14장 전극 전위

Electrode Potentials

14-3 표준전위(standard potentials)

- **표준환원전위** (standard reduction potential)
  - 표준상태에서의 환원전위
  - 표준상태 : 화학종이 고체, 액체, 농도가 1 M, 압력이 1 기압인 상태

- 환원전위 (reduction potential)
  - 환원 반응이 일어나려는 경향의 상대적 세기
  - 기준 : SHE

$$2H^+(1\ M, aq) + 2e^- = H_2(g)\quad E^0 = 0.00\ V$$

- 전위의 측정
  - $M^{n+} + ne^- = M$ E^0 ?
  - SHE || M^{n+} | M
  - E^0 (오른쪽)-E^0 (왼쪽) = E^0 (오른쪽)-0
    → E^0 (오른쪽)

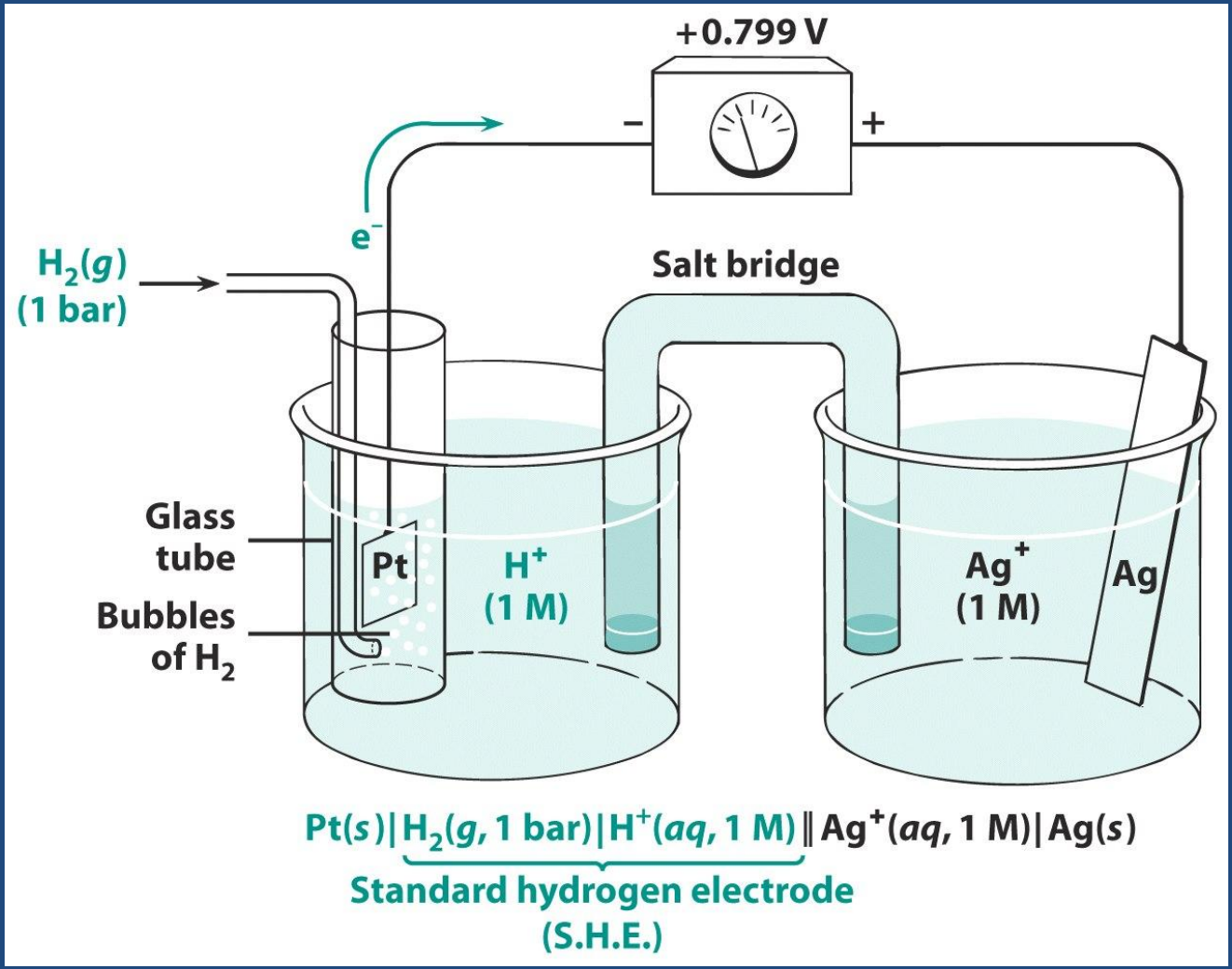


그림 14-6. 반쪽 반응 $Ag^+ + e^- = Ag(s)$ 의 표준환원전위(E^0)를 측정하기 위한 장치구성. 왼쪽 반쪽전지는 표준수소전극(SHE)이라고 부른다.

- SHE || Ag^+ | Ag E^0 = 0.799 V
  - $Ag^+ + e^- = Ag$ E^0 = 0.799 V
  - $\Delta G < 0$
  - 자발적 반응 :
  - 환원제의 세기 : H_2 Ag

- SHE || Cd^{2+} | Cd E^0 = -0.402 V
  - $Cd^{2+} + 2e^- = Cd$ E^0 = -0.402 V
  - $\Delta G > 0$, 비자발적 반응
  - 자발적 반응 :
  - 환원제의 세기 : Cd > H_2

표준전위가 의미하는 것은 무엇인가?

TABLE 14-1 Ordered redox potentials

Oxidizing agent	Reducing agent	E° (V)
$F_2(g) + 2e^- \rightleftharpoons 2F^-$		2.890
$O_3(g) + 2H^+ + 2e^- \rightleftharpoons O_2(g) + H_2O$		2.075
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$		1.507
$Ag^+ + e^- \rightleftharpoons Ag(s)$		0.799
$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$		0.339
$2H^+ + 2e^- \rightleftharpoons H_2(g)$		0.000
$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$		−0.402
$K^+ + e^- \rightleftharpoons K(s)$		−2.936
$Li^+ + e^- \rightleftharpoons Li(s)$		−3.040

Oxidizing power increases ↑

Reducing power increases ↓

- E^0 증가
  - ΔG 감소
  - 자발적 반응성 증가
  - 환원반응의 경향성 증가
  - 산화력의 증가
- 산화력 : $F_2(g) \rightarrow Li^+$
- 환원력 : $Li(s) \rightarrow F^-$

Cu in Cd^{2+} vs. Cd in Cu^{2+}

$Cu + Cd^{2+} = Cu^{2+} + Cd$ 자발적 반응의 방향은?

<형식전위 $E^{0'}$: formal potential>

- 특정 농도의 화학종을 포함하고 있는 전지의 전위

- $AgCl + e^- = Ag + Cl^-$
  - $E^0 = 0.222$ V
  - $E^0 = 0.197$ V (in 포화 KCl)

14-4 Nernst 식

$$aA + ne^- = bB$$

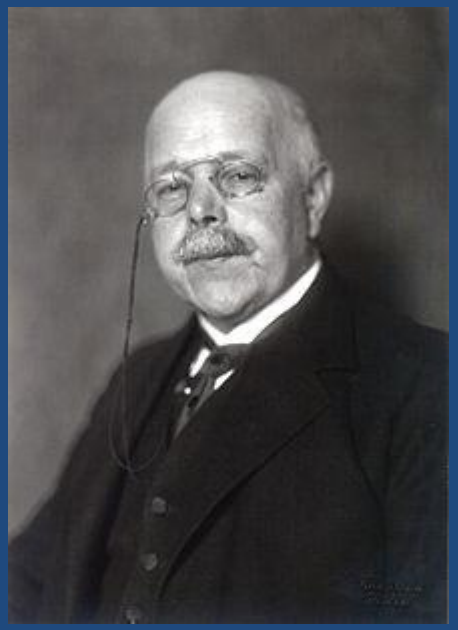
$$E = E^0 - \frac{0.05916}{n} \log \frac{[B]^b}{[A]^a}$$

- 0.05916 ?
- 단위?

Walther Hermann Nernst

The Nobel Prize in Chemistry 1920

"in recognition of his work in thermochemistry".



(1864 –1941)

German physical chemist and physicist who is known for his theories behind the calculation of chemical affinity as embodied in the third law of thermodynamics, for which he won the 1920 Nobel Prize in chemistry. Nernst helped establish the modern field of physical chemistry and contributed to electrochemistry, thermodynamics, solid state chemistry and photochemistry. He is also known for developing the Nernst equation.

Sweden 1980, Nov. 18

German 1950, July 10

복 습

- E^0?
  - $AgCl + e^- = Ag + Cl^-$ $E^0 = 0.222$ V
  - 부호? 크기?
- $Cd \mid Cd^{2+} \parallel Cl^- \mid AgCl \mid Ag$
  - $AgCl + e^- = Ag + Cl^-$ $E^0 = 0.222$ V
  - $Cd^{2+} + 2e^- = Cd$ $E^0 = -0.402$ V

$2AgCl + Cd = 2Ag + 2Cl^- + Cd^{2+}$ $E^0 = 0.624$ V

<완전한 반응식에 대한 Nernst 식>

- $Cd|Cd(NO_3)_2\,(0.01\ M)||KCl(0.5\ M)|AgCl|Ag$

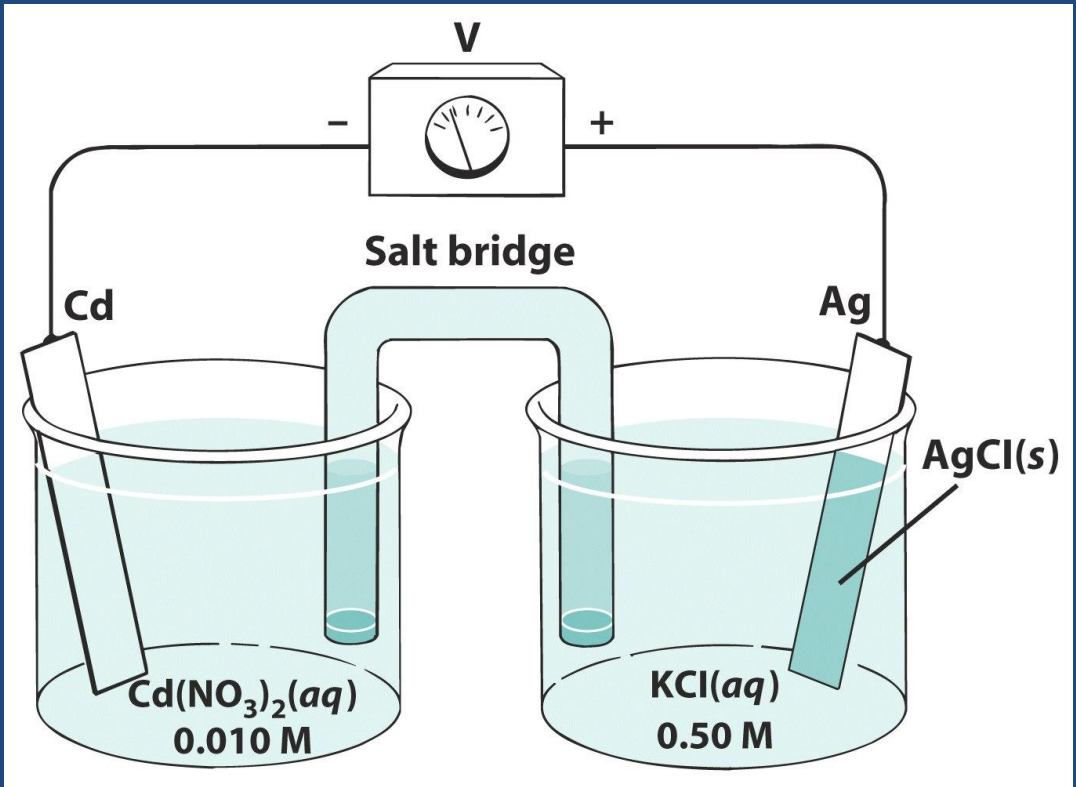
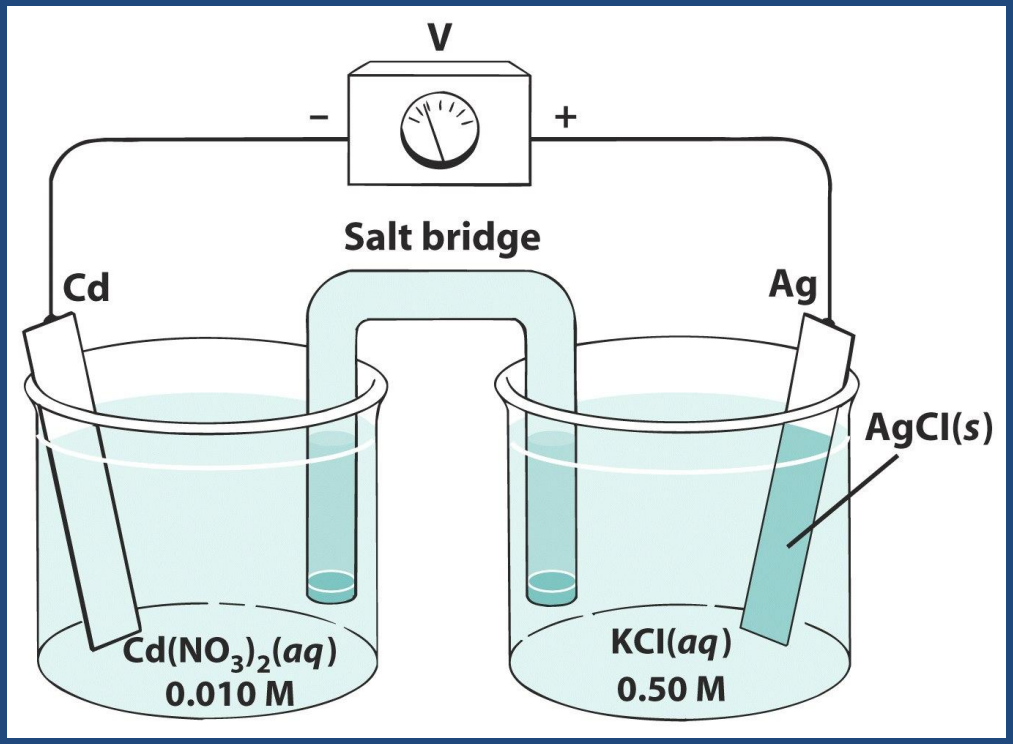


그림 14-4 또 하나의 갈바니 전지

$Cd|Cd(NO_3)_2\,(0.01\ M)||KCl(0.5\ M)|AgCl|Ag$

- E_+ (오른쪽)
  - $AgCl + e^- = Ag + Cl^-$ $E^0 = 0.222$ V
  - $E_+ = E^0 - 0.05916 \log[Cl^-]$
    $= 0.222 - 0.05916 \log 0.5 = 0.24$ V
- E_- (왼쪽)
  - $Cd^{2+} + 2e^- = Cd$ $E^0 = -0.402$ V
  - $E_- = E^0 - (0.05916/2) \log(1/0.01) = -0.461$ V
- $E = E_+ - E_- = 0.24 - (-)0.461 = 0.701$ V

$Cd|Cd(NO_3)_2\ (0.01\ M)||KCl(0.5\ M)|AgCl|Ag$



- $2AgCl + Cd = 2Ag + 2Cl^- + Cd^{2+}$
  - E = 0.701 V
  - 정반응이 자발적
  - 전자의 이동 : Cd → Ag

< 더 + 값을 갖는 전위를 향한 전자의 흐름>

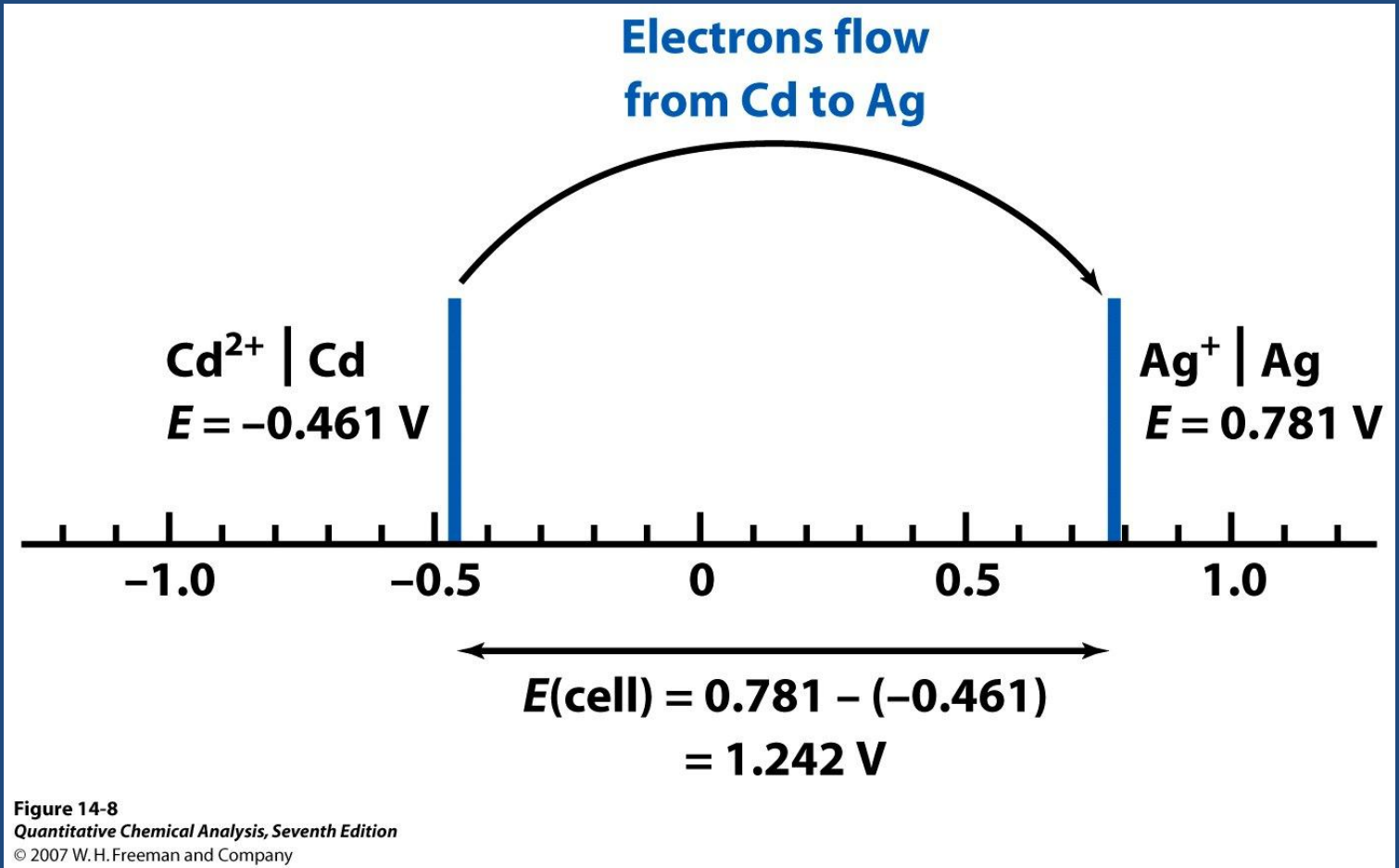


Figure 14-8
Quantitative Chemical Analysis, Seventh Edition

- 전자의 이동 : Cd → Ag

<같은 반응에 대한 다른 표현>

- **$Cd|Cd(NO_3)_2\,(0.01\ M)||KCl(0.5\ M)|AgCl|Ag$**

- $AgCl + e^- = Ag + Cl^-$ $\quad E^0 = 0.222$ V
  - $E_+ = E^0 - 0.05916 \log [Cl^-]$
  - $E_+ = 0.222 - 0.05916 \log 0.5 = 0.24$ V

- $Ag^+ + e = Ag \quad E^0 = 0.799$ V
  - $E_+ = E^0 - 0.05916 \log(1/[Ag^+])$
  - $E_+ = 0.799 - 0.05916 \log([Cl^-]/K_{sp})$
  - $E_+ = 0.799 - 0.05916 \log(0.5/1.8 \times 10^{-10}) =$ 0.24 V
  - $K_{sp} = [Ag^+][Cl^-]$

- $Pb \mid PbF_2 \mid F^- \parallel Cu^{2+} \mid Cu$
- $Pb^{2+} + 2e^- = Pb$
  - $E = E^0 - (0.05916/2) \log(1/[Pb^{2+}])$
  - $= E^0 - (0.05916/2) \log(1/[Pb^{2+}])$
  - $= E^0 - (0.05916/2) \log([F^-]^2/K_{sp})$
  - $K_{sp} = [Pb^{2+}][F^-]^2$
- $PbF_2 + 2e^- = Pb + 2F^-$
  - $E = E^0 - (0.05916/2) \log([F^-]^2)$

14-5 E^0와 평형상수

- At 평형, E=0

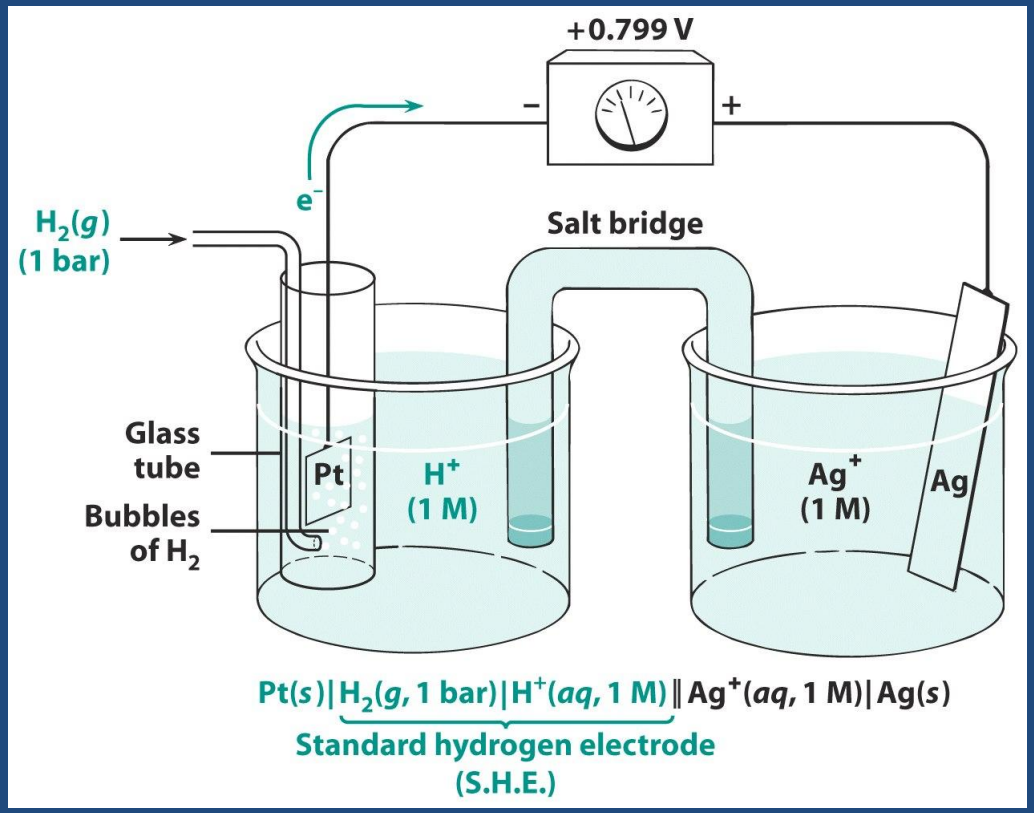
$$E = E^0 - \frac{0.05916}{n}\log K = 0$$

$$K = 10^{\frac{n \times E^0}{0.05916}}$$

14-6 기준전극(reference electrode)

SHE || Ag^+ | Ag

기준전극 지시전극



[더 편리한 기준전극]

① 은-염화은 전극 ($Ag|AgCl|Cl^-$)

– $AgCl + e^- = Ag + Cl^-$ $E^0 = 0.222$ V

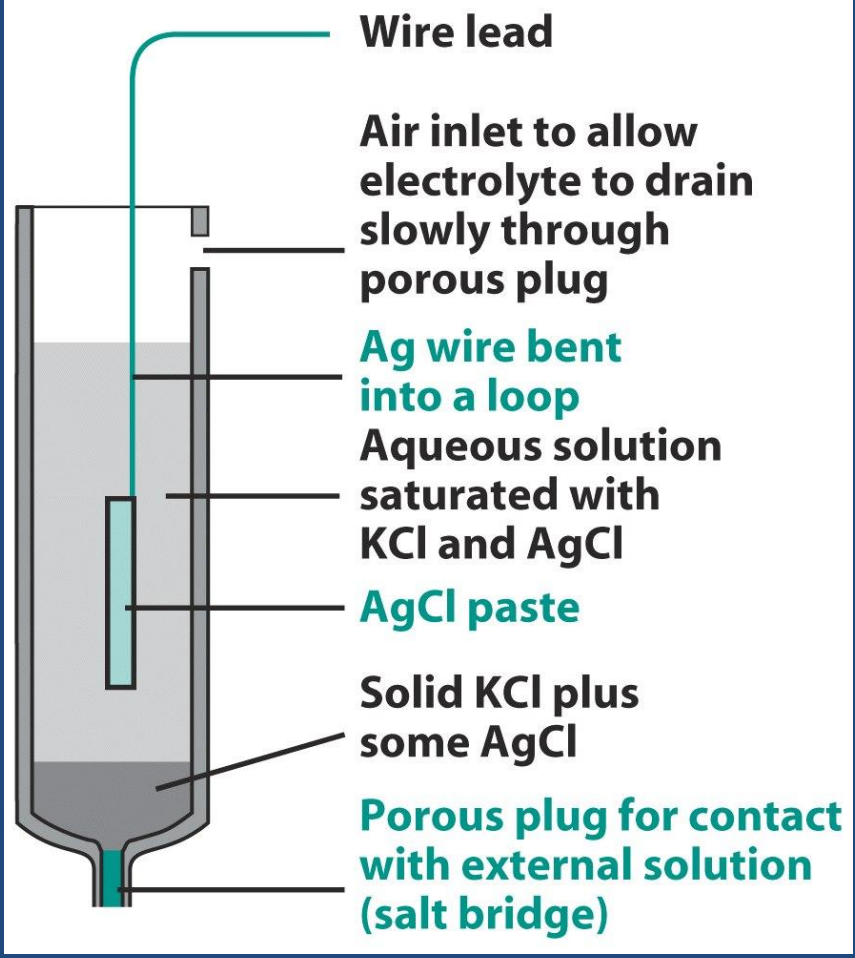


그림 14-10. 은-염화은 기준전극

[더 편리한 기준전극]

② 칼로멜 기준전극 ($Hg|Hg_2Cl_2|Cl^-$)

– $Hg_2Cl_2 + 2e^- = 2Hg + 2Cl^-$ $E^0 = 0.268$ V

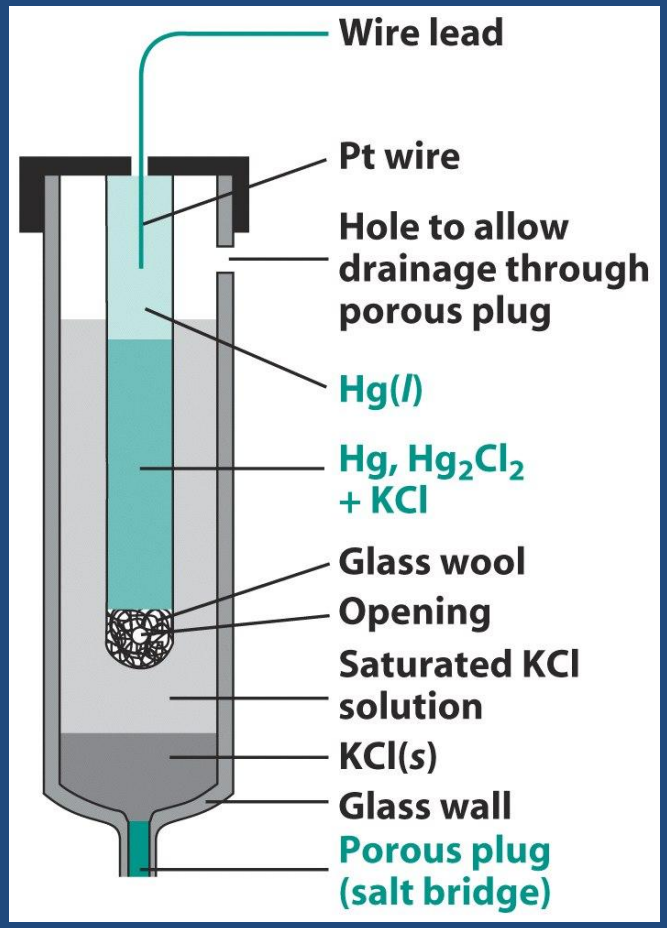


그림 14-11. 포화 칼로멜 전극

<다른 기준점에 대한 전압 변환>

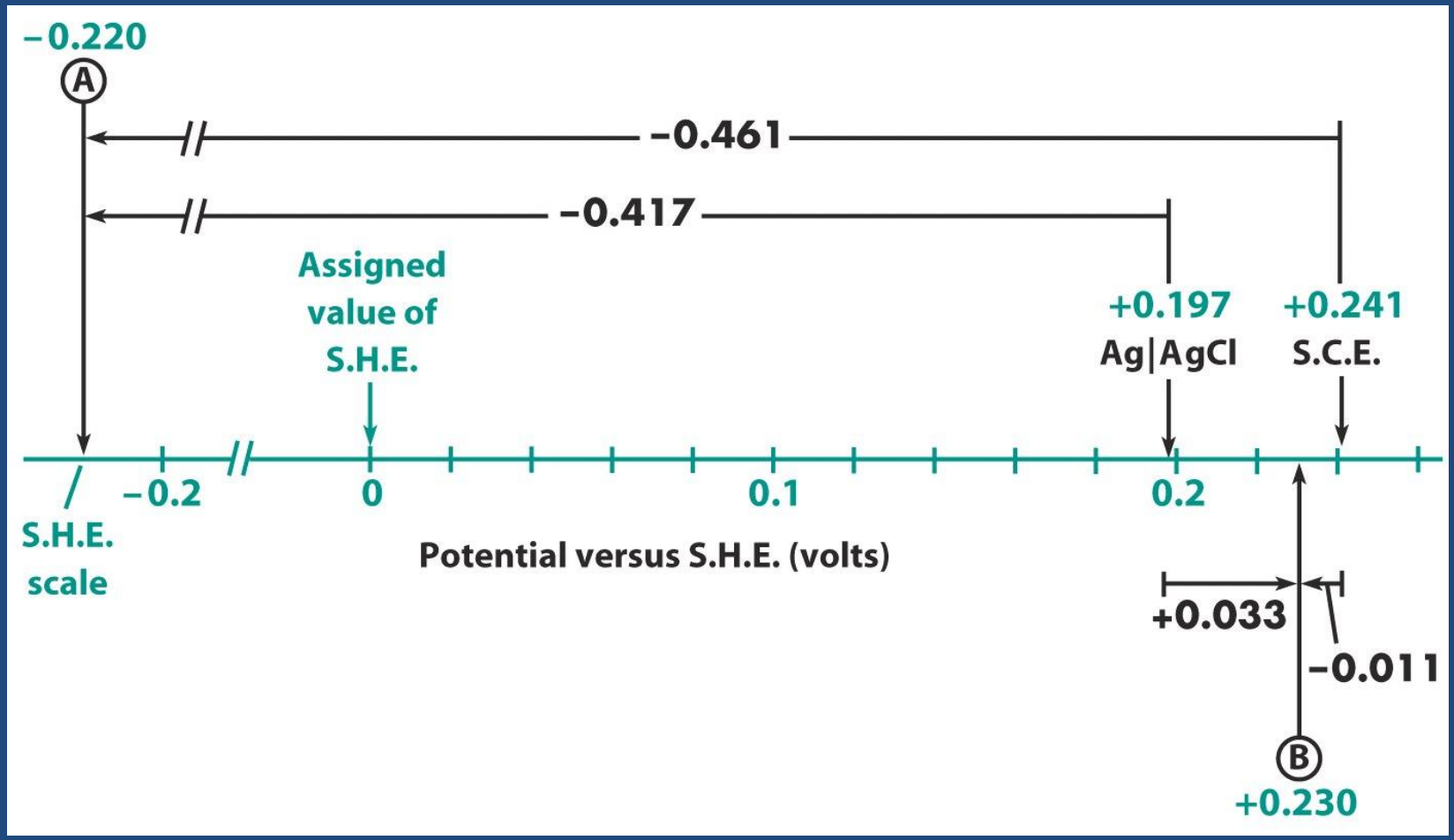


그림 14-12. 한 기준점을 다른 기준점의 전위로 바꾸는 그림