Electrochemical Equilibrium

Lectures 5 - 7

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Basic Thermodynamic Formulation

T, S thermal variables

μ_i, n_i chemical variables

ϕ, q electrical variables

$$dU = \underbrace{TdS} + \underbrace{\mu_1 dn_1 + \mu_2 dn_2} + \underbrace{\phi dq}$$

heat term

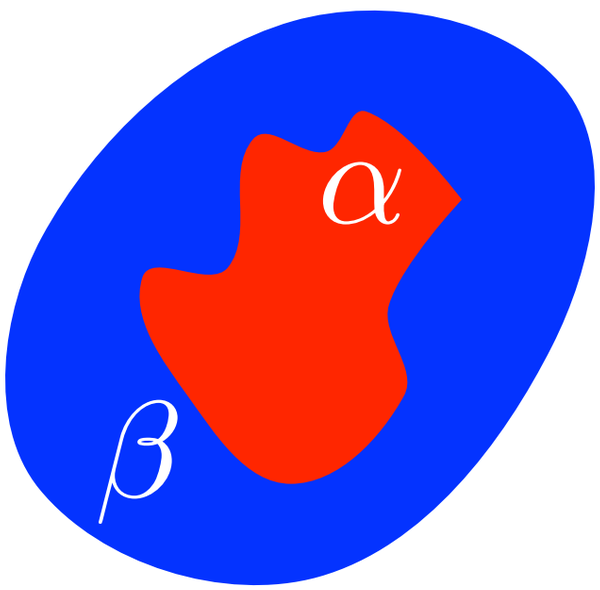
chemical work

electrical work

Basic Thermodynamic Formulation (continued)

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

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



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

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

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

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

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

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

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:

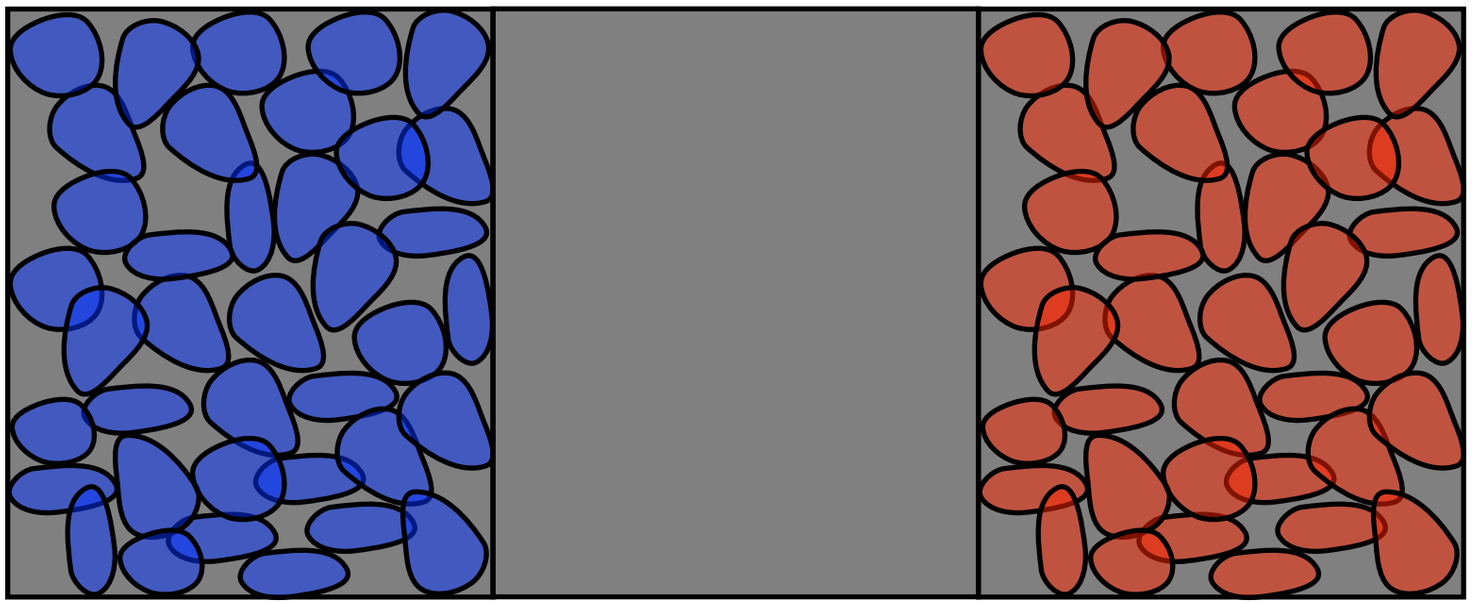
$$\eta_1^\alpha = \eta_1^\beta$$
$$\eta_2^\alpha = \eta_2^\beta$$

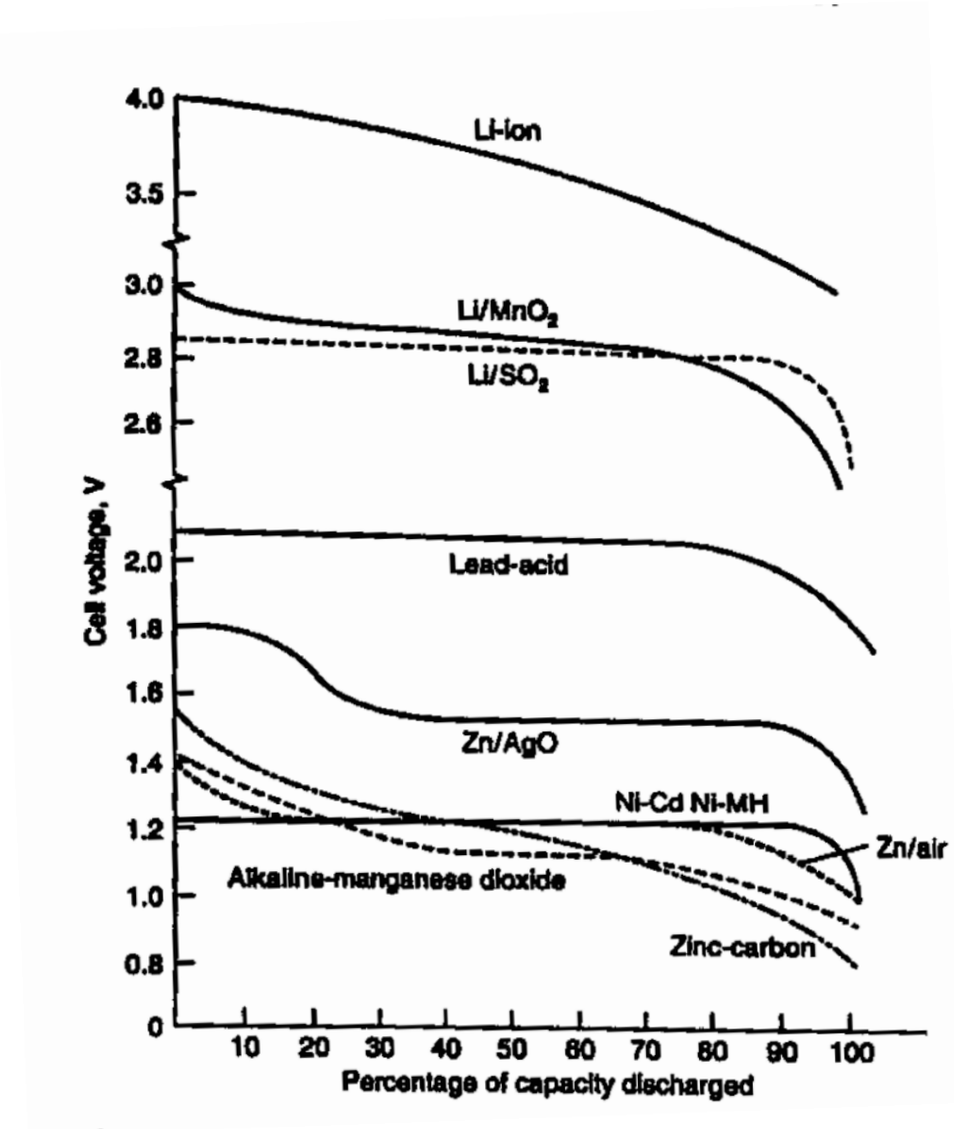
and yet, another way to look at it:

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

Electrochemical Driving Force

Anode Electrolyte Cathode





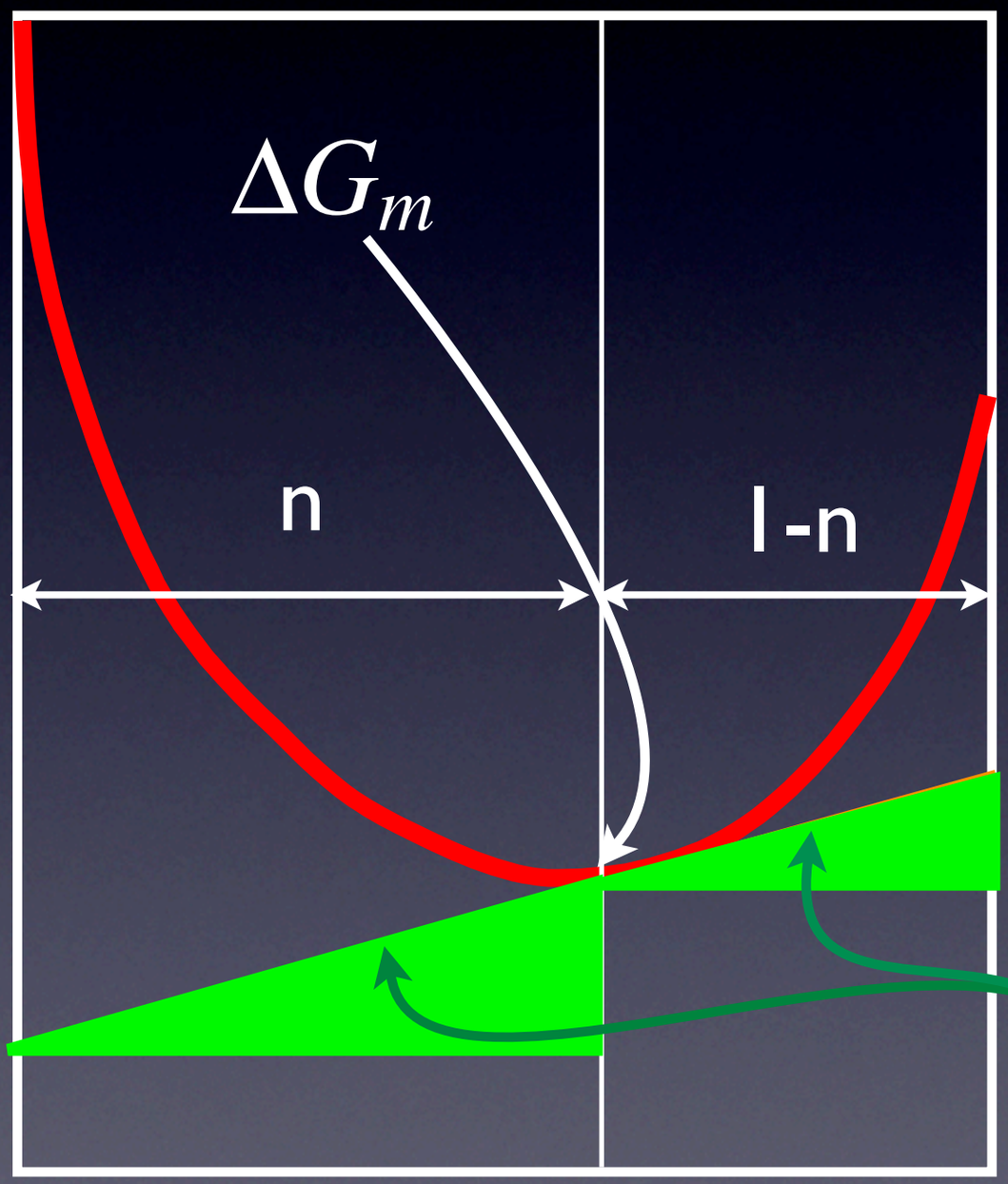
$$\varphi_a = \frac{\mu_{Li}^a}{zF} \qquad \varphi_c = \frac{\mu_{Li}^c}{zF}$$

$$\Delta\varphi = \frac{\mu_{Li}^c}{zF} - \frac{\mu_{Li}^a}{zF}$$

Method of Intercepts

ΔG_m

$$\mu_2 = \Delta G_m + \frac{\partial \Delta G_m}{\partial n}(1-n)$$



$$\mu_1 = \Delta G_m - \frac{\partial \Delta G_m}{\partial n} n$$

The Common Tangent and Lever Rule

$f_\beta + f_\alpha = 1$

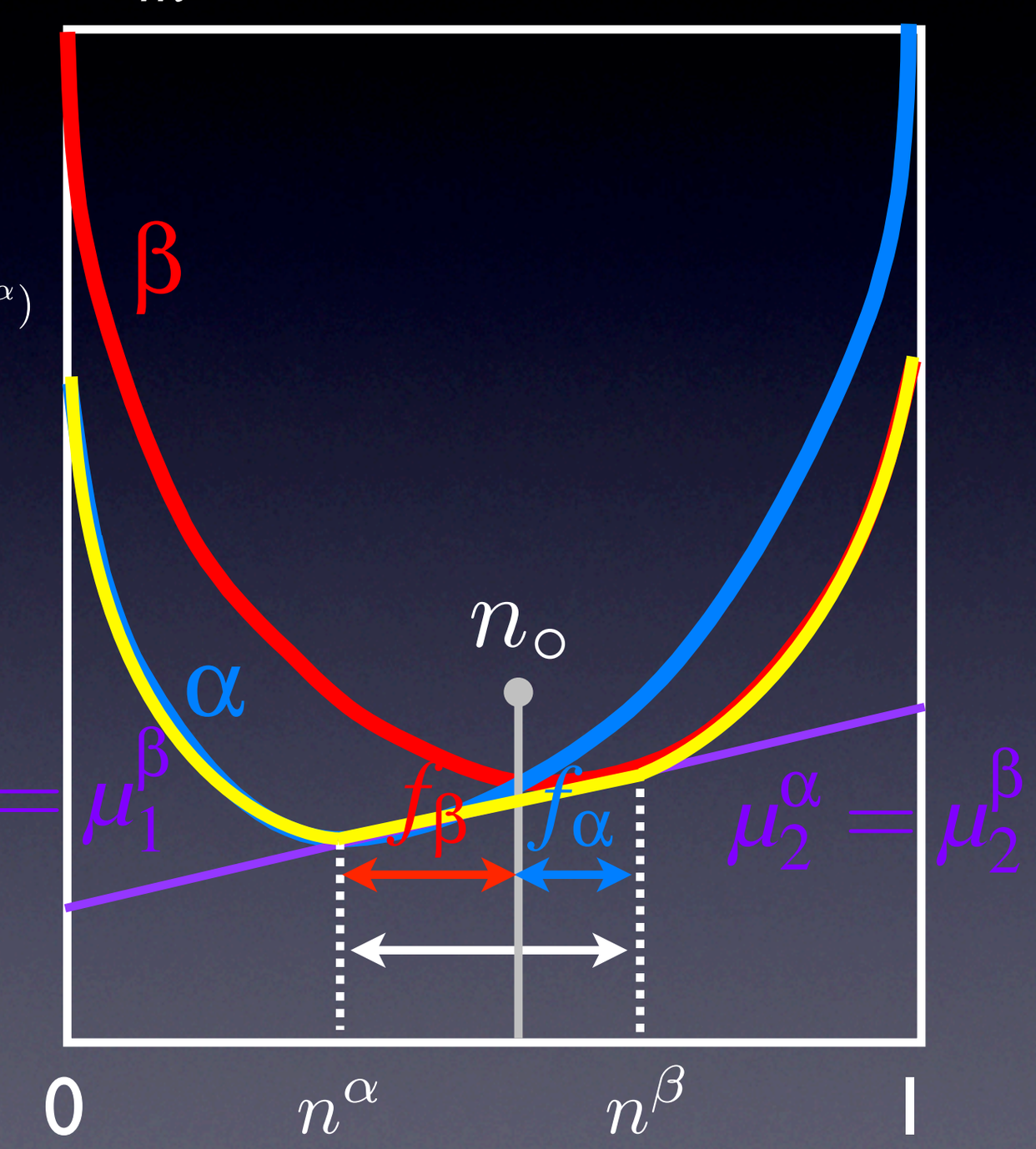
free energy in the miscibility gap:

$$\Delta G_m(n_\circ) = \Delta G_m^\alpha(n^\alpha) + \frac{\Delta G_m^\beta(n^\beta) - \Delta G_m^\alpha(n^\alpha)}{n^\beta - n^\alpha}(n_\circ - n^\alpha)$$

$$\Delta G_m(n_\circ) = \Delta G_m^\alpha(n^\alpha)\frac{n^\beta - n_\circ}{n^\beta - n^\alpha} + \Delta G_m^\beta(n^\beta)\frac{n_\circ - n_\alpha}{n^\beta - n^\alpha}$$

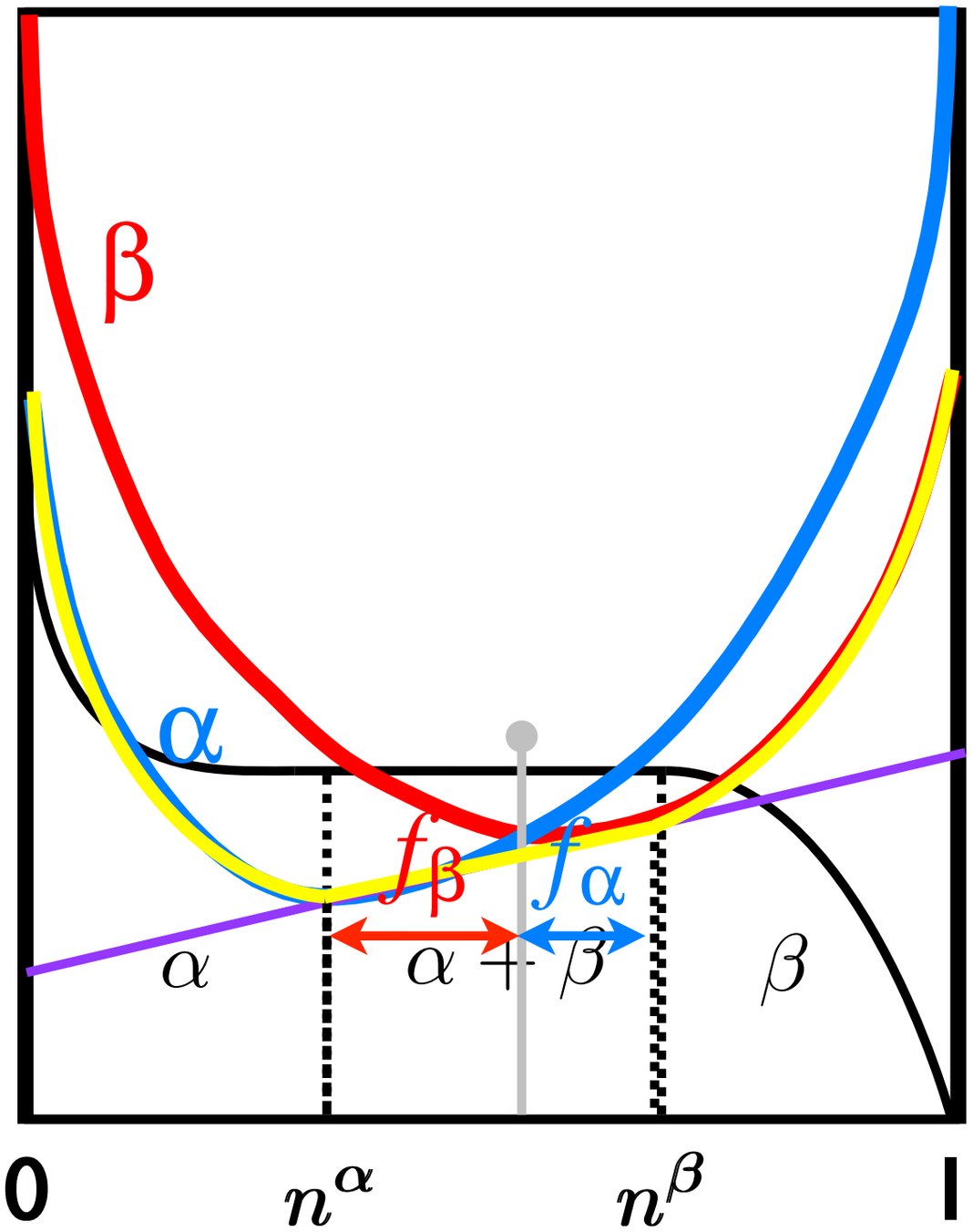
$$f_\alpha = \frac{n^\beta - n_\circ}{n^\beta - n^\alpha}$$

$$f_\beta = \frac{n_\circ - n^\alpha}{n^\beta - n^\alpha}$$

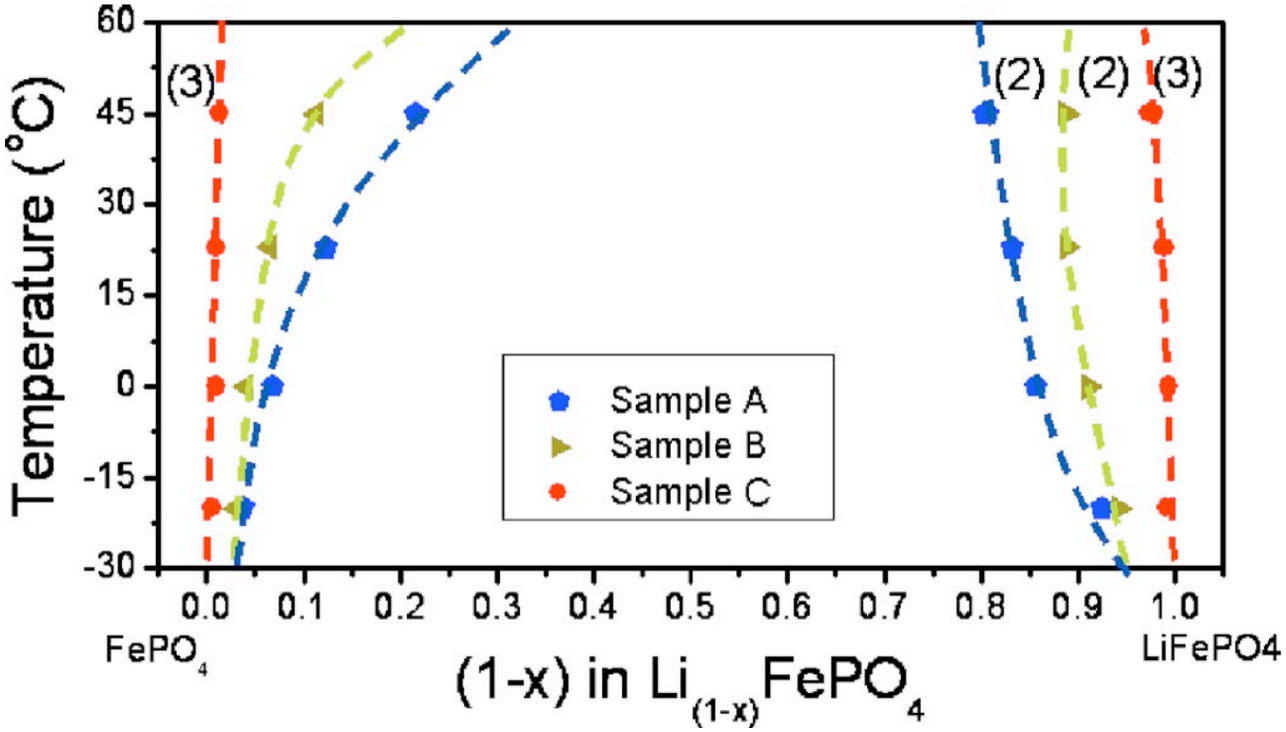


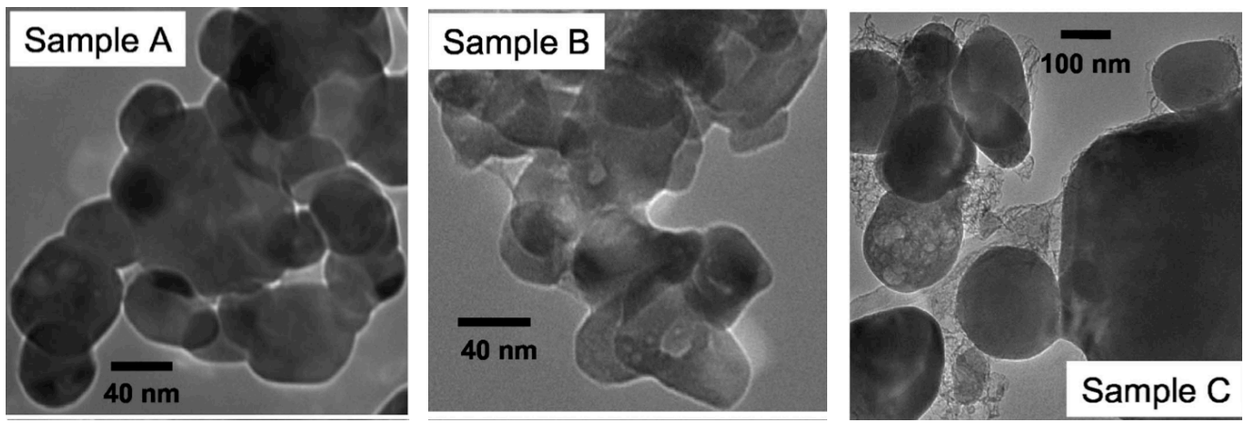
Phase Diagrams and Material Potential

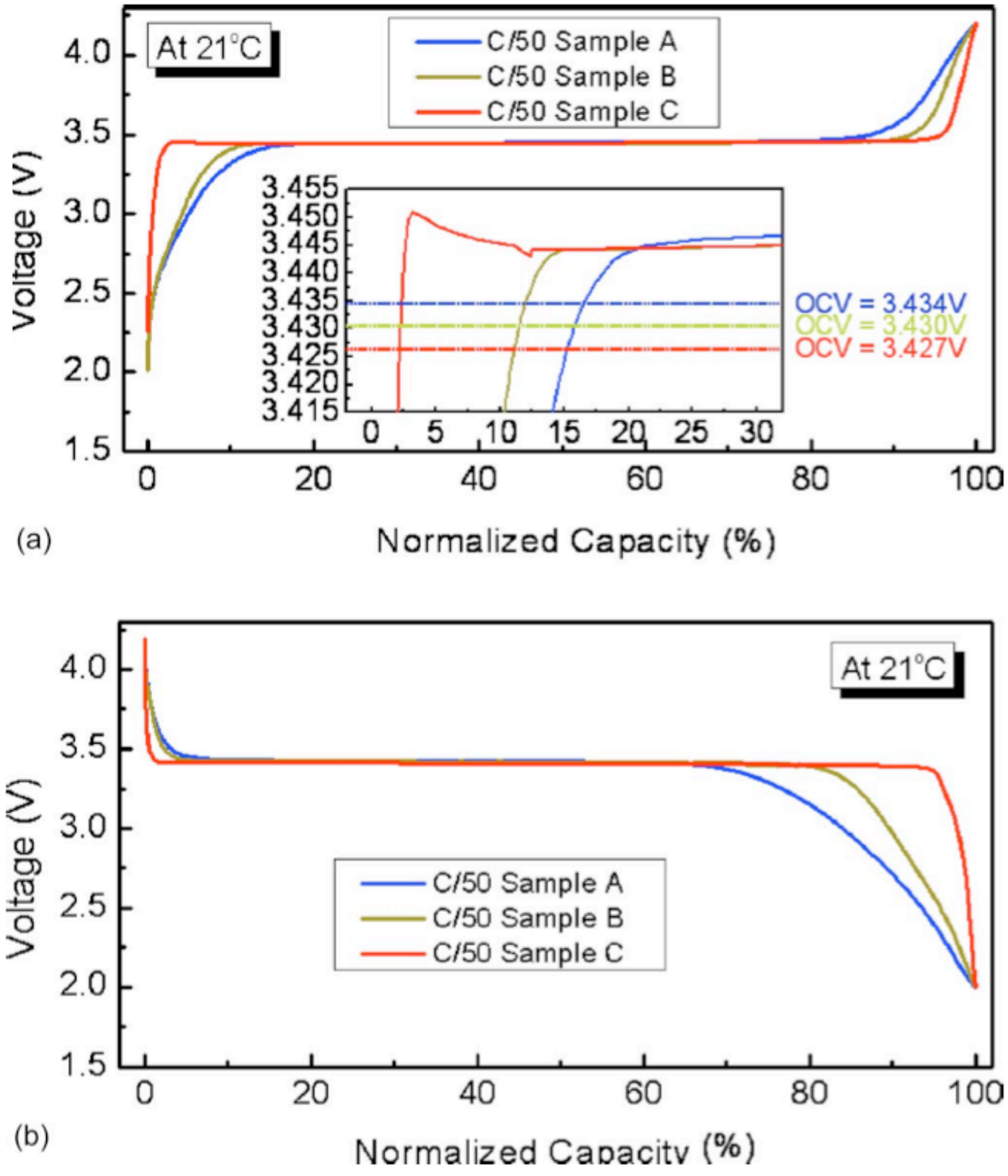
ΔG_m



The $LiFePO_4$ System

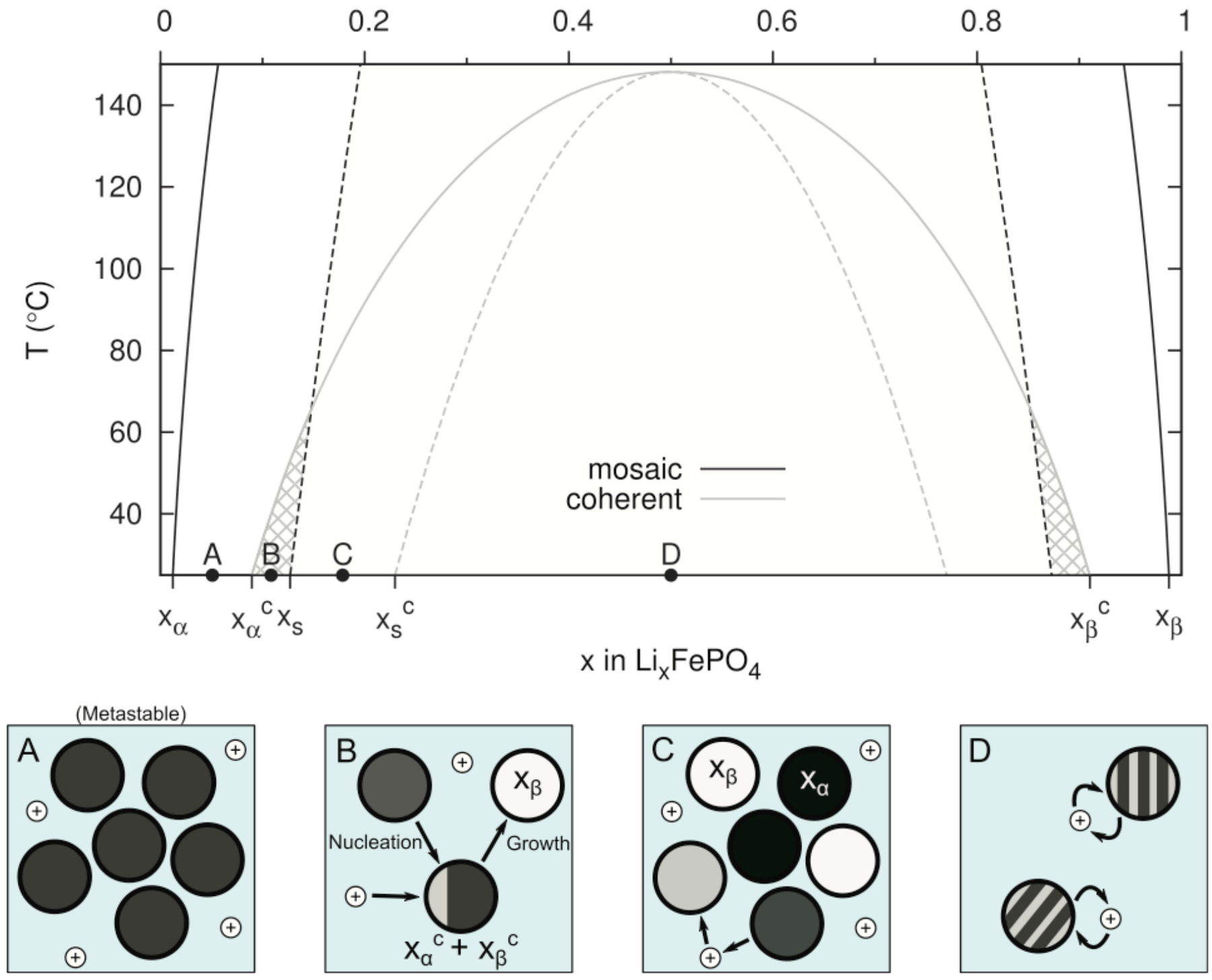






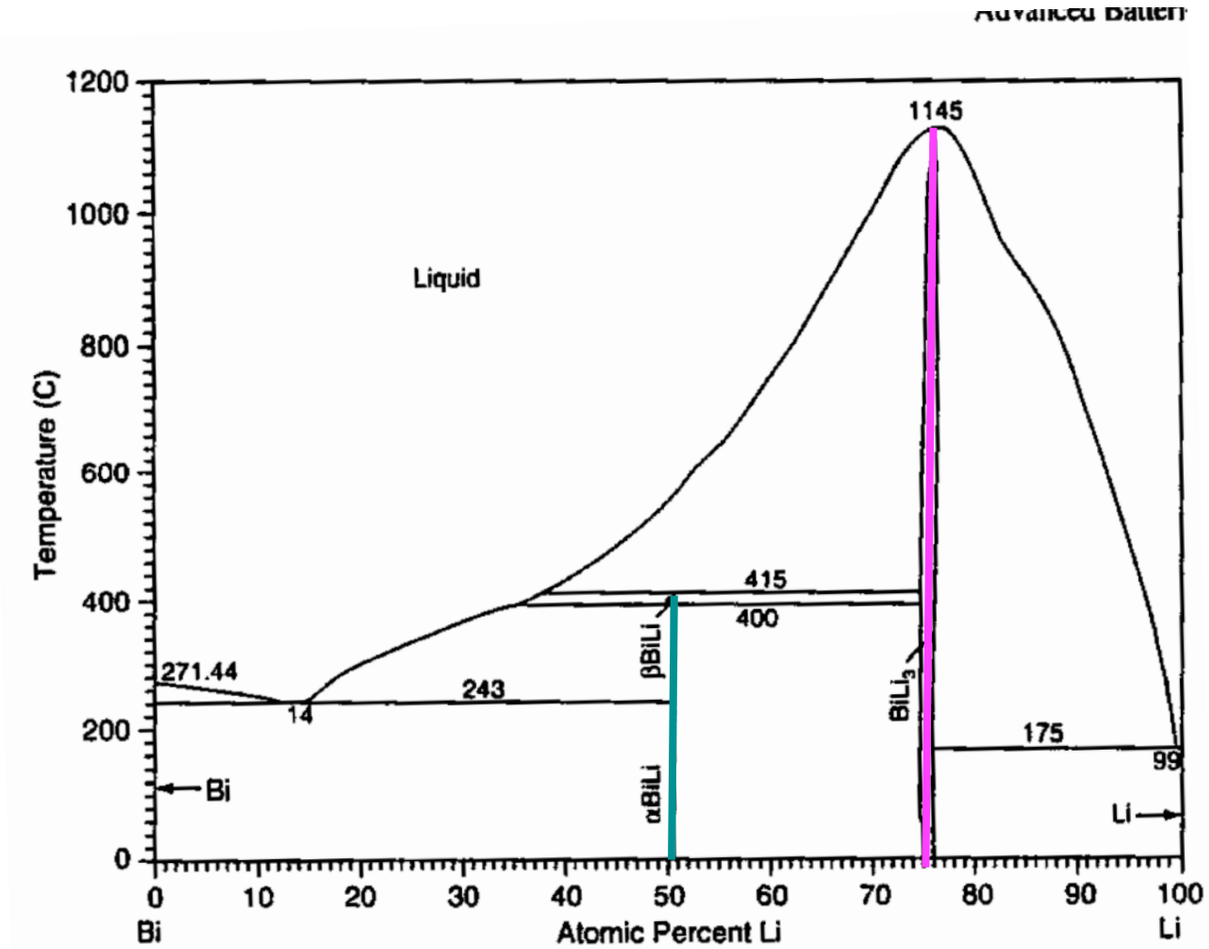
N. Meethong, H-Y. S. Huang, W. C. Carter, and Y.-M. Chiang "Size-Dependent Lithium Miscibility Gap in Nanoscale $Li_{1-x}FePO_4$." Electrochemical and Solid-State Letters, 10 (5) A134-A138 (2007).

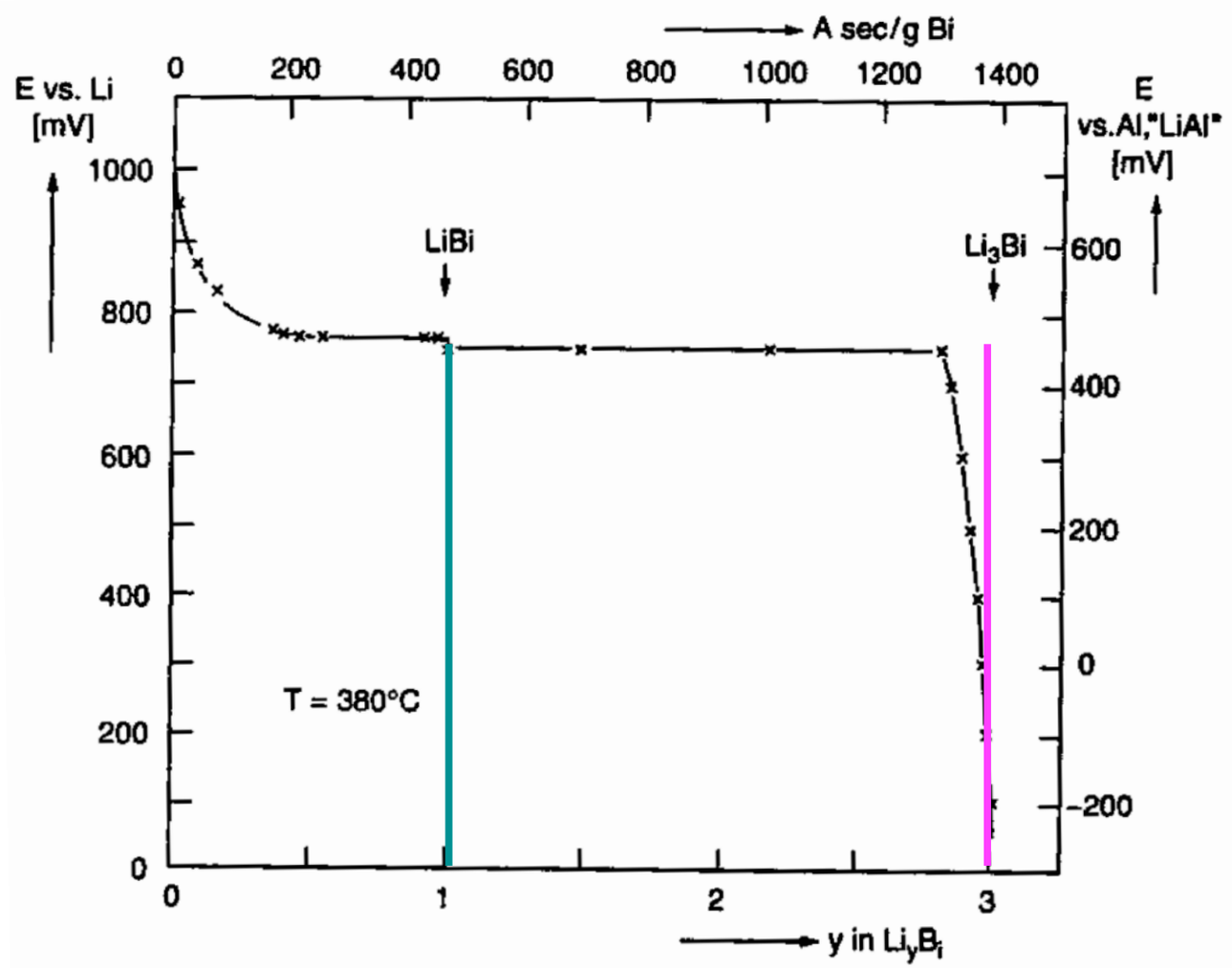
$LiFePO_4$ Intercalation Process



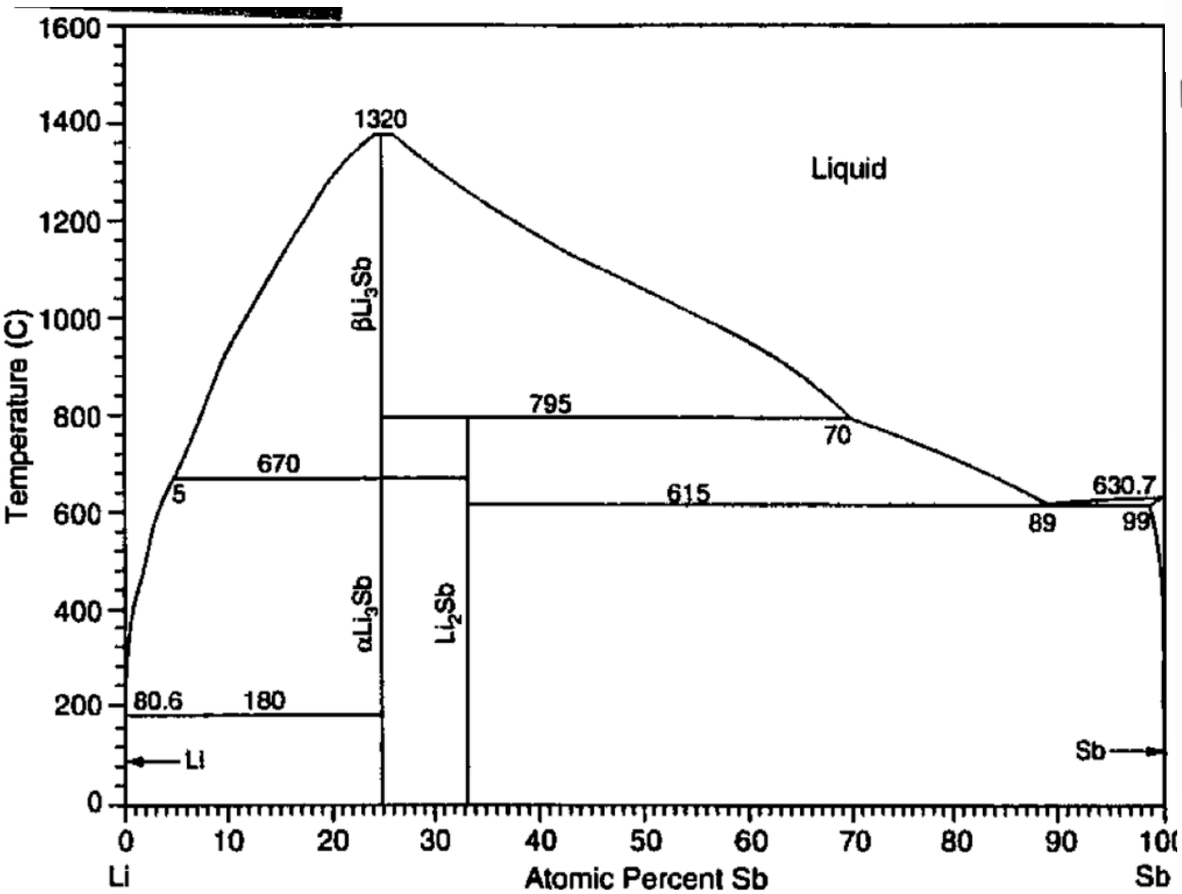
D. A. Cogswell and M. Z. Bazant "Coherency Strain and the Kinetics of Phase Separation in LiFePO4 Nanoparticles." ACS Nano (6): 2215-2225, 2012.

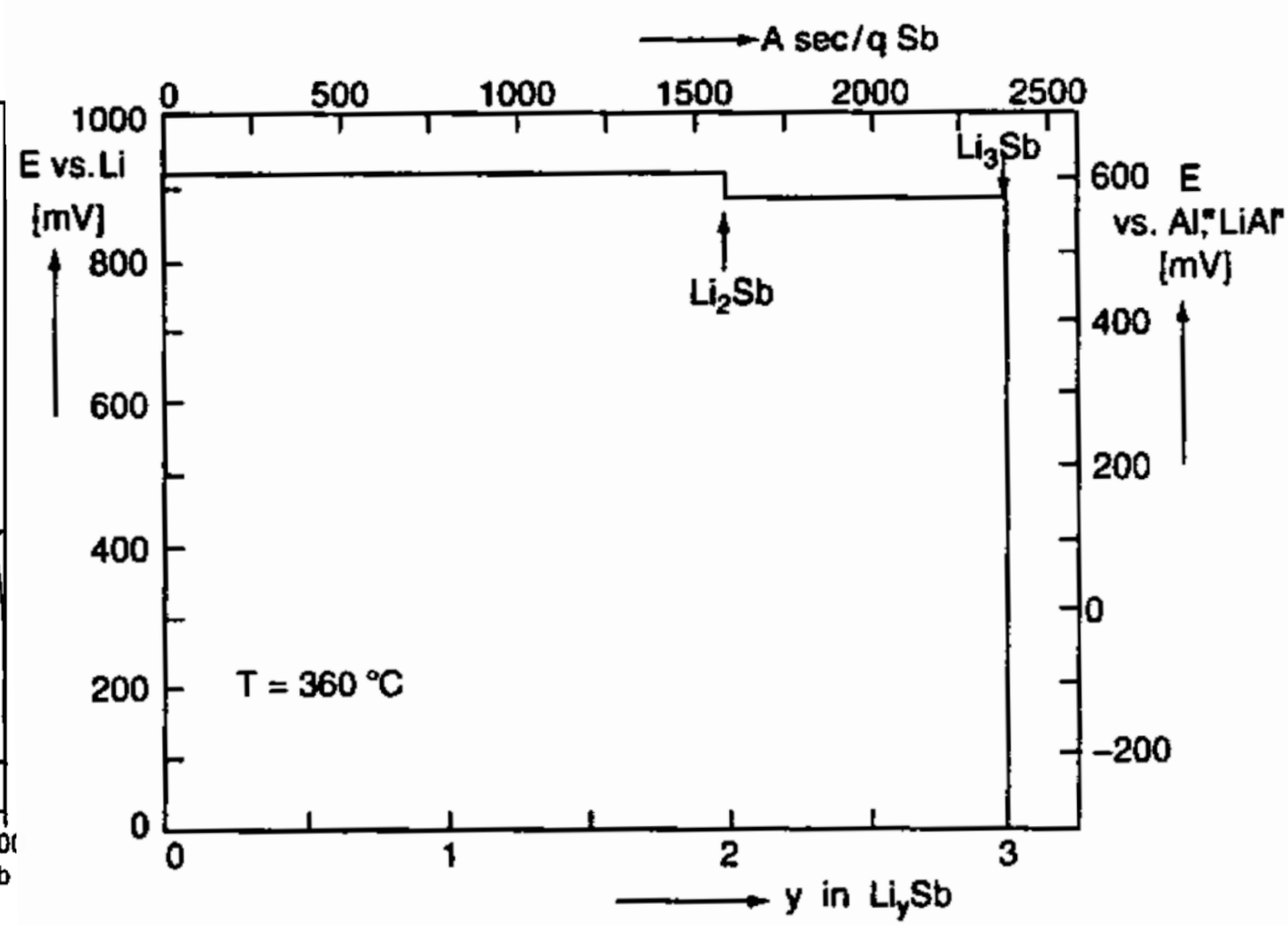
The Bi-Li System



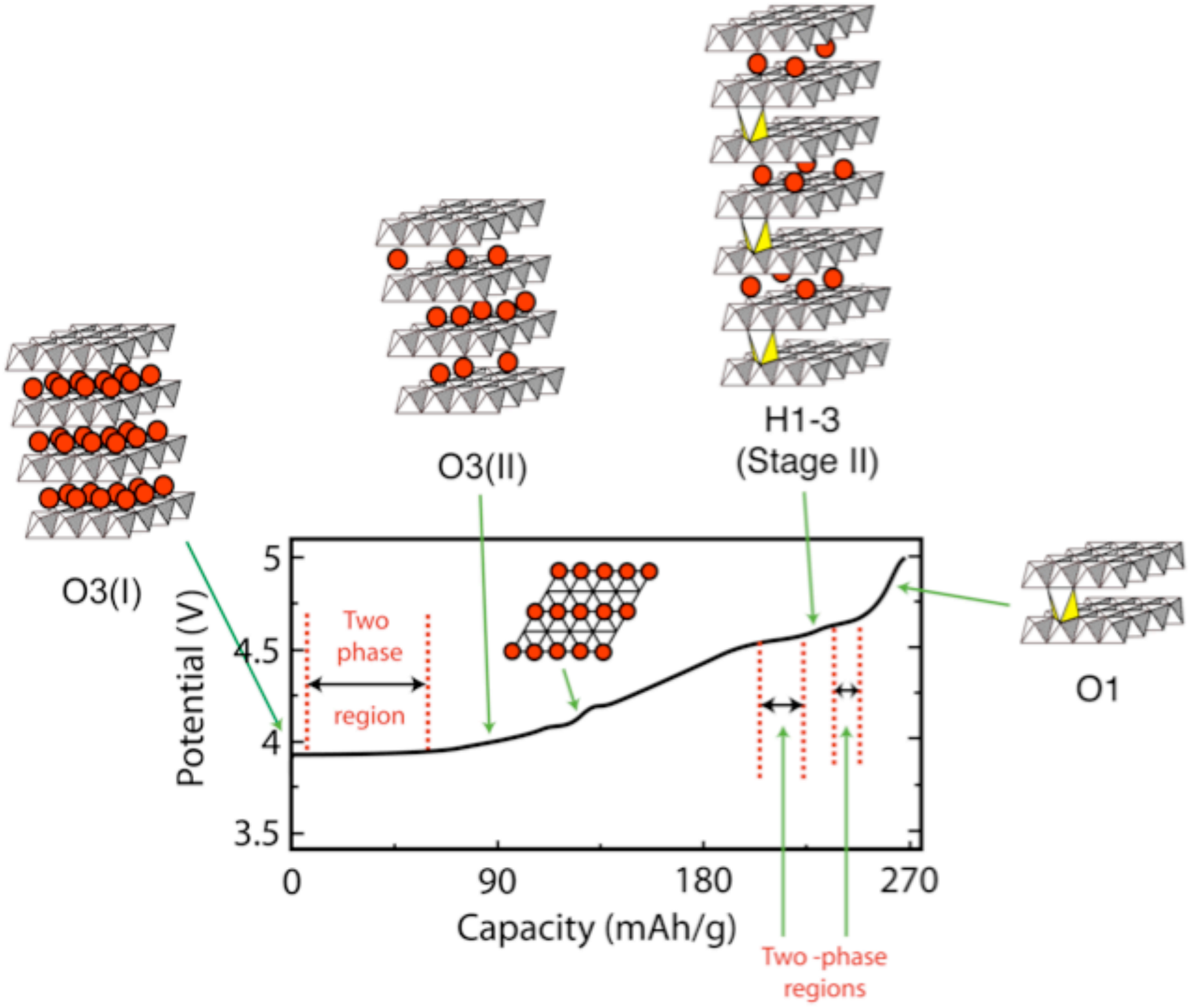


Sb-Li System


Liquid
1320
βLi3Sb
795
70
670
5
615
630.7
89
99
80.6
180
αLi3Sb
Li2Sb
Li
Sb
Temperature (C)
Atomic Percent Sb

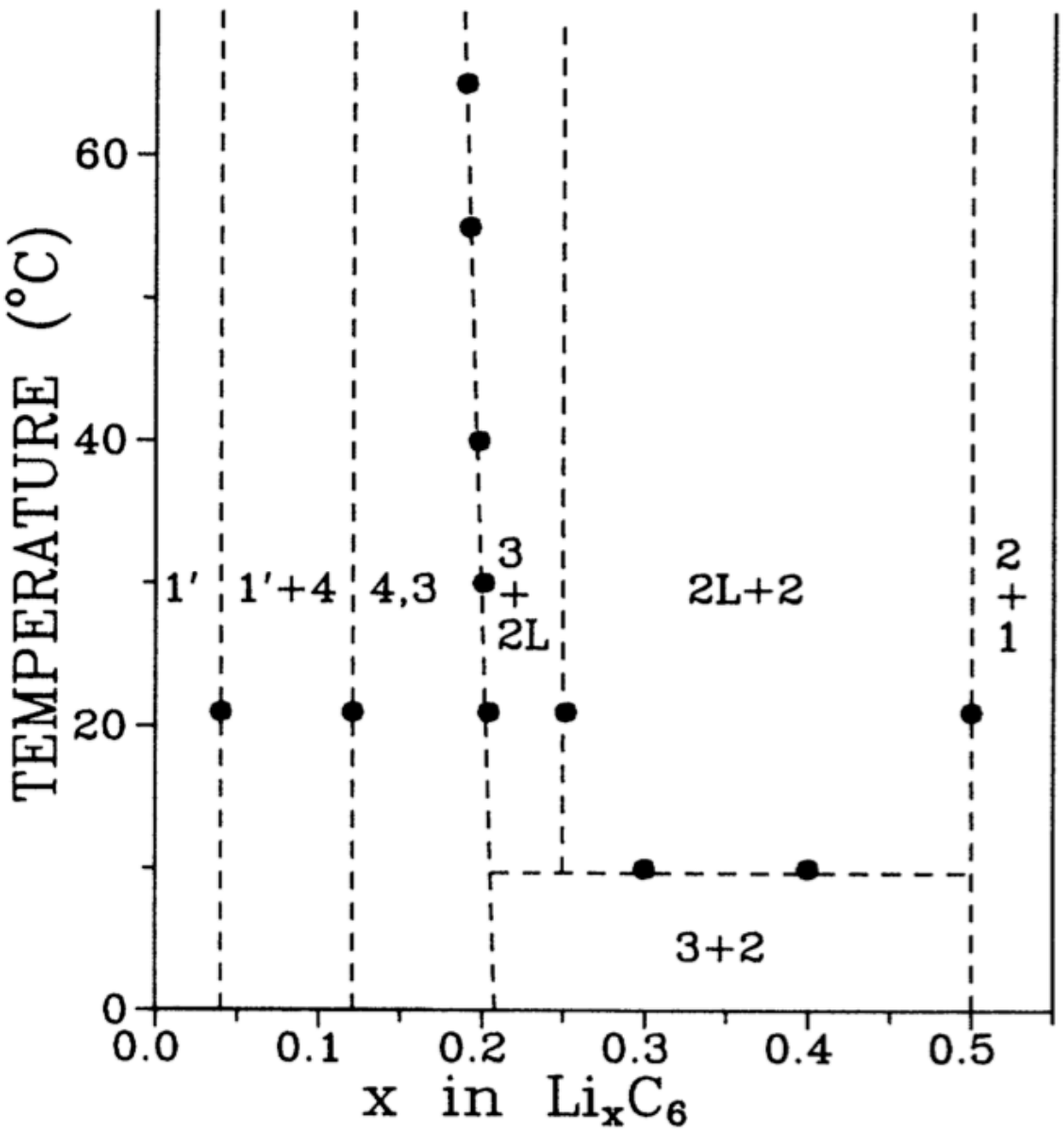

A sec/q Sb
E vs.Li [mV]
E vs. Al;LiAl [mV]
Li3Sb
Li2Sb
T = 360 °C
y in LiySb

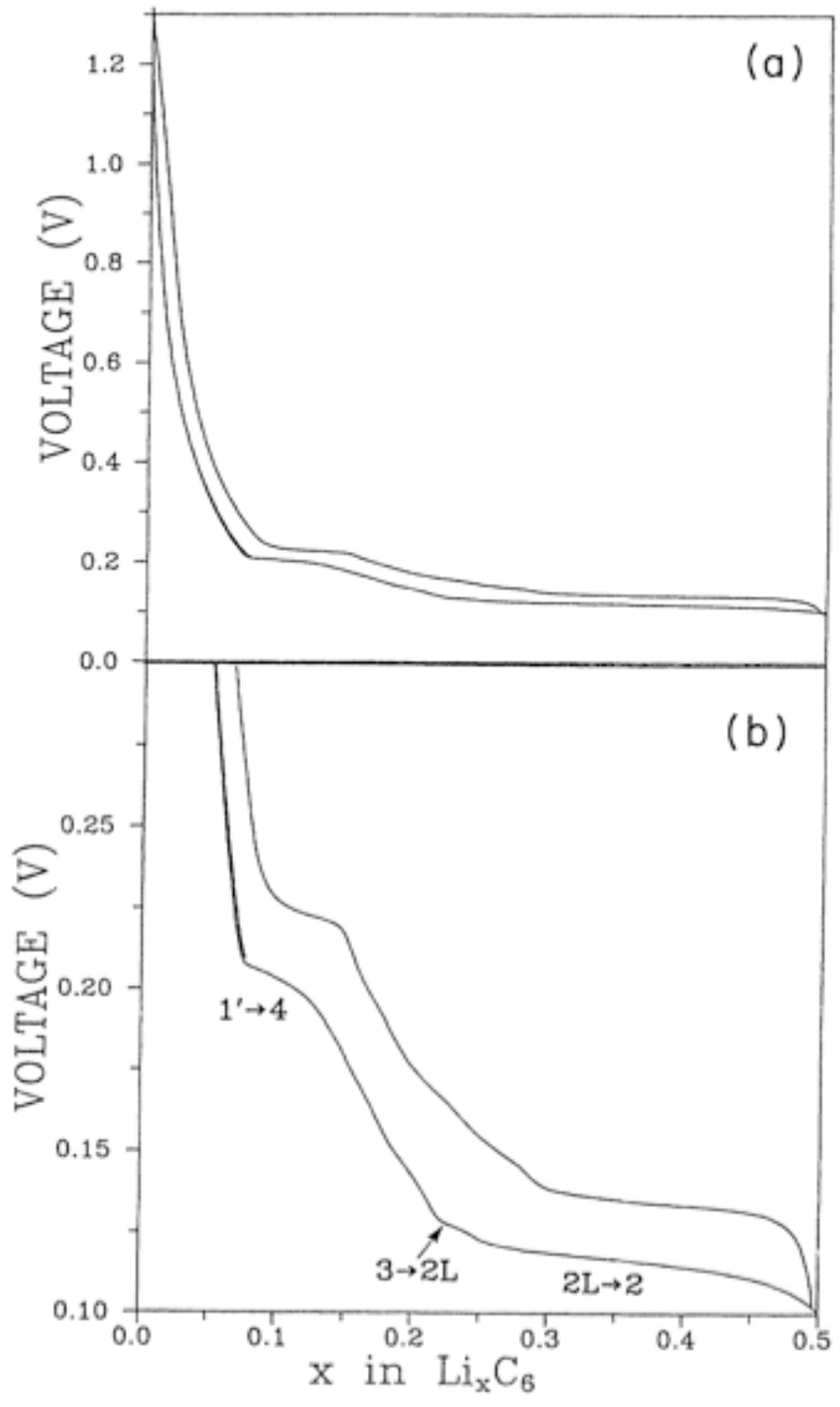
The $LiCoO_2$ System



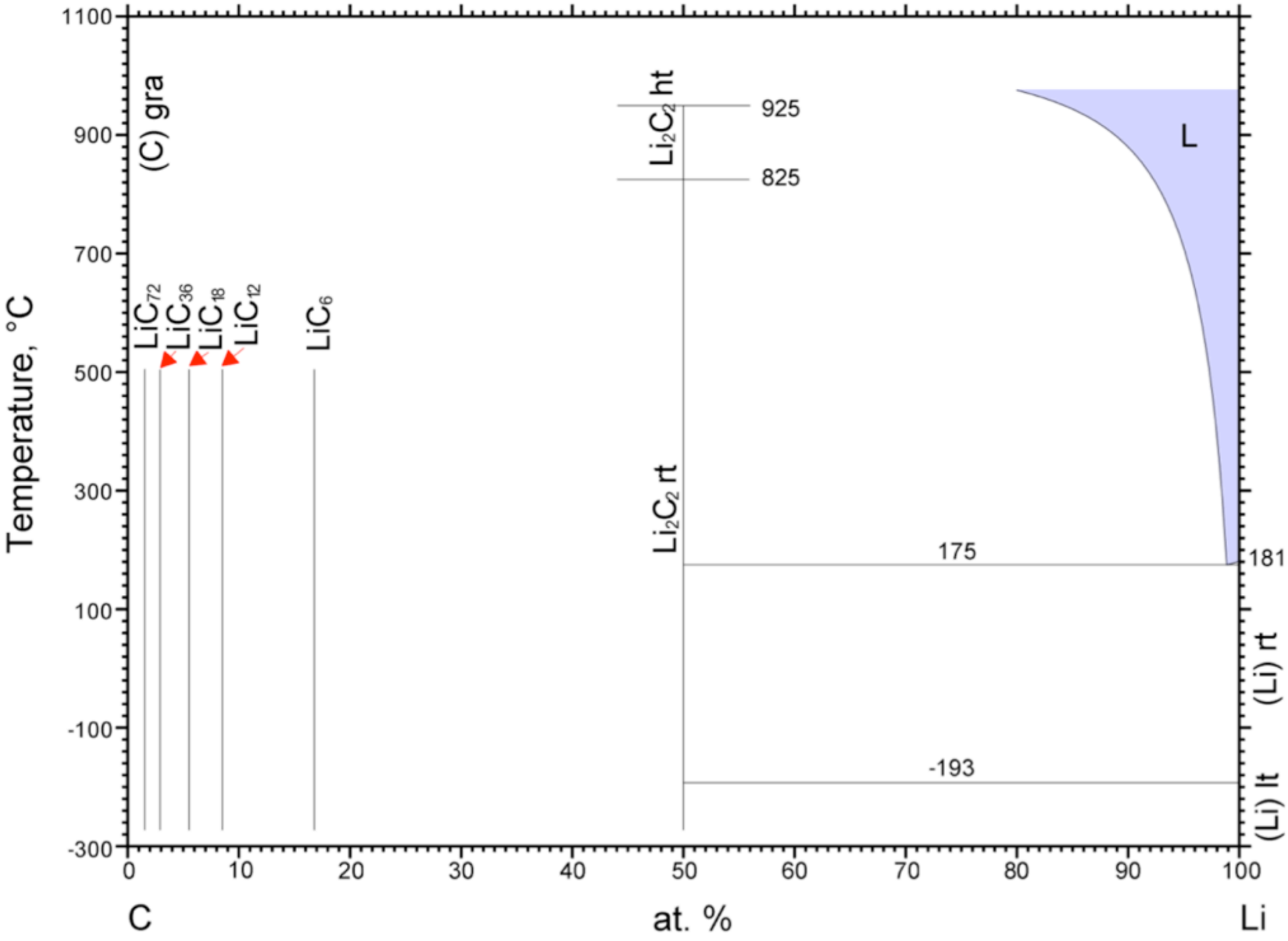
Anton Van der Ven, Purdue University, 2010

The C_6-Li System





The C-Li System



Reminder: The Electrode Potential

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or equivalently:

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and yet, another way to look at it:

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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:

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

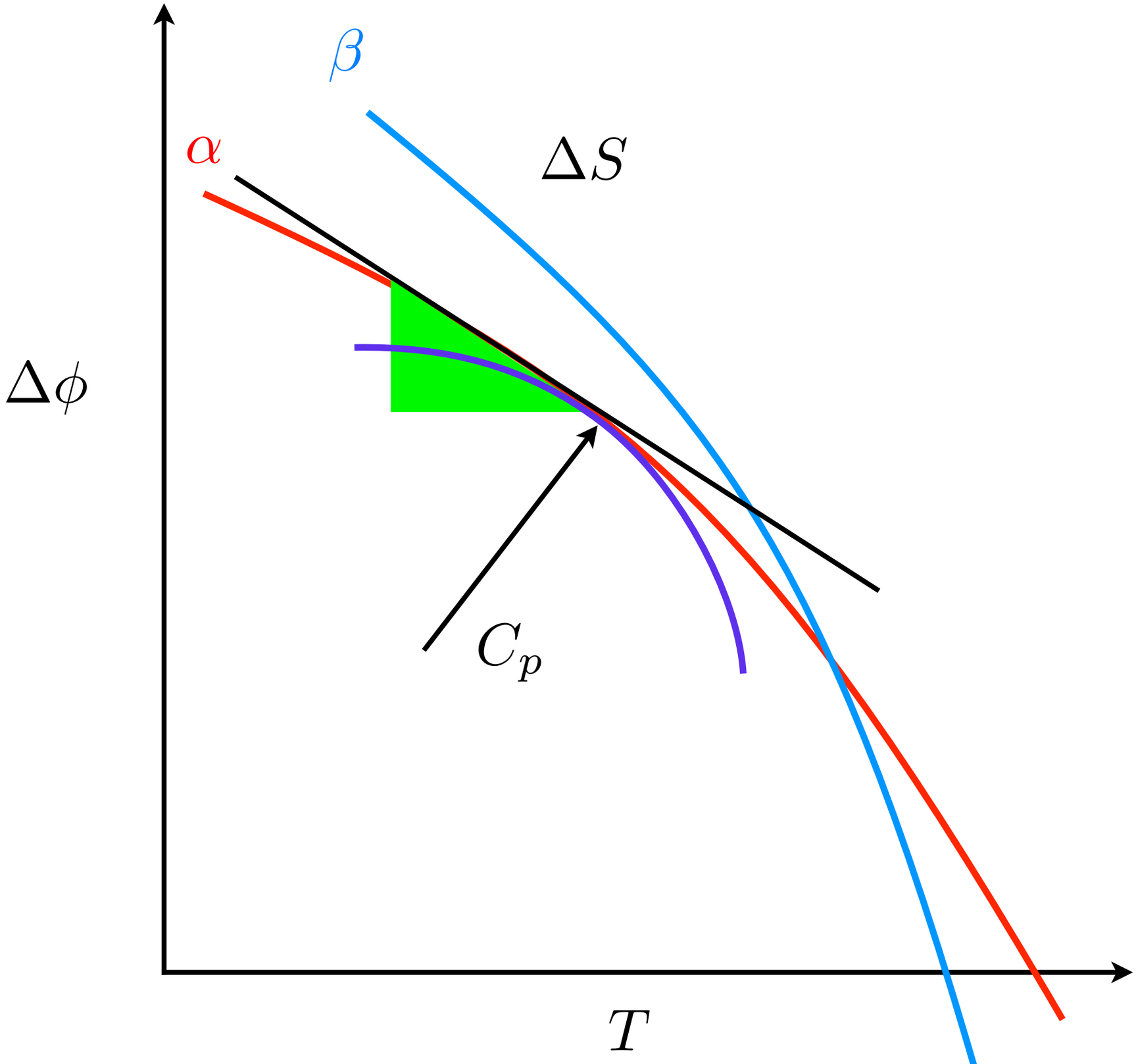
therefore:

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

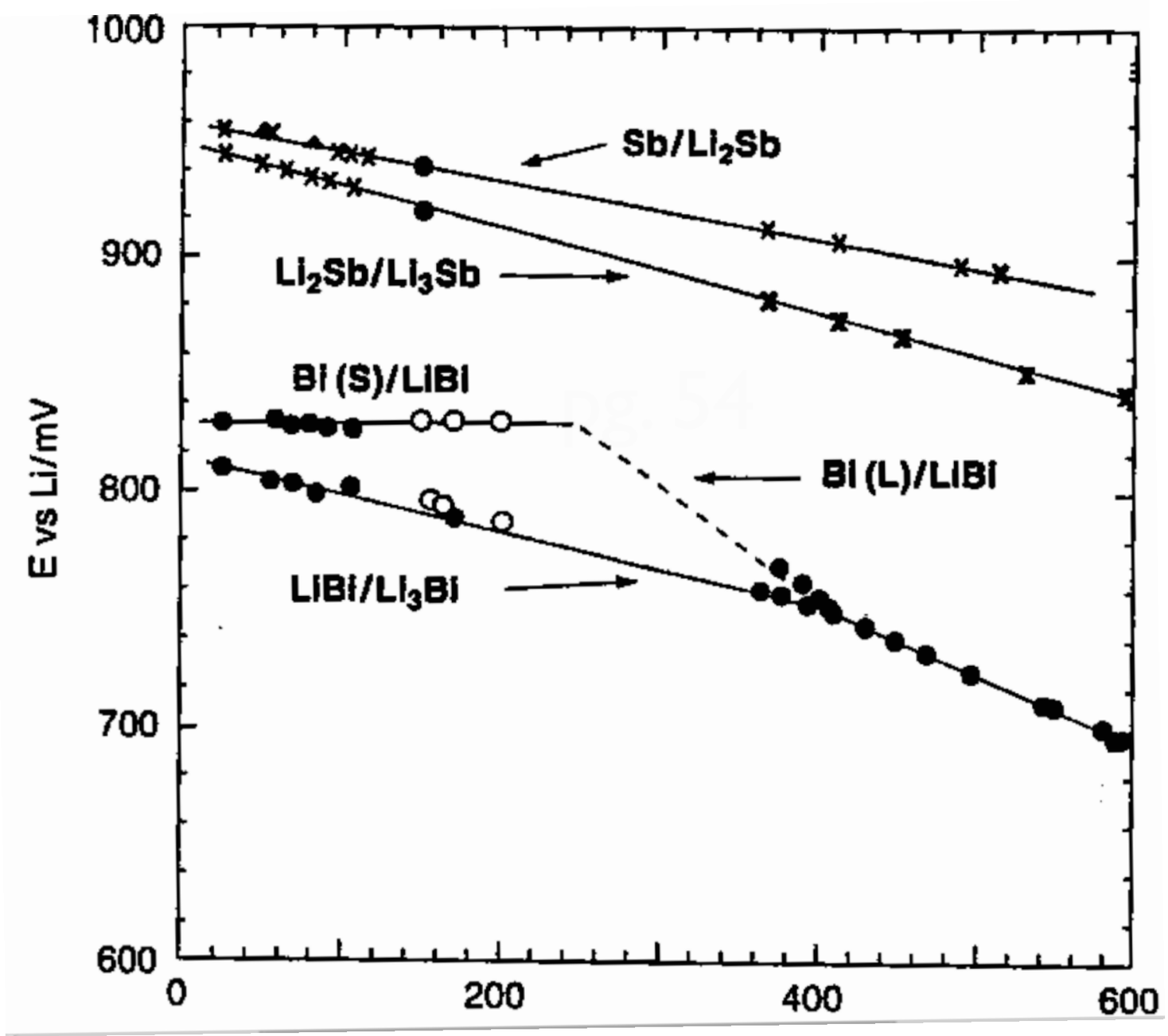
and also:

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

Thermal Effects and Phase Transitions



Li-Sb-Bi System



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