Introduction to the Materials Science of

# Rechargeable Batteries

Week 2: Thermodynamics of Battery Materials

Lecture 2.1: Electrochemical Equilibrium

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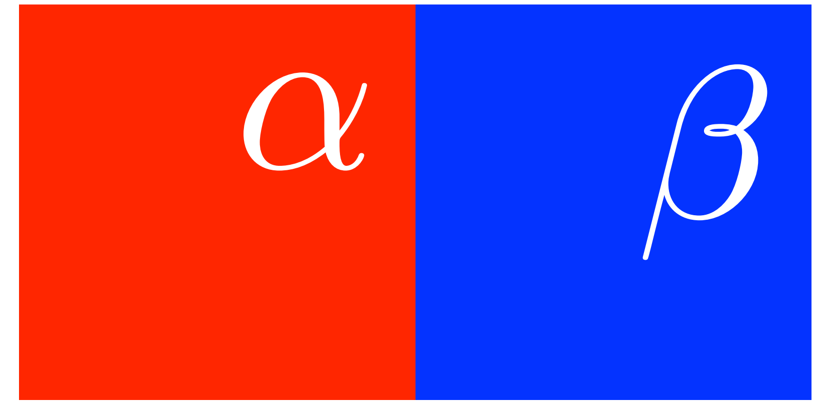
# Basic Thermodynamic Formulation




$T, S$ thermal variables

$\mu_i, n_i$ chemical variables

$\phi, q$ electrical variables

$$dU = \underbrace{TdS}_{\text{heat term}} + \underbrace{\mu_1 dn_1 + \mu_2 dn_2}_{\text{chemical work}} + \underbrace{\phi dq}_{\text{electrical work}}$$

heat term

electrical work

chemical work

# Basic Thermodynamic Formulation (continued)

$$dU^\alpha = T^\alpha dS^\alpha + \mu_1^\alpha dn_1^\alpha + \mu_2^\alpha dn_2^\alpha + \phi^\alpha dq^\alpha$$

$$dU^\beta = T^\beta dS^\beta + \mu_1^\beta dn_1^\beta + \mu_2^\beta dn_2^\beta + \phi^\beta dq^\beta$$

$$U_T = U^\alpha + U^\beta$$

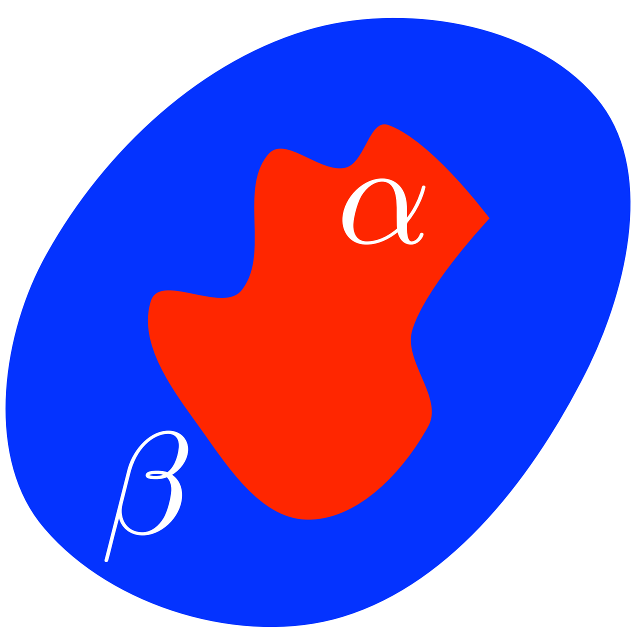
$$S_T = S^\alpha + S^\beta$$

$$n_{T,1} = n_1^\alpha + n_1^\beta$$

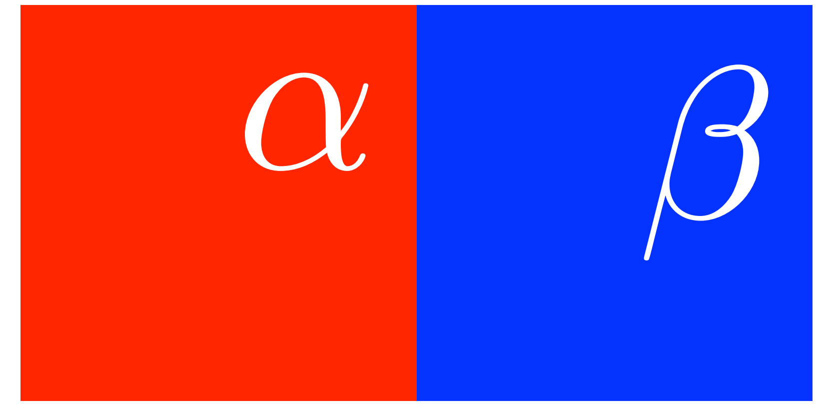
$$n_{T,2} = n_2^\alpha + n_2^\beta$$

$$q^\alpha = \sum_{i=1}^{N} F z_i n_i^\alpha$$

$$q^\beta = \sum_{i=1}^{N} F z_i n_i^\beta$$



# Deriving the Conditions of Equilibrium




Energy conservation implies:

$$0 = dU^\alpha + dU^\beta$$

Other relationships:

$$dS^\beta = -dS^\alpha \qquad dq^\beta = -dq^\alpha$$

$$dn_1^\beta = -dn_1^\alpha \qquad dn_2^\beta = -dn_2^\alpha$$

$$dq^\beta = Fz_1 dn_1^\beta + Fz_2 dn_2^\beta$$

Putting it all together:

$$0 = (T^\beta - T^\alpha)dS^\beta + (\mu_1^\beta - \mu_1^\alpha)dn_1^\beta + (\mu_2^\beta - \mu_2^\alpha)dn_2^\beta + (\phi^\beta - \phi^\alpha)dq^\beta$$

or equivalently:

$$0 = (T^\beta - T^\alpha)dS^\beta + (\mu_1^\beta + z_1 F\phi^\beta - (\mu_1^\alpha + z_1 F\phi^\alpha))dn_1^\beta + (\mu_2^\beta z_2 + F\phi^\beta - (\mu_2^\alpha + z_2 F\phi^\alpha))dn_2^\beta$$

Any fluctuation does not affect equilibrium!

# The Electrode Potential

So the conditions for equilibrium are

$$T^\alpha = T^\beta$$ we know this one

$$\mu_1^\alpha + z_1 F \phi^\alpha = \mu_1^\beta + z_1 F \phi^\beta$$
$$\mu_2^\alpha + z_2 F \phi^\alpha = \mu_2^\beta + z_2 F \phi^\beta$$

or equivalently:

$$\eta_1^\alpha = \eta_1^\beta$$

$$\eta_2^\alpha = \eta_2^\beta$$

Define this as the *electrochemical potential*

and yet, another way to look at it:

$$\Delta\phi_1^{\alpha\to\beta} = \frac{\Delta\mu_1^{\alpha\to\beta}}{z_1 F} \qquad \Delta\phi_2^{\alpha\to\beta} = \frac{\Delta\mu_2^{\alpha\to\beta}}{z_2 F}$$