



20th DISCUSSION MEETING ON THERMODYNAMICS OF ALLOYS
20 - 24 September 2026
BLED - SLOVENIA

On The Electrochemical Phase Diagrams (ECPD)

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Electrodeposition:

- **metals or alloys**
- **corrosion-resistant coatings**
- **wear-resistant coatings**
- **electronic components**
- **battery electrodes**
- **catalysts**
- **micro- and nanostructured layers**
- **potentiostatic and galvanostatic**

Galvanostatic electrodeposition:

- **constant current density**
- **control deposition rate**
- **control coating thickness**
- **composition**
- **grain size**
- **surface morphology**
- **phase constitution**

binary alloys: T, electrolyte -> which phase ? -> ECPD



Electrochemical diagrams (ECD) [1]

Binary systems: A – B

Electrolyte: A_qX_r , B_sX_t , solvent

Reduced molar fraction:

$$x_{B+}^* \equiv \frac{n_{B+}}{n_{A+} + n_{B+}}$$

Molar fractions:

$$x_{AX(e)} + x_{BX(e)} + y = 1$$

$$x_{AX(e)} = \frac{s \cdot (1 - y) \cdot (1 - x_{B+}^*)}{s - (s - q) \cdot x_{B+}^*}$$

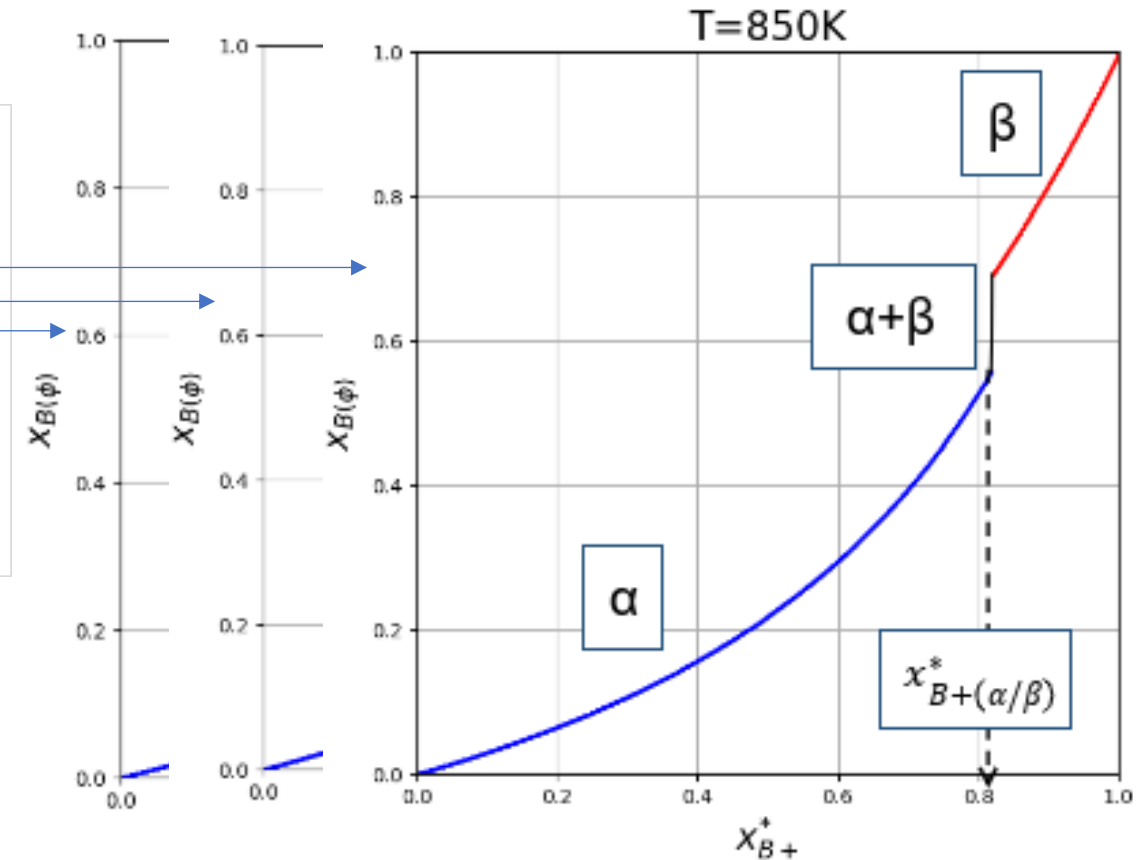
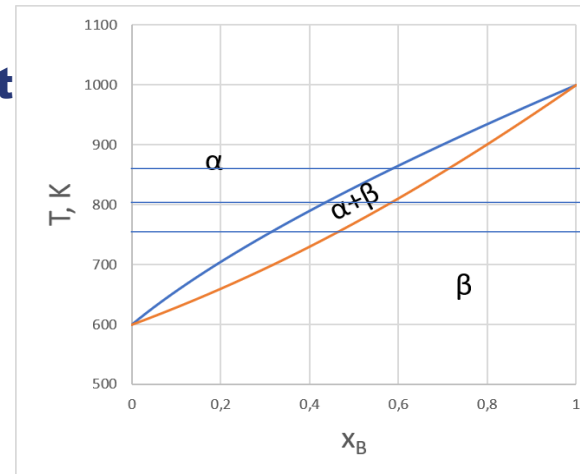
$$x_{BX(e)} = \frac{q \cdot (1 - y) \cdot x_{B+}^*}{s - (s - q) \cdot x_{B+}^*}$$

Partial cathode potentials:

$$E_{A(\phi)} = \frac{\mu_{AX(e)} - q \cdot \mu_{A(\phi)}}{a \cdot q \cdot F}$$

$$E_{B(\phi)} = \frac{\mu_{BX(e)} - s \cdot \mu_{B(\phi)}}{b \cdot s \cdot F}$$

- I. ECD rule: $E_\alpha > E_\beta \rightarrow E_\alpha$
- II. ECD rule: $E_{A(\alpha)} = E_{B(\alpha)}$
- III. ECD rule: $E_\alpha = E_\beta$



$$x_{B+}^*(\alpha/\beta) = f(T) \text{ or } T = f(x_{B+}^*(\alpha/\beta))$$



General equation of ECPD lines

Partial cathode potentials:

$$E_{A(\Phi)} = \frac{\mu_{AX(e)} - q \cdot \mu_{A(\Phi)}}{a \cdot q \cdot F}$$

$$E_{B(\Phi)} = \frac{\mu_{BX(e)} - s \cdot \mu_{B(\Phi)}}{b \cdot s \cdot F}$$

Partial chemical potentials:

$$\mu_{A(\Phi)} = \mu_{A(\Phi)}^0 + R \cdot T \cdot \ln x_{A(\Phi)} + \Delta\mu_{A(\Phi)}^E$$

$$\mu_{B(\Phi)} = \mu_{B(\Phi)}^0 + R \cdot T \cdot \ln x_{B(\Phi)} + \Delta\mu_{B(\Phi)}^E$$

$$\mu_{AX(e)} = \mu_{AX(e)}^0 + R \cdot T \cdot \ln x_{AX(e)} + \Delta\mu_{AX(e)}^E$$

$$\mu_{BX(e)} = \mu_{BX(e)}^0 + R \cdot T \cdot \ln x_{BX(e)} + \Delta\mu_{BX(e)}^E$$

$$E_{A(\Phi)} = E_{A(\Phi)}^0 + \frac{R \cdot T}{a \cdot q \cdot F} \cdot \ln \frac{x_{AX(e)}}{(x_{A(\Phi)})^q} + \frac{\Delta\mu_{AX(e)}^E - q \cdot \Delta\mu_{A(\Phi)}^E}{a \cdot q \cdot F}$$

$$E_{B(\Phi)} = E_{B(\Phi)}^0 + \frac{R \cdot T}{b \cdot s \cdot F} \cdot \ln \frac{x_{BX(e)}}{(x_{B(\Phi)})^s} + \frac{\Delta\mu_{BX(e)}^E - s \cdot \Delta\mu_{B(\Phi)}^E}{b \cdot s \cdot F}$$

$$x_{AX(e),\Phi/\Psi} = \frac{s \cdot (1 - y) \cdot (1 - x_{B+(\Phi/\Psi)}^*)}{s - (s - q) \cdot x_{B+(\Phi/\Psi)}^*} \quad x_{BX(e)} = \frac{q \cdot (1 - y) \cdot x_{B+(\Phi/\Psi)}^*}{s - (s - q) \cdot x_{B+(\Phi/\Psi)}^*}$$

$$\begin{aligned} & E_{A(\Phi)}^0 + \frac{R \cdot T}{a \cdot q \cdot F} \cdot \ln \frac{x_{AX(e),\Phi/\Psi}}{(x_{A(\Phi)})^q} + \frac{\Delta\mu_{AX(e),\Phi/\Psi}^E - q \cdot \Delta\mu_{A(\Phi)}^E}{a \cdot q \cdot F} = \\ & = E_{B(\Phi)}^0 + \frac{R \cdot T}{b \cdot s \cdot F} \cdot \ln \frac{x_{BX(e),\Phi/\Psi}}{(x_{B(\Phi)})^s} + \frac{\Delta\mu_{BX(e),\Phi/\Psi}^E - s \cdot \Delta\mu_{B(\Phi)}^E}{b \cdot s \cdot F} \end{aligned}$$



Simplified equation of ECPD lines

$$E^0_{A(\Phi)} + \frac{R \cdot T}{a \cdot q \cdot F} \cdot \ln \frac{x_{AX(e),\Phi/\Psi}}{(x_{A(\Phi)})^q} + \frac{\Delta\mu^E_{AX(e),\Phi/\Psi} - q \cdot \Delta\mu^E_{A(\Phi)}}{a \cdot q \cdot F} = E^0_{B(\Phi)} + \frac{R \cdot T}{b \cdot s \cdot F} \cdot \ln \frac{x_{BX(e),\Phi/\Psi}}{(x_{B(\Phi)})^s} + \frac{\Delta\mu^E_{BX(e),\Phi/\Psi} - s \cdot \Delta\mu^E_{B(\Phi)}}{b \cdot s \cdot F}$$

$$x_{AX(e),\Phi/\Psi} = \frac{s \cdot (1 - y) \cdot (1 - x^*_{B+(\Phi/\Psi)})}{s - (s - q) \cdot x^*_{B+(\Phi/\Psi)}} \quad x_{BX(e),\Phi/\Psi} = \frac{q \cdot (1 - y) \cdot x^*_{B+(\Phi/\Psi)}}{s - (s - q) \cdot x^*_{B+(\Phi/\Psi)}}$$

Active compounds: A_qX_r , B_sX_t

charges of cations: $a = b(\equiv c)$ $q = s(\equiv u)$ $r = t$

$$x^*_{B+(\alpha/\beta)} = \frac{1}{1 + \left(K^0_{B(\Phi)} \cdot K^E_{B(\Phi)}\right)^{-\frac{1}{c \cdot u}} \cdot \left(\frac{x_{A(\Phi)}}{x_{B(\Phi)}}\right)^u}$$

$$K^0_{B(\Phi)} \equiv \exp \left(c^2 \cdot u^2 \cdot F \cdot \frac{E^0_{A(\Phi)} - E^0_{B(\Phi)}}{R \cdot T} \right)$$

$$K^E_{B(\Phi)} \equiv \exp \left[c \cdot u \cdot \frac{(\Delta\mu^E_{AX(e),\alpha/\beta} - \Delta\mu^E_{BX(e),\alpha/\beta}) - u \cdot (\Delta\mu^E_{A(\Phi)} - \Delta\mu^E_{B(\Phi)})}{R \cdot T} \right]$$



ECPD lines of a simple binary solid solution system

Active compounds: A_qX_r , B_sX_t

charges of cations: $a = b(\equiv c)$

$q = s(\equiv u)$ $r = t$

Electrolyte: ideal solution

$$\Delta\mu_{AX(e),s/l}^E = \Delta\mu_{BX(e),s/l}^E = 0$$

Electrodeposited alloy:

- **ideal solution in solid phase**
- **ideal solution in liquid phase**

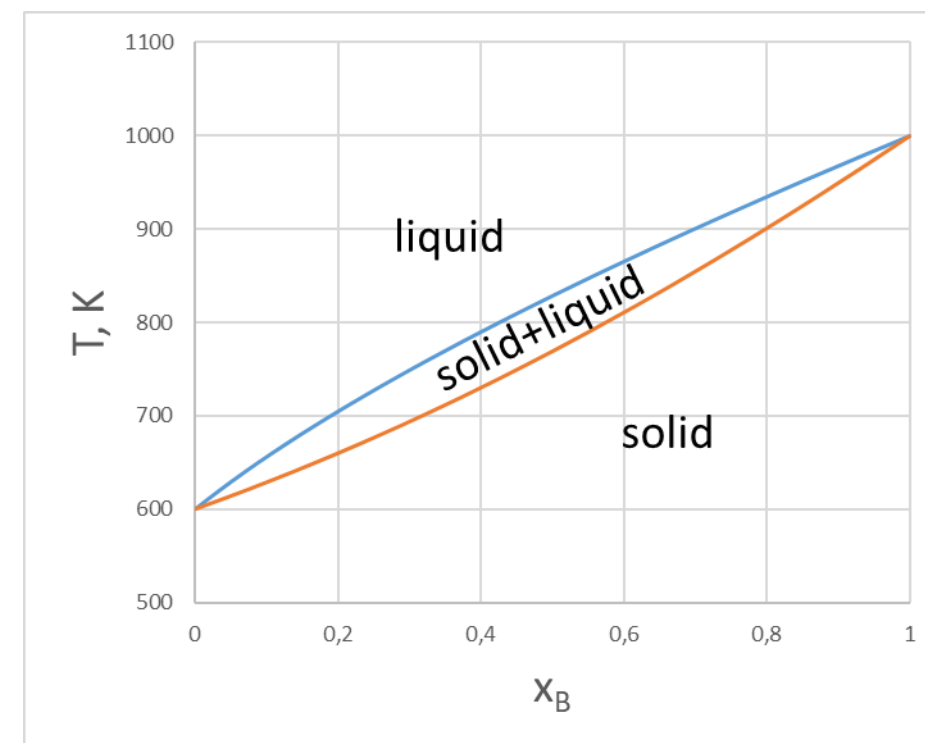
$$\Delta\mu_{A(\phi)}^E = \Delta\mu_{B(\phi)}^E = 0$$

$$x_{B(\alpha)} = K_B \cdot \frac{K_A - 1}{K_A - K_B} \quad x_{B(l)} = \frac{K_A - 1}{K_A - K_B}$$

$$K_A \equiv \exp\left(\frac{\mu_{A(l)}^0 - \mu_{A(\alpha)}^0}{R \cdot T}\right) \quad K_{B(l)}^0 = \exp\left(c^2 \cdot u^2 \cdot F \cdot \frac{E_{A(l)}^0 - E_{B(l)}^0}{R \cdot T}\right)$$

$$K_B \equiv \exp\left(\frac{\mu_{B(l)}^0 - \mu_{B(\alpha)}^0}{R \cdot T}\right)$$

$$x_{B+(s/l)}^* = \frac{1}{1 + \left(K_{B(l)}^0\right)^{-\frac{1}{c \cdot u}} \cdot \left(\frac{1 - K_B}{K_A - 1}\right)^u}$$





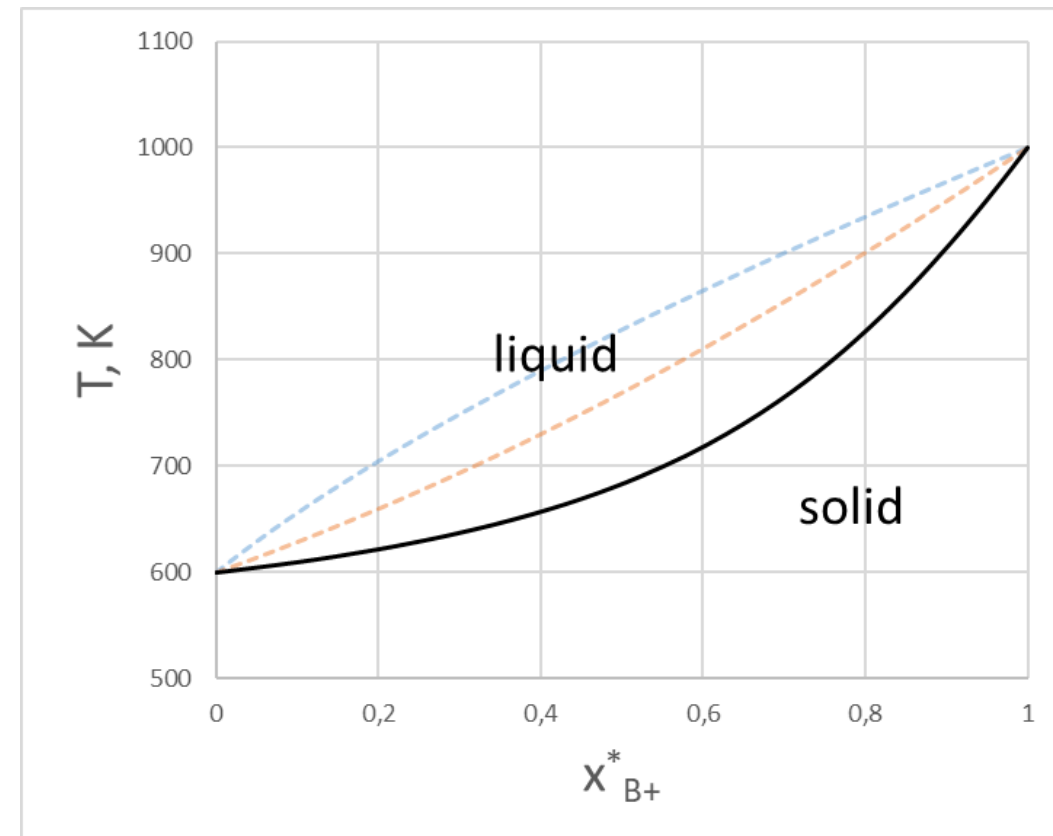
ECPD lines of a simple binary solid solution system

quantity [unit]	value
$T_{m,A}^0$ [K]	600
$T_{m,B}^0$ [K]	1000
$\Delta_m S_m^0 \left[\frac{J}{mol \cdot K} \right]$	10
$a = b \equiv c$ [-]	2
$q = s \equiv u$ [-]	1
$\Delta E_l^0 = E_{A(l)}^0 - E_{B(l)}^0$ [V]	0,05

$$\mu_{A(\alpha)}^0 = \mu_{B(\alpha)}^0 = 0$$

$$\mu_{i(l)}^0 = \Delta_m S_{m,i}^0 \cdot (T_{m,i}^0 - T)$$

$$x_{B+(s/l)}^* = \frac{1}{1 + \left(K_{B(l)}^0 \right)^{-\frac{1}{c \cdot u}} \cdot \left(\frac{1 - K_B}{K_A - 1} \right)^u}$$





ECPD lines of a simple binary system with miscibility gap

Active compounds: A_qX_r , B_sX_t

charges of cations: $a = b(\equiv c)$

$q = s(\equiv u)$ $r = t$

Electrolyte: ideal solution

$$\Delta\mu_{AX(e),\alpha1/\alpha2}^E = \Delta\mu_{BX(e),\alpha1/\alpha2}^E = 0$$

Electrodeposited alloy:

- **phase separation in solid phase**
- **regular solution in solid phase**

$$T = \frac{L_0}{R} \cdot \frac{1 - 2 \cdot x_{B(\alpha1)}}{\ln \frac{1 - x_{B(\alpha1)}}{x_{B(\alpha1)}}}$$

$$\Delta\mu_{A(\alpha1)}^E = L_0 \cdot x_{B(\alpha1)}^2$$

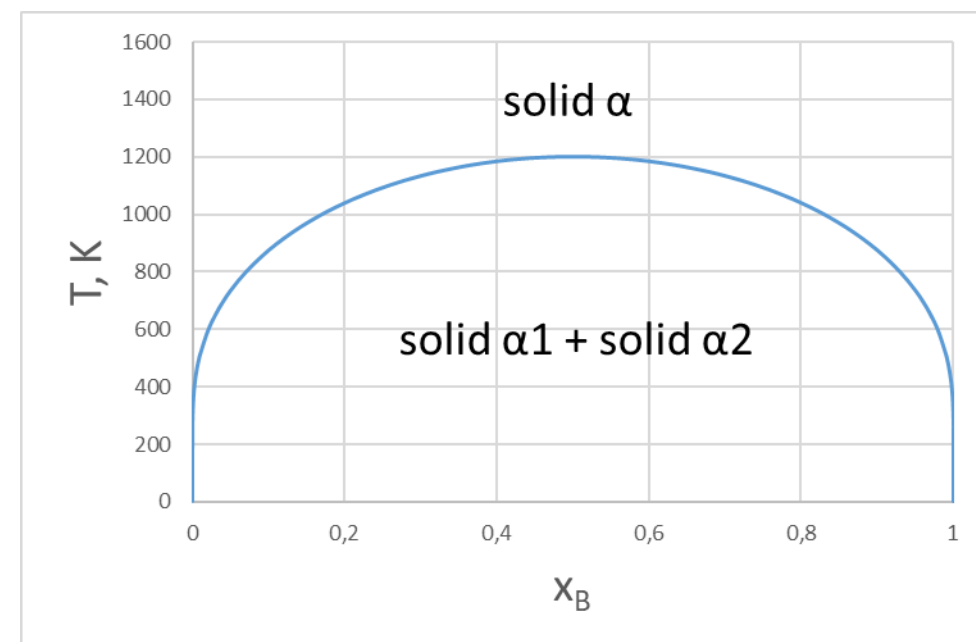
$$\Delta\mu_{A(\alpha2)}^E = L_0 \cdot x_{B(\alpha2)}^2$$

$$\Delta\mu_{B(\alpha1)}^E = L_0 \cdot (1 - x_{B(\alpha1)})^2$$

$$\Delta\mu_{B(\alpha2)}^E = L_0 \cdot (1 - x_{B(\alpha2)})^2$$

$$K_{B(\alpha)}^0 = \exp \left(c^2 \cdot u^2 \cdot F \cdot \frac{E_{A(\alpha)}^0 - E_{B(\alpha)}^0}{R \cdot T} \right)$$

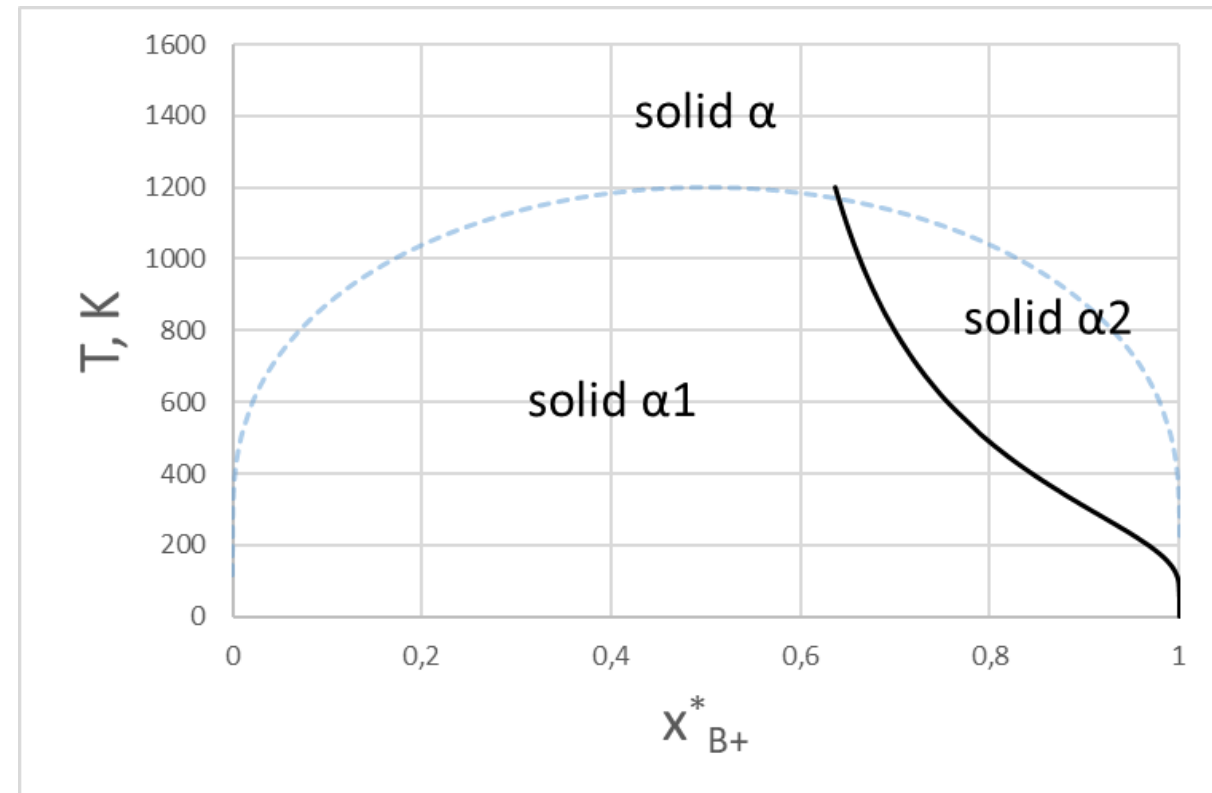
$$x_{B+(\alpha1/\alpha2)}^* = \frac{1}{1 + \left(K_{B(\alpha)}^0 \right)^{-\frac{1}{c \cdot u}}}$$





ECPD lines of a simple binary system with miscibility gap

quantity [unit]	value
$T^0_{m,A} [K]$	600
$T^0_{m,B} [K]$	1000
$\Delta_m S^0_m \left[\frac{J}{mol \cdot K} \right]$	10
$L_0 \left[\frac{kJ}{mol} \right]$	20
$a = b \equiv c [-]$	2
$q = s \equiv u [-]$	1
$\Delta E_s^0 = E_{A(s)}^0 - E_{B(s)}^0 [V]$	0,029



$$x_{B+(\alpha1/\alpha2)}^* = \frac{1}{1 + \left(K_{B(\alpha)}^0 \right)^{-\frac{1}{c \cdot u}}}$$



ECPD lines of a simple binary eutectic system

Active compounds: A_qX_r , B_sX_t

charges of cations: $a = b(\equiv c)$

$q = s(\equiv u)$ $r = t$

Electrolyte: ideal solution

$$\Delta\mu_{AX(e),l/\alpha}^E = \Delta\mu_{BX(e),l/\beta}^E = 0$$

Electrodeposited alloy:

- ideal solution in liquid phase
- immiscible α , β in solid phase

$$\mu_{A(\alpha)}^0 = \mu_{A(l)}^0 + R \cdot T \cdot \ln(1 - x_{B(l/\alpha)})$$

$$\mu_{B(\beta)}^0 = \mu_{B(l)}^0 + R \cdot T \cdot \ln x_{B(l/\beta)}$$

$$x_{B(l/\alpha)} = 1 - \frac{1}{K_{A(\alpha)}}$$

$$K_{B(\alpha/\beta)}^0 = \exp\left(c^2 \cdot u^2 \cdot F \cdot \frac{E_{A(\alpha)}^0 - E_{B(\beta)}^0}{R \cdot T}\right)$$

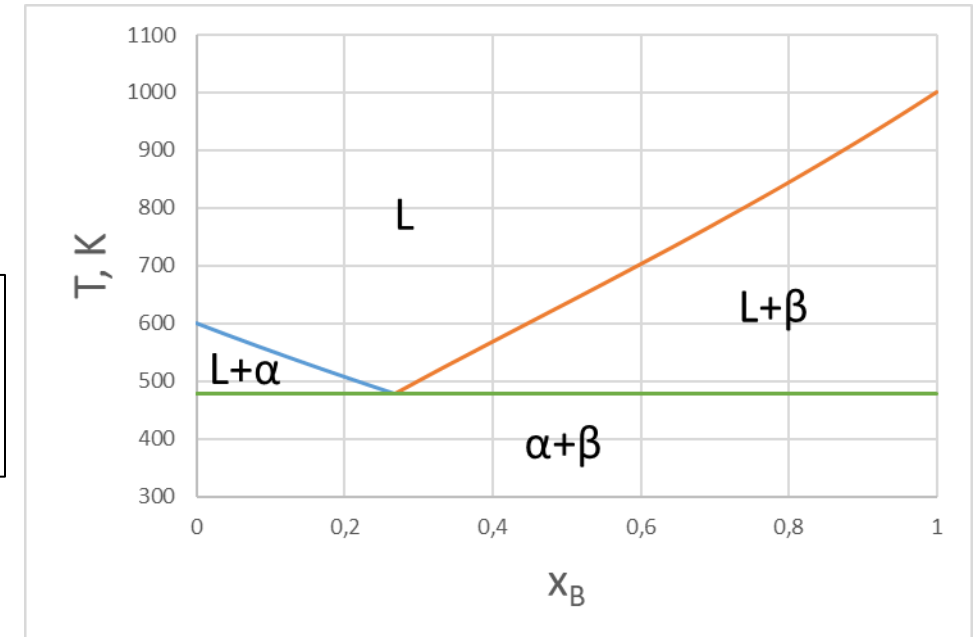
$$x_{B(l/\beta)} = \frac{1}{K_{B(\beta)}}$$

$$\Delta\mu_{A(l)}^E = \Delta\mu_{B(l)}^E = 0$$

$$x_{B+(\alpha/\beta)}^* = \frac{1}{1 + \left(K_{B(\alpha/\beta)}^0\right)^{-\frac{1}{c \cdot u}}}$$

$$x_{B+(l/\alpha)}^* = \frac{1}{1 + \left(K_{B(l)}^0\right)^{-\frac{1}{c \cdot u}} \cdot \left(K_{A(\alpha)} - 1\right)^{-u}}$$

$$x_{B+(l/\beta)}^* = \frac{1}{1 + \left(K_{B(l)}^0\right)^{-\frac{1}{c \cdot u}} \cdot \left(K_{B(\beta)} - 1\right)^u}$$





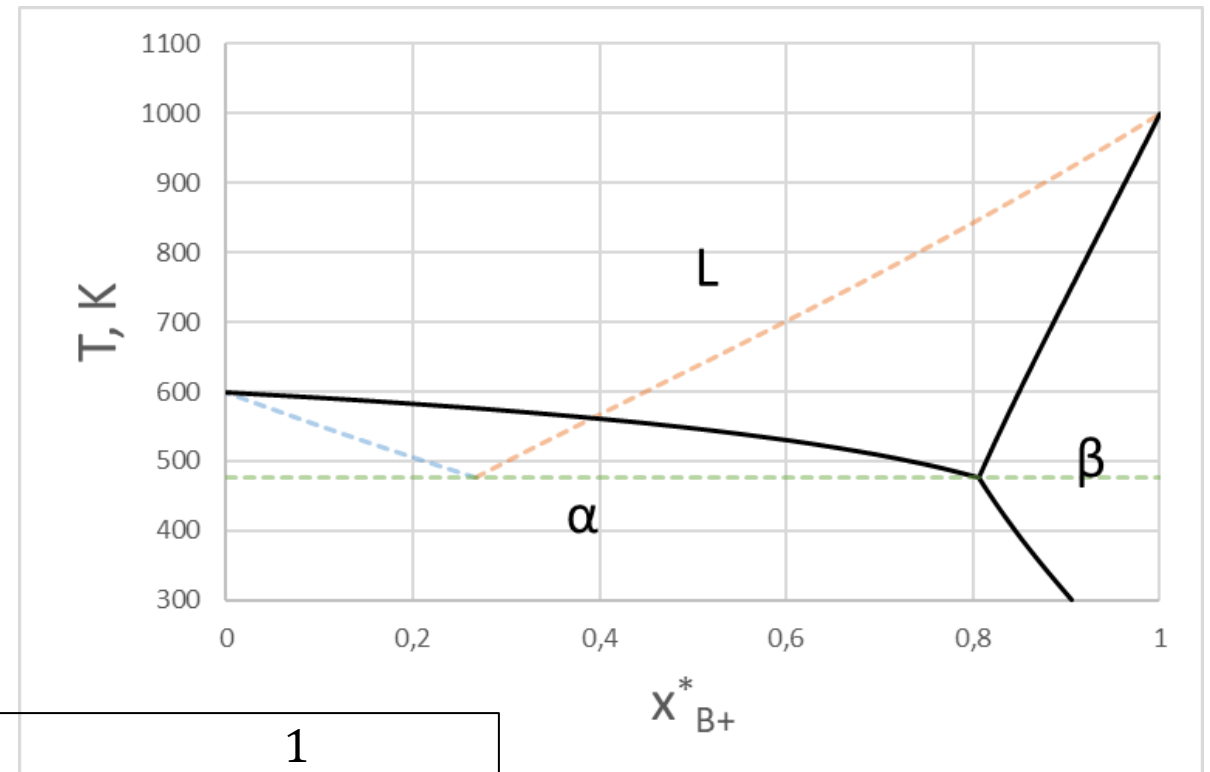
ECPD lines of a simple binary eutectic system

quantity [unit]	value
$T^0_{m,A} [K]$	600
$T^0_{m,B} [K]$	1000
$\Delta_m S^0_m \left[\frac{J}{mol \cdot K} \right]$	10
$a = b \equiv c [-]$	2
$q = s \equiv u [-]$	1
$\Delta E^0_l = E^0_{A(l)} - E^0_{B(l)} [V]$	0,05
$\Delta E^0_s = E^0_{A(s)} - E^0_{B(s)} [V]$	0,029

$$x_{B+(l/\alpha)}^* = \frac{1}{1 + \left(K_{B(l)}^0 \right)^{-\frac{1}{c \cdot u}} \cdot (K_{A(\alpha)} - 1)^{-u}}$$

$$x_{B+(l/\beta)}^* = \frac{1}{1 + \left(K_{B(l)}^0 \right)^{-\frac{1}{c \cdot u}} \cdot (K_{B(\beta)} - 1)^u}$$

$$x_{B+(\alpha/\beta)}^* = \frac{1}{1 + \left(K_{B(\alpha/\beta)}^0 \right)^{-\frac{1}{c \cdot u}}}$$





Experimental data:

- **Ag-Cu** Kun Hee Lee, et al.: "Properties of nanocrystalline CuAg foil prepared via electrodeposition." *Journal of Alloys and Compounds* 881 (2021): 160522.

- cathode: Ni covered by chromate
- bath temperature: 60 °C
- current density: 7,5 mA/cm²
- electrolyte:

result:

- supersaturated Cu(FCC) nanocrystals
- after heat treatment: Ag precipitates

- CuCN: 0.78 M
- AgCN: 0.12, 2.5, 3.7 mM
- KCN: 2.08 M
- Rochelle salt: 79 mM
- KOH: 0.27 M
- K₂CO₃: 0.36 M
- saccharin: 0.5 mM
- PAT: 75 μM
- PEI: 3 mM
- Triton-X: 5 mM

$$x_{CuCN(e)} \cong 0.013$$

$$x_{AgCN(e)} \cong 2.03 \cdot 10^{-6}, 4.23 \cdot 10^{-6}, 6.26 \cdot 10^{-6}$$

$$x_{Cu+}^* = 0.9998, 0.9996, 0.9995$$

$$x_{Ag+}^* = 1.53 \cdot 10^{-4}, 3.20 \cdot 10^{-4}, 4.74 \cdot 10^{-3}$$

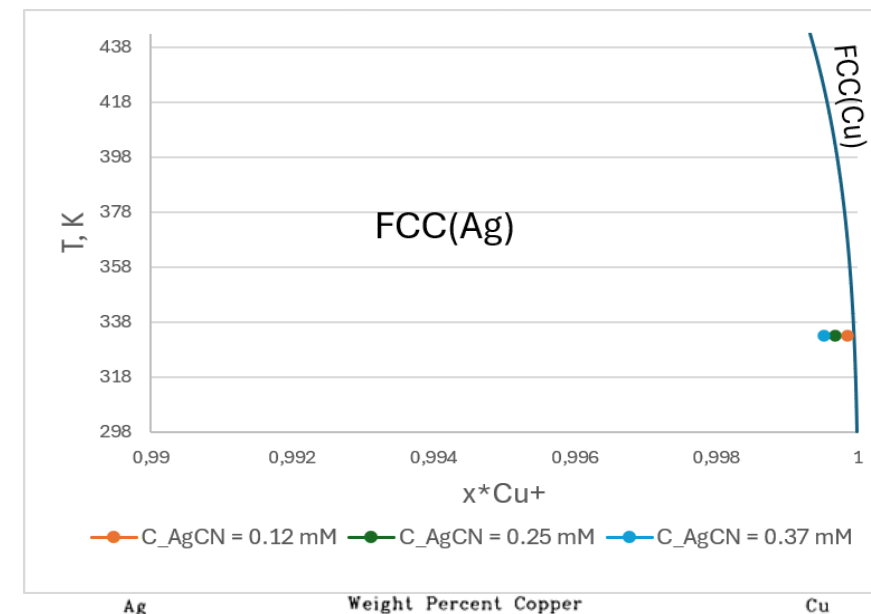
$$\gamma \cong 0.987 \quad \text{diluted solution}$$

$$E^0_{Cu(FCC)} \cong 0.521 \text{ V}$$

$$E^0_{Ag(FCC)} \cong 0.799 \text{ V}$$

$$E^0_{Cu(FCC)} - E^0_{Ag(FCC)} \cong -0.278 \text{ V}$$

$$x_{Cu+(FCC1/FCC2)}^* = \frac{1}{1 + \left(K_{Cu(FCC1/FCC2)}^0\right)^{-1}}$$





Experimental data:

• **Co-Cu** **A. E. Mohamed, et al.: "Electrodeposition of Co-Cu alloy coatings from glycinate baths." Journal of Applied Electrochemistry 33.11 (2003): 1085-1092.**

- **cathode: steel**
- **bath temperature: 10 – 55 °C (25 °C)**
- **current density: 1.5 – 10.8 mA/cm²**
- **electrolyte:**

result:

- **Cu is more preferable < 24 mA/cm²**
- **one FCC phase (XRD)**

- **CuSO₄*5H₂O: 0.04 M**
- **CoSO₄*7H₂O : 0.106 M**
- **Na₂SO₄: 0.14 M**
- **glycine: 1.06 M**

$$x_{CuSO_4(e)} \cong 7.03 \cdot 10^{-4}$$

$$x_{CoSO_4(e)} \cong 1.86 \cdot 10^{-3}$$

$$x_{Cu+}^* \cong 0.273$$

$$x_{Co+}^* \cong 0.727$$

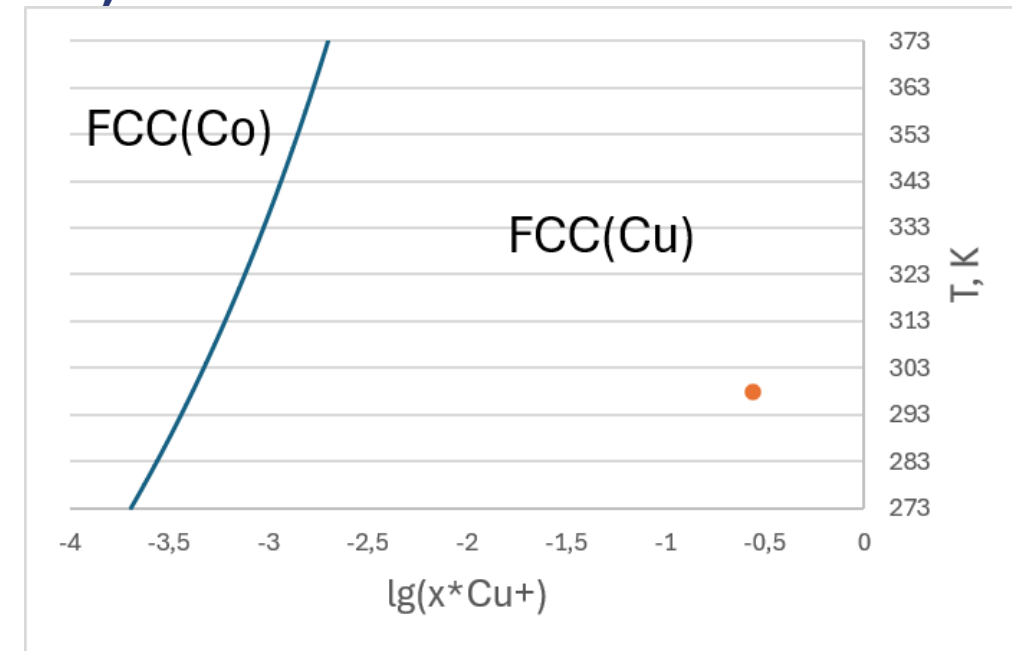
$$y \cong 0.997 \quad \text{diluted solution}$$

$$E^0_{Cu(FCC)} \cong -1.2 \text{ V}$$

$$E^0_{Co(FCC)} \cong -1.3 \text{ V}$$

$$E^0_{Co(FCC)} - E^0_{Cu(FCC)} \cong -0.1 \text{ V}$$

$$x_{Cu+(FCC1/FCC2)}^* = \frac{1}{1 + \left(K_{Cu(FCC1/FCC2)}^0 \right)^{-\frac{1}{2}}}$$





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Thank you for your attention!