电化学

电化学热力学和
电极过程动力学

特点、要点、难点

电化学热力学

$\Delta G = -zFE$, $\bar{\mu}_i$, $Nernst$方程

化学电池 → 浓差电池

$$E\ ,\varphi\ ,\left(\frac{\partial E}{\partial T}\right)_P ,\varphi_l$$

$$\Delta G, \Delta H, \Delta S \Lambda\ , K_a^{\theta}, K_{sp} \Lambda\ , \gamma_{\pm}, t_i$$

电化学系统的热力学的特点

Thermodynamic of Electrochemical Systems

$$dG = SdT + Vdp$$

多相，多组分

$$dG = SdT + Vdp + \sum_{\alpha=1}^{\pi}\sum_{i=1}^{K}\left(\mu_i^{\alpha} dn_i^{\alpha}\right)$$

带电粒子，多相，多组分

$$dG = SdT + Vdp + \sum_{\alpha=1}^{\pi}\sum_{i=1}^{K}\left(\mu_i^{\alpha} dn_i^{\alpha} + z_i F \phi^{\alpha} dn_i^{\alpha}\right)$$

要点：电化学势

恒温恒压下**荷电粒子*i***从α相转移到β相

$$\Delta G_i^{\alpha\rightarrow\beta} = \mu_i^\beta - \mu_i^\alpha + z_i e_0(\phi^\beta - \phi^\alpha)$$

平衡时： $\mu_i^\beta + z_i e_0 \phi^\beta = \mu_i^\alpha + z_i e_0 \phi^\alpha$

$$\overline{\mu}_i^\beta = \overline{\mu}_i^\alpha$$

i 粒子在两相间的电化学势相等

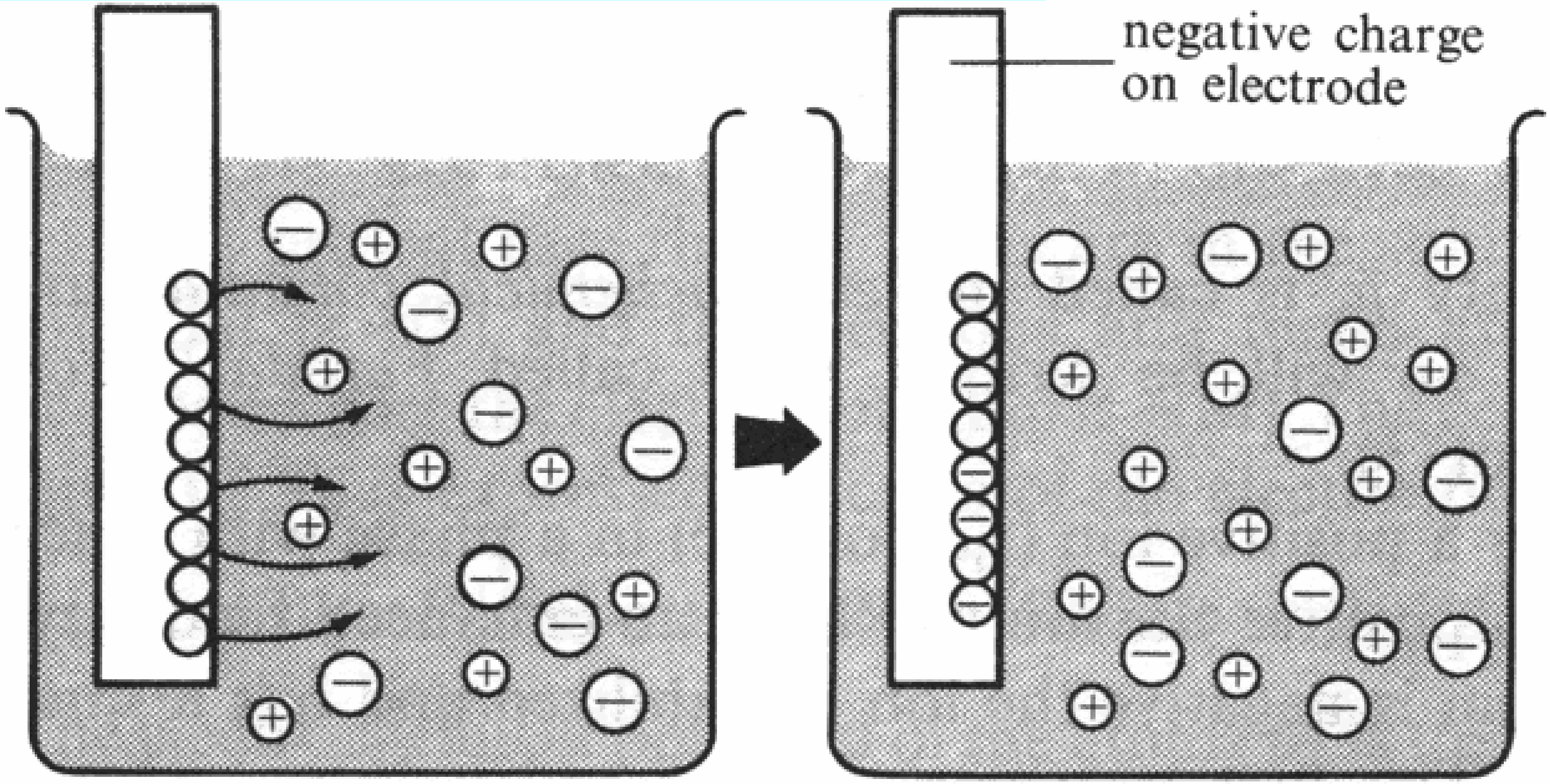
单电极的Nenster方程的推导

a. 从半电池考虑(可逆电池)

b. 从电化学势考虑

$$M^{z+} + ze \rightleftharpoons M$$

$$M^{z+} + ze \rightleftharpoons M$$



$$\Delta\varphi_{M/M^{z+}} = \phi(M) - \phi(Sol)$$

$$M^{z+} + ze \rightleftharpoons M$$

$$\Delta \varphi_{M/M^{z+}} = \phi(M) - \phi(Sol)$$

平衡时： $\mu_i^{\beta} + z_i e_0 \phi^{\beta} = \mu_i^{\alpha} + z_i e_0 \phi^{\alpha}$

$$\overline{\mu}_i^{\beta} = \overline{\mu}_i^{\alpha}$$

两相间建立平衡电势

平衡时电化学势

$$\bar{\mu}_{M^{z+}}(Sol) = \bar{\mu}_{M^{z+}}(M)$$

$$\bar{\mu}_{M^{z+}}(Sol) = \bar{\mu}_{M}(M) - z\bar{\mu}_{e}(M)$$

$$M^{z+} \rightleftharpoons M - ze$$

[illegible]

$$= \overline{\mu}_M(M) = \mu_M(M) \qquad (M\text{为中性})$$

$$\Delta\varphi_{M/M^{z+}} = \phi(M) - \phi(Sol)$$

$$= \frac{1}{zF}[\mu_{M^{z+}}(Sol) + z\mu_e(M) - \mu_M(M)]$$

$$\Theta \qquad \mu_i = \mu_i^{\ominus} + RT\ln a_i$$

$$\mu_M(M) = \mu_M^{\ominus}(M)$$

纯物质为标准态

$$=\frac{1}{zF}[\mu^{o}_{M^{z+}}(sol)+z\mu_e(M)-\mu^{o}_{M}(M)]+\frac{RT}{zF}\ln a_{M^{z+}}$$

标准电极电势

$$\Delta\varphi^{o}_{M/M^{z+}}=\frac{1}{zF}[\mu^{o}_{M^{z+}}(Sol)+z\mu_e(M)-\mu^{o}_{M}(M)]$$

大块金属中一摩尔M 分离为M^{z+} 和z个电子且达到平衡的化学势变化

$$M^{z+}+ze \rightleftharpoons M$$

单电极的Nernst方程电极电势表达式

$$\Delta\varphi_{M/M^{z+}} = \Delta\varphi^{\ominus}_{M/M^{z+}} - \frac{RT}{zF}\ln\frac{1}{a_{M^{z+}}}$$

$$= \frac{1}{zF}[\mu^{\ominus}_{M^{z+}} + z\mu_e(M) - \mu^{\ominus}_{M}(M)] + \frac{RT}{zF}\ln a_{M^{z+}}$$

$$\Delta\bar{\varphi}^{o}_{M/M^{z+}} = \frac{1}{zF}[\bar{\mu}^{o}_{M^{z+}}(Sol) + z\mu_e(M) - \bar{\mu}^{o}_{M}(M)]$$

电极过程动力学特点

如何控制电化学过程

加快或减缓电化学反应速度

电　流

$$Ox + ze \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Red \quad (单电极)$$

净阴极电流密度

$$j_c = \overrightarrow{j} - \overleftarrow{j}$$

$$Ox + ze \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Red$$

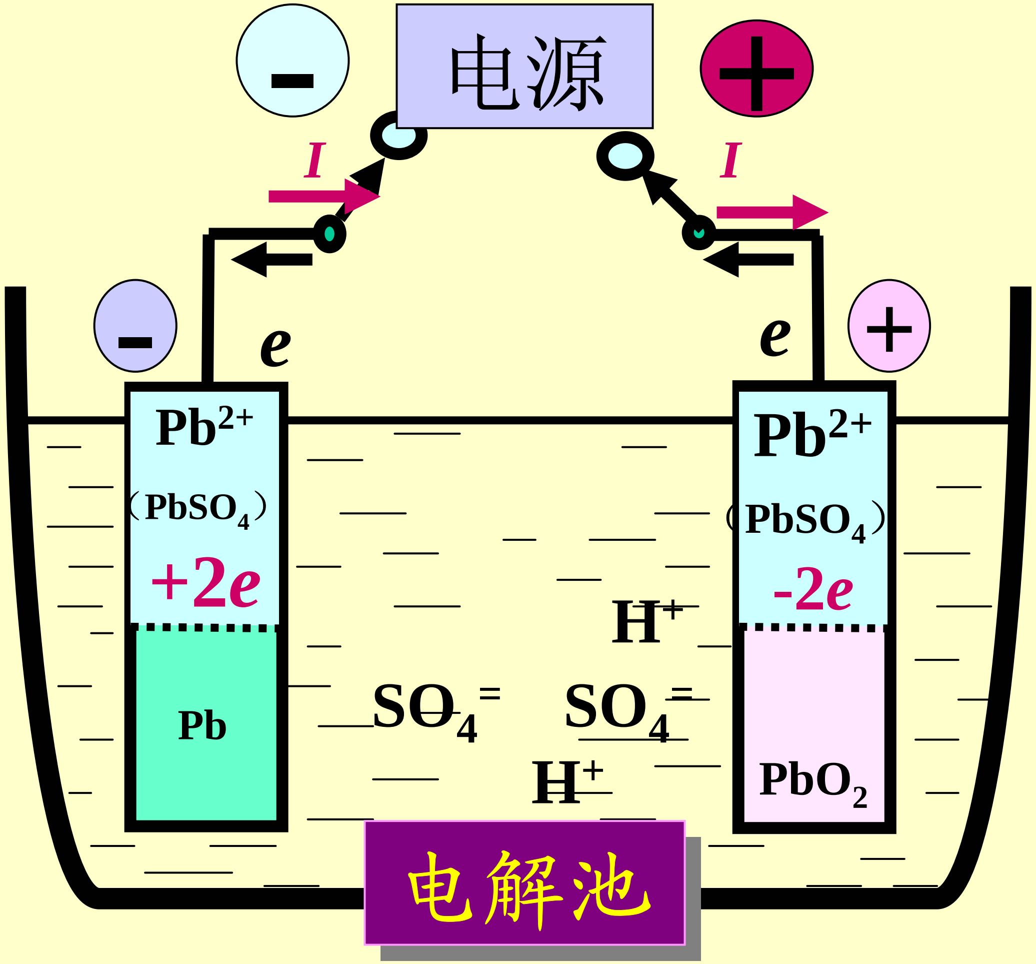
净电流密度 $$j_c = \vec{j} - \overleftarrow{j}$$

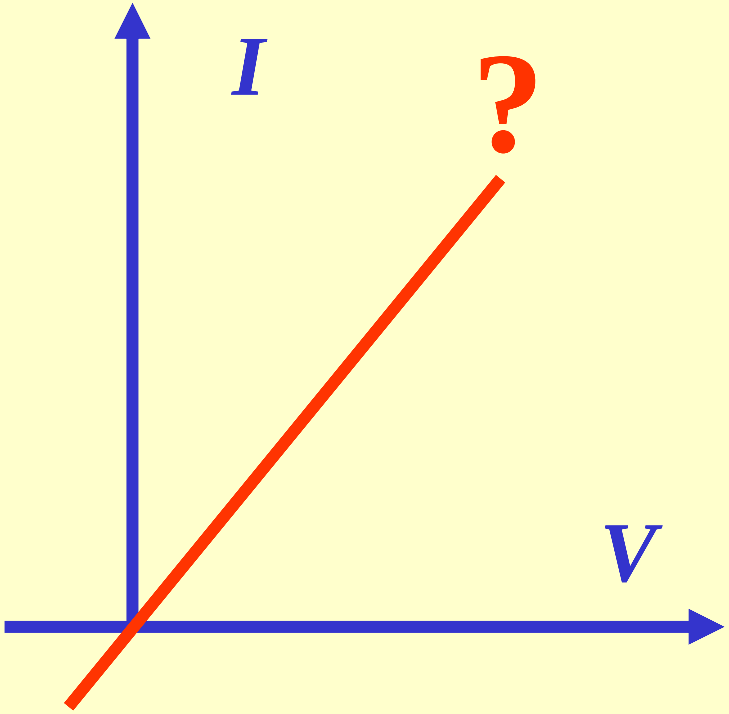
$$Red - ze \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} Ox$$

净电流密度 $$j_a = \overleftarrow{j} - \vec{j}$$

要点:如何检测和分析电解池中的电流?

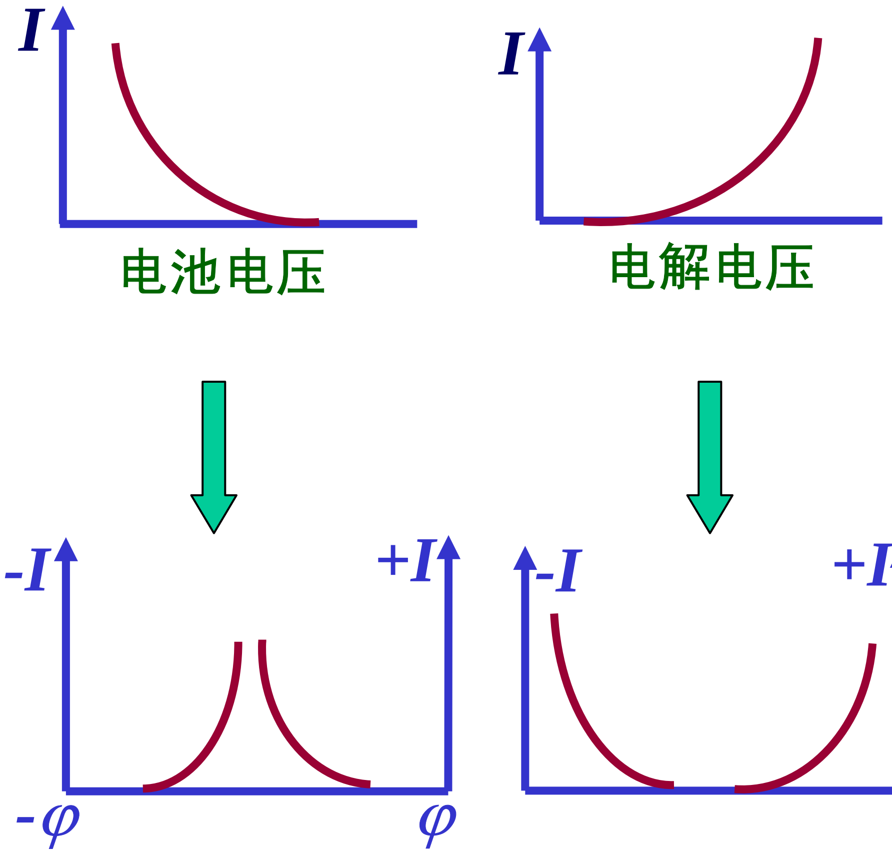
电解池中的$I-V$曲线? ? ?





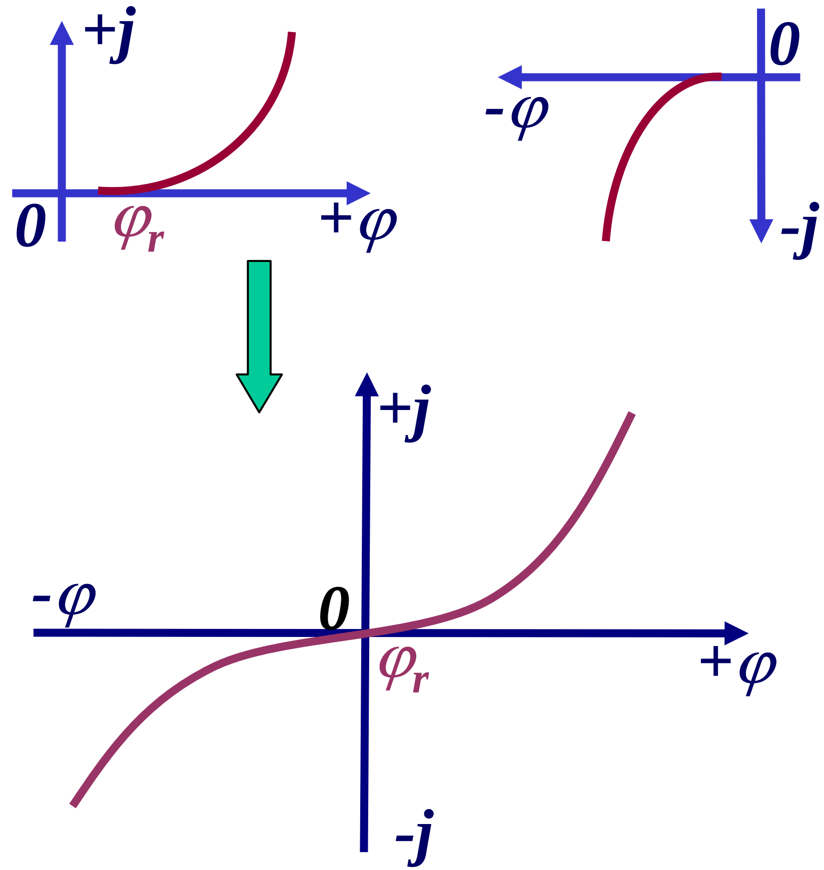
电池电动势(唯一)

原电池	电解池
输出电压	电解电压

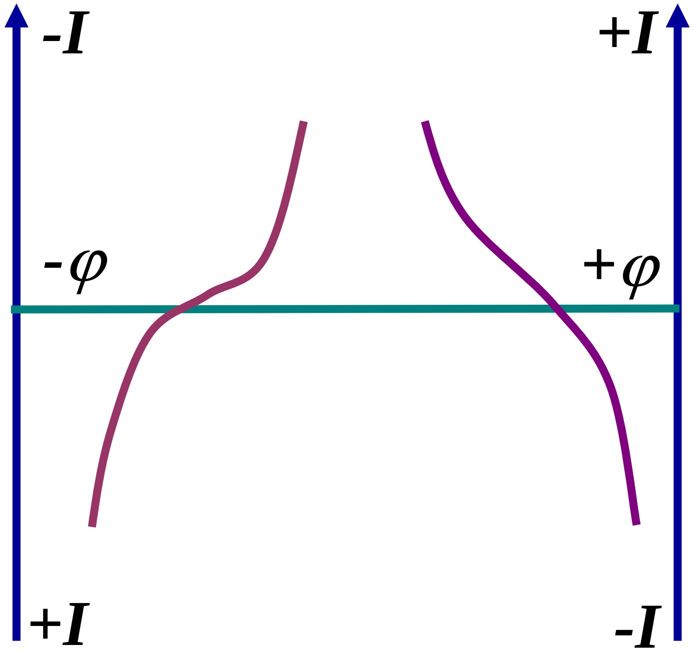


电极电势(唯一)

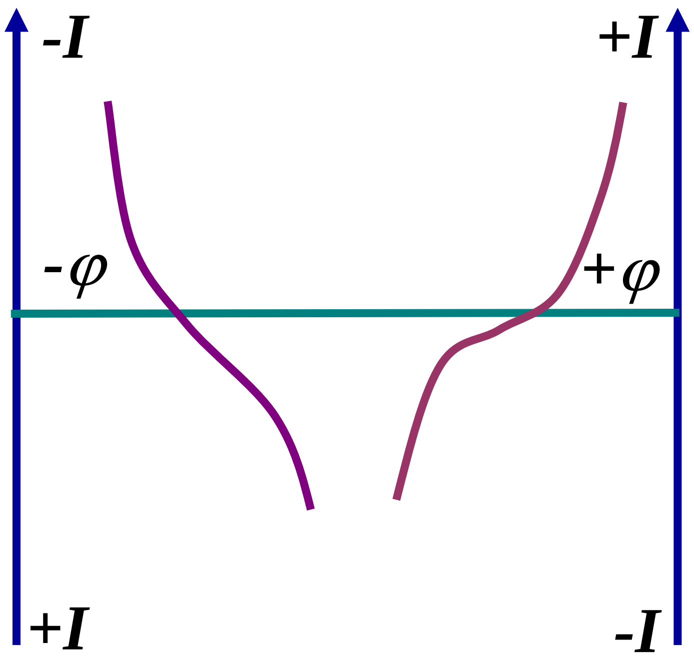
阳极	阴极
阳极电位	阴极电位



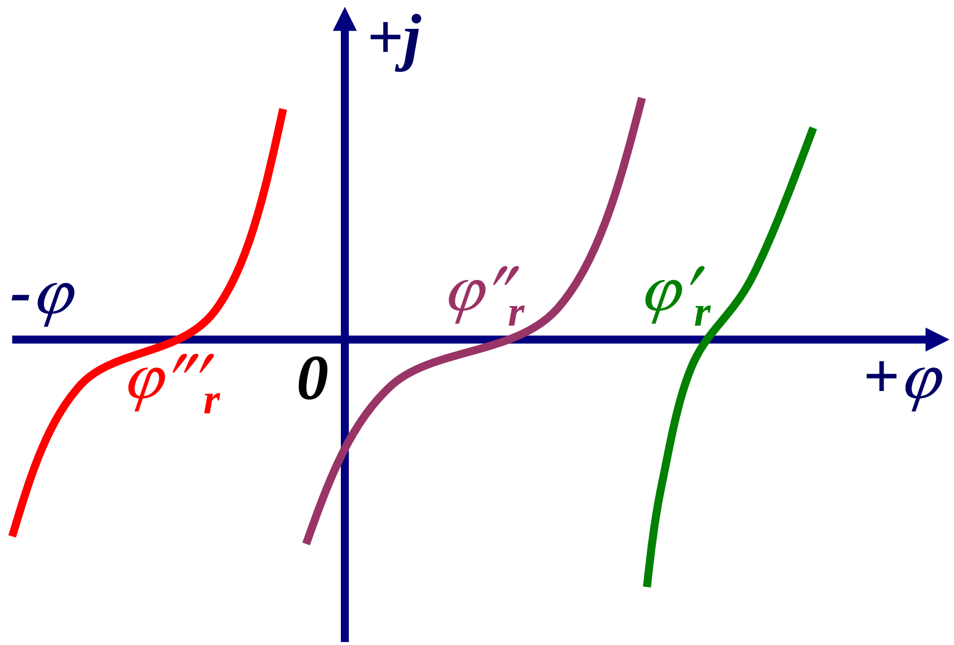
极化曲线

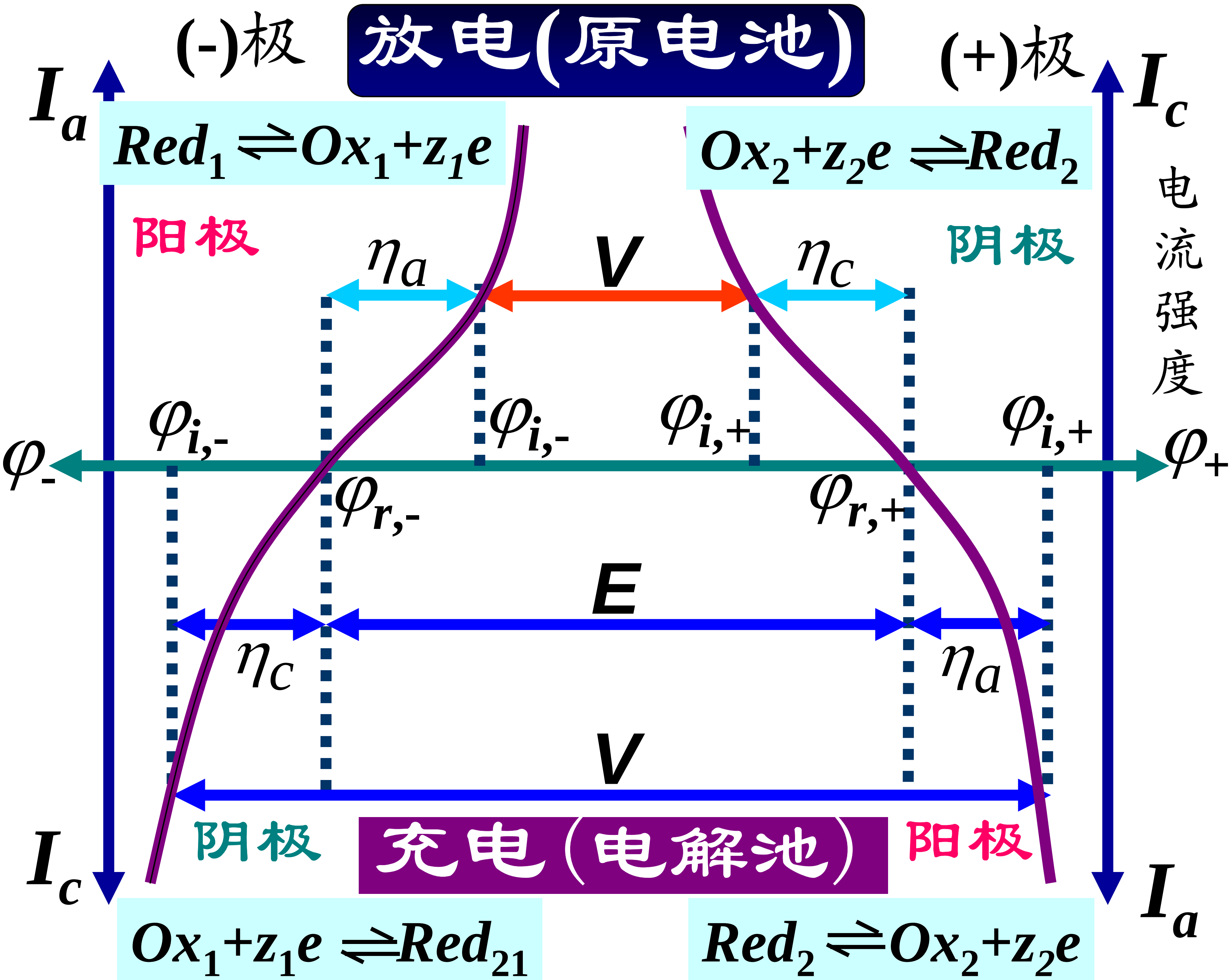


电化学池

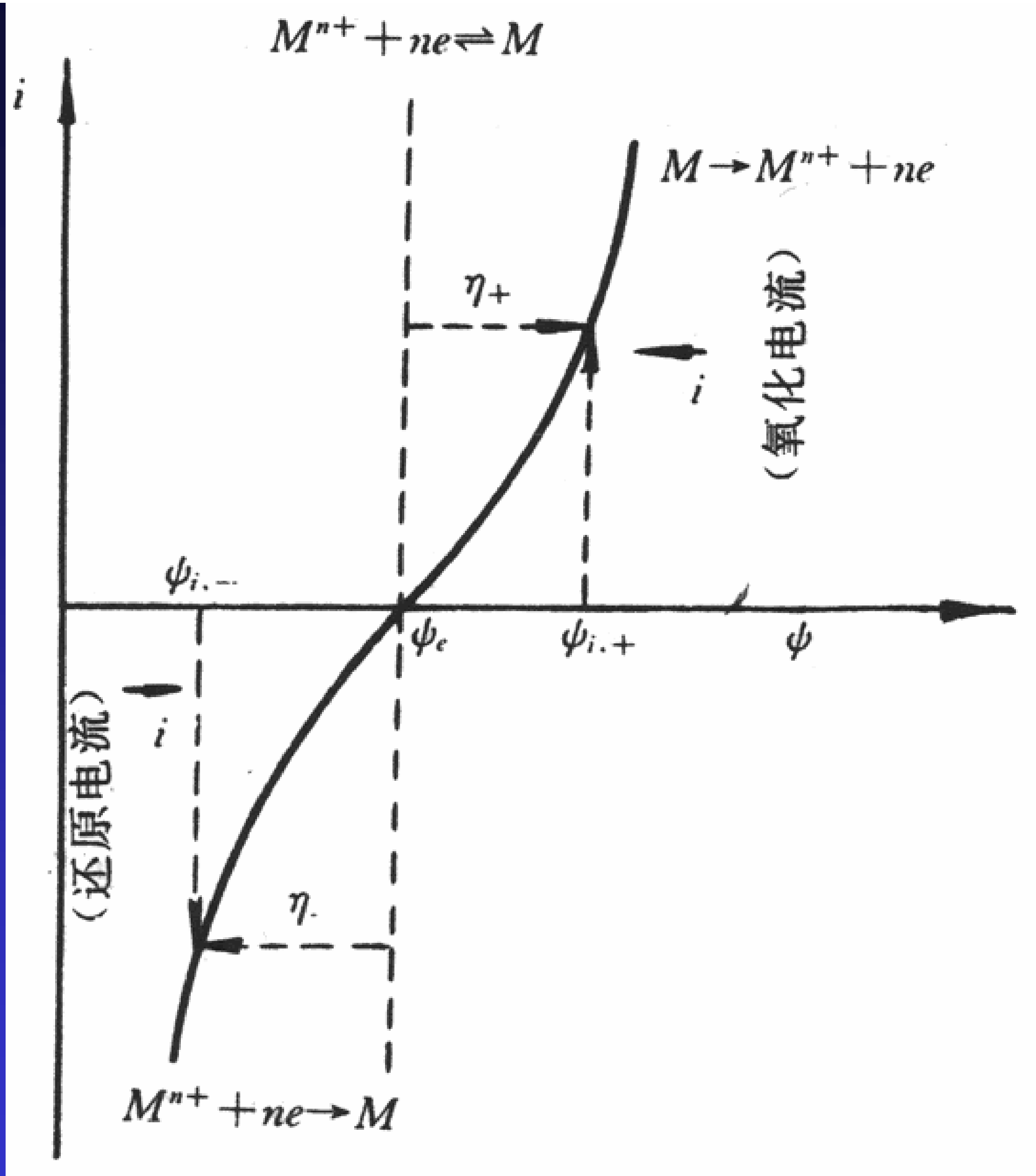


电极

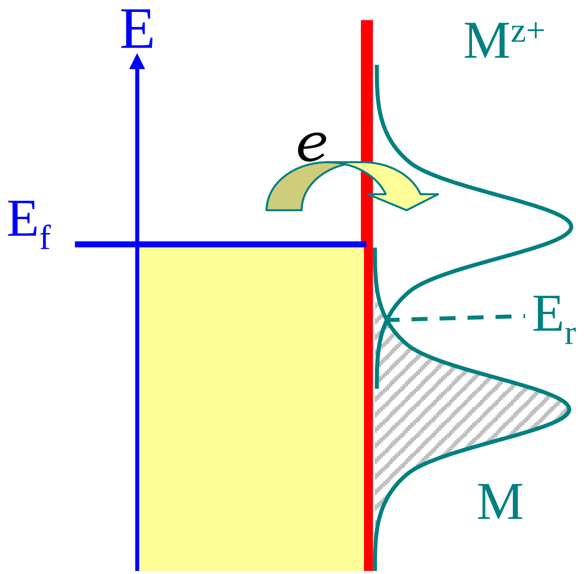


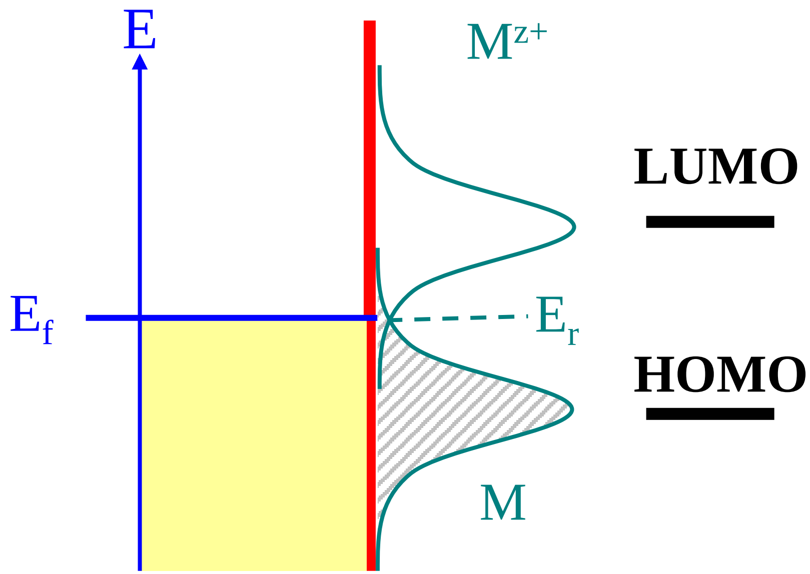


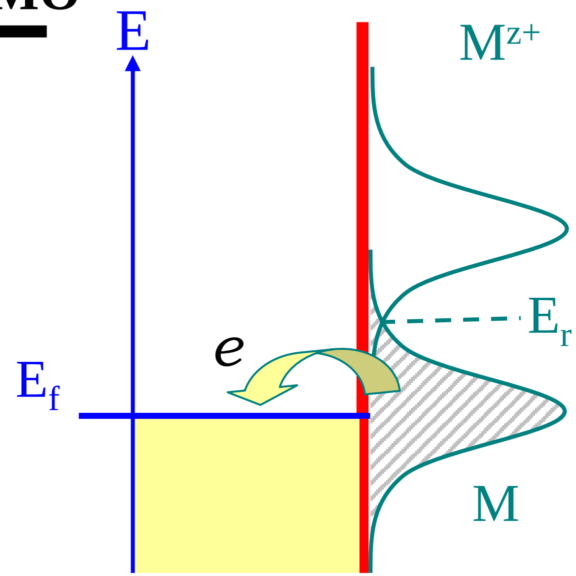
放电(原电池)
(-)极
(+)极
I_a
I_c
$Red_1 \rightleftharpoons Ox_1+z_1e$
$Ox_2+z_2e \rightleftharpoons Red_2$
阳极
阴极
电流强度
η_a
η_c
V
$\varphi_{i,-}$
$\varphi_{i,+}$
φ_-
φ_+
$\varphi_{r,-}$
$\varphi_{r,+}$
E
η_c
η_a
V
阴极
充电(电解池)
阳极
I_c
I_a
$Ox_1+z_1e \rightleftharpoons Red_{21}$
$Red_2 \rightleftharpoons Ox_2+z_2e$

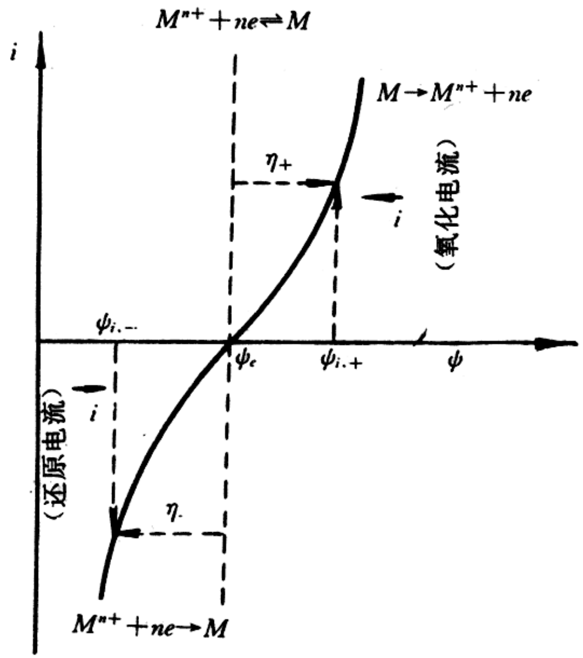


电极反应的j-φ关系









施加负电压

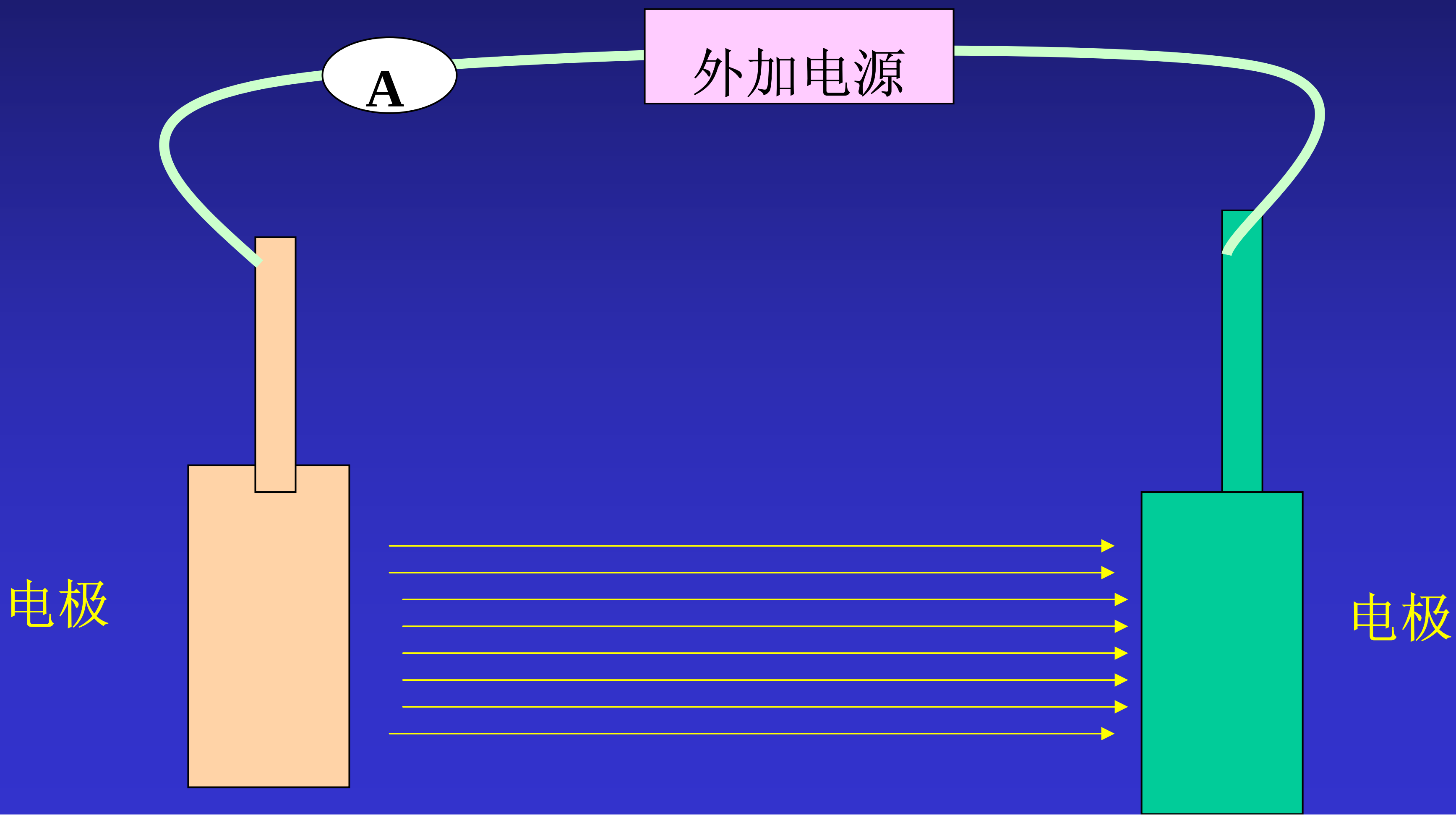
金属内电子能
量升高，容易
给出电子

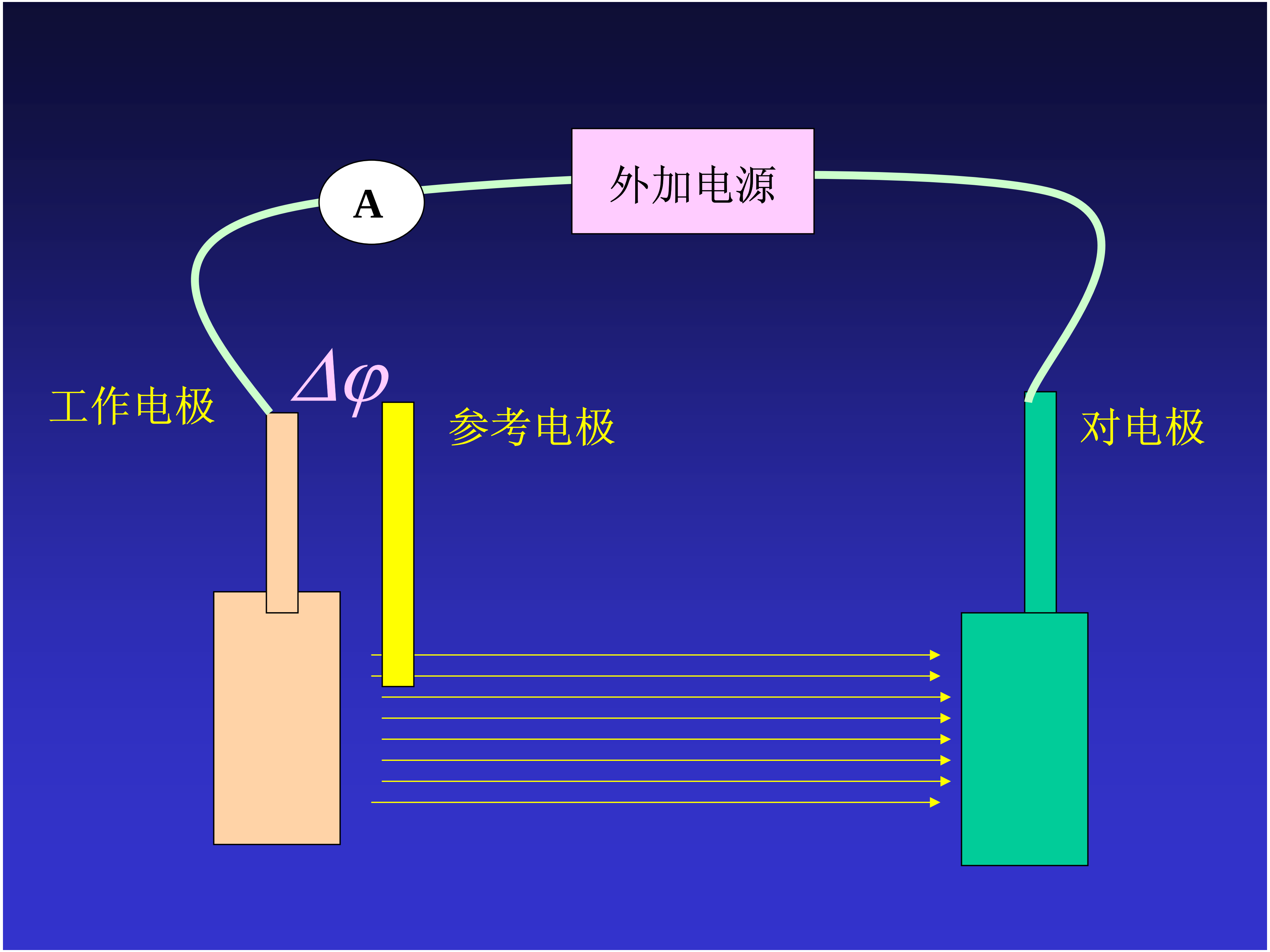
施加正电压

金属内电子能
量降低，容易
接受电子

何为正确的V – I 关系？

如何将实际复杂的工作体系分解为几部分后分别研究

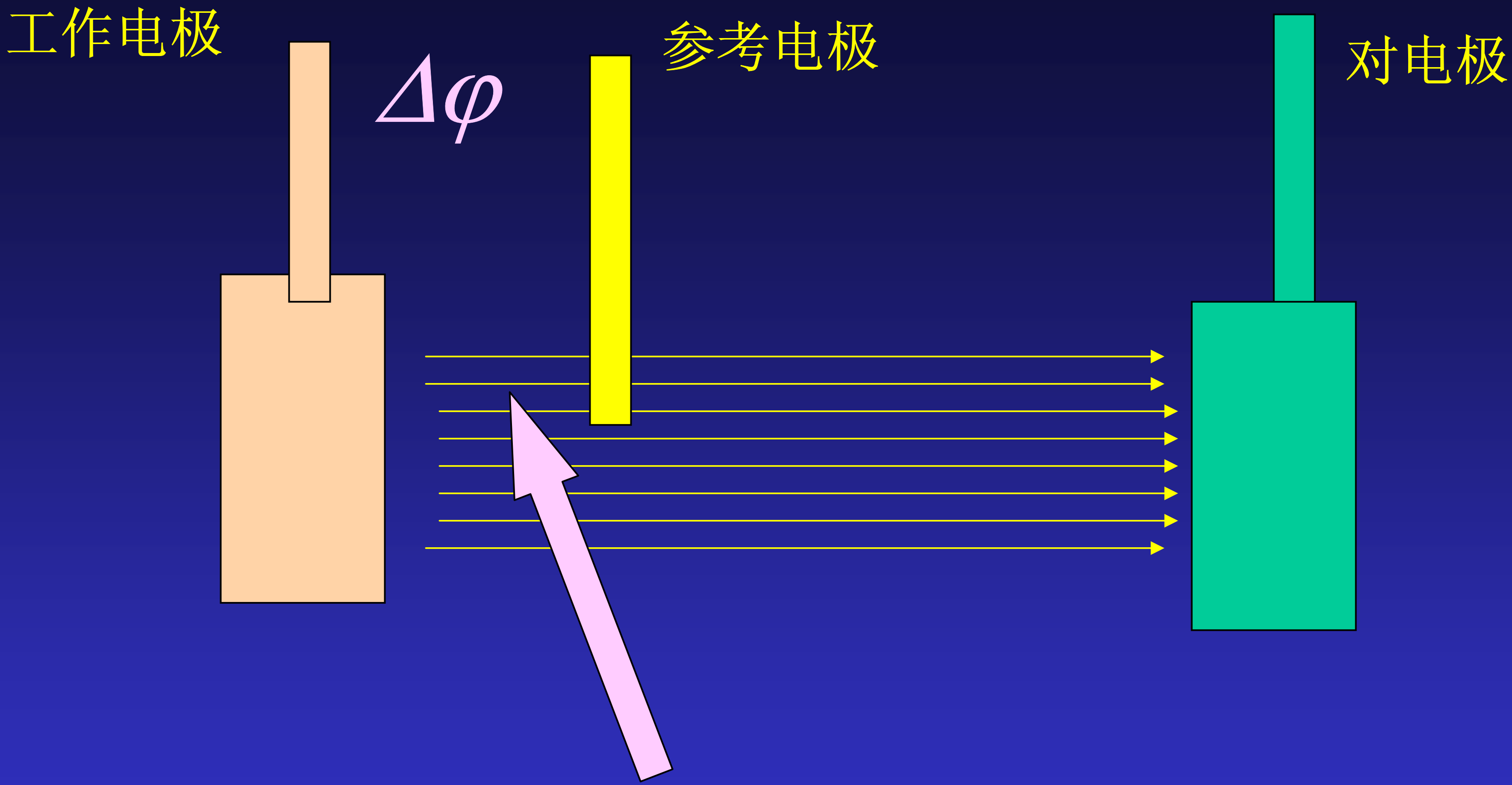



外加电源
A
Δφ
工作电极
参考电极
对电极

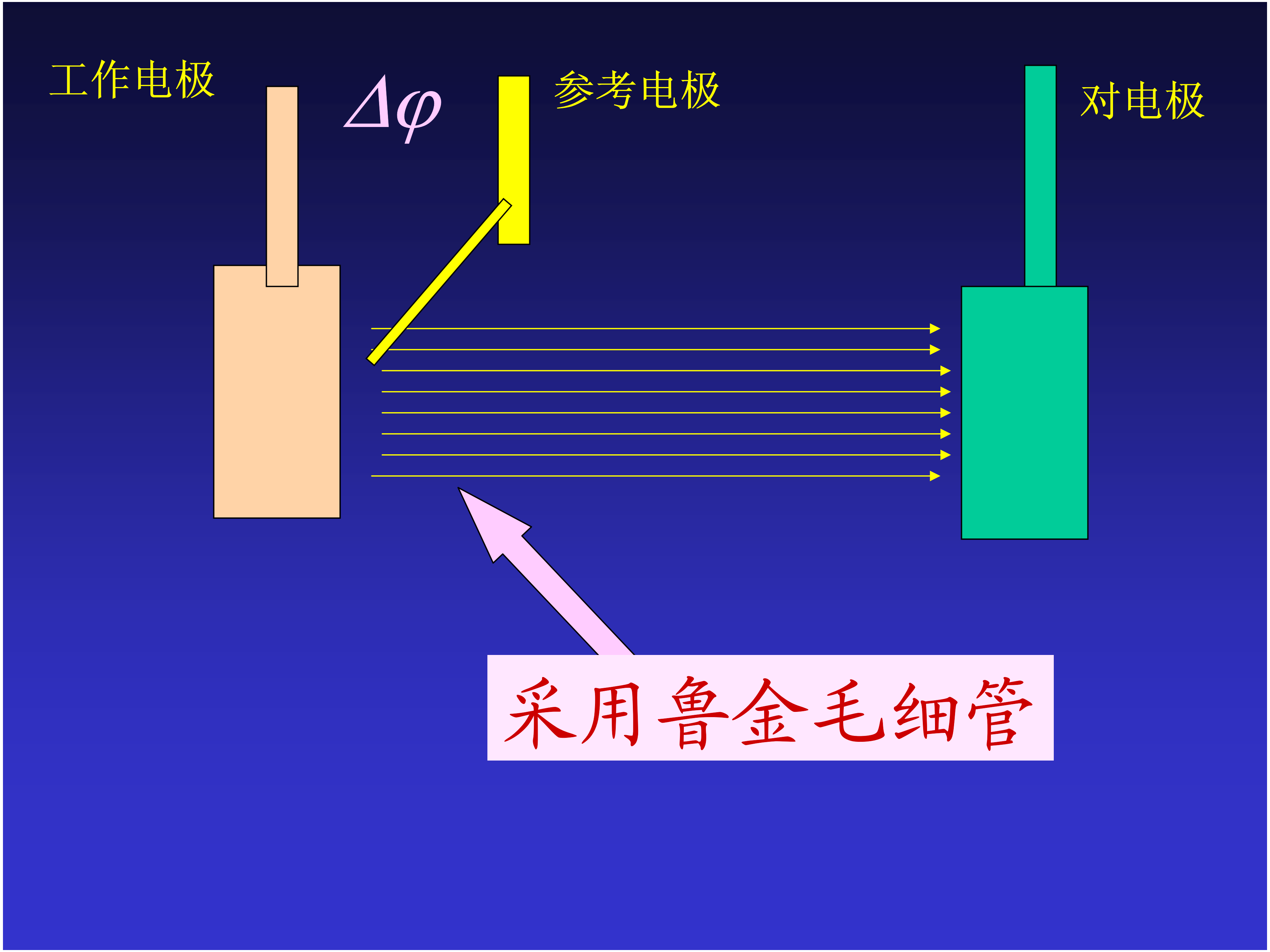
针对单一电极的超电势的测量

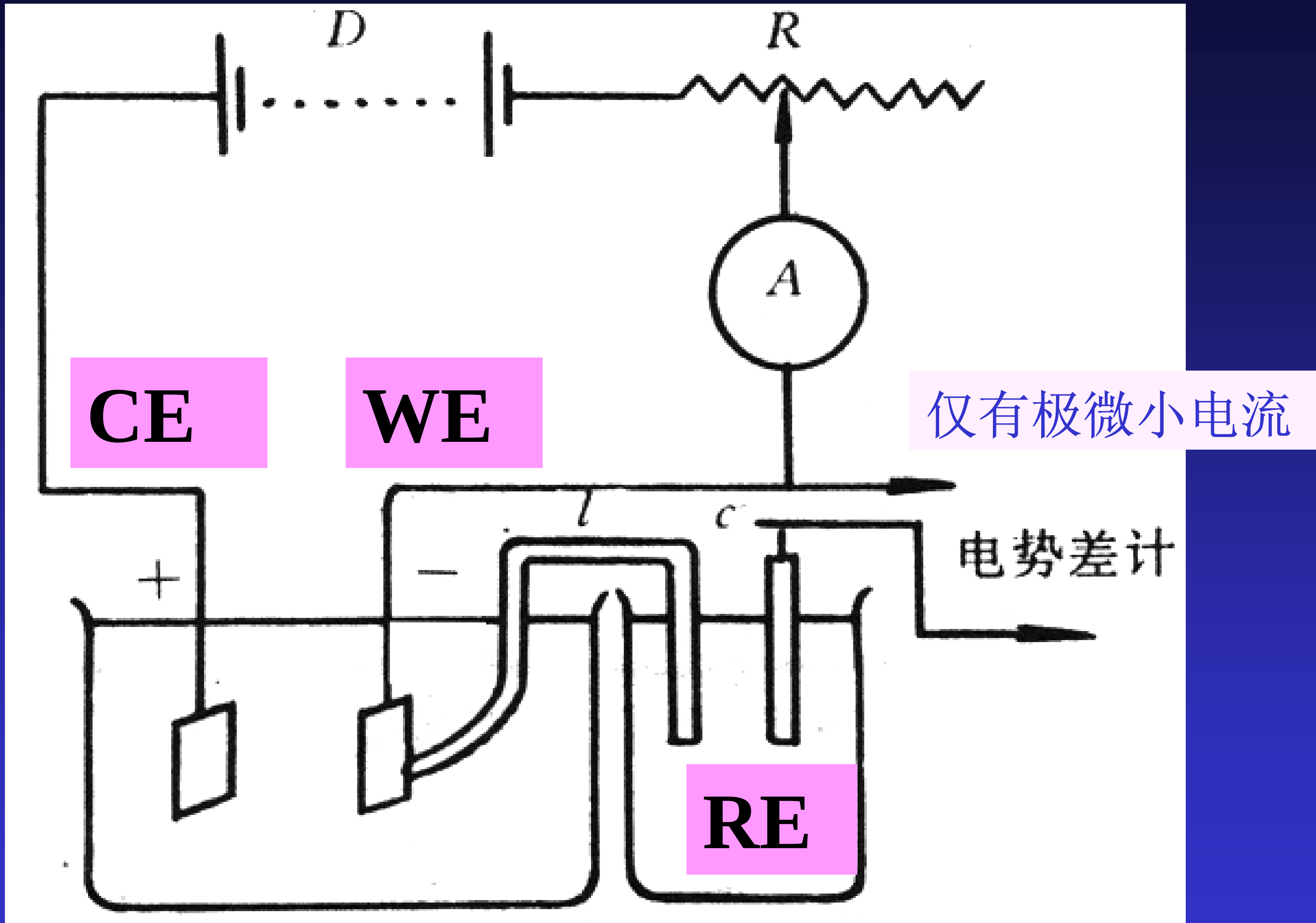
三电极体系及其特点

- 研究(工作)电极 Working Electrode
- 参比(参考)电极 Reference Electrode
- 辅助(对)电极 Counter Electrode

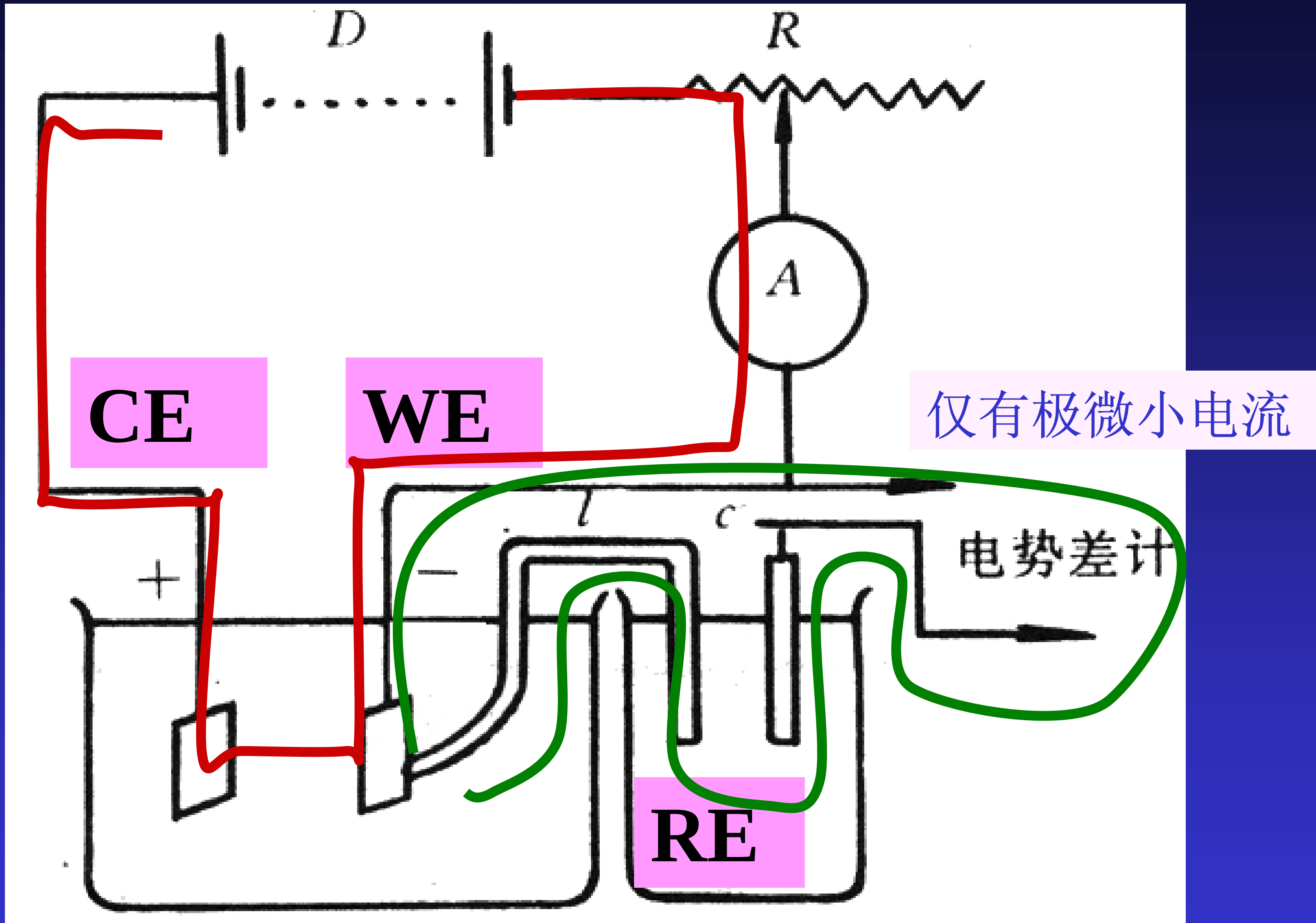


$$\Delta\varphi(\text{测量}) = \Delta\varphi + I \times R_l'$$


工作电极
Δφ
参考电极
对电极
采用鲁金毛细管



用三电极体系测量电极电势的装置



用三电极体系测量电极电势的装置

甘汞电极
(氯化亚汞电极)

二级基准电极，

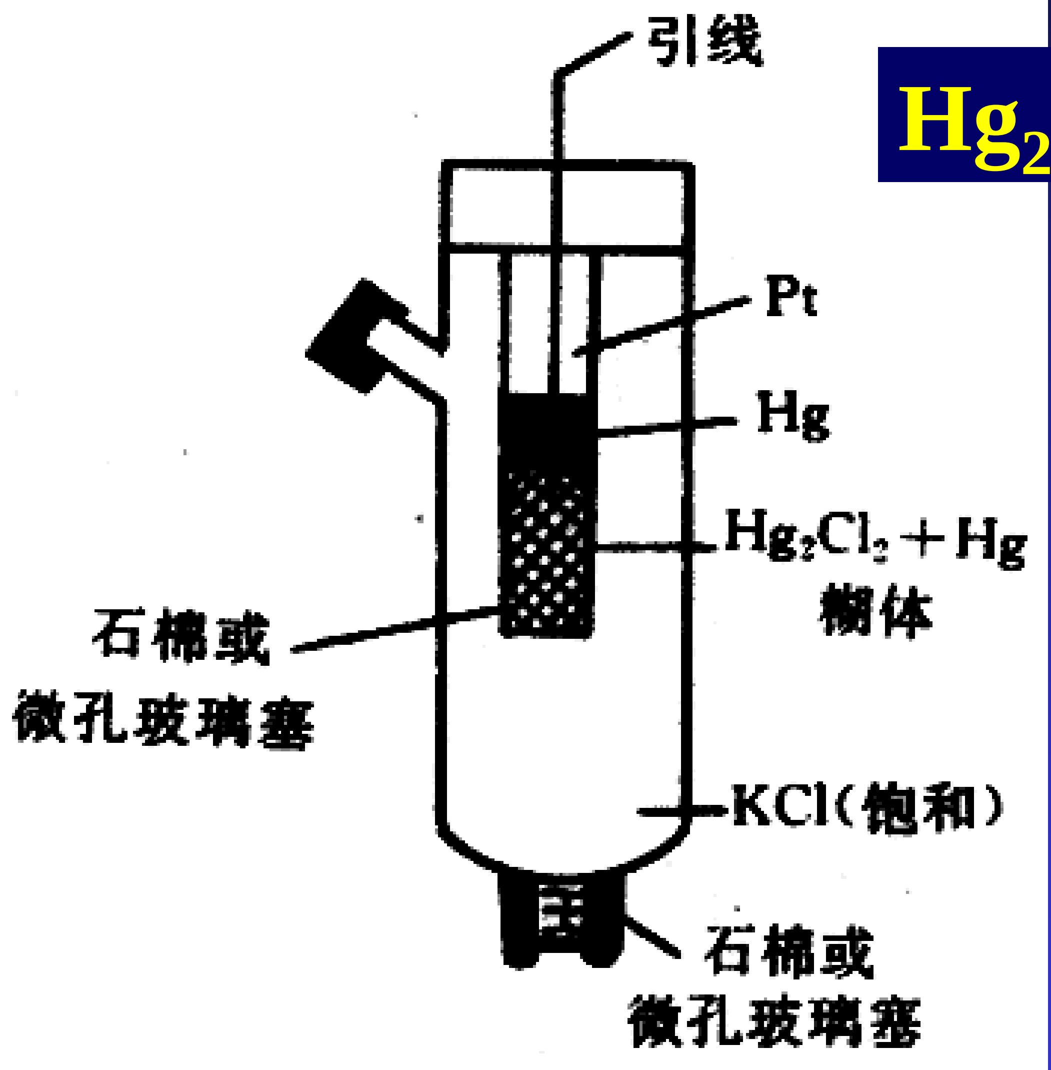
参比电极

Pt,Hg|Hg_2Cl_2(*s*),KCl(*a*)

$Hg_2Cl_2+2e \rightleftharpoons 2Hg+2Cl^-$

$$\varphi_{Hg_2/Hg_2Cl_2} = \varphi^{\ominus} - \frac{RT}{F}\ln a_{Cl^-}$$

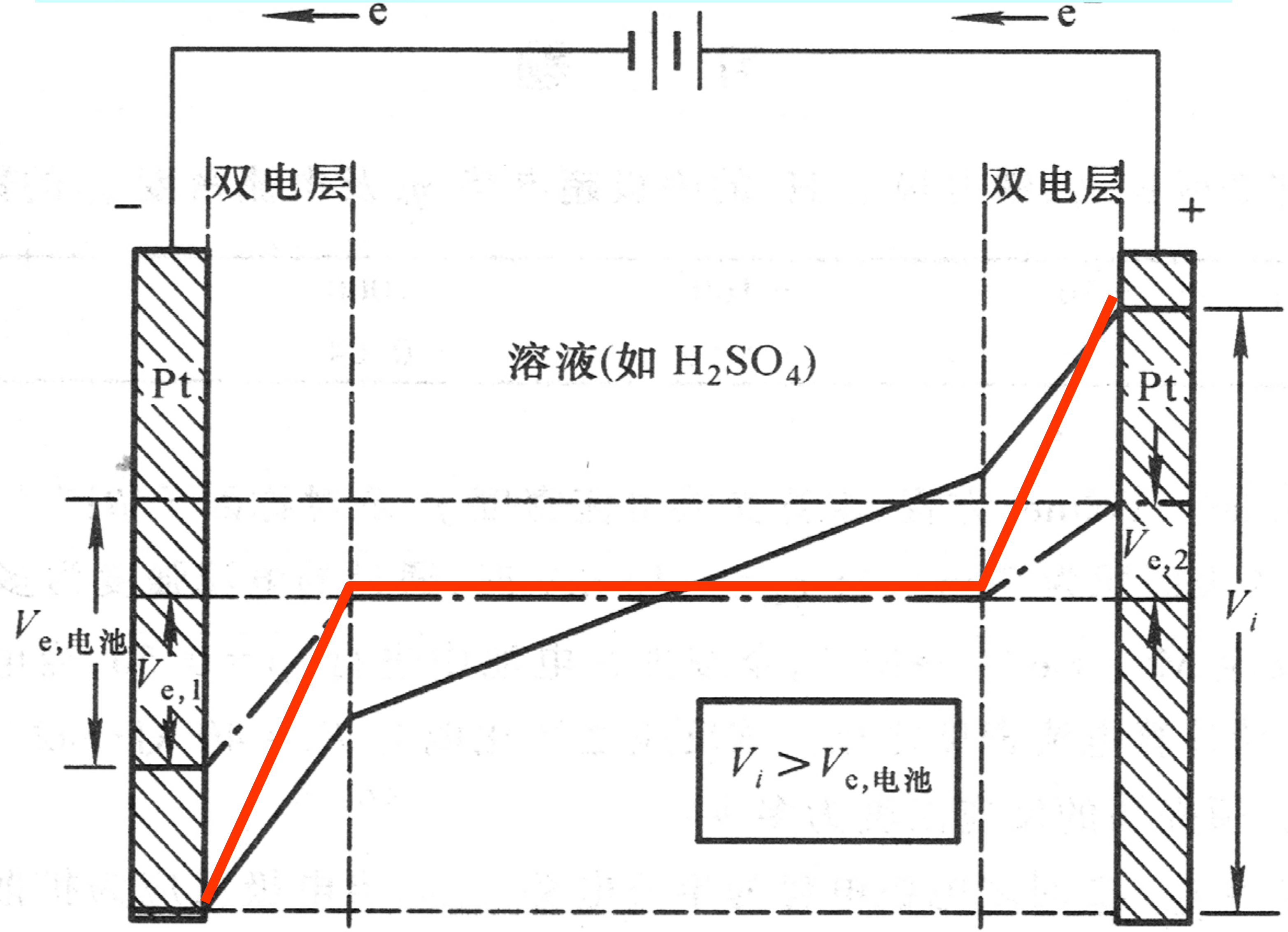
甘汞电极

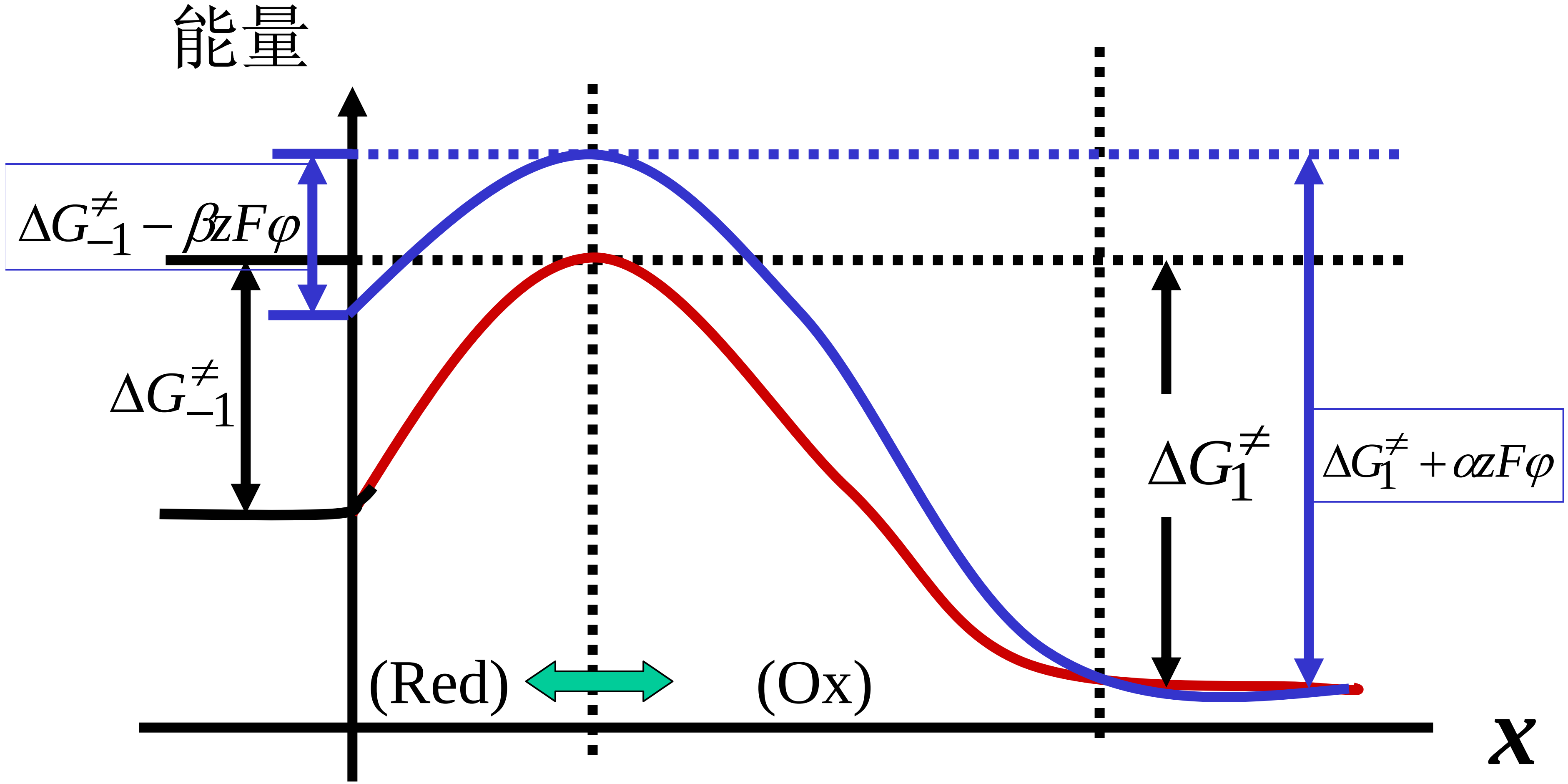


$$Hg_2Cl_2+2e \rightleftharpoons 2Hg+2Cl^-$$

饱和甘汞电极最常用，配**KCl**盐桥。但是温度系数较大，

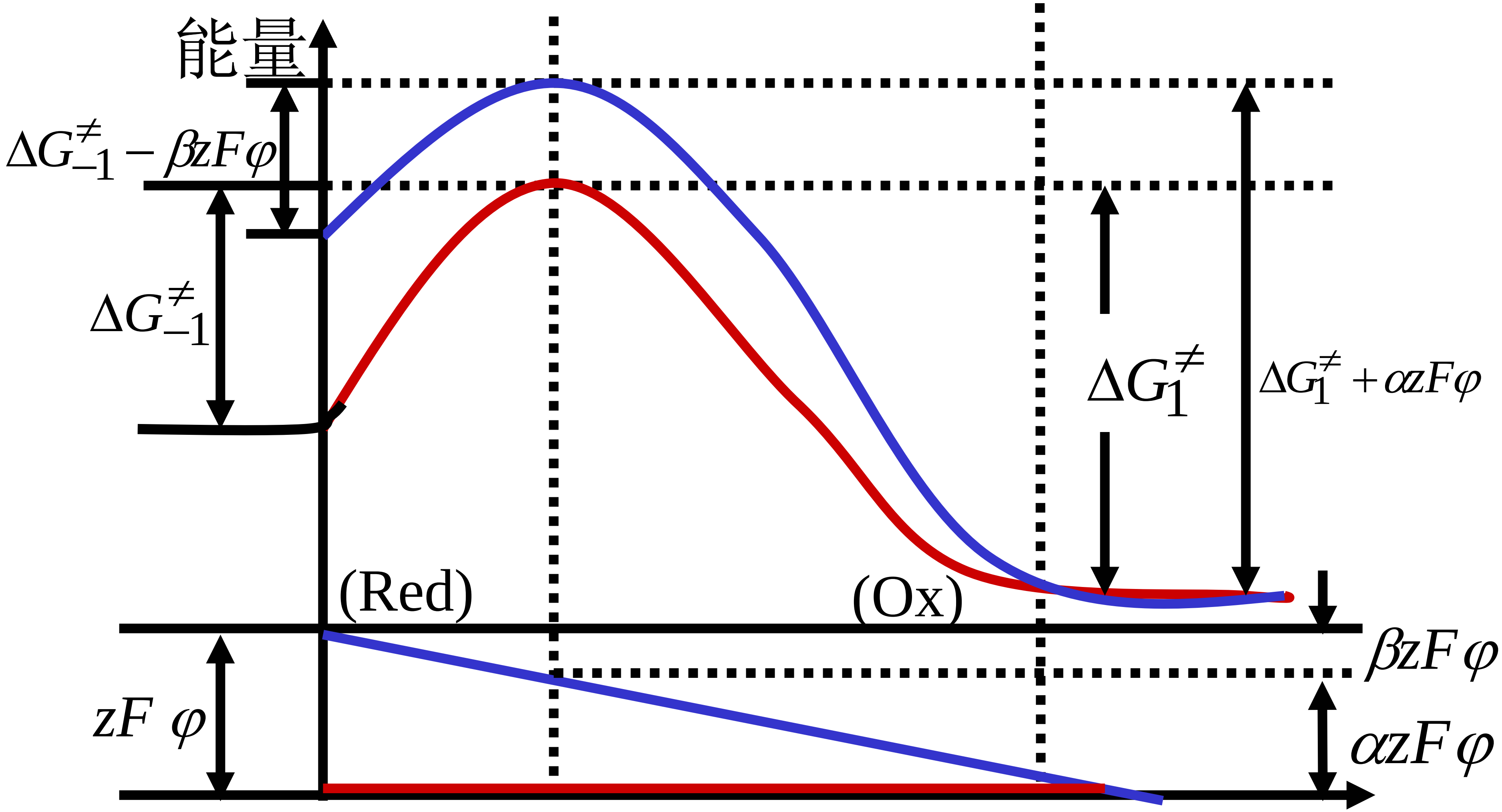
双电极电解池的电势分布应主要降在双电层区间

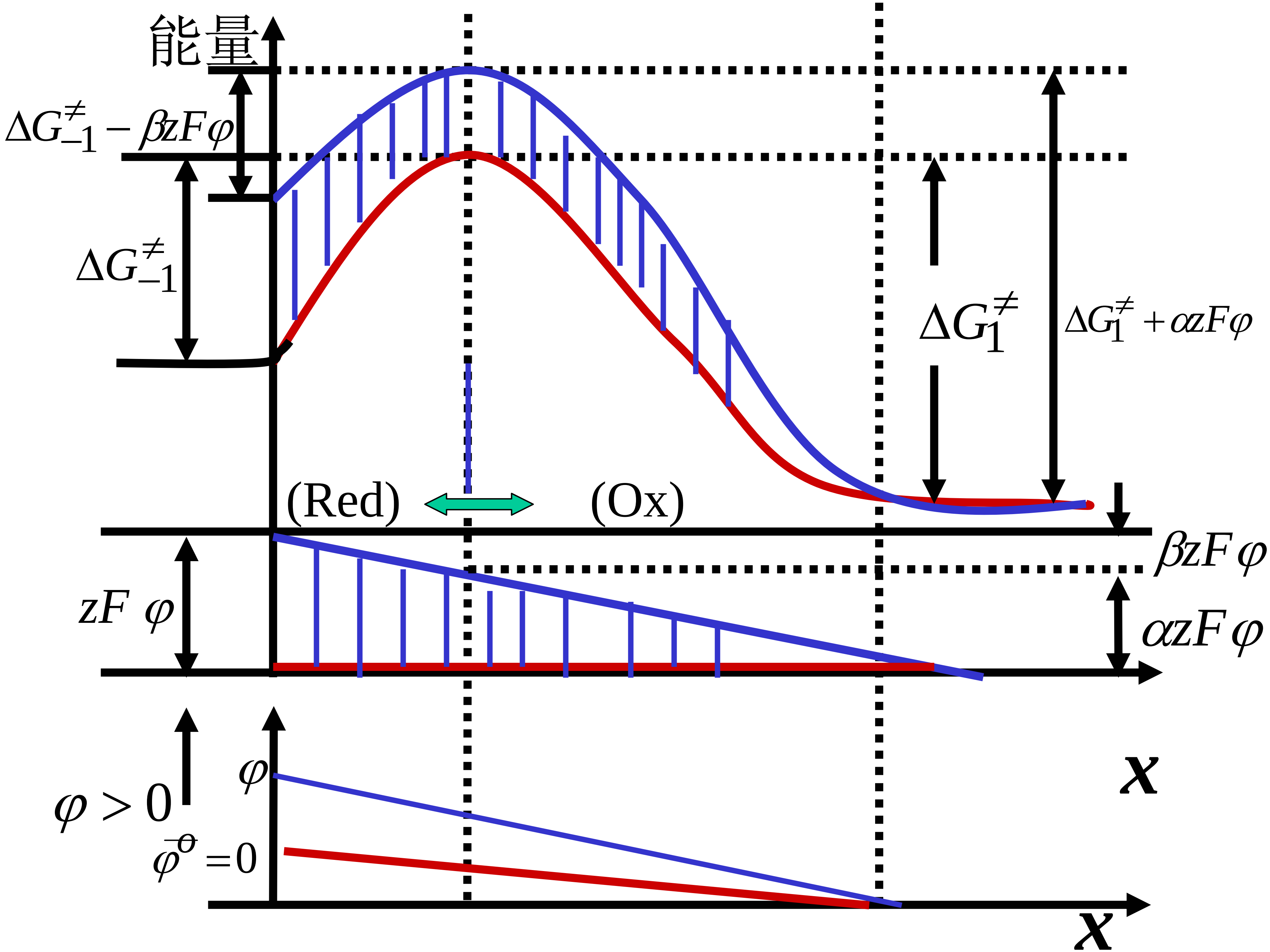




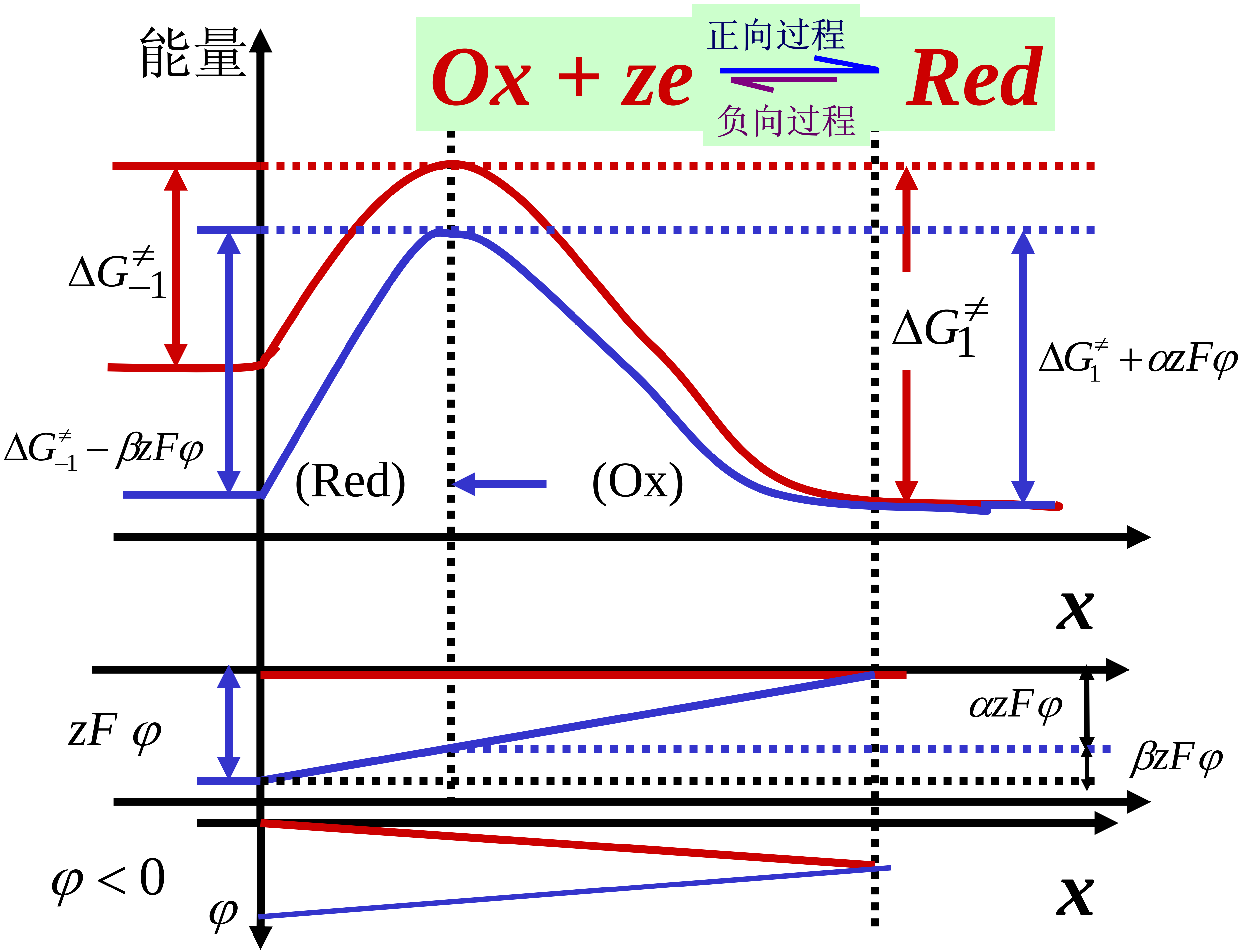
改变$\Delta_r G$，直接影响电极动力学过程

$$\mathbf{Ox + ze \underset{\text{阳极过程}}{\overset{\text{阴极过程}}{\rightleftharpoons}} Red}$$


能量
$\Delta G^{\neq}_{-1} - \beta zF\varphi$
$\Delta G^{\neq}_{-1}$
$\Delta G^{\neq}_{1}$
$\Delta G^{\neq}_{1} + \alpha zF\varphi$
(Red)
(Ox)
$\beta zF\varphi$
$zF\ \varphi$
$\alpha zF\varphi$



能量
$\Delta G^{\neq}_{-1} - \beta zF\varphi$
$\Delta G^{\neq}_{-1}$
$\Delta G^{\neq}_{1}$
$\Delta G^{\neq}_{1} + \alpha zF\varphi$
(Red)
(Ox)
$\beta zF\varphi$
$zF\ \varphi$
$\alpha zF\varphi$
x
φ
$\varphi > 0$
$\varphi^{\theta} = 0$
x



能量
Ox + ze
正向过程
负向过程
Red
$\Delta G^{\neq}_{-1}$
$\Delta G^{\neq}_{-1} - \beta zF\varphi$
(Red)
(Ox)
$\Delta G^{\neq}_{1}$
$\Delta G^{\neq}_{1} + \alpha zF\varphi$
x
$zF\ \varphi$
$\alpha zF\varphi$
$\beta zF\varphi$
$\varphi < 0$
φ
x

$$\Theta \qquad \alpha F\varphi + \beta F\varphi = F\varphi$$

$$\alpha + \beta = 1$$

α，*β*分别表示对所研究电极施加*φ*（*Δφ*）后分别对其正向和负向过程活化能的影响程度

“电荷传递系数”（对称因