

Lecture #15 of 20+

Liquid-Junction Potentials

Chapter 2

Q: What's in this set of lectures?

A: B&F Chapter 2 main concepts:

- “Section 2.1”: Salt; Activity; Underpotential deposition
- Section 2.3: Transference numbers; Liquid-junction potentials
- Sections 2.2 & 2.4: Donnan potentials; Membrane potentials; pH meter; Ion-selective electrodes



$$E = E^0 - \frac{RT}{nF} \ln \frac{a_R}{a_O}$$

← activity of R
← activity of O

the *standard potential*

(look it up in the back of your book or in the CRC table)

... the activity is the product of the activity coefficient and the concentration...
 ... divided by the standard-state concentration, which is (nearly) always 1 M...

$$E = E^0 - \frac{RT}{nF} \ln \frac{\gamma_R C_R / C_R^0}{\gamma_O C_O / C_O^0}$$

$$E = E^0 - \frac{RT}{nF} \ln \frac{\gamma_R}{\gamma_O} - \frac{RT}{nF} \ln \frac{C_R / C_R^0}{C_O / C_O^0}$$

(UPDATED)

$$E = \boxed{E^0 - \frac{RT}{nF} \ln \frac{\gamma_R}{\gamma_O}} - \frac{RT}{nF} \ln \frac{C_R/C_R^0}{C_O/C_O^0}$$

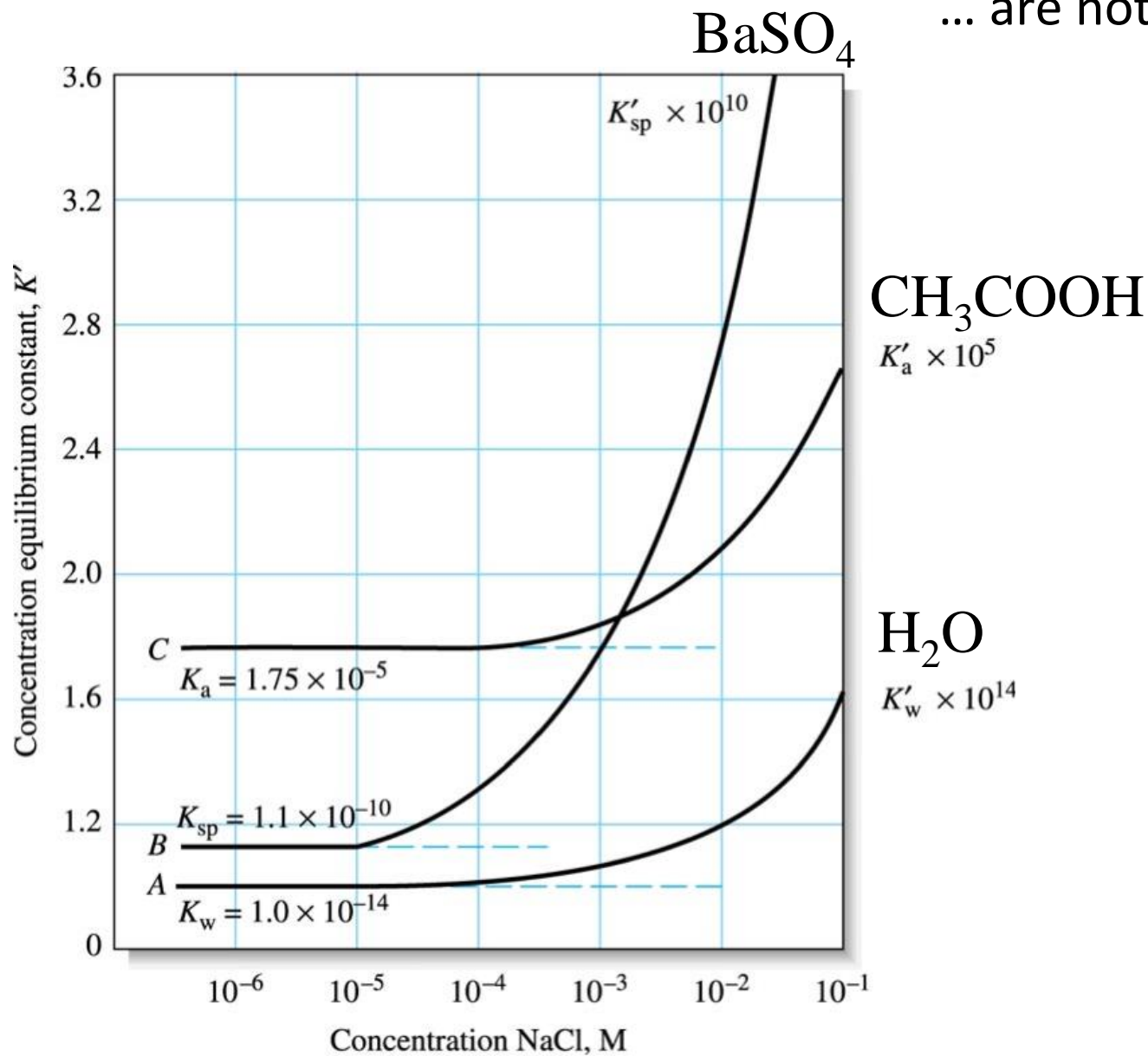
$E^{0'}$

$$E = E^{0'} - \frac{RT}{nF} \ln \frac{C_R/C_R^0}{C_O/C_O^0}$$

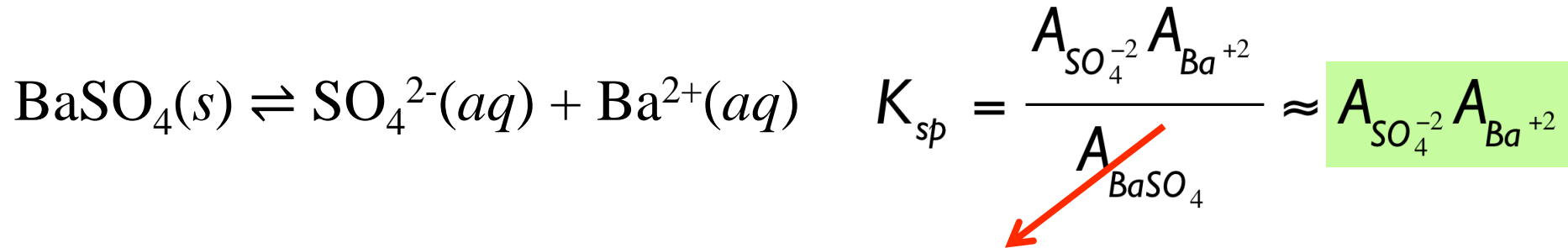
the *formal potential*... this depends on the identity and concentration of all ionizable species present in solution

However, (concentration) equilibrium “constants” ...

... are not constants...

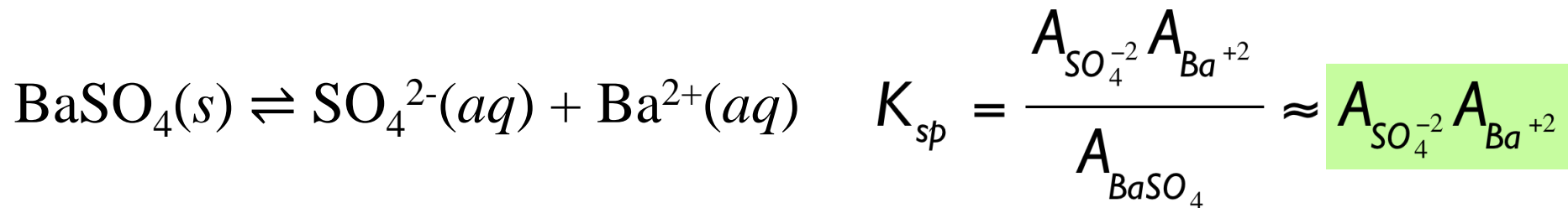


... let's focus on the solubility of BaSO₄...



A (activity) = 1.0 for any pure solid compound
in its standard state at room temperature

... let's focus on the solubility of BaSO₄...



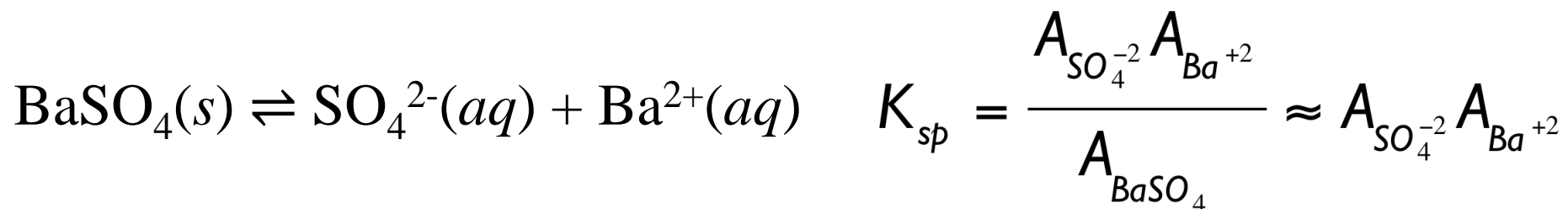
$$K_{sp} = \gamma_{\text{SO}_4^{2-}} [\text{SO}_4^{2-}] \gamma_{\text{Ba}^{2+}} [\text{Ba}^{2+}]$$

the *activity coefficient*
for SO₄²⁻

the *concentration*
of SO₄²⁻

(already divided by the standard-state concentration)

... let's focus on the solubility of BaSO₄...



$$K_{sp} = \gamma_{\text{SO}_4^{-2}} [\text{SO}_4^{-2}] \gamma_{\text{Ba}^{+2}} [\text{Ba}^{+2}]$$

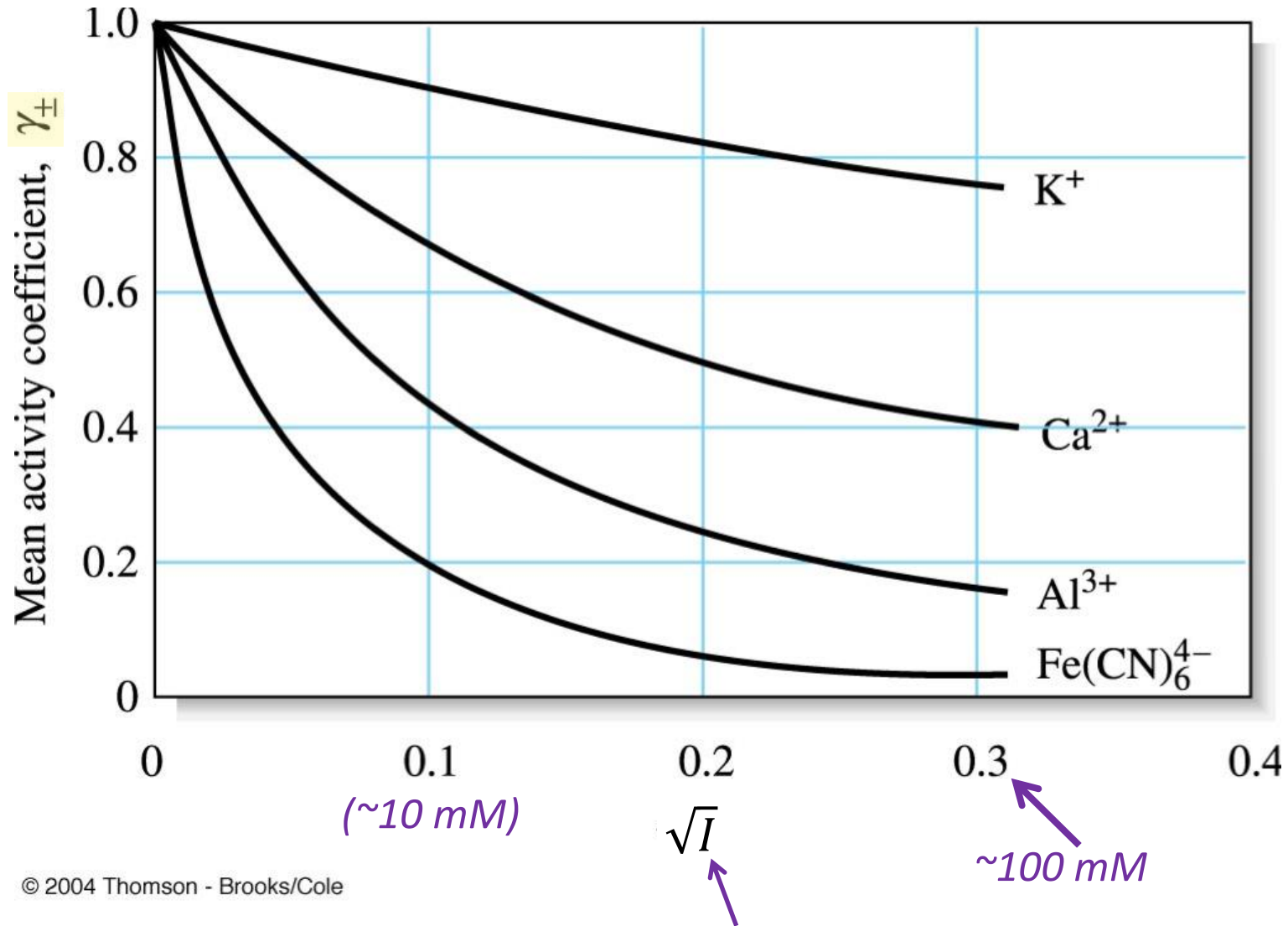
↑
the *thermodynamic equilibrium constant*

$$K'_{sp} = \frac{K_{sp}}{\gamma_{\text{SO}_4^{-2}} \gamma_{\text{Ba}^{+2}}} = [\text{SO}_4^{-2}] [\text{Ba}^{+2}]$$

↑
the *concentration equilibrium constant*

(with each concentration already divided by its standard-state concentration)

... the greater the charge on an ion, the greater the **depression** of its activity coefficient by an inert salt...



Ionic strength, $I = 0.5(z_A^2[A] + z_B^2[B] + z_C^2[C] + \dots)$

... so, for NaCl, what is I ? **[NaCl]!**

Fig. 10-3, p. 272 in Skoog & West

... the greater the charge on an ion, the greater the **depression** of its activity coefficient by an inert salt... **but at high concentration, this trend flips!**

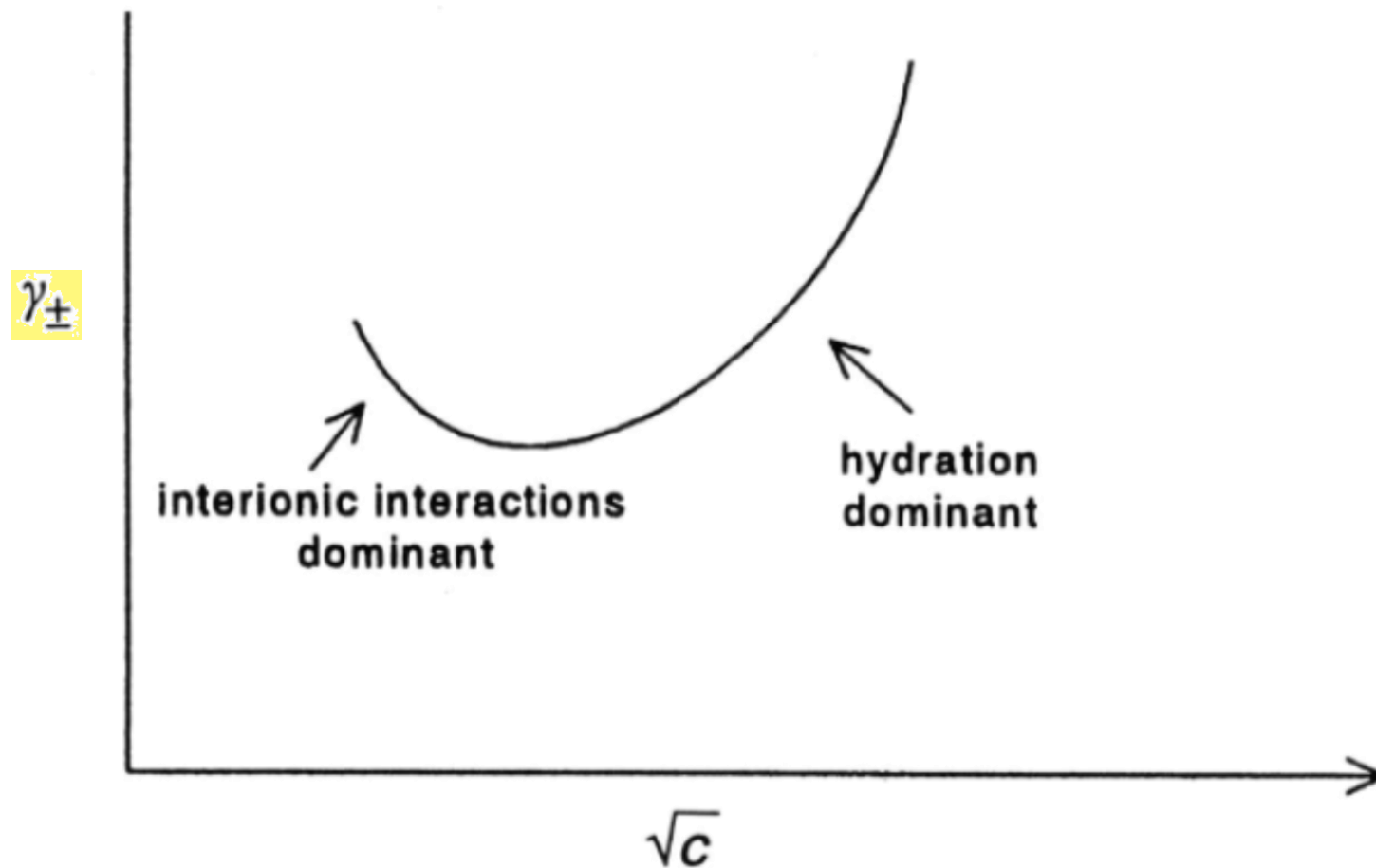
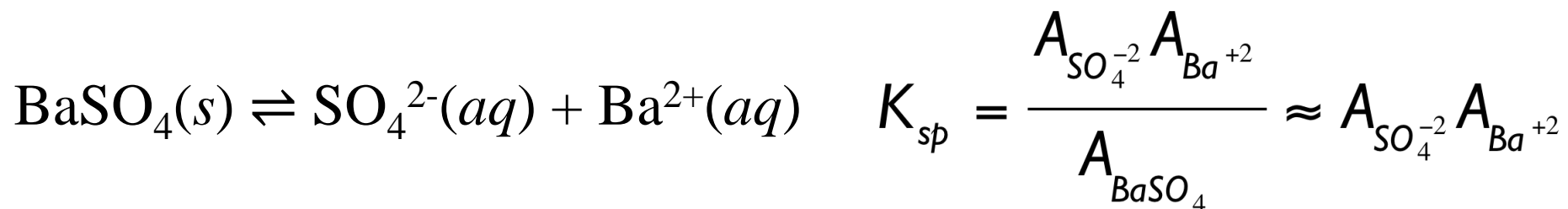


Fig. 2.18. Schematic of the observed trend of γ_{\pm} versus \sqrt{c} curve for salts showing a minimum.

... let's focus on the solubility of BaSO₄...

(UPDATED) 582



$$K_{sp} = \gamma_{\text{SO}_4^{-2}} [\text{SO}_4^{-2}] \gamma_{\text{Ba}^{+2}} [\text{Ba}^{+2}]$$

$$K_{sp}' = \frac{K_{sp}}{\gamma_{\text{SO}_4^{-2}} \gamma_{\text{Ba}^{+2}}} = [\text{SO}_4^{-2}] [\text{Ba}^{+2}]$$

... but what are these values? That is, how do we calculate them...
... and **why** do they depend on the concentration of salt?

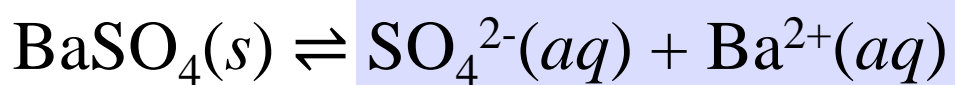
(with each concentration already divided by its standard-state concentration)

... in all three of these cases, $K' > K$, at not too large of an ionic strength

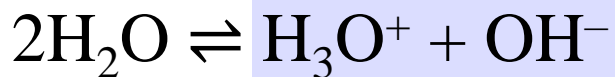
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less ionic

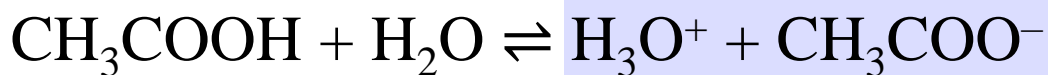
more ionic



$$K_{sp} = \frac{A_{\text{SO}_4^{2-}} A_{\text{Ba}^{2+}}}{A_{\text{BaSO}_4}} \approx A_{\text{SO}_4^{2-}} A_{\text{Ba}^{2+}}$$



$$K_w = A_{\text{H}_3\text{O}^+} A_{\text{OH}^-}$$



$$K_a = \frac{A_{\text{H}_3\text{O}^+} A_{\text{CH}_3\text{COO}^-}}{A_{\text{CH}_3\text{COOH}}}$$

general observation: K' always shifts (from K) to favor the **most ionic state** of the equilibrium

$$E = E^{0'} - \frac{RT}{nF} \ln \frac{C_R / C_R^0}{C_O / C_O^0}$$

Question: How, qualitatively, is the equilibrium potential for Fe²⁺/Fe³⁺ affected by the addition of a supporting electrolyte, KF, at a concentration of 0.1 M?



$$E = E^0 - \frac{RT}{nF} \ln \frac{\gamma_R}{\gamma_O} - \frac{RT}{nF} \ln \frac{C_R / C_R^0}{C_O / C_O^0}$$

... now, $\gamma_{\text{Fe}^{3+}} < \gamma_{\text{Fe}^{2+}}$, agreed?...

Debye–Hückel equation

(in water at 25 °C)

$$-\log \gamma_x = \frac{0.51z_x^2\sqrt{I}}{1 + 3.3\alpha_x\sqrt{I}}$$

α = effective diameter of hydrated ion (nm)

TABLE 10-2

Activity Coefficients for Ions at 25 °C

Ion	Activity Coefficient at Indicated Ionic Strength					
	α_x , nm	0.001	0.005	0.01	0.05	0.1
H ₃ O ⁺	0.9	0.967	0.934	0.913	0.85	0.83
Li ⁺ , C ₆ H ₅ COO ⁻	0.6	0.966	0.930	0.907	0.83	0.80
Na ⁺ , IO ₃ ⁻ , HSO ₃ ⁻ , HCO ₃ ⁻ , H ₂ PO ₄ ⁻ , H ₂ AsO ₄ ⁻ , OAc ⁻	0.4–0.45	0.965	0.927	0.902	0.82	0.77
OH ⁻ , F ⁻ , SCN ⁻ , HS ⁻ , ClO ₃ ⁻ , ClO ₄ ⁻ , BrO ₃ ⁻ , IO ₃ ⁻ , MnO ₄ ⁻	0.35	0.965	0.926	0.900	0.81	0.76
K ⁺ , Cl ⁻ , Br ⁻ , I ⁻ , CN ⁻ , NO ₂ ⁻ , NO ₃ ⁻ , HCOO ⁻	0.3	0.965	0.925	0.899	0.81	0.75
Rb ⁺ , Cs ⁺ , Tl ⁺ , Ag ⁺ , NH ₄ ⁺	0.25	0.965	0.925	0.897	0.80	0.75
Mg ²⁺ , Be ²⁺	0.8	0.872	0.756	0.690	0.52	0.44
Ca ²⁺ , Cu ²⁺ , Zn ²⁺ , Sn ²⁺ , Mn ²⁺ , Fe ²⁺ , Ni ²⁺ , Co ²⁺ , Phthalate ²⁻	0.6	0.870	0.748	0.676	0.48	0.40
Sr ²⁺ , Ba ²⁺ , Cd ²⁺ , Hg ²⁺ , S ²⁻	0.5	0.869	0.743	0.668	0.46	0.38
Pb ²⁺ , CO ₃ ²⁻ , SO ₃ ²⁻ , C ₂ O ₄ ²⁻	0.45	0.868	0.741	0.665	0.45	0.36
Hg ₂ ²⁺ , SO ₄ ²⁻ , S ₂ O ₃ ²⁻ , Cr ₄ ²⁻ , HPO ₄ ²⁻	0.40	0.867	0.738	0.661	0.44	0.35
Al ³⁺ , Fe ³⁺ , Cr ³⁺ , La ³⁺ , Ce ³⁺	0.9	0.737	0.540	0.443	0.24	0.18
PO ₄ ³⁻ , Fe(CN) ₆ ³⁻	0.4	0.726	0.505	0.394	0.16	0.095
Th ⁴⁺ , Zr ⁴⁺ , Ce ⁴⁺ , Sn ⁴⁺	1.1	0.587	0.348	0.252	0.10	0.063
Fe(CN) ₆ ⁴⁻	0.5	0.569	0.305	0.200	0.047	0.020

Source: Reprinted with permission from J. Kielland, *J. Am. Chem. Soc.*, 1937, 59, 1675. Copyright 1937 American Chemical Society.

Debye–Hückel equation

(in water at 25 °C)

$$-\log \gamma_x = \frac{0.51z_x^2\sqrt{I}}{1 + 3.3\alpha_x\sqrt{I}}$$

α = effective diameter of hydrated ion (nm)

... the derivation is long... but the main idea is that you balance thermal motion (Boltzmann) with electrostatics (Poisson/Gauss)...

Physicist & P-Chemist



Peter Joseph William Debye
(1884–1966)

Physicist & P-Chemist



Erich Armand Arthur Joseph Hückel
(1896–1980)

from Wiki

Debye–Hückel equation (in water at 25 °C)

$$-\log \gamma_x = \frac{0.51z_x^2\sqrt{I}}{1 + 3.3\alpha_x\sqrt{I}}$$

α = effective diameter of hydrated ion (nm)

... the “limiting law” is when $I \rightarrow 0$ (< 10 mM)...

... and then the Debye–Hückel equation simplifies to just the numerator:

$$-\log \gamma_x = 0.51z_x^2\sqrt{I}$$

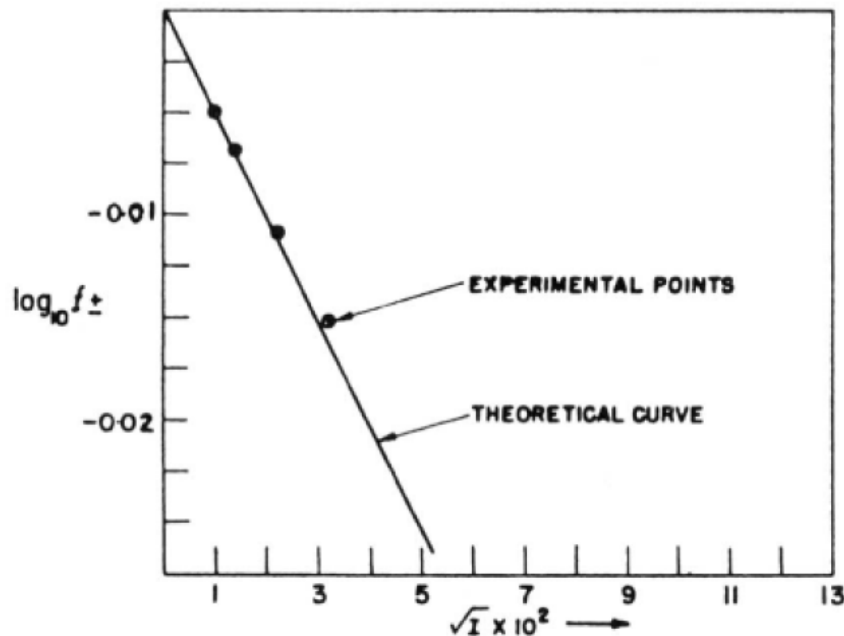


Fig. 3.23. The comparison of the experimentally observed mean activity coefficients of HCl and those that are calculated from the Debye–Hückel limiting law.

Question: How, qualitatively, is the equilibrium potential for $\text{Fe}^{2+}/\text{Fe}^{3+}$ affected by the addition of a supporting electrolyte, KF, at a concentration of 0.1 M? (UPDATED)



$$E = E^0 - \frac{RT}{nF} \ln \frac{\gamma_R}{\gamma_O} - \frac{RT}{nF} \ln \frac{C_R/C_R^0}{C_O/C_O^0}$$

... now, $\gamma_{\text{Fe}^{3+}} < \gamma_{\text{Fe}^{2+}}$, agreed?... So...

$$\frac{\gamma_R}{\gamma_O} > 1.0 \quad \text{and} \quad \ln \frac{\gamma_R}{\gamma_O} > 0$$

... and we conclude that in the presence of added salt... you tell me!

Question: How, qualitatively, is the equilibrium potential for $\text{Fe}^{2+}/\text{Fe}^{3+}$ affected by the addition of a supporting electrolyte, KF, at a concentration of 0.1 M? (UPDATED)



$$E = E^0 - \frac{RT}{nF} \ln \frac{\gamma_R}{\gamma_O} - \frac{RT}{nF} \ln \frac{C_R/C_R^0}{C_O/C_O^0}$$

no added salt...



$$\gamma_O \approx \gamma_R \approx 1.0$$

$$\ln \frac{\gamma_R}{\gamma_O} \approx 0$$

with added salt...



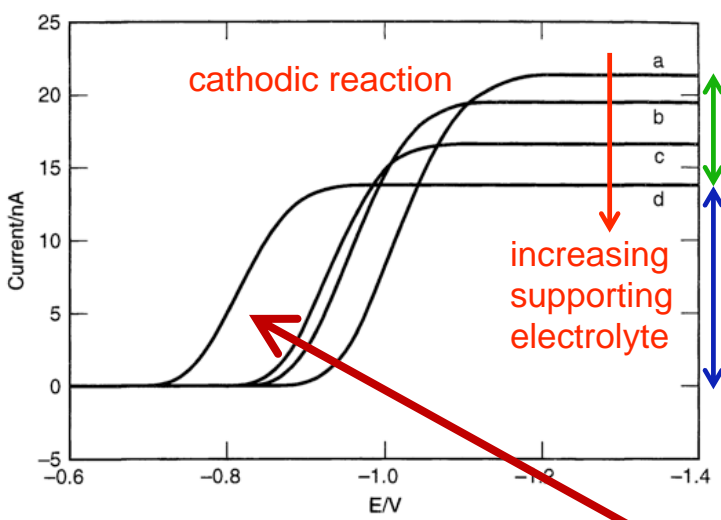
$$\frac{\gamma_R}{\gamma_O} > 1.0 \quad \text{and} \quad \ln \frac{\gamma_R}{\gamma_O} > 0$$

ANSWER: $E^{0'}$ shifts to more negative potentials

Question: What if the redox species were positive/neutral charged, like $Tl^{+}/^0$, and we increased the concentration of supporting electrolyte to ~ 0.1 M? (UPDATED)



$$E = E^0 - \frac{RT}{nF} \ln \frac{\gamma_R}{\gamma_O} - \frac{RT}{nF} \ln \frac{C_R/C_R^0}{C_O/C_O^0}$$



$I_{m-Tl^{+}}$, to bring Tl^{+} to the electrode
 $I_{d-Tl^{+}}$, to bring Tl^{+} to the electrode

with added salt...

$$\frac{\gamma_R}{\gamma_O} > 1.0 \text{ and } \ln \frac{\gamma_R}{\gamma_O} > 0$$

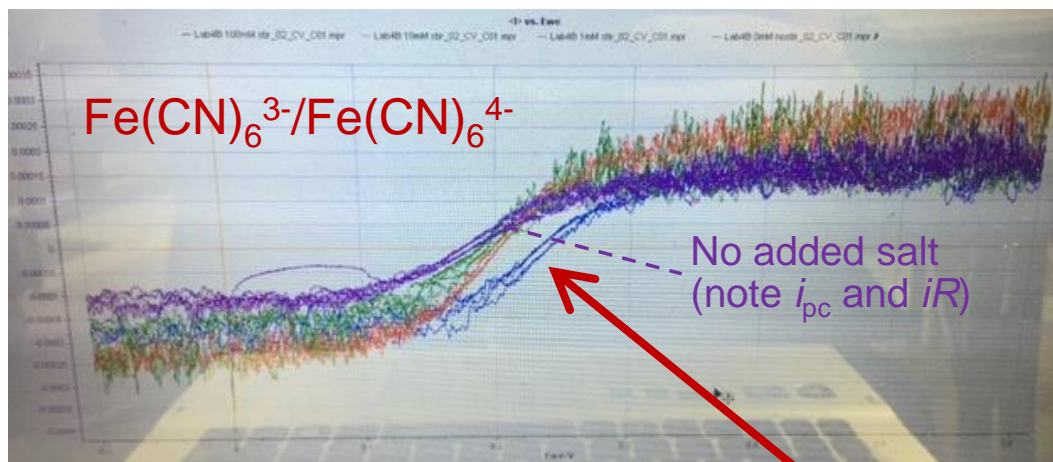
Figure 4.3.5 Voltammograms for reduction of 0.65 mM Tl_2SO_4 at a mercury film on a silver ultramicroelectrode (radius, 15 μm) in the presence of (a) 0, (b) 0.1, (c) 1, and (d) 100 mM $LiClO_4$. The potential was controlled vs. a Pt wire QRE whose potential was a function of solution composition. This variability is the basis for the shifts in wave position along the potential axis. [Reprinted with permission from M. Ciszowska and J. G. Osteryoung, *Anal. Chem.*, **67**, 1125 (1995). Copyright 1995, American Chemical Society.]

ANSWER: E^0 shifts to more negative potentials (which are more positive in TX!)

Question: What if the redox species were negatively charged, like $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}/[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$, and we increased the concentration of supporting electrolyte to $\sim 0.1 \text{ M}$? **(FROM LAB!)** **(UPDATED)**



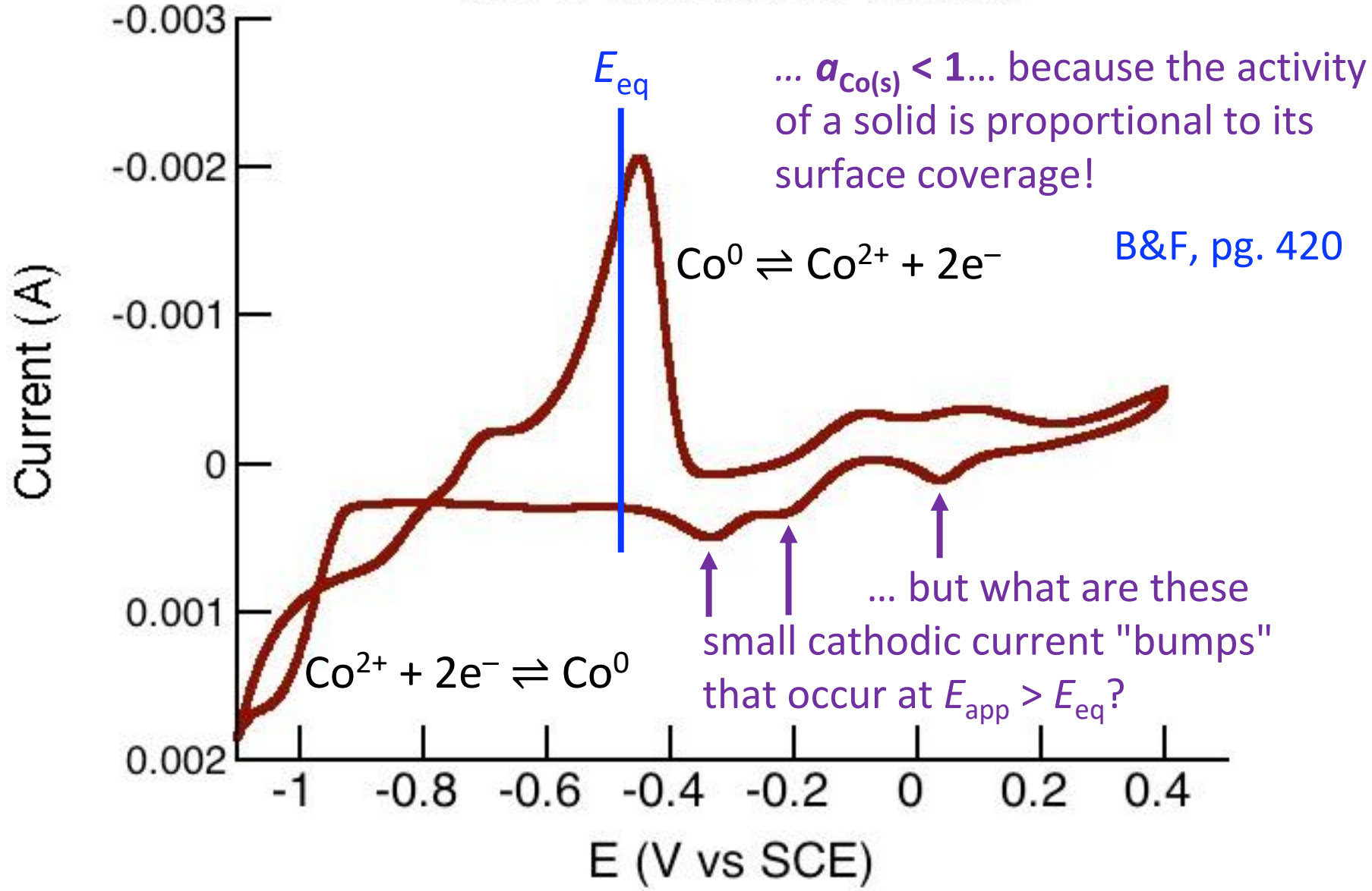
$$E = E^0 - \frac{RT}{nF} \ln \frac{\gamma_R}{\gamma_O} - \frac{RT}{nF} \ln \frac{C_R/C_R^0}{C_O/C_O^0}$$



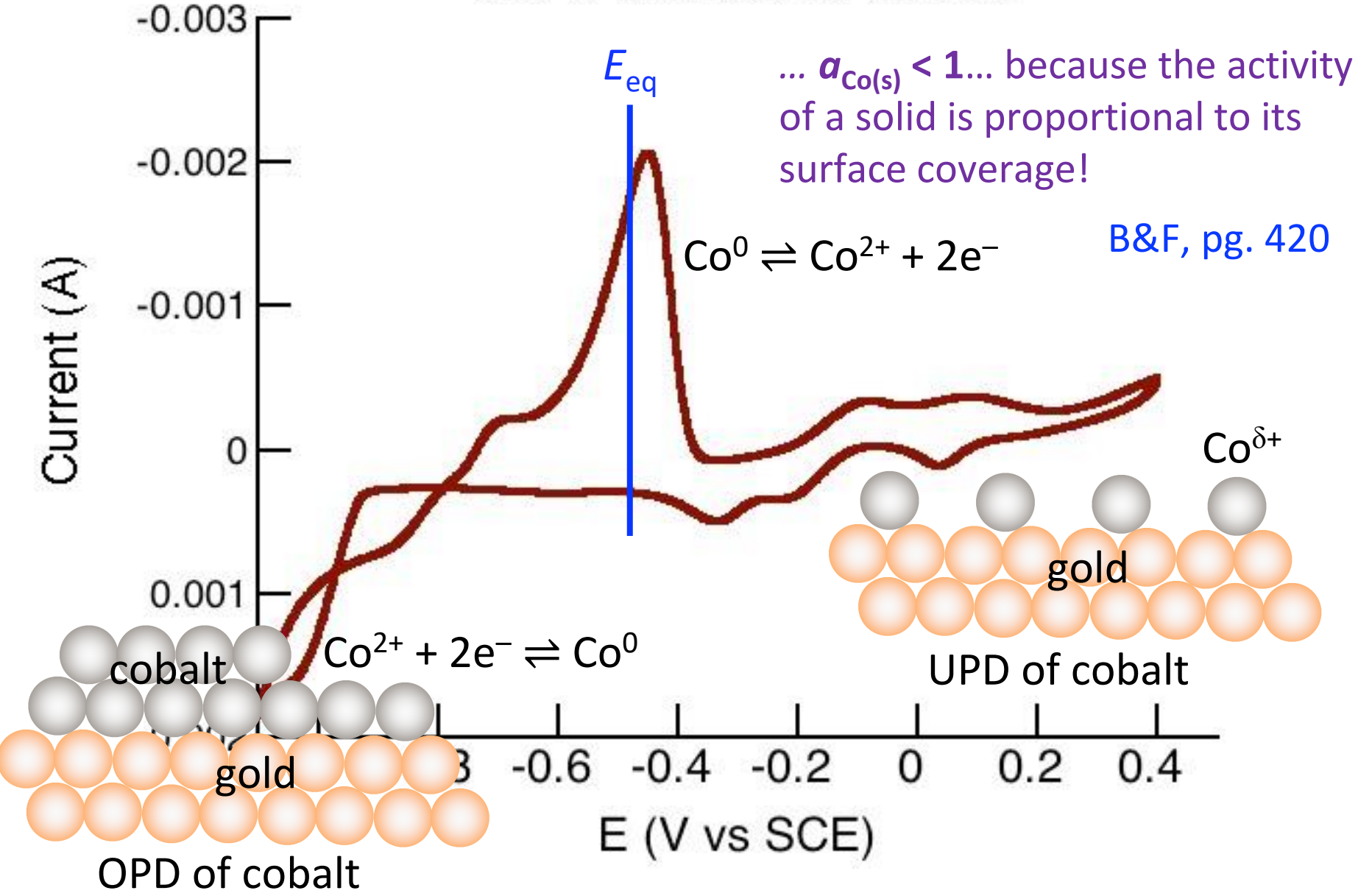
$$\frac{\gamma_R}{\gamma_O} < 1.0 \text{ and } \ln \frac{\gamma_R}{\gamma_O} < 0$$

ANSWER: E^0 shifts to more positive potentials

UPD of cobalt on Au thin film



UPD of cobalt on Au thin film



Q: What's in this set of lectures?

A: B&F Chapter 2 main concepts:

- “Section 2.1”: Salt; Activity; Underpotential deposition
- Section 2.3: Transference numbers; Liquid-junction potentials
- Sections 2.2 & 2.4: Donnan potentials; Membrane potentials; pH meter; Ion-selective electrodes

Now on to two general liquid junctions that we care about (the most)...

595

an SCE

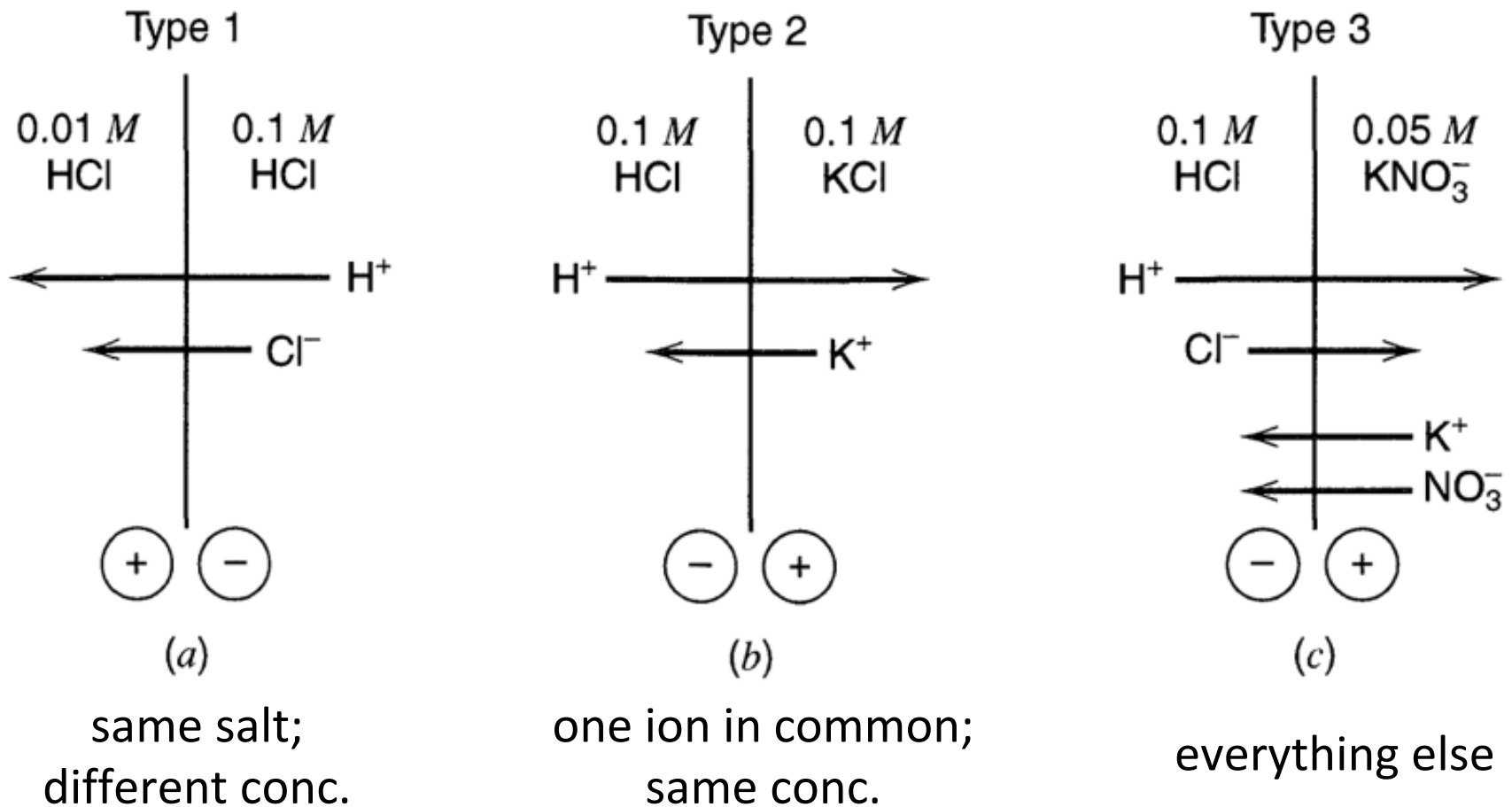


an ISE (for nitrate ions)

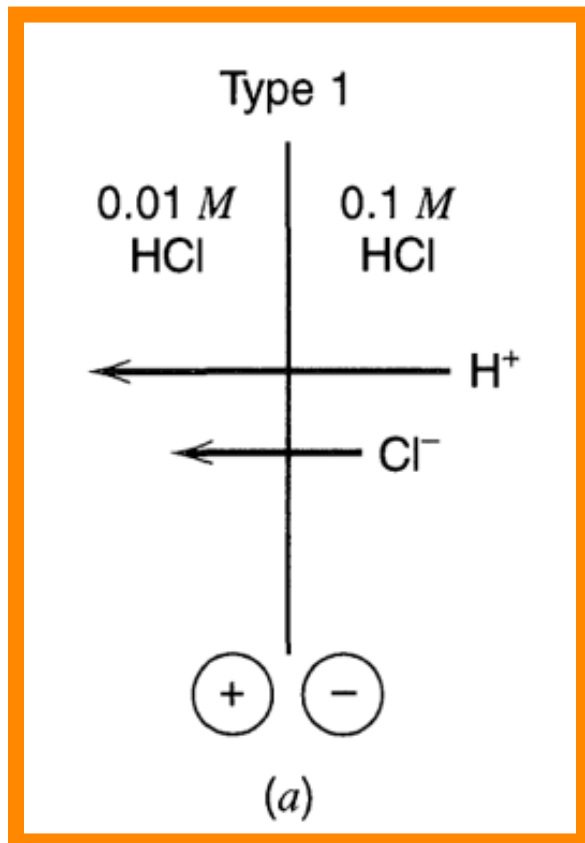


... liquid junctions:

when two ionic solutions are separated across an interface that prevents bulk mixing of the ions, but has ionic permeability, a potential (drop) develops called the *liquid junction potential*.



- ... example "1":
- starting at the side with larger ion concentration
 - the ion the with larger mobility will impart its charge to the opposite side of the junction



same salt;
different conc.

... conceptually, let's think about a condition in the limit where $t_{H^+} \rightarrow 1$ (say $t_{H^+} \approx 0.9$)...

... as H^+ diffuses down its concentration gradient, an electrostatic force is exerted on Cl^- to pull it along (at a larger flux) while at the same time slowing down transport of H^+

... this happens until t_{i-} -effective = 0.5 for both H^+ and Cl^- , and at which time the system has attained steady-state mass transport and has generated a maximum liquid-junction potential.

... FYI, in semiconductor physics this same process results in a Demper potential... and the transport process is called ambipolar diffusion

Recall that *transport number*, t_i , (or *transference number*) is based on ...

$$u_i = \frac{v}{\mathcal{E}} = \frac{|z_i|e}{6\pi\eta r} \quad \text{units: cm}^2/(\text{s V})$$

(Stokes' law)

... and that the ionic conductivity, κ or σ , is defined as...

$$\kappa = F \sum_i |z_i| u_i C_i \quad \text{units: S/cm or } 1/(\Omega \text{ cm})$$

Siemens

... so t_i is the fraction of the solution conductivity attributable to ion "i"

$$t_i = \frac{|z_i| u_i C_i}{\sum_j |z_j| u_j C_j}$$

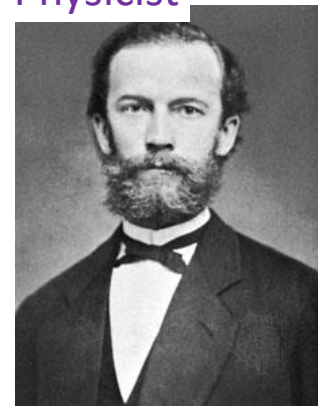
The Kohlrausch law (empirical) and Debye–Hückel–Onsager equation (theoretical) predict that the molar conductivity is proportional to the square root of the salt concentration

$$\Lambda \propto (C)^{1/2}$$

Friedrich Wilhelm Georg Kohlrausch
(1840–1910)

from Wiki

Physicist



Recall that *transport number*, t_i , (or *transference number*) is based on ...

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$$\Lambda \propto (C)^{1/2}$$

P-Chemist & Physicist



Lars Onsager
from Wiki (1903–1976)

"equivalent"
molar (ionic)
conductivity

TABLE 2.3.2 Ionic Properties at Infinite Dilution in Aqueous Solutions at 25°C

Ion	$\lambda_0, \text{cm}^2 \Omega^{-1} \text{equiv}^{-1a}$	$u, \text{cm}^2 \text{sec}^{-1} \text{V}^{-1b}$
H ⁺	349.82	3.625×10^{-3}
K ⁺	73.52	7.619×10^{-4}
Na ⁺	50.11	5.193×10^{-4}
Li ⁺	38.69	4.010×10^{-4}
NH ₄ ⁺	73.4	7.61×10^{-4}
$\frac{1}{2}\text{Ca}^{2+}$	59.50	6.166×10^{-4}
OH ⁻	198	2.05×10^{-3}
Cl ⁻	76.34	7.912×10^{-4}
Br ⁻	78.4	8.13×10^{-4}
I ⁻	76.85	7.96×10^{-4}
NO ₃ ⁻	71.44	7.404×10^{-4}
OAc ⁻	40.9	4.24×10^{-4}
ClO ₄ ⁻	68.0	7.05×10^{-4}
$\frac{1}{2}\text{SO}_4^{2-}$	79.8	8.27×10^{-4}
HCO ₃ ⁻	44.48	4.610×10^{-4}
$\frac{1}{3}\text{Fe}(\text{CN})_6^{3-}$	101.0	1.047×10^{-3}
$\frac{1}{4}\text{Fe}(\text{CN})_6^{4-}$	110.5	1.145×10^{-3}

= F

... and recall the Einstein–Smoluchowski equation to calculate D_i ,

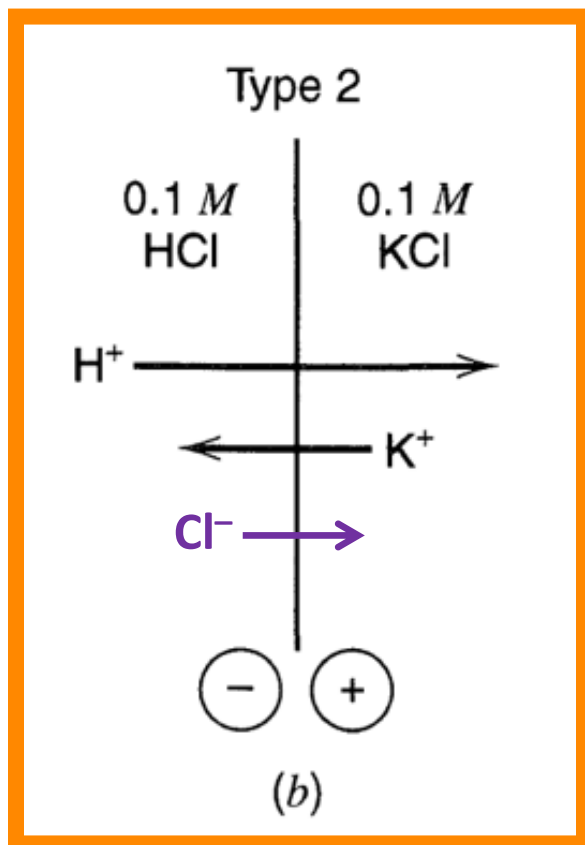
$$\mu_i = \frac{|z_i|FD_i}{RT}$$

^aFrom D. A. MacInnes, "The Principles of Electrochemistry," Dover, New York, 1961, p. 342

^bCalculated from λ_0 .

... example "2":

- compare dissimilar ions (cations or anions)
- the ion with the larger mobility will impart its charge to the opposite side of the junction



one ion in common;
same conc.

... the sign of the liquid-junction potential is obvious for Types 1 and 2 (but not Type 3) based on the mobilities of the individual ions...

... and so when in doubt, think logically about the sign of the potential to verify answers...

... and yes, Cl⁻ will migrate/drift based on the electric potential formed by cation transport

TABLE 2.3.2 Ionic Properties at Infinite Dilution in Aqueous Solutions at 25°C

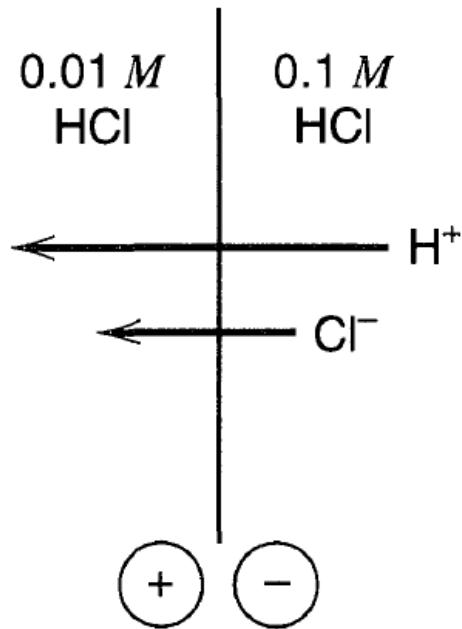
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^aFrom D. A. MacInnes, "The Principles of Electrochemistry," Dover, New York, 1961, p. 342

^bCalculated from λ_0 .

we use t_i values, which are based on *kinetic transport* to determine the liquid-junction potential (for derivations, see B&F, pp. 70 – 72)...

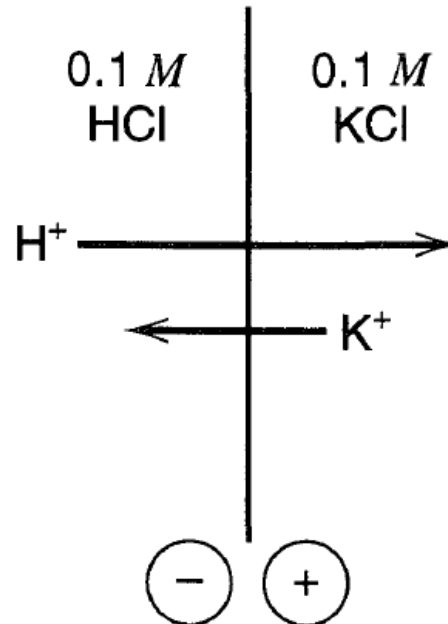
Type 1



(a)

same salt;
different concentrations

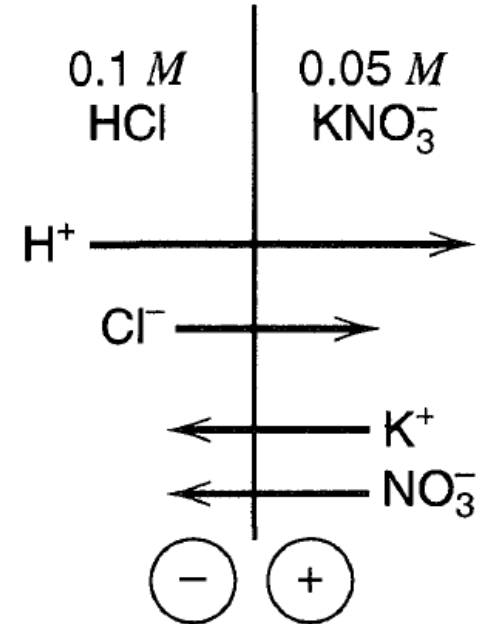
Type 2



(b)

same cation or anion;
different counter ion;
same concentration

Type 3



(c)

no common ions,
and/or one common
ion; different concs

we use t_i values, which are based on **kinetic transport** to determine the liquid-junction potential (for derivations, see B&F, pp. 70 – 72)...

Type 1
$$E_j = (\phi^\beta - \phi^\alpha) = (t_+ - t_-) \frac{RT}{F} \ln \frac{a^{(\alpha)}}{a^{(\beta)}} \dots \text{use the activity of the entire salt}$$

Type 2
$$E_j = \pm \frac{RT}{F} \ln \frac{\sum_i |z_i| u_i C_i(\alpha)}{\sum_i |z_i| u_i C_i(\beta)}$$
 ... use the conductivity due to all ions, even the common one (with a few assumptions, pg. 72)

... sign depends on the charge of the dissimilar ion:

(+) when cations are dissimilar, and (-) when anions are dissimilar

Type 3
$$E_j = \frac{\sum_i \frac{|z_i| u_i}{z_i} [C_i(\beta) - C_i(\alpha)]}{\sum_i |z_i| u_i [C_i(\beta) - C_i(\alpha)]} \frac{RT}{F} \ln \frac{\sum_i |z_i| u_i C_i(\alpha)}{\sum_i |z_i| u_i C_i(\beta)}$$
 the *Henderson Eq.* (with a few assumptions, pg. 72)

... as written, these equations calculate E_j at β vs α

example: B&F Problem 2.14d

Calculate E_j for NaNO_3 (0.10 M) | NaOH (0.10M)
 α | β

1. What Type? Type 2
2. Polarity?

TABLE 2.3.2 Ionic Properties at Infinite Dilution in Aqueous Solutions at 25°C

Ion	$\lambda_0, \text{cm}^2 \Omega^{-1} \text{equiv}^{-1a}$	$u, \text{cm}^2 \text{sec}^{-1} \text{V}^{-1b}$
H ⁺	349.82	3.625×10^{-3}
K ⁺	73.52	7.619×10^{-4}
Na ⁺	50.11	5.193×10^{-4}
Li ⁺	38.69	4.010×10^{-4}
NH ₄ ⁺	73.4	7.61×10^{-4}
$\frac{1}{2}\text{Ca}^{2+}$	59.50	6.166×10^{-4}
OH ⁻	198	2.05×10^{-3}
Cl ⁻	76.34	7.912×10^{-4}
Br ⁻	78.4	8.13×10^{-4}
I ⁻	76.85	7.96×10^{-4}
NO ₃ ⁻	71.44	7.404×10^{-4}
OAc ⁻	40.9	4.24×10^{-4}
ClO ₄ ⁻	68.0	7.05×10^{-4}
$\frac{1}{2}\text{SO}_4^{2-}$	79.8	8.27×10^{-4}
HCO ₃ ⁻	44.48	4.610×10^{-4}
$\frac{1}{3}\text{Fe}(\text{CN})_6^{3-}$	101.0	1.047×10^{-3}
$\frac{1}{4}\text{Fe}(\text{CN})_6^{4-}$	110.5	1.145×10^{-3}

^aFrom D. A. MacInnes, "The Principles of Electrochemistry," Dover, New York, 1961, p. 342

^bCalculated from λ_0 .

Calculate E_j for NaNO_3 (0.10 M) | NaOH (0.10M)

α | β

1. What Type? **Type 2**

2. Polarity? **Polarity should be clear... compare mobilities... μ_{OH^-} is larger...
... so NaNO_3 side will be (-)... and so β vs α will be (+)**

3. Calculate it:

$$E_j = -\frac{RT}{F} \ln \frac{\sum_i |z_i| u_i C_i(\alpha)}{\sum_i |z_i| u_i C_i(\beta)}$$

... (-) due to anions moving

$$E_j = -0.05916 \log \left(\frac{\mu_{\text{NO}_3^-} + \mu_{\text{Na}^+}}{\mu_{\text{OH}^-} + \mu_{\text{Na}^+}} \right)$$

← as predicted, a (+) LJ potential correlates with the compartment in the denominator, β , vs α

$$E_j = -0.05916 \log \left(\frac{7.404 + 5.913}{20.5 + 5.913} \right) = 0.0176 \text{ V} = \mathbf{+17.6 \text{ mV}}$$

... a rather large E_j (at β vs α)!

TABLE 2.3.2 Ionic Properties at Infinite Dilution in Aqueous Solutions at 25°C

Ion	$\lambda_0, \text{cm}^2 \Omega^{-1} \text{equiv}^{-1a}$	$u, \text{cm}^2 \text{sec}^{-1} \text{V}^{-1b}$
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... so, why do trained electrochemists prefer to use saturated KCl (or KNO₃) as the salt to fill reference electrodes?

... similar mobilities and thus, similar t_i 's and thus,...

... vanishingly small LJ potentials!

^aFrom D. A. MacInnes, "The Principles of Electrochemistry," Dover, New York, 1961, p. 342

^bCalculated from λ_0 .