PMT 3205

Físico-Química para Metalurgia e Materiais I

3. *[Bodsworth & Appleton, problem 3.5, p.55]* O titânio apresenta as formas alotrópicas α e β. A temperatura de transformação do Ti hexagonal compacto (α) em Ti cúbico de corpo centrado (β) é 1155 K. Calcular a temperatura do **ponto de fusão hipotético** para o **Ti (α)**.

DADOS:

$c_{p(\alpha)} = 5{,}28 + 2{,}4 \times 10^{-3}.T$ (cal/mol.K)

$T_{\alpha\rightarrow\beta} = 1155$ K

$\Delta H_{\alpha\rightarrow\beta} = +830$ cal/mol

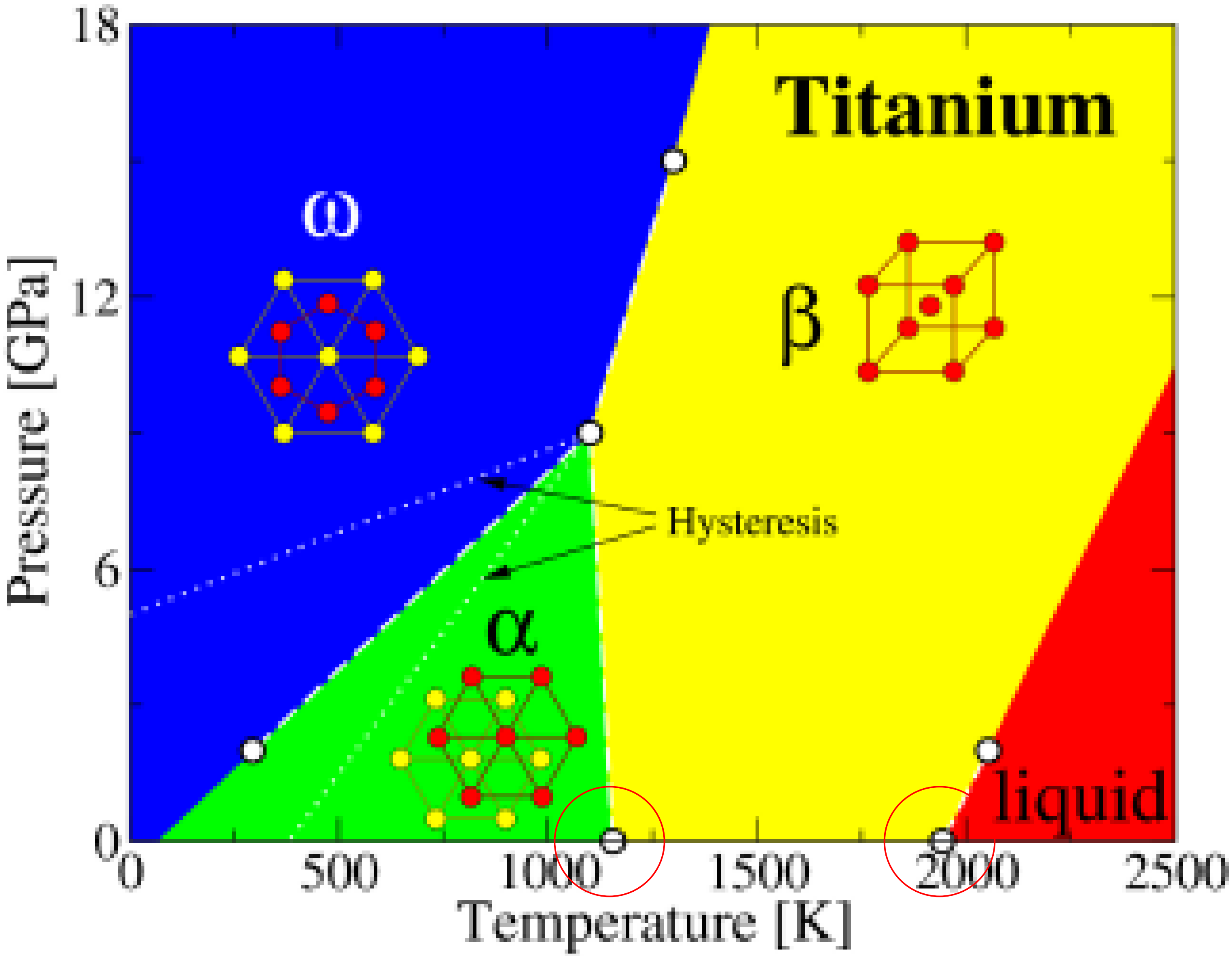
$c_{p(\beta)} = 6{,}91$ cal/mol.K

$T_{\beta\rightarrow l} = 1933$ K

$\Delta H_{\beta\rightarrow l} = +4500$ cal/mol

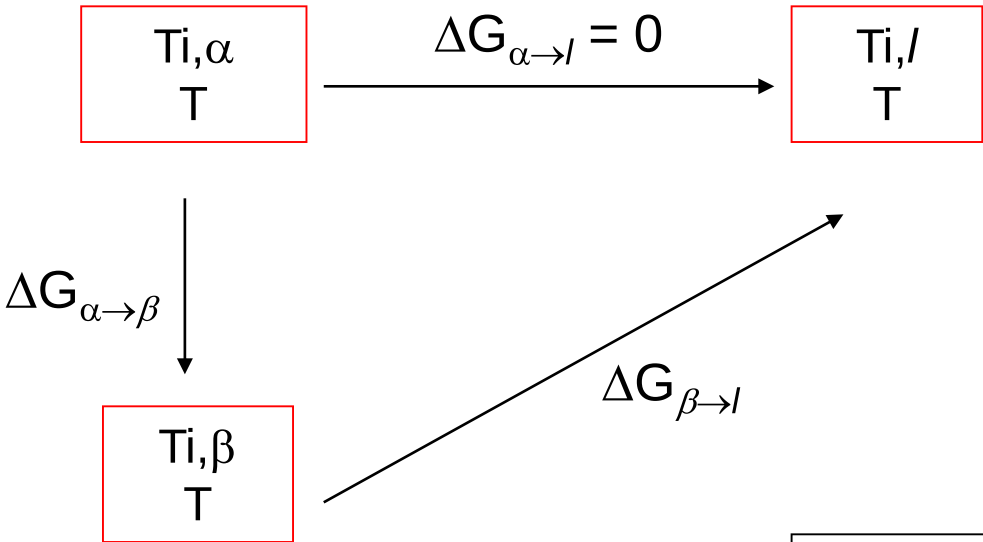
$c_{p(l)} = 8{,}00$ cal/mol.K

$S_{298,Ti} = 7{,}3$ cal/mol.K



Titanium
ω
β
α
liquid
Hysteresis
Pressure [GPa]
Temperature [K]
18
12
6
0
0
500
1000
1500
2000
2500

Solução usando Termodinâmica do *loop*



$$\Delta G_{\alpha \to l} = 0$$

$$\Delta G_{\alpha \to \beta} + \Delta G_{\beta \to l} = 0$$

$$\Delta G_{\alpha \to \beta} = \Delta G_{l \to \beta}$$

Equação de Gibbs-Helmholtz

METMAT

$$d\left(\frac{\Delta G_{\alpha\to\beta}}{T}\right)_P = -\frac{\Delta H_{\alpha\to\beta}}{T^2}dT$$

$$\int d\left(\frac{\Delta G_{\alpha\to\beta}}{T}\right)_P = -\int \frac{\Delta H_{\alpha\to\beta}}{T^2}dT$$

$$\Delta G_{\alpha\to\beta} = -T\int \frac{\Delta H_{\alpha\to\beta}}{T^2}dT$$

$$\Delta G_{\alpha\to\beta} = -T\int \frac{\Delta H_{\alpha\to\beta}}{T^2}\,dT$$

$$\Delta G_{\alpha\to\beta} = -T\int \frac{(\Delta H_{T_1,\alpha\to\beta} + \int_{T_1}^{T} \Delta c_p\,dT)}{T^2}\,dT$$

$$\Delta G_{\alpha\to\beta} = -T\int \frac{(830 + \int_{1155}^{T} (6{,}91 - 5{,}28 - 2{,}4x10^{-3}T)dT}{T^2}\,dT$$

$$\Delta G_{\alpha\to\beta} = 0 \;\; ; \quad T_{\alpha\to\beta} = 1155K \;\; ; \quad cte = -9{,}634$$

$$\Delta G_{\alpha\to\beta} = -1{,}63T\,\mathit{ln}T + 1{,}2x10^{-3}T^2 + 9{,}63T + 548{,}18 \text{ (cal/mol)}$$

METMAT

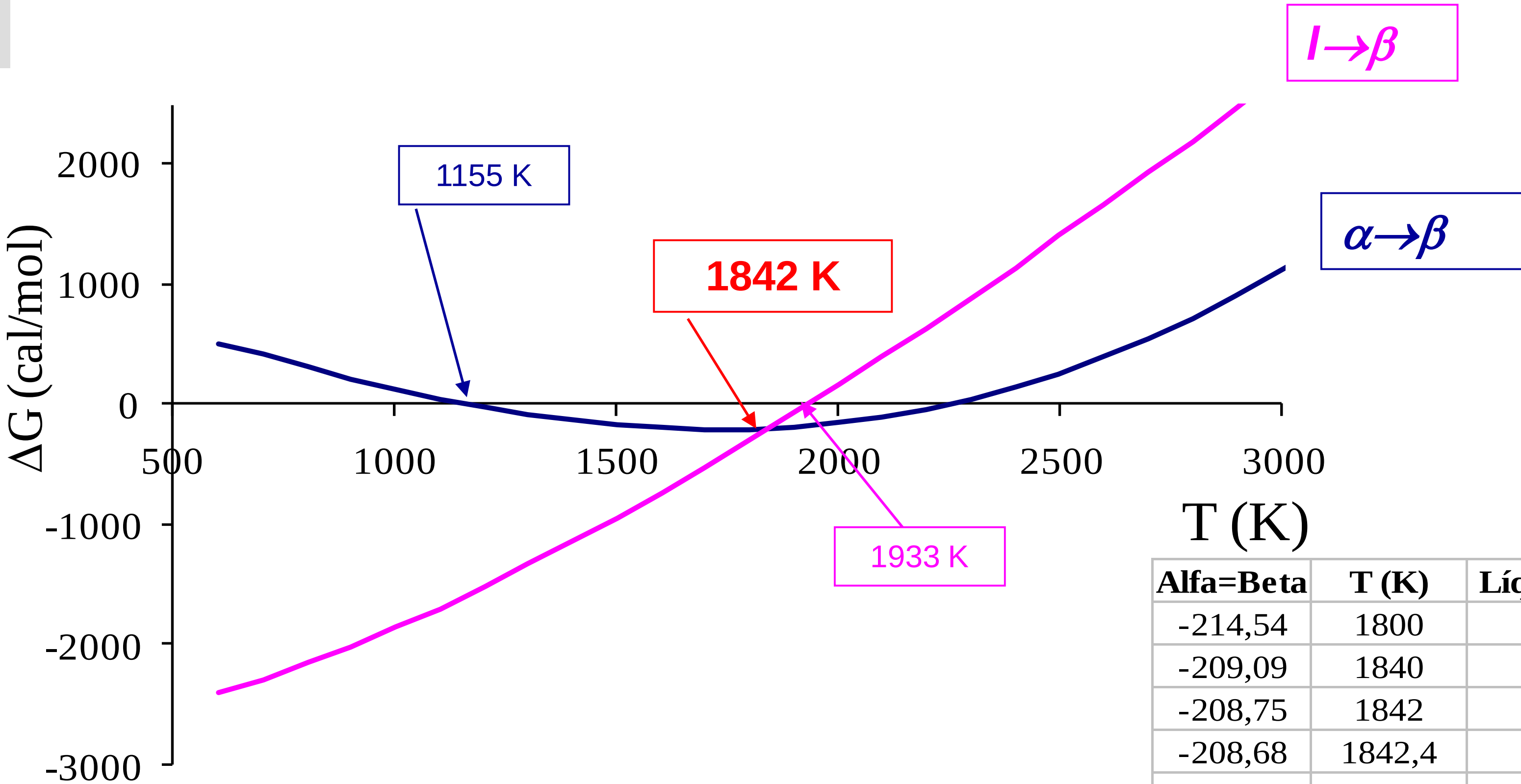
$$\Delta G_{l\rightarrow\beta} = -T\int \frac{\Delta H_{l\rightarrow\beta}}{T^2}\, dT$$

$$\Delta G_{l\rightarrow\beta} = -T\int \frac{(\Delta H_{T_1, l\rightarrow\beta} + \int_{T_1}^{T} \Delta c_p\, dT)}{T^2}\, dT$$

$$\Delta G_{l\rightarrow\beta} = -T\int \frac{(-4500 + \int_{1933}^{T} (6{,}91 - 8{,}0)\, dT}{T^2}\, dT$$

$$\Delta G_{l\rightarrow\beta} = 0 \;;\quad T_{l\rightarrow\beta} = 1933\text{K} \;;\quad cte = 7{,}01$$

$$\Delta G_{l\rightarrow\beta} = 1{,}09T\,lnT - 7{,}01T - 2393 \text{ (cal/mol)}$$



Alfa=Beta	T (K)	Líquido=Beta	Diferença
-214,54	1800	-304,78	90,24
-209,09	1840	-214,29	5,20
-208,75	1842	-209,74	0,99
-208,68	1842,4	-208,83	0,15
-208,68	1842,41	-208,81	0,12
-208,68	1842,42	-208,79	0,10
-208,68	1842,43	-208,76	0,08
-208,68	1842,44	-208,74	0,06
-208,68	1842,45	-208,72	0,04
-208,67	1842,46	-208,69	0,02
-208,67	**1842,47**	**-208,67**	**0,00**
-208,67	1842,48	-208,65	-0,02
-208,67	1842,49	-208,63	-0,04
-208,67	1842,5	-208,60	-0,06
-208,67	1842,51	-208,58	-0,09
-208,66	1842,52	-208,56	-0,11
-208,66	1842,53	-208,53	-0,13

Resposta: (ΔG em **cal/mol**)

$\Delta G_{\alpha\rightarrow\beta} = -1,63T\,lnT + 1,2x10^{-3}T^2 + 9,63T + 548,18$

$\Delta G_{l\rightarrow\beta} = 1,09T\,lnT - 7,01T - 2393,03$

T = 1842K

Solução usando a definição de G

$$\Delta G_{\alpha\to l} = 0$$
$$G_l - G_\alpha = 0$$
$$G_\alpha = G_l$$

$$G_\alpha = G_l$$
$$G_\alpha = H_\alpha - TS_\alpha$$
$$G_l = H_l - TS_l$$

$$G_\alpha = \left(H_{298} + \int_{298}^{T} c_{p,\alpha} dT \right) - T\left(S_{298} + \int_{298}^{T} \frac{c_{p,\alpha}}{T} dT \right)$$

$$G_l = \left(H_{298} + \int_{298}^{1155} c_{p,\alpha} dT + \Delta H_{\alpha\to\beta} + \int_{1155}^{1933} c_{p,\beta} dT + \Delta H_{\beta\to l} + \int_{1933}^{T} c_{p,l} dT \right) -$$
$$- T\left(S_{298} + \int_{298}^{1155} \frac{c_{p,\alpha}}{T} dT + \frac{\Delta H_{\alpha\to\beta}}{1155} + \int_{1155}^{1933} \frac{c_{p,\beta}}{T} dT + \frac{\Delta H_{\beta\to l}}{1933} + \int_{1933}^{T} \frac{c_{p,l}}{T} dT \right)$$

$$G_\alpha = 28{,}78T - 1{,}20x10^{-3}T^2 - 5{,}28T\,\mathit{ln}\,T - 1680$$

$$G_l = 45{,}42T - 8{,}0T\,\mathit{ln}\,T + 1261{,}21$$

$$G_\beta = \left(H_{298} + \int_{298}^{1155} c_{p,\alpha}\,dT + \Delta H_{\alpha\to\beta} + \int_{1155}^{T} c_{p,\beta}\,dT \right) - \\ - T\left(S_{298} + \int_{298}^{1155} \frac{c_{p,\alpha}}{T}\,dT + \frac{\Delta H_{\alpha\to\beta}}{1155} + \int_{1155}^{T} \frac{c_{p,\beta}}{T}\,dT \right)$$

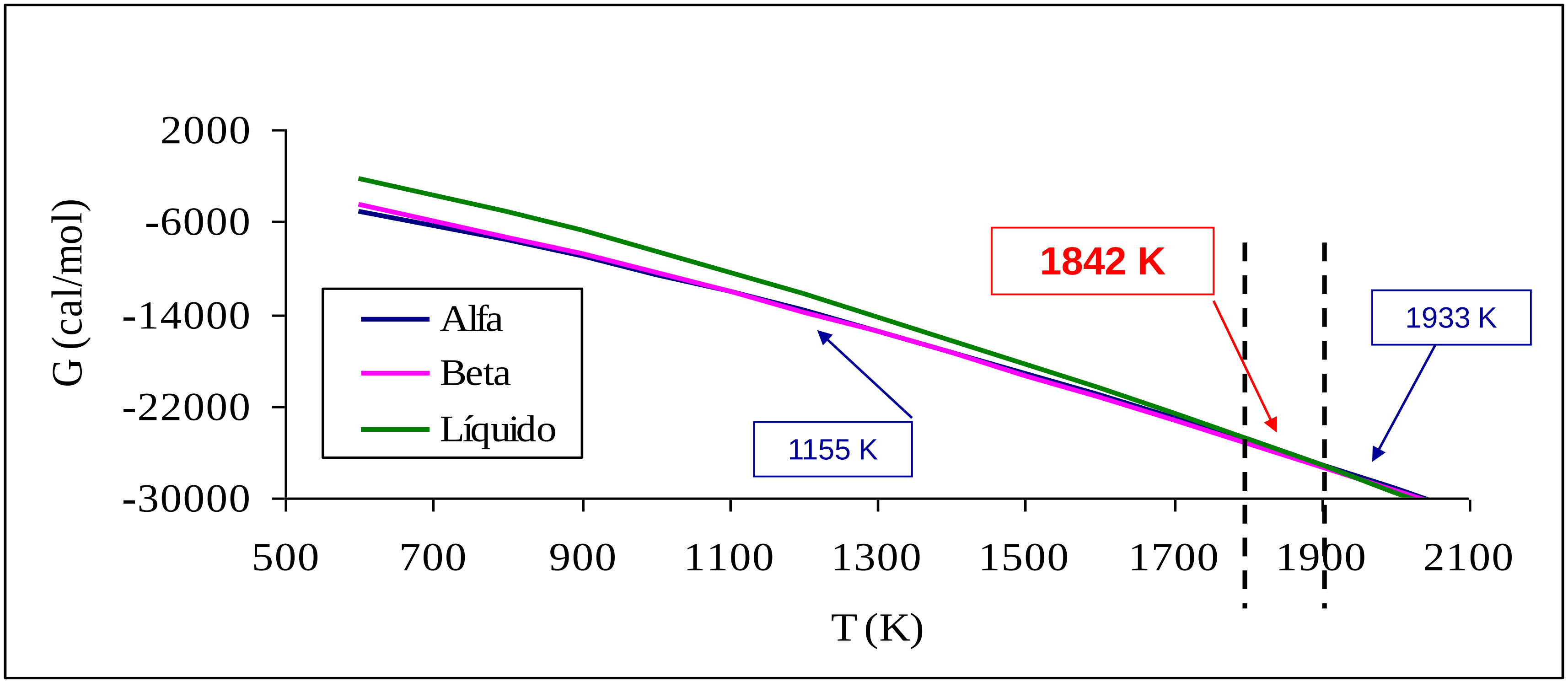
$$G_\alpha = 28{,}78T - 1{,}20x10^{-3}T^2 - 5{,}28T\,lnT - 1680$$

$$G_l = 45{,}42T - 8{,}0T\,lnT + 1261{,}21$$

$$G_\beta = 38{,}41T - 6{,}91T\,lnT - 1131{,}82$$

Equilíbrios Estáveis e Metaestável

	(kcal/mol)	(kcal/mol)	(kcal/mol)
T(K)	**Gα**	**Gβ**	**Gl**
1155	**-13,0**	**-13,0**	-11,4
1842,47	**-25,9**	-26,1	**-25,9**
1933	-27,8	**-28,0**	**-28,0**



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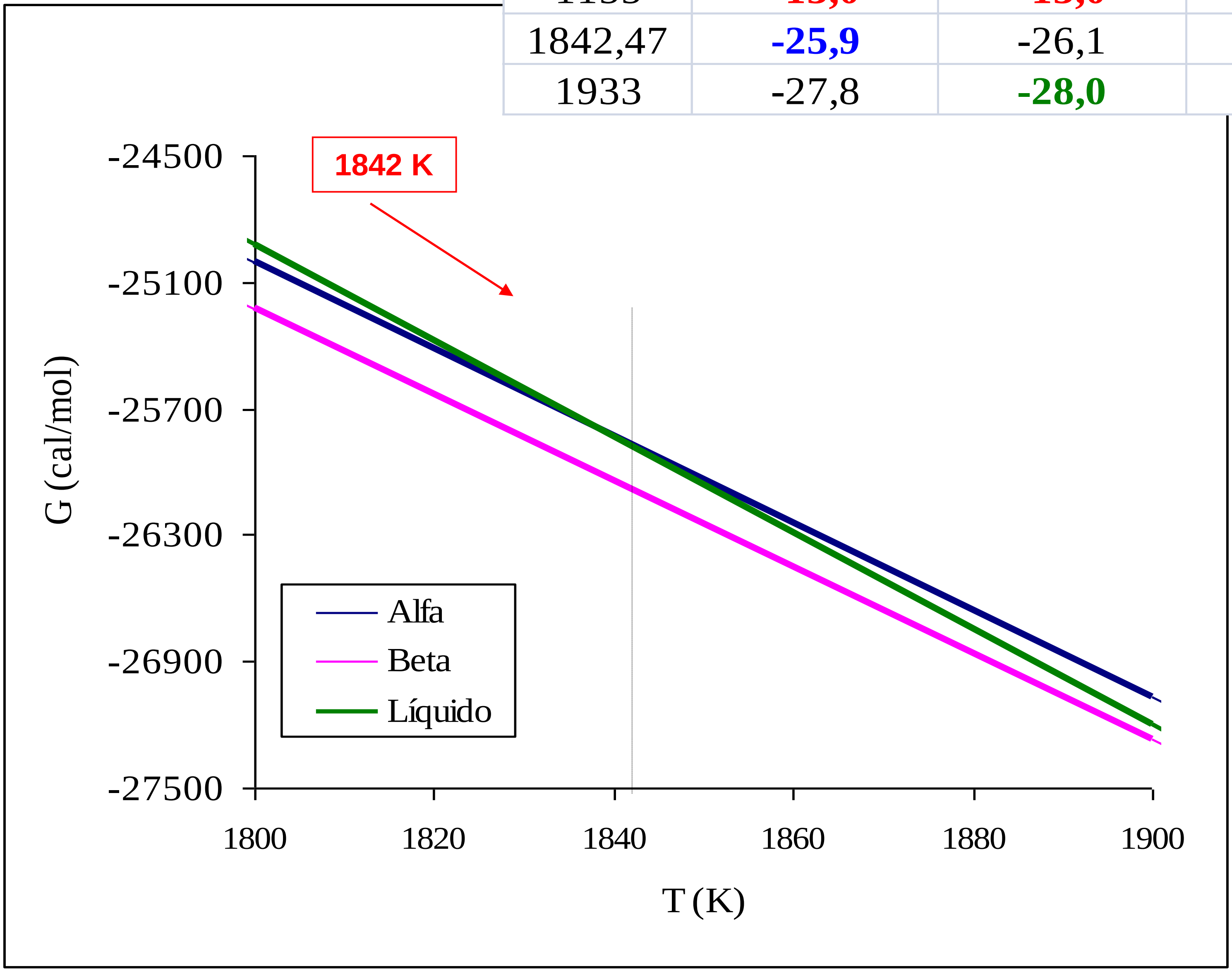
Intervalo do equilíbrio Metaestável

	(kcal/mol)	(kcal/mol)	(kcal/mol)
T(K)	G_α	G_β	G_l
1155	-13,0	-13,0	-11,4
1842,47	-25,9	-26,1	-25,9
1933	-27,8	-28,0	-28,0



Intervalo do equilíbrio Metaestável:

	(kcal/mol)	(kcal/mol)	(kcal/mol)
T(K)	**Gα**	**Gβ**	**Gl**
1155	**-13,0**	**-13,0**	-11,4
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