Introduction to the Materials Science of

Rechargeable Batteries

Week 2: Thermodynamics of Battery Materials

Lecture 2.4: Thermal Effects in the Equilibrium Potential

By R. Edwin Garcia

Associate Professor of Materials Engineering

Purdue University

Reminder: 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:

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

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

and yet, another way to look at it:

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

Thermal Effects

$$\Delta G = \Delta H - T\Delta S$$

$$\frac{\partial \Delta G/T}{\partial 1/T} = \Delta H$$

$$\frac{\partial \Delta G}{\partial T} = -\Delta S$$

However, we also concluded that:

$$\Delta G/zF = \Delta\phi$$

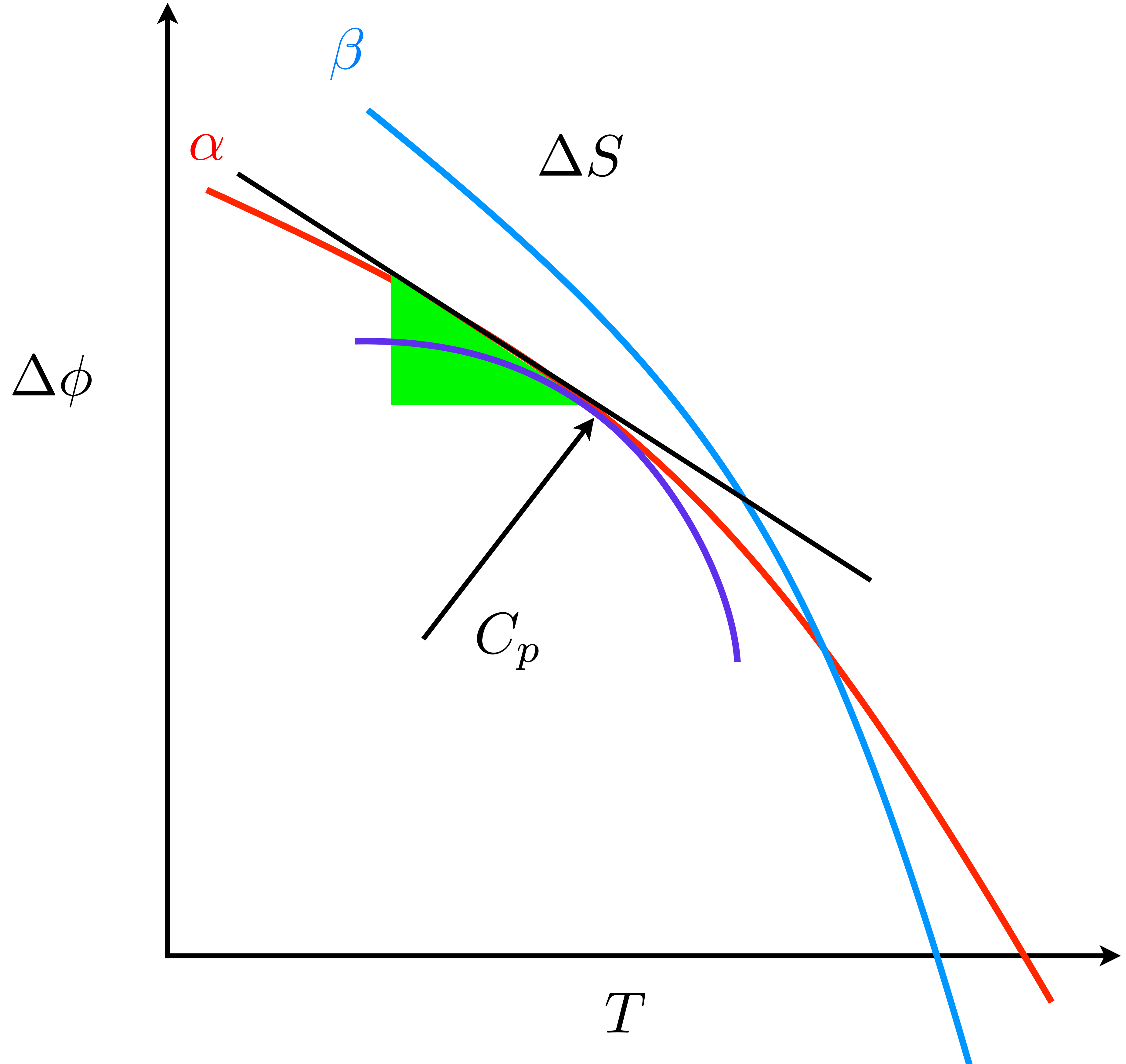
therefore:

$$\frac{\partial \Delta\phi}{\partial T} = -\frac{\Delta S}{zF} \qquad \Delta H = zF\left(\Delta\phi - \frac{\partial \Delta\phi}{\partial T}T\right)$$

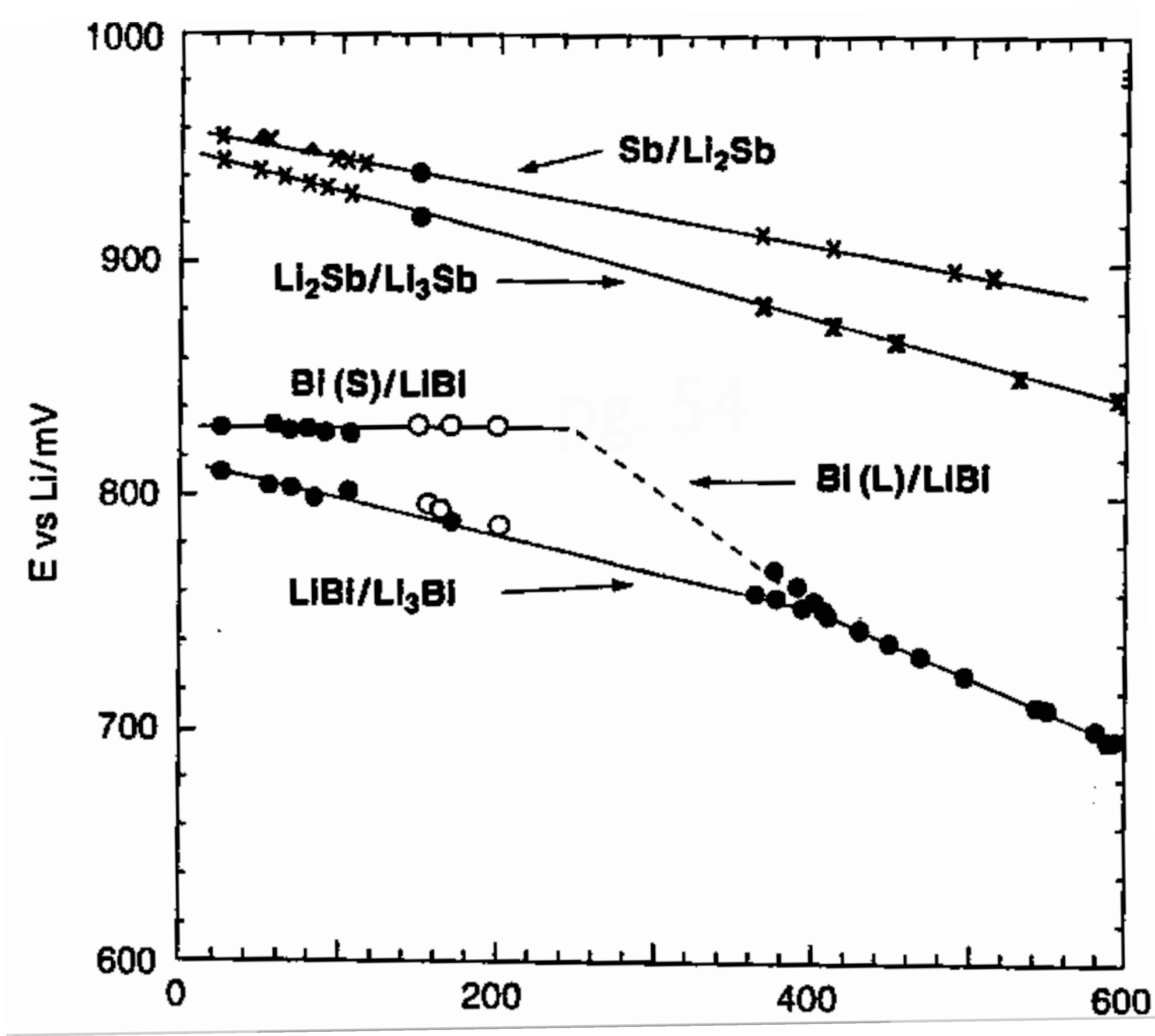
and also:

$$\frac{\partial^2 \Delta\phi}{\partial T^2} = -\frac{C_p}{zFT}$$

Thermal Effects and Phase Transitions



Li-Sb-Bi System



T