动势都会改变。

(4) 总电动势E与 E_c , E_j 的关系



$$E_1 = E_c + E_j$$



$$E_2 = E_c$$

$$E_j = E_1 - E_2$$

9.8 电动势测定的应用

一、求电解质溶液的平均活度因子



$$E = E^\theta - \frac{RT}{F} \ln a_{H^+} a_{Cl^-} = \varphi^\theta_{AgCl/Ag} - \frac{2RT}{F} \ln \frac{m_{HCl}}{m^\theta} - \frac{2RT}{F} \ln \gamma_\pm$$

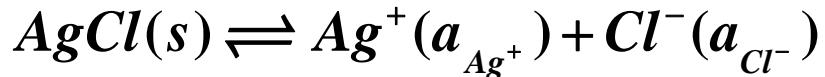
(1) 求 γ_\pm

(2) 求 $\varphi^\theta_{AgCl/Ag}$

当浓度很低时, $\ln \gamma_\pm = -A |Z + Z -| \sqrt{I} = -A \sqrt{m_{HCl}}$

$$\varphi^\theta_{AgCl/Ag} = E + \frac{2RT}{F} \ln \frac{m_{HCl}}{m^\theta} - \frac{2RTA}{F} \sqrt{m_{HCl}}$$

二、求难溶盐的活度积



$$K_{ap} = \frac{a_{Ag^+} a_{Cl^-}}{a_{AgCl}} = a_{Ag^+} a_{Cl^-}$$

设计电池为 $Ag(s) | Ag^+(a_{Ag^+}) \parallel Cl^-(a_{Cl^-}) | AgCl(s) + Ag(s)$

电池的标准电动势

$$E^\theta = \varphi^\theta_{AgCl/Ag} - \varphi^\theta_{Ag^+/Ag} = 0.2224 - 0.779 = -0.5767V$$

$$\Delta_r G_m^\theta = -zE^\theta F = -RT \ln K_{ap}$$

$$K_{ap} = \exp\left(\frac{zE^\theta F}{RT}\right) = \exp\left[\frac{1 \times (-0.5767) \times 96500}{8.314 \times 298}\right] = 1.76 \times 10^{-10}$$

用类似的方法可以求解离常数、水的离子积常数和络合常数

三、pH的测定

玻璃电极|待测溶液|甘汞电极

$$E = \varphi_{\text{甘汞电极}} - \varphi_{\text{玻璃电极}}$$

$$= \varphi_{\text{甘汞电极}} - (\varphi_{\text{玻璃电极}}^\theta + \frac{RT}{F} \ln a_{H^+})$$

$$= \varphi_{\text{甘汞电极}} - \varphi_{\text{玻璃电极}}^\theta - \frac{2.303RT}{F} pH$$

$$= \text{常数} - 0.05916 pH$$

- Nernst

WALTHER NERNST (1864-1941), German physical chemist, did much of the early important work in electrochemistry, studying the thermodynamics of galvanic cells and the diffusion of ions in solution. Besides his scientific researches, he developed the Nernst lamp, which used a ceramic body. This lamp never achieved commercial importance since the tungsten lamp was developed soon afterwards.

His electrical piano, which used radio amplifiers instead of a sounding board, was totally rejected by musicians. Nernst was the first to enunciate the third law of thermodynamics, and received the Nobel Prize in chemistry in 1920 for his thermochemical work.

下列电池在298K时的电动势 $E = 0.165V$



电池反应（1个电子得失）的 $\Delta_r H_m = 50kJ \cdot mol^{-1}$,

已知 $AgBr(s)$ 的 $K_{sp} = 1.0 \times 10^{-12}$, $\varphi_{Ag^+ / Ag}^\theta = 0.799V$

(1)写出电极反应和电池反应

(2) 计算电池的 E^θ 值

(3) 计算可逆电池产生 $1mol$ 电子电量时的热效应

(4) $0.1mol \cdot Kg^{-1} HBr$ 溶液的平均活度系数