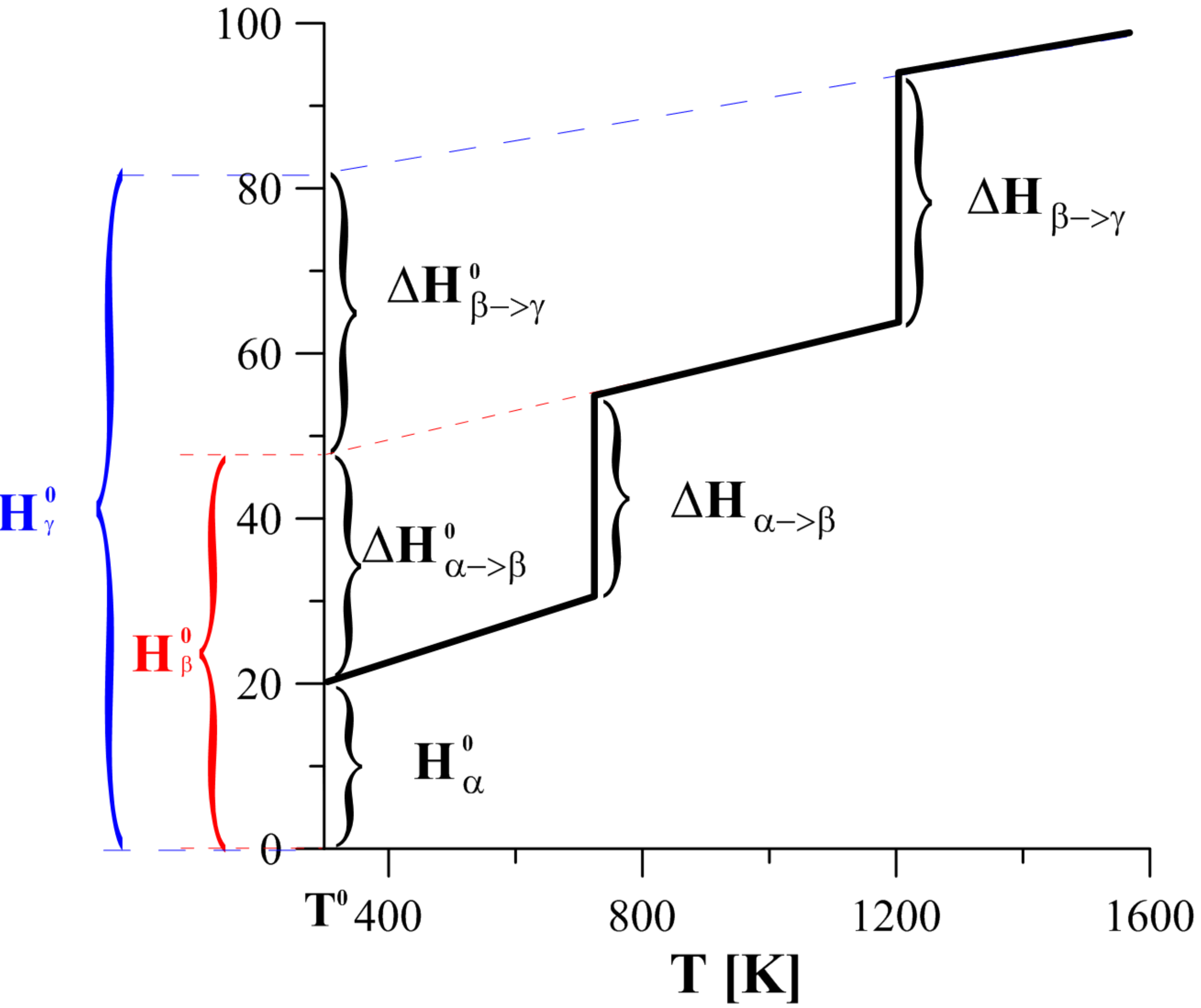


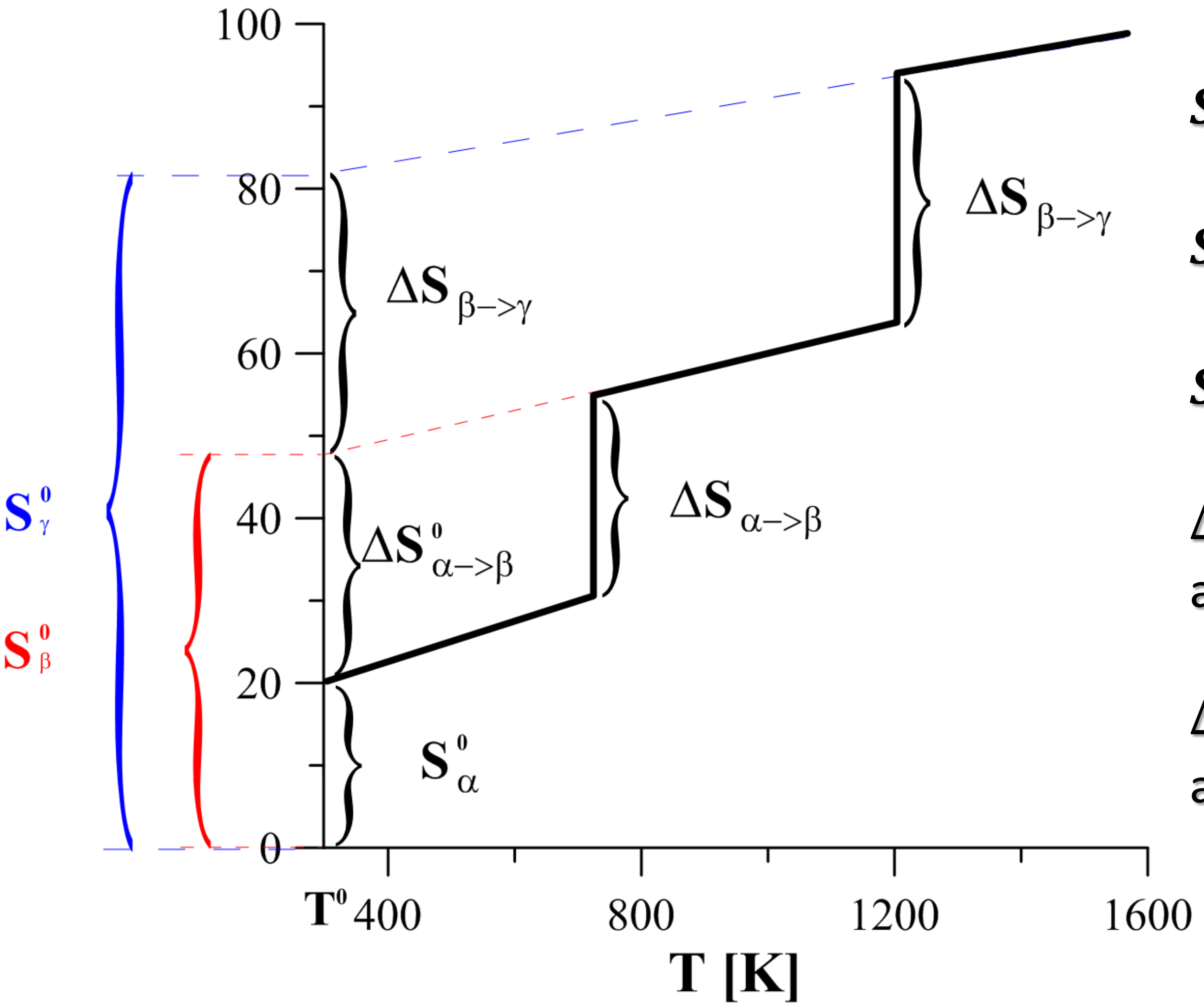
H^0_α - the standard enthalpy of α phase

H^0_β - the standard enthalpy of β phase

H^0_γ - the standard enthalpy of γ phase

$\Delta H_{\alpha\rightarrow\beta}$ - the transition enthalpy of α to β phase at T_{t1}

$\Delta H_{\beta\rightarrow\gamma}$ - the transition enthalpy of β to γ phase at T_{t2}



$S^0_\alpha = S^0_{X(\alpha)}$ - the standard entropy of α phase

$S^0_\beta = S^0_{X(\beta)}$ - the standard entropy of β phase

$S^0_\gamma = S^0_{X(\gamma)}$ - the standard entropy of γ phase

$\Delta S_{\alpha\to\beta} = \Delta S_{(\alpha\to\beta)}$ - the transition entropy of α to β phase at T_{t1}

$\Delta S_{\beta\to\gamma} = \Delta S_{(\beta\to\gamma)}$ - the transition entropy of β to γ phase at T_{t2}

Exercise 1

Calculate the change in the enthalpy and entropy of solid and liquid zinc in the temperature range from T^0 = 298.16 K to T = 1000 K, step =100 K based on following data:

MPT=692.655K   BPT= 1180K

s -	4.956	2.99E-3	.199E+5	0.	298.14	$H_s^0 = 0.$	$S_s^0 = 9.95$
l -	7.5	3*0.			692.655	$\Delta H_{s\to l} = 1750.$	
g -	4.968	3*0.			1180.	$\Delta H_{l\to g} = 27569.$	

Calculation of the standard enthalpy and entropy of the liquid phase $H^0_{lT^0}$ and $S^0_{lT^0}$

Step I. *Establishing the equations for Cp and enthalpis and entropies of solid, liquid and gas Zn*

$$C_{p(s)} = a + b \cdot T + c \cdot T^{-2} + d \cdot T^2$$

$$C_{p(s)} = 4.956 + 2.99E{-}3 \cdot T + .199E{+}5 \cdot T^{-2} + 0 \cdot T^2$$

$$C_{p(s)} = 4.956 + 2.99 \cdot 10^{-3} \cdot T + 0.199 \cdot 10^{5} \cdot T^{-2}$$

$C_{p(l)} = 7.5$ $\quad$ $C_{p(g)} = 4.968,$ $\quad$ (b=0, c=0, d=0)

$H^0_{(s)}=0$ $\quad$ $\Delta H_{s\rightarrow l}=1750$ $\quad$ $\Delta H_{l\rightarrow g} = 27569$ $\quad$ $S^0_s = 9.95$

$$\Delta S_{s\rightarrow l} = \frac{\Delta H_{s\rightarrow l}}{T_{t1}} = \frac{1750}{692.655} = 2.5265 \qquad \Delta S_{l\rightarrow g} = \frac{\Delta H_{l\rightarrow g}}{T_{t2}} = \frac{27569}{1180} = 23.3636$$

Step 2. *Calculation of the standard enthalpy of liquid and gas phase for Zn*

$$H^0_{(l)} = H^0_{(s)} + \int_{T^0}^{T_m} C_{p(s)}\,dT + \Delta H_{(s\to l)} - \int_{T_m}^{T^0} C_{p(l)}\,dT$$

$$H^0_{(g)} = H^0_{(l)} + \int_{T_m}^{T_b} C_{p(l)}\,dT + \Delta H_{(l\to g)} - \int_{T_b}^{T^0} C_{p(g)}\,dT$$

$$H^0_{(l)} = 0 + \int_{T^0}^{T_m} (4.956 + 2.99\cdot 10^{-3}\cdot T + 0.199\cdot 10^{5}\cdot T^{-2})\,dT + 1750 - \int_{T_m}^{T^0} 7.5\,dT$$

$$H^0_{(g)} = H^0_{(l)} + \int_{T_m}^{T_b} 7.5\,dT + \Delta H_{(l\to g)} - \int_{T_b}^{T^0} 4.968\,dT$$

Step 2. *Calculation of the standard entropy of liquid and gas phase for Zn*

$$S^0_{(l)} = S^0_{(s)} + \int_{T^0}^{T_m} \frac{C_{p(s)}}{T} dT + \Delta S_{(s\to l)} - \int_{T_m}^{T^0} \frac{C_{p(l)}}{T} dT$$

$$S^0_{(g)} = S^0_{(l)} + \int_{T_m}^{T_b} \frac{C_{p(l)}}{T} C_{p(l)} dT + \Delta S_{(l\to g)} - \int_{T_b}^{T^0} \frac{C_{p(g)}}{T} dT$$

$$S^0_{(l)} = 9.95 + \int_{T^0}^{T_m} \frac{(4.956 + 2.99 \cdot 10^{-3} \cdot T + 0.199 \cdot 10^{5} \cdot T^{-2})}{T} dT + \frac{1750}{692.655} - \int_{T_m}^{T^0} \frac{7.5}{T} dT$$

$$S^0_{(g)} = S^0_{(l)} + \int_{T_m}^{T_b} \frac{7.5}{T} dT + \Delta S_{(l\to g)} - \int_{T_b}^{T^0} \frac{4.968}{T} dT$$

Calculated the standard entropy and enthalpy of liquid and gas Zn

$$\boldsymbol{H^0_{(l)} = 1368.8\ [cal \cdot mol^{-1}]}$$

$$\boldsymbol{H^0_{(g)} = 31170.65\ [cal \cdot mol^{-1}]}$$

$$\boldsymbol{S^0_{(l)} = 11.603\left[cal \cdot K^{-1} \cdot mol^{-1}\right]}$$

$$\boldsymbol{S^0_{(g)} = 38.450\left[cal \cdot K^{-1} \cdot mol^{-1}\right]}$$

Step III. Calculation of the enthalpy and entropy of solid, liquid and gas Zn

$$H_{Zn(l)} = H^0_{Zn(l)} + a_{(l)}(T - T^0) = 1368.8 + 7.5 \cdot (T - 298.16)$$

$$H_{Zn(g)} = H^0_{Zn(g)} + a_{(g)}(T - T^0) = 31170.65 + 4.968 \cdot (T - 298.16)$$

$$S_{Zn(l)} = S^0_{Zn(l)} + a_{(l)} \cdot ln\left(\frac{T}{T^0}\right) = 11.603 + 7.5 \cdot ln\left(\frac{T}{298.16}\right)$$

$$S_{Zn(g)} = S^0_{Zn(g)} + a_{(g)} ln\left(\frac{T}{T^0}\right) = 38.450 + 4.968 \cdot ln\left(\frac{T}{298.16}\right)$$

Step III. Calculation of the enthalpy and entropy of solid, liquid and gas Zn

$$H_{Zn(s)} = H^0_{Zn(s)} + a_{(s)} \cdot (T - T^0) + b_{Zn(s)} \cdot \frac{T^2 - T^{02}}{2} + c_{Zn(s)} \cdot \frac{T - T^0}{T \cdot T^0}$$

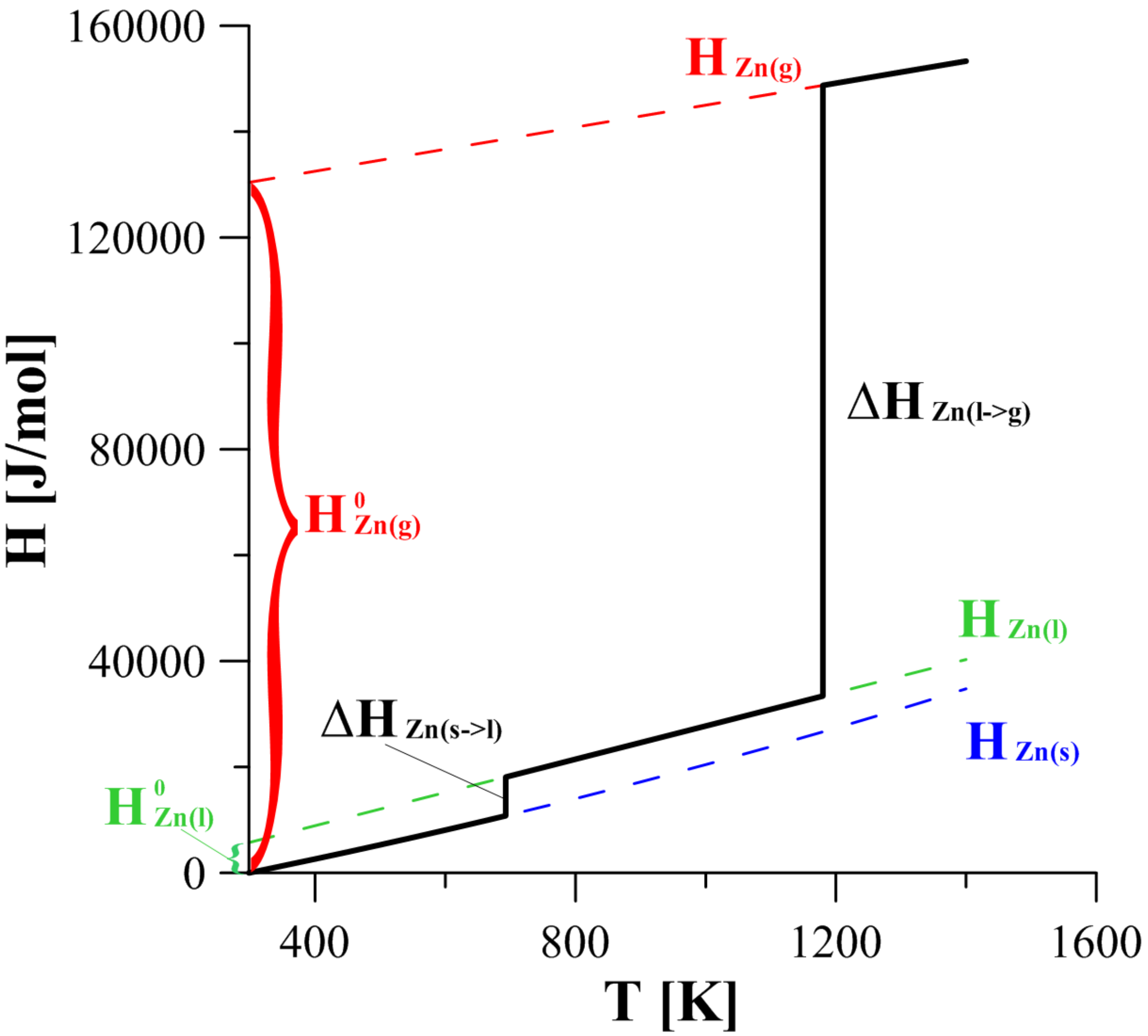
$$H_{Zn(s)} = 0 + 4.956 \cdot (T - 298.16) + 0.00299 \cdot \frac{T^2 - 298.16^2}{2} + 19900 \cdot \frac{T - 298.16}{T \cdot T^0}$$

$$S_{Zn(s)} = a_{(s)} \cdot ln\left(\frac{T}{T^0}\right) + b_{(s)}b \cdot (T - T^0) + c_{(s)} \cdot \frac{T^2 - T^{02}}{2 \cdot T^2 \cdot T^{02}}$$

$$S_{Zn(s)} = 4.956 \cdot ln\left(\frac{T}{298.16}\right) + 0.00299 \cdot (T - T^0) + 19900 \cdot \frac{T^2 - T^{02}}{2 \cdot T^2 \cdot T^{02}}$$

T(K)	$H_{(s)}$	$H_{(l)}$	$H_{(g)}$
298.2	0	5727	130418
400	2628	8923	132535
450	3954	10492	133574
500	5306	12061	134614
550	6687	13630	135653
600	8096	15199	136692
650	9534	16768	137732
692.7	10785	18107	138618
700	11002	18337	138771
750	12500	19906	139810
800	14029	21475	140850
900	17177	24613	142928
1000	20449	27751	145007
1100	23844	30889	147085
1180	26648	33400	148748
1200	27362	34027	149164
1300	31005	37165	151243
1400	34772	40303	153321

T(K)	$S_{(s)}$	$S_{(l)}$	$S_{(g)}$
298.2	41.632	48.548	160.875
400	49.208	57.769	166.982
450	52.33	61.465	169.431
500	55.179	64.771	171.621
550	57.81	67.762	173.602
600	60.262	70.492	175.410
650	62.564	73.004	177.074
692.7	64.428	74.998	178.395
700	64.740	75.329	178.615
750	66.807	77.494	180.049
800	68.780	79.520	181.39
900	72.487	83.216	183.838
1000	75.932	86.522	186.028
1100	79.167	89.513	188.01
1180	81.628	91.716	189.469
1200	82.228	92.243	189.818
1300	85.143	94.755	191.482
1400	87.934	97.08	193.022



$$H^0_{(s)} = H^0_{Zn(s)}$$

$$H^0_{(l)} = H^0_{Zn(l)}$$

$$H^0_{(g)} = H^0_{Zn(g)}$$

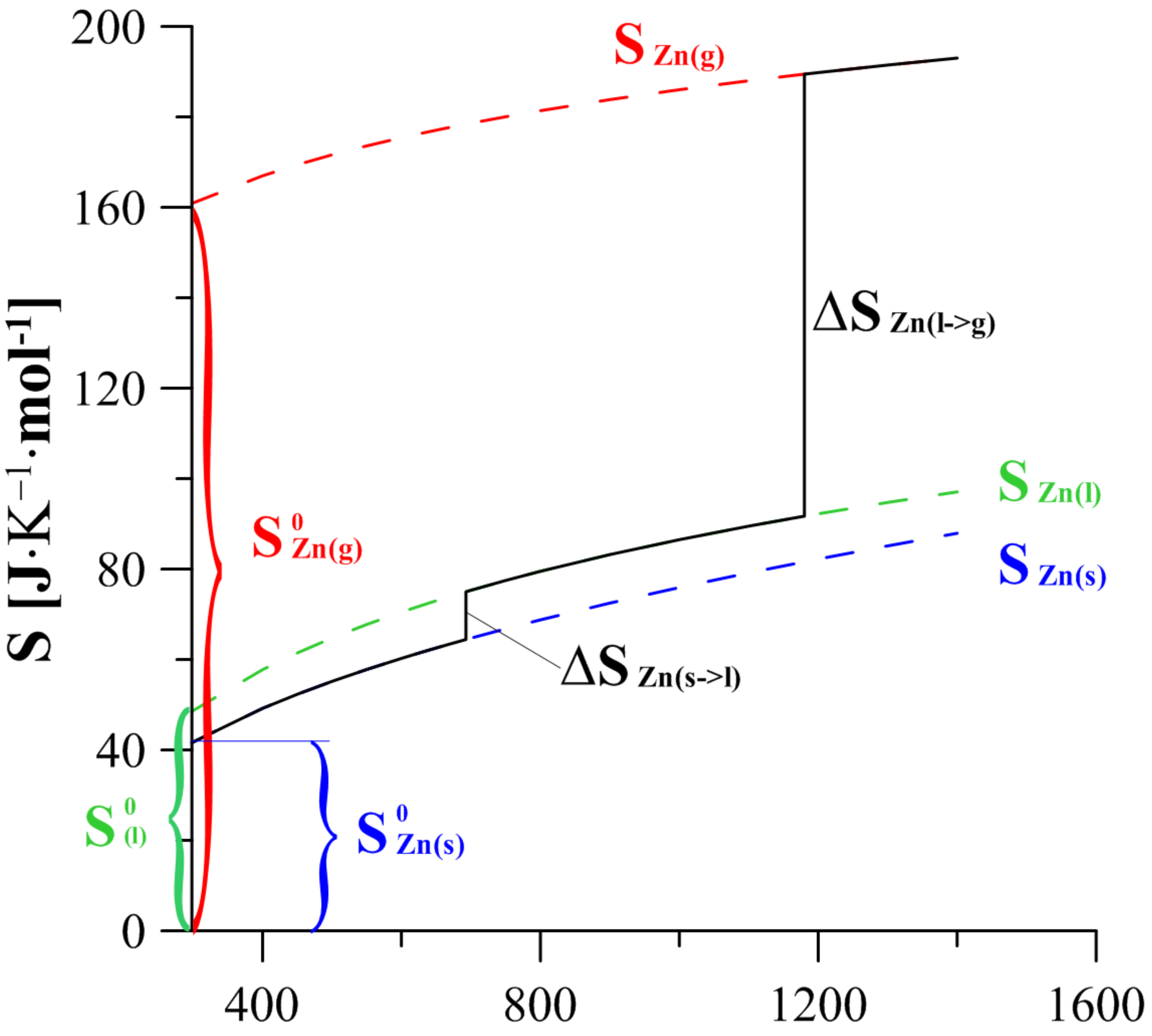
$$H_{(s)T} = H_{Zn(s)}$$

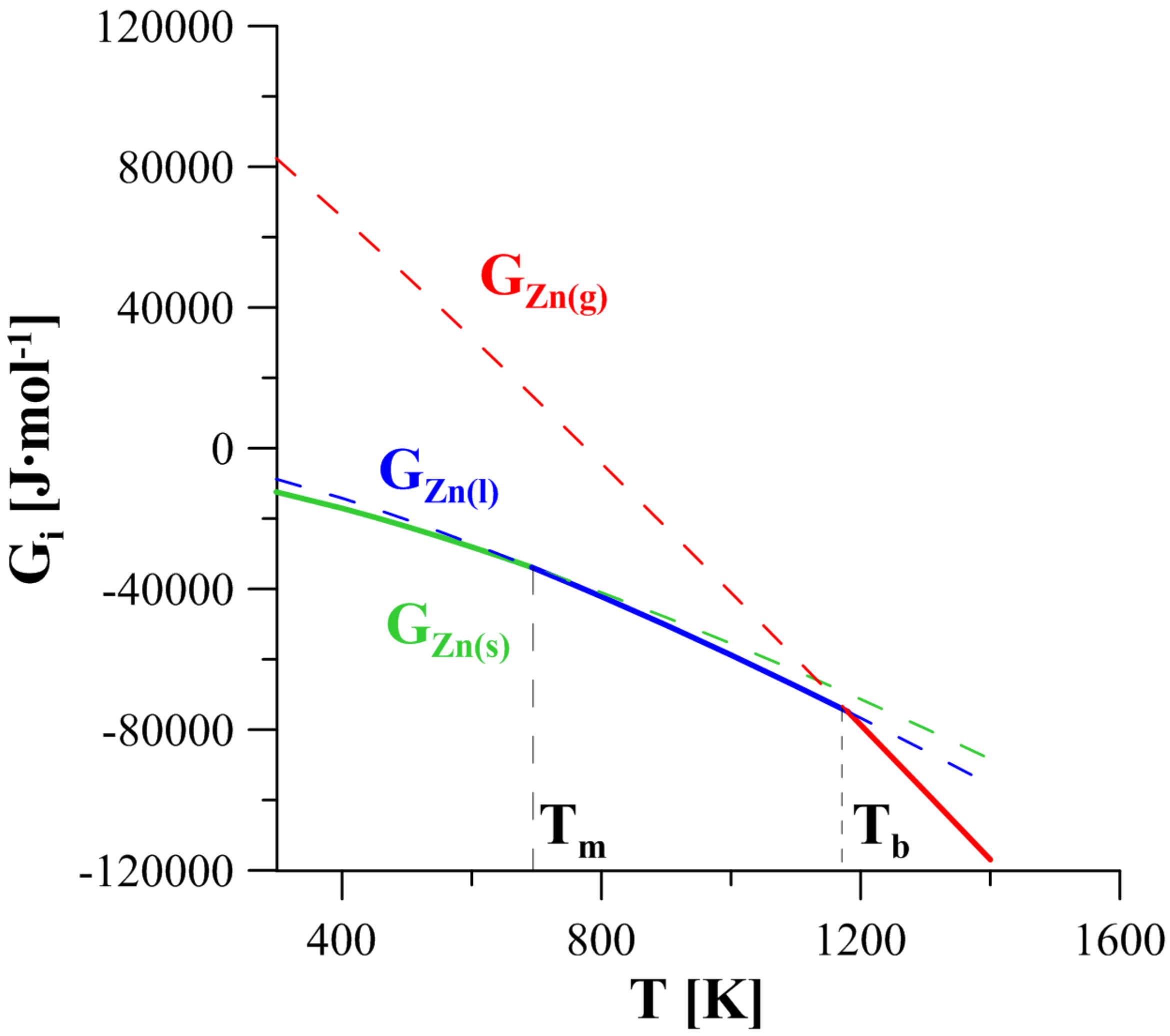
$$H_{(l)T} = H_{Zn(l)}$$

$$H_{(g)T} = H_{Zn(g)}$$

$$\Delta H_{(s\rightarrow l)T_m} = \Delta H_{Zn(s\rightarrow l)}$$

$$\Delta H_{(l\rightarrow g)T_b} = \Delta H_{Zn(l\rightarrow g)}$$


200
160
120
80
40
0
S [J·K⁻¹·mol⁻¹]
400
800
1200
1600
S Zn(g)
ΔS Zn(l->g)
S Zn(l)
S Zn(s)
S ⁰ Zn(g)
ΔS Zn(s->l)
S ⁰ (l)
S ⁰ Zn(s)


120000
80000
40000
0
-40000
-80000
-120000
G_i [J·mol^{-1}]
$G_{Zn(g)}$
$G_{Zn(l)}$
$G_{Zn(s)}$
T_m
T_b
400
800
1200
1600
T [K]

The change of the Gibbs Energy of the chemical reaction

A + B = C w T [K] = const

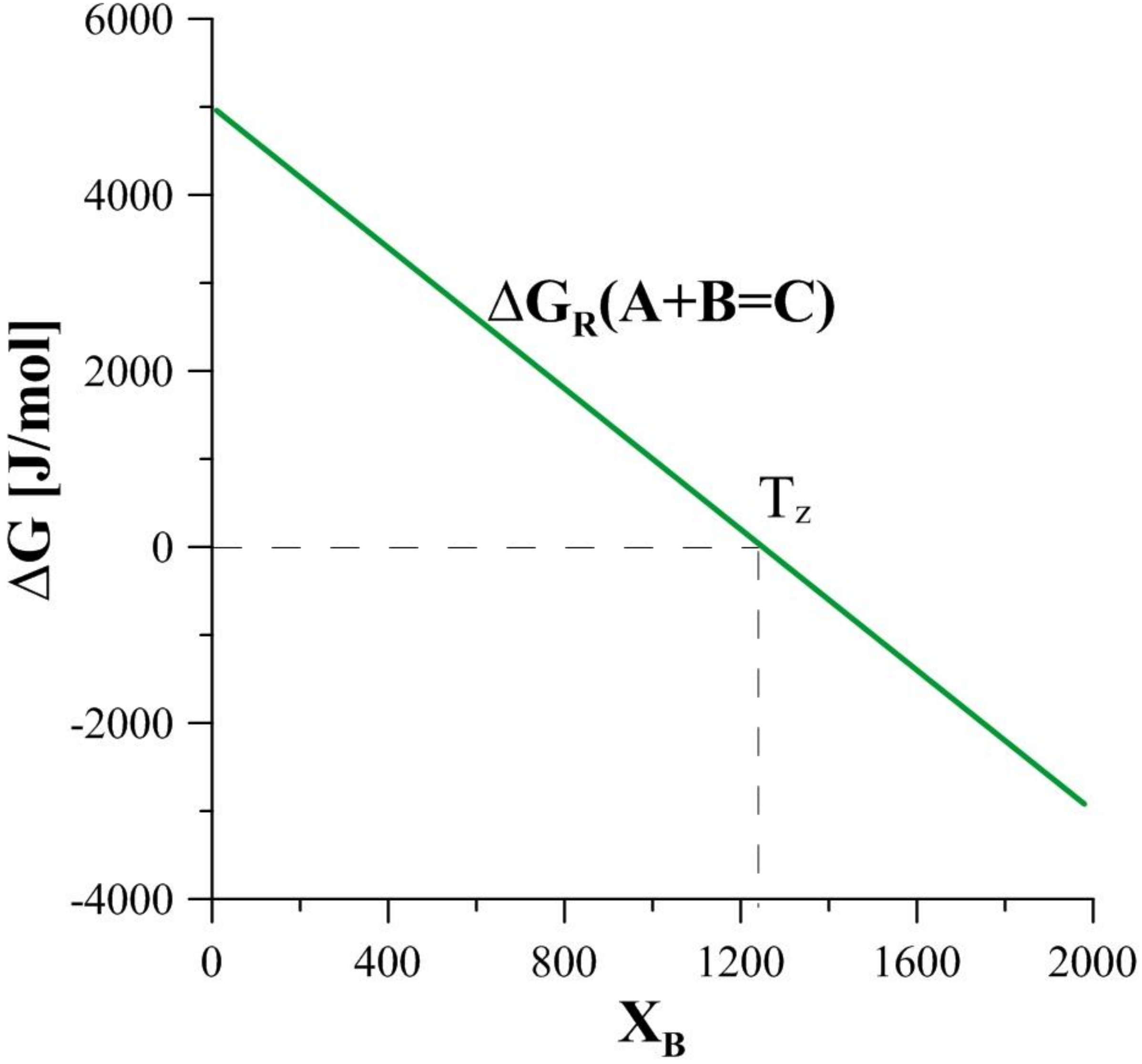
$$\Delta G_R = \Delta G_p - \Delta G_{sub}$$

$$\Delta G_R = \Delta G_C - (\Delta G_A + \Delta G_B)$$

$$\Delta G_R = \Delta G_C - \Delta G_A - \Delta G_B$$

$$G_2 - G_1 = \int_1^2 C_p dT - T \int_1^2 \frac{C_p}{T} dT$$

$$C_p = a + bT + \frac{c}{T^2} + dT^2 + \cdots$$


6000
4000
2000
0
-2000
-4000
ΔG [J/mol]
ΔG_R(A+B=C)
T_Z
0
400
800
1200
1600
2000
X_B

Binary solutions

$$G_A = G_A^0 + RTlnX_A + G_A^{ex}$$

$$G_B = G_B^0 + RTlnX_B + G_B^{ex}$$

$$G_{AB} = X_A G_A + X_B G_B$$

$$G_{AB} = X_A(G_A^0 + RTlnX_A + G_A^{ex}) + X_B(G_B^0 + RTlnX_B + G_B^{ex})$$

$$X_A = 1 - X_B$$

$$X_B = 1 - X_A$$

Binary solutions - continuation

$$G_{AB}^{0} = X_A G_A^0 + X_B G_B^0$$

$$\Delta G_{AB} = X_A(RTlnX_A + G_A^{ex}) + X_B(RTlnX_B + G_B^{ex})$$

Roztwory doskonałe

$$G_{AB}^{id} = G_{AB}^{0} + X_A RTlnX_A + X_B RTlnX_B$$

$$\Delta G_{AB}^{id} = X_A RTlnX_A + X_B RTlnX_B$$

Excess Gibbs free energy

$$G_{AB}^{ex} = X_A G_A^{ex} + X_B G_B^{ex}$$

$$G_{AB}^{ex} = X_A TRln\gamma_A + X_B RTln\gamma_B$$

$$\Delta G_{AB} = X_A(RTlnX_A + G_A^{ex}) + X_B(RTlnX_B + G_B^{ex})$$

$$\Delta G_{AB} = X_A RTlnX_A\gamma_A + X_B RTlnX_B\gamma_B$$

$$a_A = X_A\gamma_A$$

$$a_B = X_B\gamma_B$$

$$\Delta G_{AB} = X_A RTlna_A + X_B RTlna_B$$

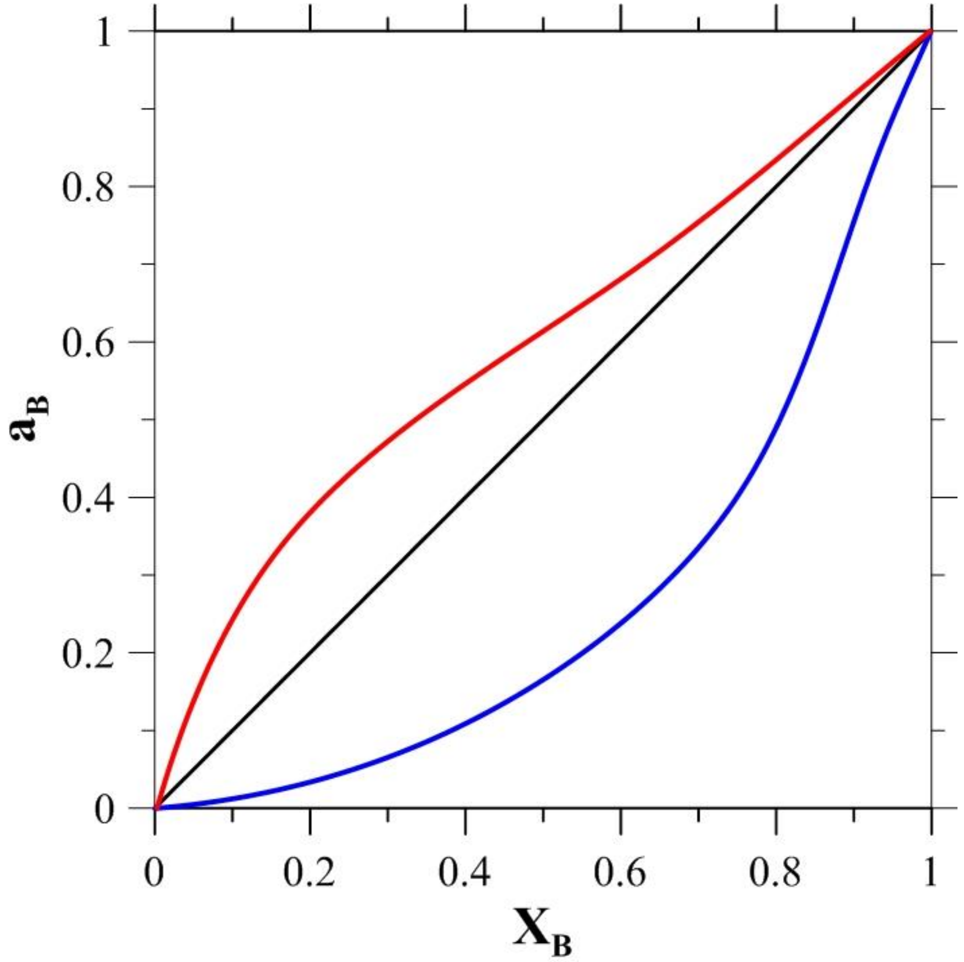
Partial Gibbs free energy of component

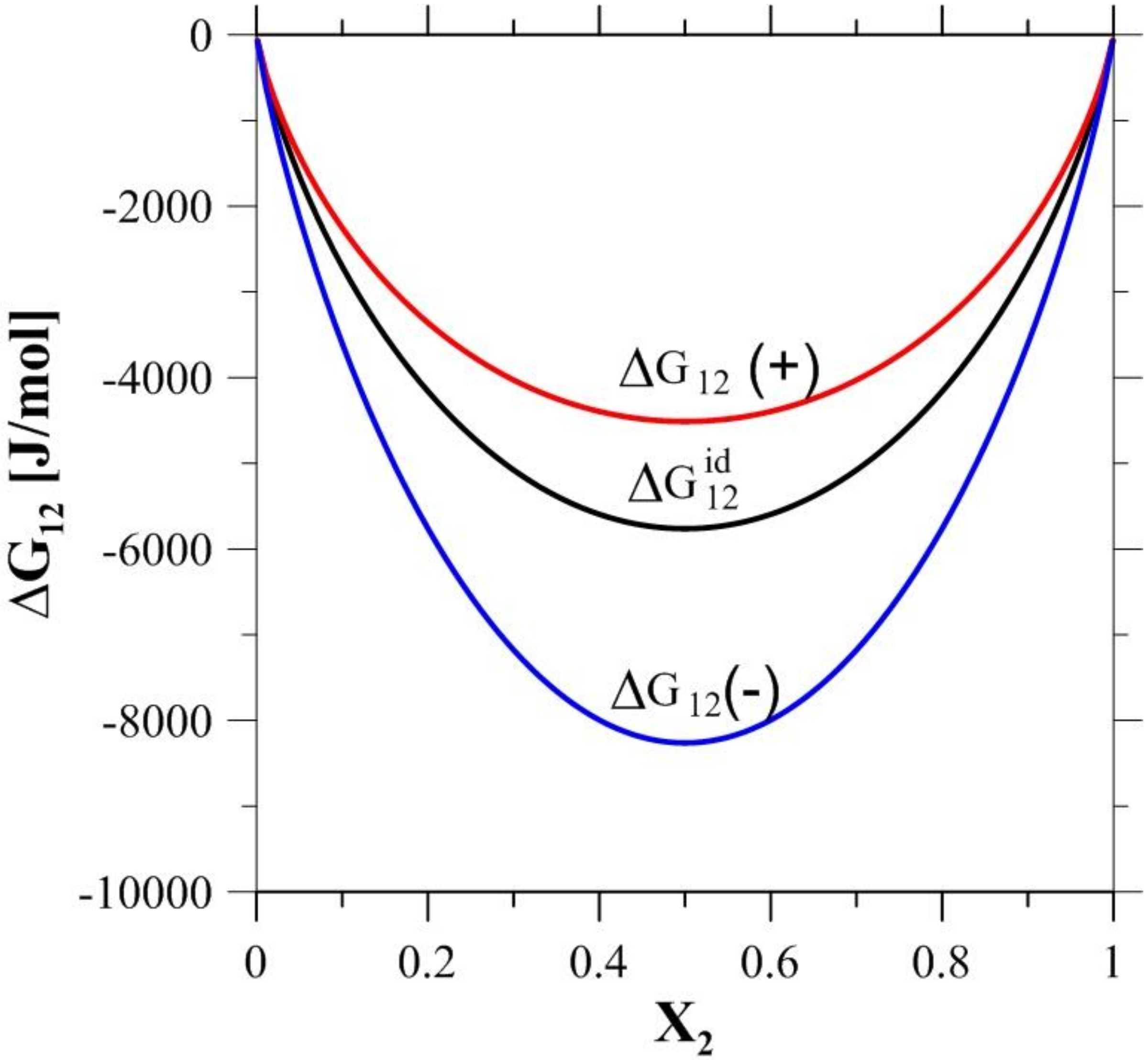
$$\Delta G_{AB} = X_A RT \ln a_A + X_B RT \ln a_B$$

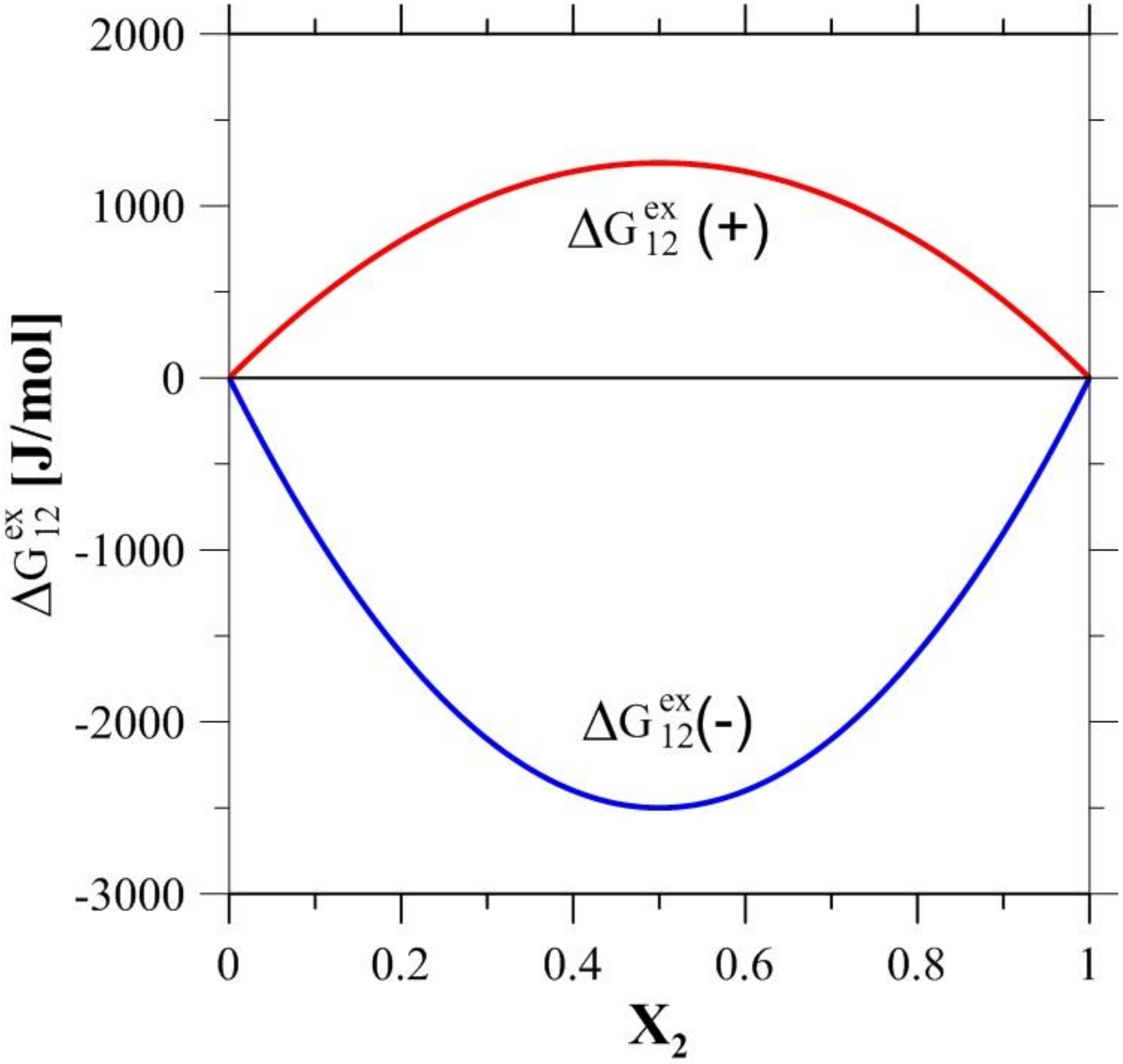
$$\Delta G_A = RT \ln a_A$$

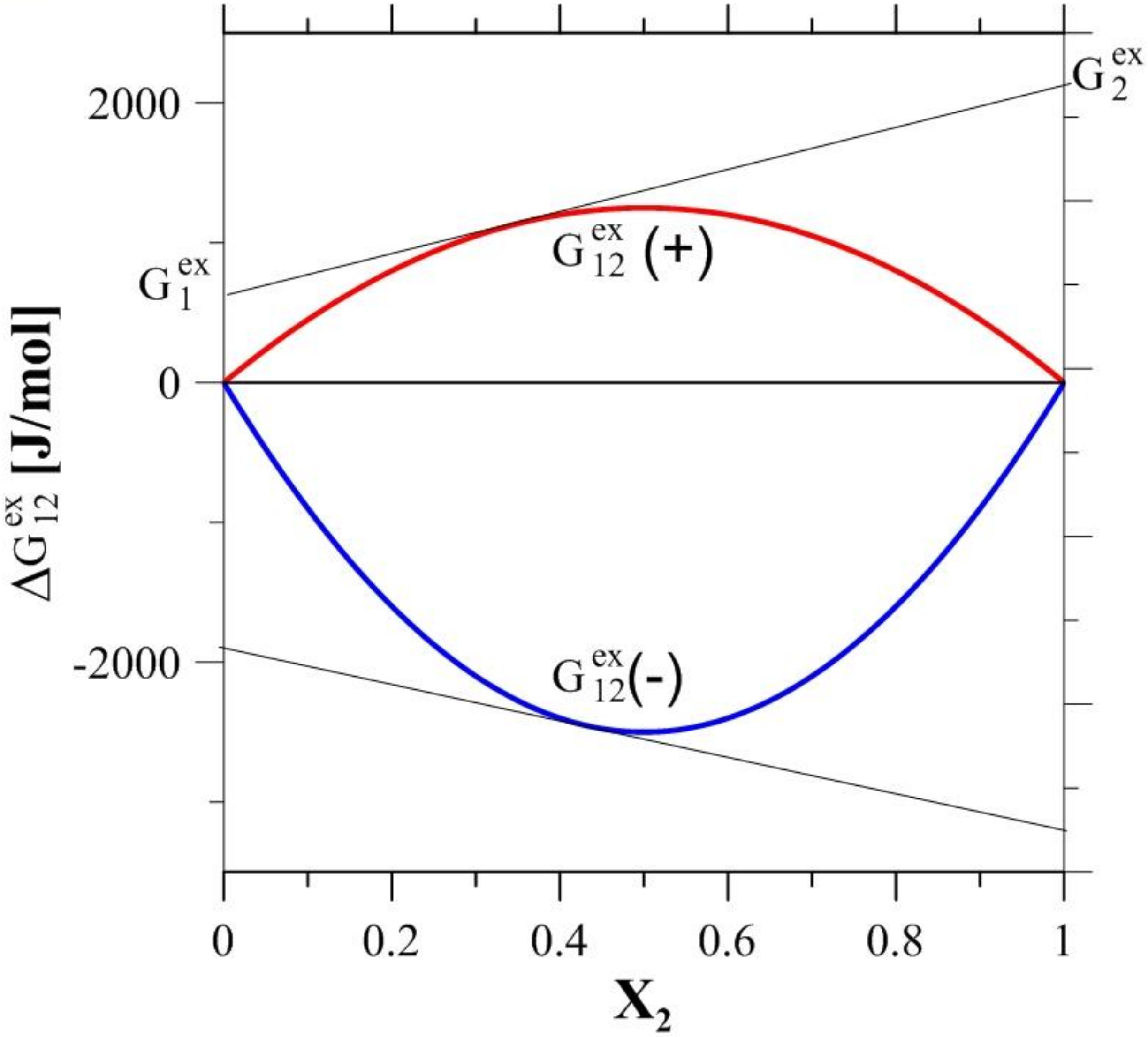
$$\Delta G_B = RT \ln a_B$$

Component activity




0
-2000
-4000
-6000
-8000
-10000
0
0.2
0.4
0.6
0.8
1
ΔG_{12} [J/mol]
X_2
ΔG_{12} (+)
ΔG_{12}^{id}
ΔG_{12}(-)


2000
1000
0
-1000
-2000
-3000
ΔG_{12}^{ex} [J/mol]
ΔG_{12}^{ex} (+)
ΔG_{12}^{ex}(-)
0
0.2
0.4
0.6
0.8
1
X_2


G_2^{ex}
2000
G_{12}^{ex} (+)
G_1^{ex}
0
ΔG_{12}^{ex} [J/mol]
-2000
G_{12}^{ex}(-)
0
0.2
0.4
0.6
0.8
1
X_2

Gibbs-Duhem equation

$$X_1 dG_1^{ex} + X_2 dG_2^{ex} = 0 \quad , \qquad \text{T=const}$$

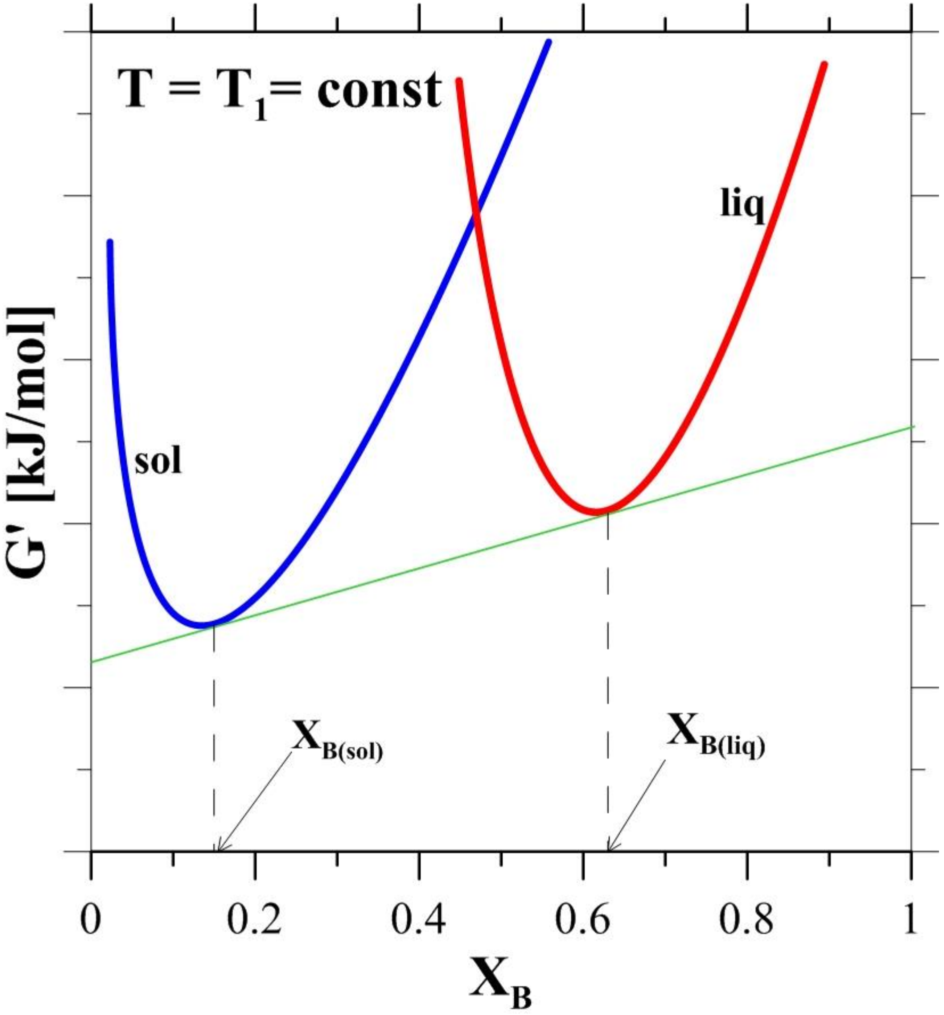
$$G_1^{ex} = G_1^{ex}(T, X_2)$$

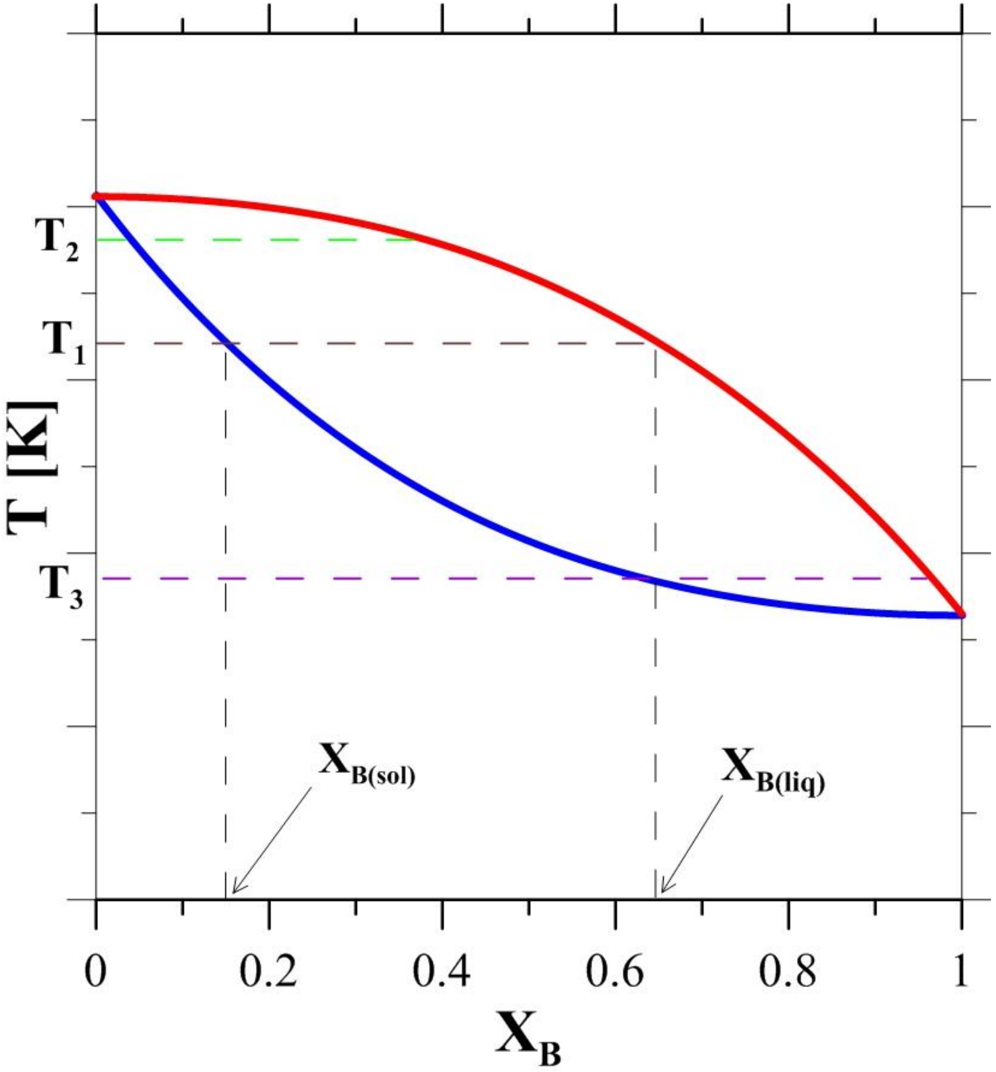
$$G_2^{ex} = G_2^{ex}(T, X_2)$$

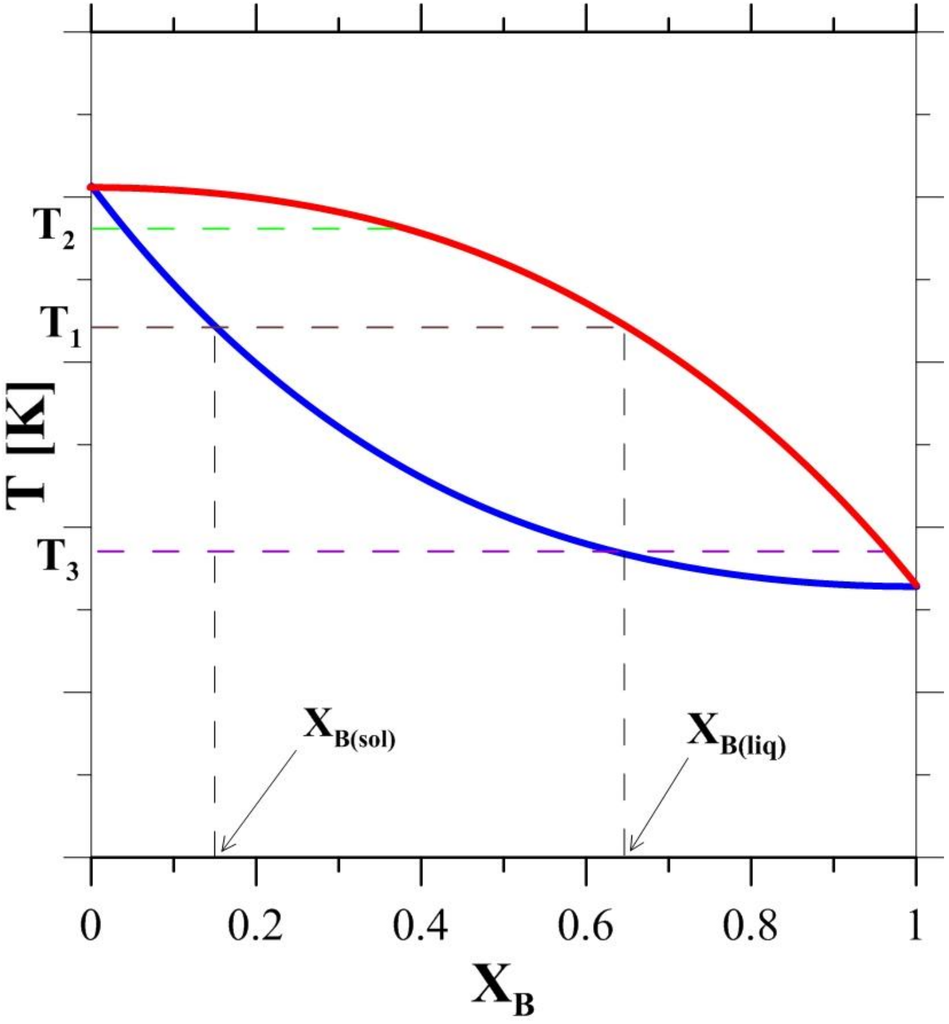
$$dG_1^{ex} = \left(\frac{dG_1^{ex}}{dX_2}\right)_{\mathrm{T}}$$

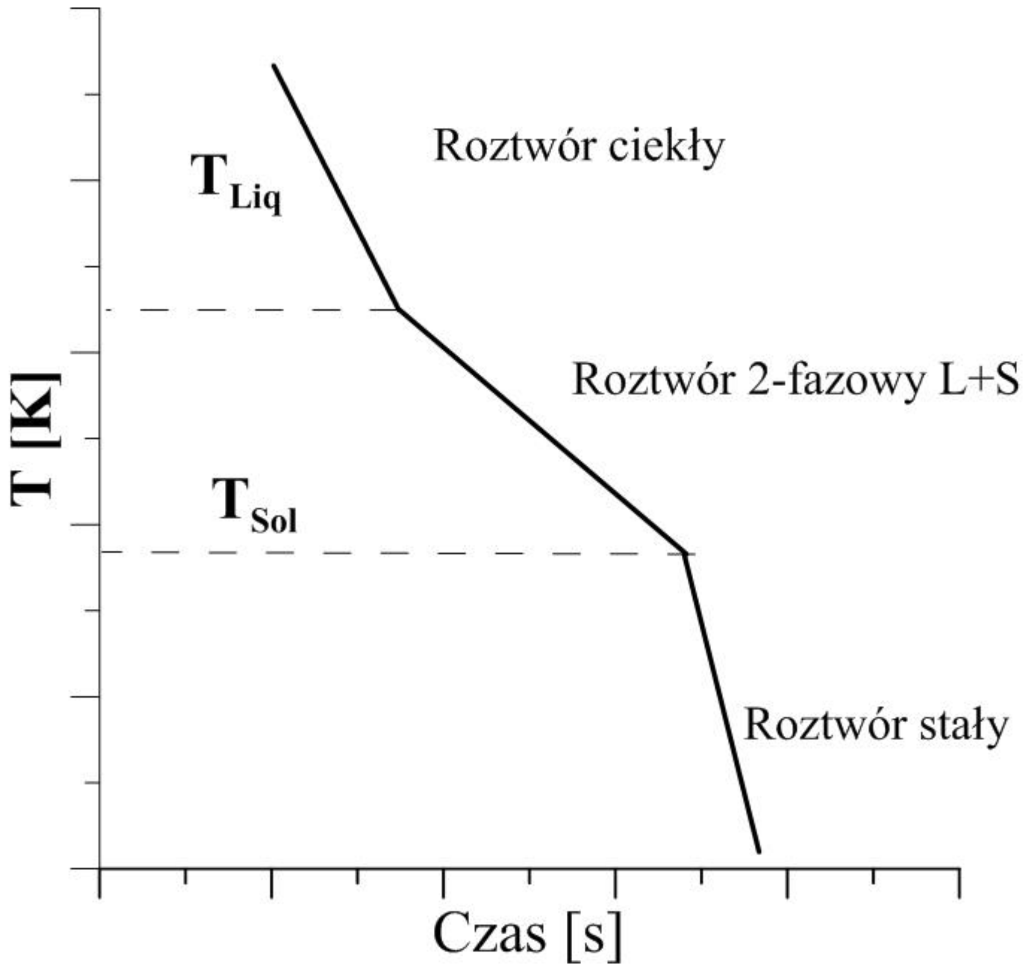
$$dG_2^{ex} = \left(\frac{dG_2^{ex}}{dX_2}\right)_{\mathrm{T}}$$

Interphase equilibria– Thermodynamic analysis




T [K]
T_2
T_1
T_3
$X_{B(sol)}$
$X_{B(liq)}$
0
0.2
0.4
0.6
0.8
1
X_B


T$_2$
T$_1$
T [K]
T$_3$
X$_{B(sol)}$
X$_{B(liq)}$
0
0.2
0.4
0.6
0.8
1
X$_B$


T$_{Liq}$
Roztwór ciekły
Roztwór 2-fazowy L+S
T [K]
T$_{Sol}$
Roztwór stały
Czas [s]

Applying the Gibbs-Duhem equation

a) Partial function of component 2 is known

$$X_1 dG_1^{ex} + X_2 dG_2^{ex} = 0\,, \qquad G_2^{ex} = \mathrm{V}(X_2), \qquad \mathrm{T{=}const}$$

$$G_1^{ex} = G_1^{ex}(X_2) \qquad G_2^{ex} = G_2^{ex}(X_2)$$

$$dG_1^{ex} = \left(\frac{dG_1^{ex}}{dX_2}\right)_{\mathrm{T}} \qquad dG_2^{ex} = \left(\frac{dG_2^{ex}}{dX_2}\right)_{\mathrm{T}}$$

$$X_1 \frac{dG_1^{ex}}{dX_2} = -X_2 \frac{dG_2^{ex}}{dX_2}$$

$$\frac{dG_1^{ex}}{dX_2} = -\frac{X_2}{1 - X_2}\frac{dG_2^{ex}}{dX_2}$$

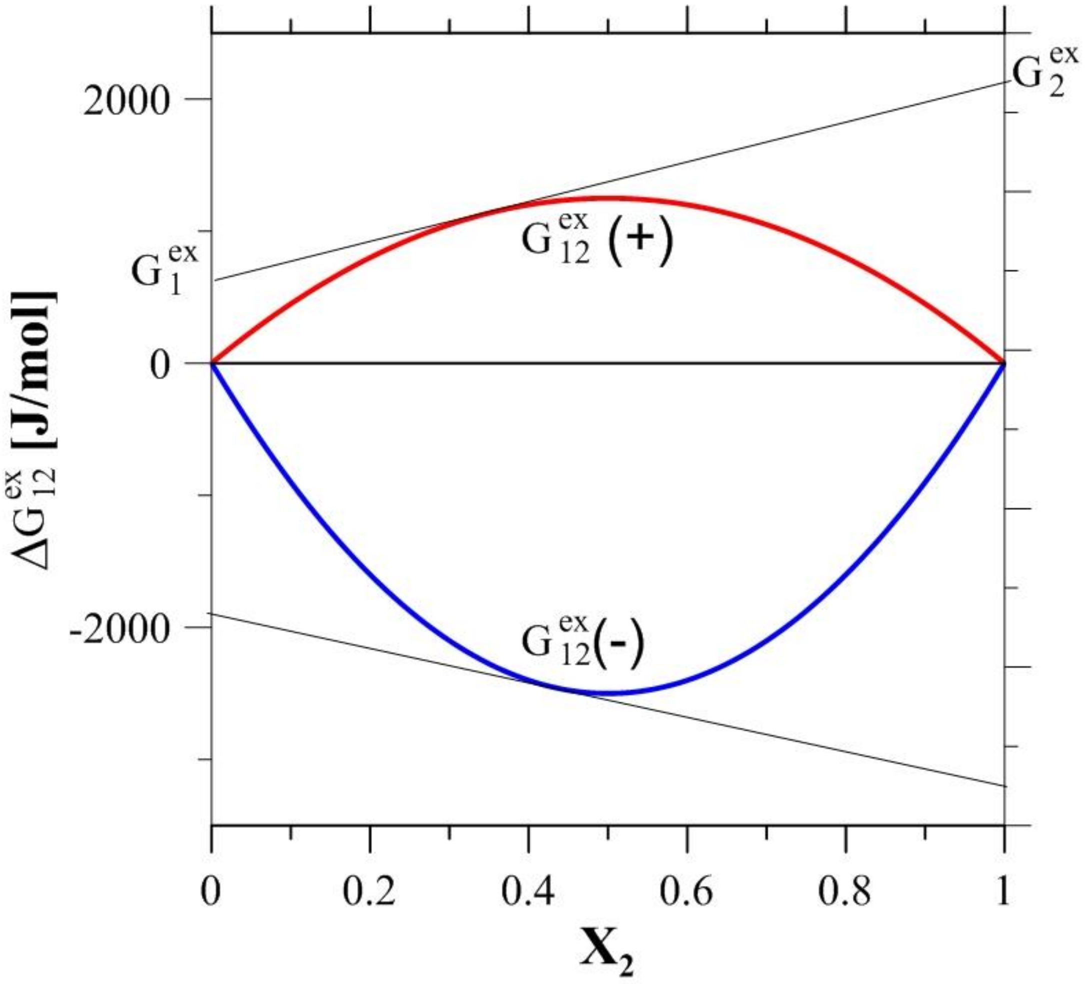
Applying the Gibbs-Duhem equation

$$\frac{dG_1^{ex}}{dX_2} = -\frac{X_2}{1-X_2}\frac{dG_2^{ex}}{dX_2}$$

$$\int \frac{dG_1^{ex}}{dX_2} dX_2 = \int -\frac{X_2}{1-X_2}\frac{dG_2^{ex}}{dX_2} dX_2$$

$$\int \frac{dG_1^{ex}}{dX_2} dX_2 = \int -\frac{X_2}{1-X_2}\frac{d\mathrm{V}(X_2)}{dX_2} dX_2$$

$$G_1^{ex} = W(X_2) + C$$



$$\boldsymbol{G_1^{ex} = W(X_2) + C}$$

To calculate C constant the G_1^{ex} value for any X_2 (X_1) value must be known.

From the figur on the left side one can notice that:

for **X_2= 0 (X_1= 1),** $\boldsymbol{G_1^{ex} = 0}$

and it gives

$$\boldsymbol{C = -W(X_2 = 0)}$$

Example:

The partial excess Gibbs energy of component A in binary liquid alloys A-B is given by following equation:

$$\boldsymbol{G_B^{ex} = 2500(1 - X_B)^2} \qquad \text{T = const.}$$

Calculate the excess Gibbs Energy the component B.

$$\boldsymbol{\frac{dG_B^{ex}}{dX_B} = 5000(1 - X_B)}$$

From the Gibbs-Duhem equation it is known that:

$$\boldsymbol{\frac{dG_A^{ex}}{dX_B} = -\frac{X_B}{1 - X_B}\frac{dG_B^{ex}}{dX_B}}$$

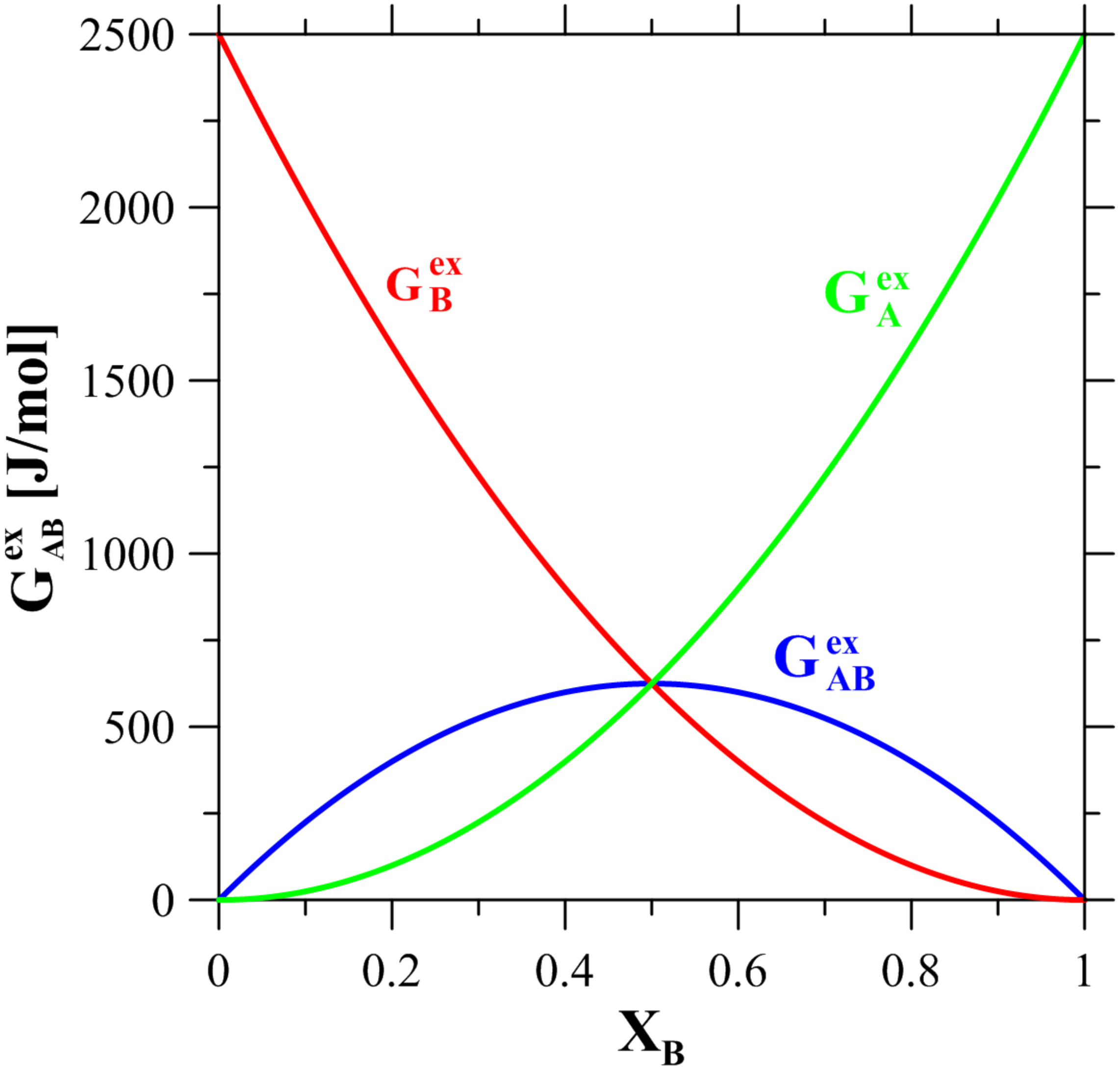
$$\int \frac{dG_A^{ex}}{dX_B}\,dX_B = 5000\int -\frac{X_B}{\cancel{1-X_B}}\,\cancel{(1-X_B)}\,dX_B$$

$$G_A^{ex} = 5000\frac{X_B^2}{2} = 2500X_B^2$$

$$G_B^{ex} = 2500(1-X_B)^2 = 2500X_A^2$$

$$G_{AB}^{ex} = X_A G_A^{ex} + X_B G_B^{ex}$$

$$G_{AB}^{ex} = 2500X_A X_B$$



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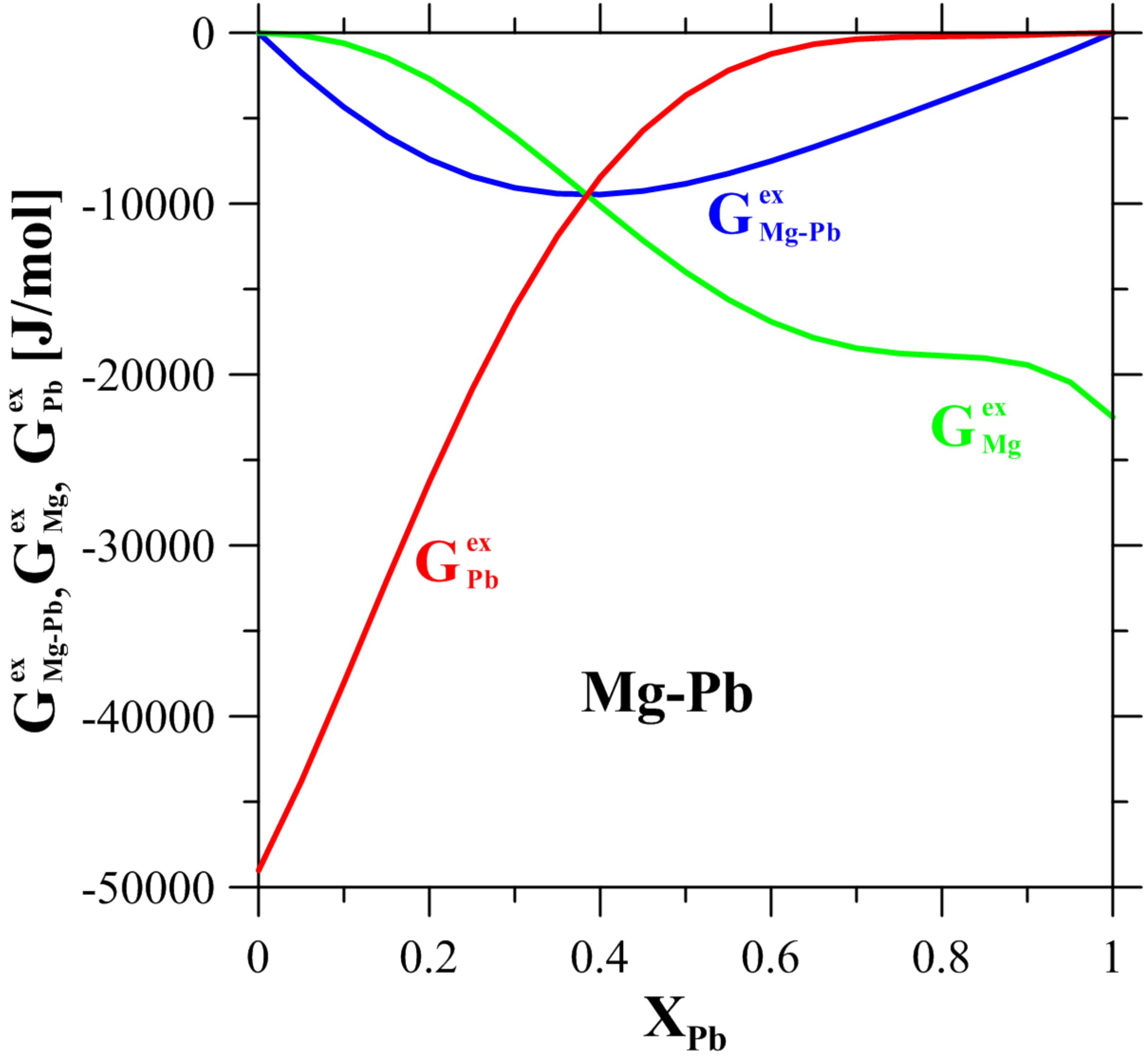
International interdisciplinary PhD Studies in Materials Science with English as the language of instruction
Project co-financed by the European Union within the European Social Funds


0
-10000
-20000
-30000
-40000
-50000
$G^{ex}_{Mg\text{-}Pb}, G^{ex}_{Mg}, G^{ex}_{Pb}$ [J/mol]
0
0.2
0.4
0.6
0.8
1
X_{Pb}
$G^{ex}_{Mg\text{-}Pb}$
G^{ex}_{Mg}
G^{ex}_{Pb}
Mg-Pb

Applying the Gibbs-Duhem equation

b) Molar Gibbs energy of solution (1-2) is known

$$G^{ex} = X_1 G_1^{ex} + X_2 G_2^{ex} = (1 - X_2) G_1^{ex} + X_2 G_2^{ex}$$

$$\frac{dG^{ex}}{dX_2} = d(G_1^{ex} + X_2 G_1^{ex}) + X_2 G_2^{ex}$$

$$\frac{dG^{ex}}{dX_2} = \frac{dG_1}{dX_2} - \left(G_1^{ex} + X_2 \frac{dG_1^{ex}}{dX_2} \right) + G_2^{ex} + X_2 \frac{dG_2^{ex}}{dX_2}$$

$$\frac{dG^{ex}}{dX_2} = \frac{dG_1}{dX_2} - G_1^{ex} - X_2 \frac{dG_1^{ex}}{dX_2} + G_2^{ex} + X_2 \frac{dG_2^{ex}}{dX_2}$$

$$\frac{dG^{ex}}{dX_2} = \frac{dG_1^{ex}}{dX_2} - G_1^{ex} - X_2\frac{dG_1^{ex}}{dX_2} + G_2^{ex} + X_2\frac{dG_2^{ex}}{dX_2}$$

$$\frac{dG^{ex}}{dX_2} = \frac{dG_1}{dX_2} - G_1^{ex} - (1 - X_1)\frac{dG_1^{ex}}{dX_2} + G_2^{ex} + X_2\frac{dG_2^{ex}}{dX_2}$$

$$\frac{dG^{ex}}{dX_2} = \frac{dG_1}{dX_2} - G_1^{ex} + G_2^{ex} - (1 - X_1)\frac{dG_1^{ex}}{dX_2} + X_2\frac{dG_2^{ex}}{dX_2}$$

$$\frac{dG^{ex}}{dX_2} = \frac{dG_1}{dX_2} + G_2^{ex} - G_1^{ex} - \frac{dG_1^{ex}}{dX_2} + X_1\frac{dG_1^{ex}}{dX_2} + X_2\frac{dG_2^{ex}}{dX_2}$$

$$\frac{dG^{ex}}{dX_2} = G_2^{ex} - G_1^{ex} / * X_2$$

$$X_2 \frac{dG^{ex}}{dX_2} = X_2 G_2^{ex} - X_2 G_1^{ex}$$

$$X_2 \frac{dG^{ex}}{dX_2} = X_2 G_2^{ex} - (1 - X_1) G_1^{ex}$$

$$X_2 \frac{dG^{ex}}{dX_2} = X_2 G_2^{ex} - G_1^{ex} + X_1 G_1^{ex}$$

$$G_1^{ex} = G^{ex} - X_2 \frac{dG^{ex}}{dX_2}$$

$$G_2^{ex} = G^{ex} + X_1 \frac{dG^{ex}}{dX_1} = G^{ex} + (1 - X_1) \frac{dG^{ex}}{dX_2}$$

Measurement of the thermodynamic properties

$$G_{AB} = X_A(G_A^0 + RTlnX_A + G_A^{ex}) + X_B(G_B^0 + RTlnX_B + G_B^{ex})$$

$$G_{AB} = X_AG_A^0 + X_BG_B^0 + X_ARTlnX_A + X_BRTlnX_B + X_AG_A^{ex} + X_BG_B^{ex}$$

$$G_{AB}^{id} = [X_AG_A^0 + X_BG_B^0 + X_ARTlnX_A + X_BRTlnX_B]$$

$$G_{AB}^{ex} = X_AG_A^{ex} + X_BG_B^{ex}$$

$$G = H - TS$$

$$G_i = H_i - TS_i$$

Electromotive force measurements of activity (Au-Li)

$$\mathrm{Li_{(l)}} \parallel \mathrm{(KCl\text{-}LiCl)_{eut}} \parallel \mathrm{Au\text{-}Li_{(s,\,l)}}$$

$$\Delta G_{Li} = -nFE = RTln(X_{Li})$$

$$a_{\mathrm{Li}} = exp\left(\frac{-n \cdot F \cdot E}{R \cdot T}\right)$$

$$G_{Li}^{E} = \Delta G_{Li} - RTln(X_{Li}) = -nFE - RTln(X_{Li})$$

$$\Delta S_{Li} = -\left(\frac{d\Delta G_{Li}}{dT}\right)_p = nF\left(\frac{dE}{dT}\right)_p = nFB$$

$$\Delta H_{Li} = \Delta G_{Li} + T\Delta S_{Li} = -nF\left[E - nF\left(\frac{dE}{dT}\right)_p\right] = -nFA$$

$$S_{Li}^{E} = \Delta S_{Li} + R\ln(X_{Li})$$

where: F – Faraday constant, R – universal gas constant, T – absolute temperature [K],
E – electromotive force as a function *T*, X_{Li}- concentration of lithium in the alloy, a_{Li} – activity of Li

ΔG_{Li} – change in the partial free enthalpy of lithium, ΔS_{Li} – change in the partial entropy of lithium, ΔH_{Li} – change in the partial enthalpy of lithium, S_{Li}^{E} – partial excess entropy of lithium.

The calorimetric study of the mixing enthalpy

$$H_{DISS-X} = \left(\Delta H_{Signal} \cdot K\right) - \left(H_X^{T_R \rightarrow T_M} \cdot n_X\right)$$

$$\Delta H_{mix} = \frac{\sum H_{DISS-X}}{n_{Au} + n_{Li} + n_{Sn}}$$

where ΔH_{Signal} is the heat effect measured after each drop of metal samples (Au, Li or Sn) into the metallic bath (Au, Li, Au-Li or Au-Sn), K is the calibration constant, T_R and T_M are the drop temperature (room temperature) and the calorimeter temperature of the respective measurement in Kelvin.

$H_X^{T_R \rightarrow T_M}$ is the enthalpy change of the pure metals (Au, Li or Sn) from the room temperature (T_R) to the measurement temperature (T_M), n_{Au}, n_{Li} and n_{Sn} are the numbers of moles of gold, lithium and tin, respectively. $H_{DISS\text{-}X}$ is the enthalpy of dissolution of pure gold, lithium or tin.

Direct reaction method

$$\boldsymbol{X_A}\mathbf{A}_{(\mathbf{T_R})} + \boldsymbol{X_B}\mathbf{B}_{(\mathbf{T_R})} = \mathbf{A}_{\boldsymbol{X_A}}\mathbf{B}_{\boldsymbol{X_B}\ (\mathbf{T})} + \mathbf{Q}$$

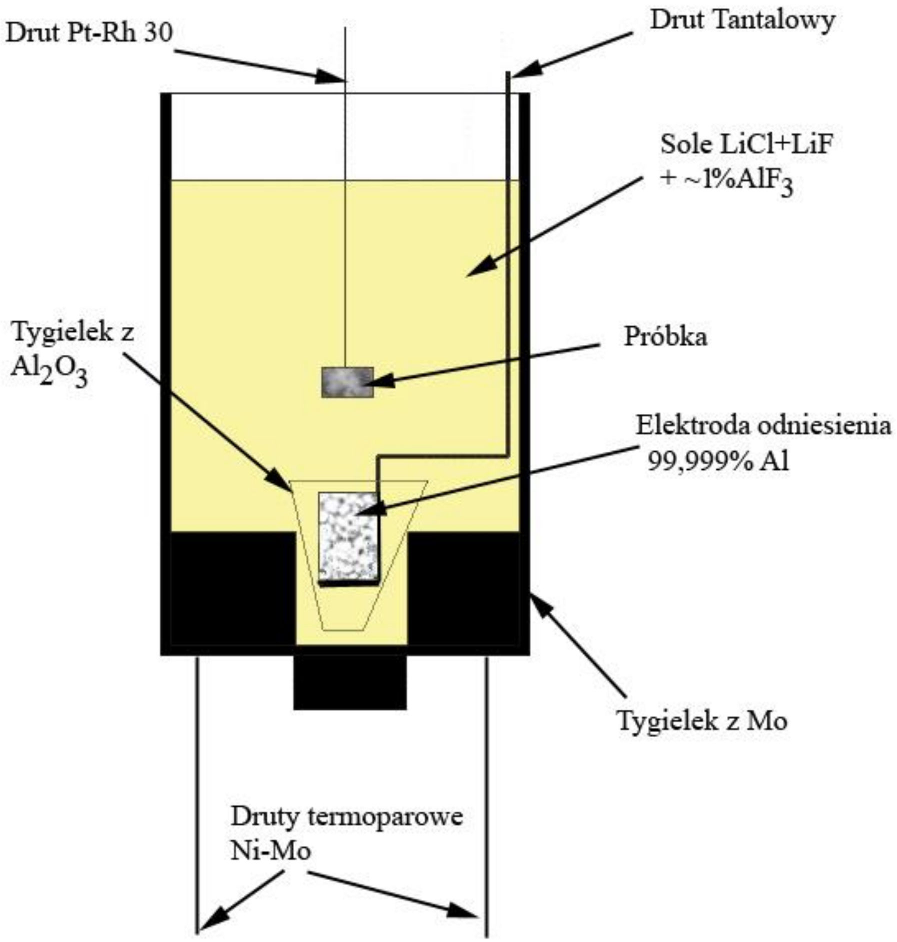
where: T_R is the temperature of the components before the introduction into the reaction zone (crucible), T is the temperature at which the reaction goes on (crucible), and Q is the heat effect measured by the calorimeter. In such a case, the formation enthalpy $\Delta_f H$ at temperature T is calculated according to the following equation:

$$\mathbf{\Delta_f H = Q - (X_A \Delta H_A + X_B \Delta H_B)}$$

Where: X_A and X_B are the mole fractions of the reacted components (A, B) and ΔH_A and ΔH_B are the enthalpy changes of the solid metals (Au or Li) between temperatures T_R and T.

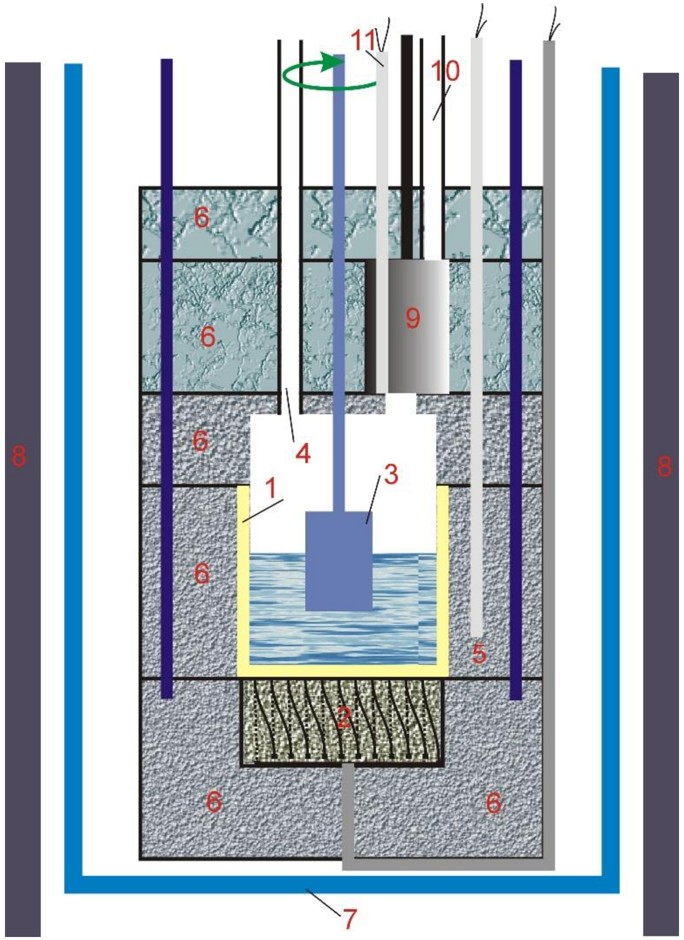
Task to do:

Korzystając z definicji funkcji mola roztworu funkcji namiarowej oraz równania Gibbsa –Duhema wyprowadzić równanie dla nadmiarowej energii swobodnej Gibbsa składnika 2 – pisemnie.



$Al\ (s)\ \|\ (LiCl - LiF)_{eut} + AlF_3\ \|\ Al\text{-}Ni\text{-}Ti\ (s)$

Entalpię tworzenia faz w układach trójskładnikowych określa się z wykorzystaniem zależności:



Schemat bloku kalorymetru typu rozpuszczania

1. **Tygiel alundowy.**
2. **Stos termoparowy NiAl-NiCr.**
3. **Mieszadełko.**
4. **Doprowadzenie próbek do kąpieli z temperatury pokojowej.**
5. **Termopara mierząca temperaturę w tyglu.**
6. **Korpus bloku kalorymetrycznego.**
7. **Pojemnik ze stali żaroodpornej.**
8. **Piec kalorymetru.**
9. **Pojemnik pośredni.**
10. **Doprowadzenie próbek do pojemnika pośredniego.**
11. **Termopara mierząca temperaturę w pojemniku pośrednim.**

$$\Delta_f H = X_A \Delta H_A^{ef} + X_B \Delta H_B^{ef} + X_C \Delta H_C^{ef} - \Delta H^{ef}_{A_{X_A} B_{X_B} C_{X_C}}$$

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