METMAT

PMT 3205

Físico-Química para Metalurgia e Materiais I

Equação de Gibbs-Helmholtz

- A integração da Equação de Gibbs-Helmholtz determina a equação da energia livre de Gibbs (G) em função da temperatura (T) para o sistema mantido a **pressão (P) constante**.

$$d\left(\frac{G}{T}\right)_P = -\frac{HdT}{T^2}$$

ou

$$d\left(\frac{\Delta G}{T}\right)_P = -\frac{\Delta HdT}{T^2}$$

Equação de Gibbs-Helmholtz

G = H - TS

Mas, numa transformação :

dG = VdP - SdT

que para processos a **P constante** fornece:

$$-S = \left(\frac{\partial G}{\partial T}\right)_P \qquad G = H + T\left(\frac{\partial G}{\partial T}\right)_P$$

Re-arranjando:

$$-H = T\left(\frac{\partial G}{\partial T}\right)_P - G$$

e multiplicando por: $\dfrac{dT}{T^2}$

$$-\frac{HdT}{T^2} = \frac{TdG - GdT}{T^2}$$

Lembrando:

$$d\left(\frac{X}{Y}\right) = \frac{YdX - XdY}{Y^2}$$

$$-\frac{HdT}{T^2} = \frac{TdG - GdT}{T^2} = d\left(\frac{G}{T}\right)$$

$$d\left(\frac{G}{T}\right)_P = -\frac{H}{T^2}dT$$

$$d\left(\frac{\Delta G}{T}\right)_P = -\frac{\Delta H}{T^2}dT$$

SEMELHANÇA FORMAL

Exercícios

1. Calcular a variação de entropia do universo e a **variação da energia livre de Gibbs** quando um átomo-grama de Cu super-resfriado a 1340 K solidifica irreversivelmente nesta temperatura a 1 atm de pressão.

Dados:

$c_{p(s)} = 5,41 + 1,5\times10^{-3}.T$ (cal/atg.K)

$c_{p(l)} = 7,5$ cal/atg.K

$\Delta H_{s\rightarrow l} = 3100$ cal/atg

$T_{s\rightarrow l} = 1356$ K

[Resposta: $\Delta S_{Cu} = -2,29$ cal/K; $\Delta S_{ME} = +2,31$ cal/K; $\Delta S_{UNIV} = +0,02$ cal/K; $\Delta G_{Cu} = -37,0$ cal/mol]

$\Delta S_{sistema} = ?$

Cu(*l*): 1340K → Cu(*s*): 1340K

↓ ↑

Cu(*l*): 1356K → Cu(*s*): 1356K

$$\Delta S_{Cu} = \int_{1340}^{1356} \frac{C_{p,l}}{T} dT + \frac{(-3100)}{1356} + \int_{1356}^{1340} \frac{C_{p,s}}{T} dT$$

$$\Delta S_{Cu} = 0{,}089 - 2{,}286 - 0{,}088$$

$$\Delta S_{Cu} = -2{,}285 \text{cal} / K$$

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$Cu(l)$: 1340K → $Cu(s)$: 1340K

$\Delta S_{meio} = ?$

$$\Delta S_{meio} = \frac{\Delta H_{meio}}{T_{meio}} = \frac{-\Delta H_{Sistema}}{T_{meio}}$$

$$\Delta H_{Sistema} = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta c_p dT$$

$$\Delta H_{Cu} = \Delta H_{1356} + \int_{1356}^{1340} (c_{p,s} - c_{p,l})dT$$

$$\Delta H_{Cu} = -3100 + \int_{1356}^{1340} (5{,}41 + 1{,}5x10^{-3}T - 7{,}5)dT$$

$$\Delta H_{Cu} = -3098{,}91 \text{ cal/mol}$$

$$\Delta S_{meio} = \frac{\Delta H_{meio}}{T_{meio}} = \frac{-\Delta H_{Sistema}}{T_{meio}}$$

$$\Delta S_{meio} = \frac{-(-3098{,}91)}{1340} = +2{,}313 \text{ cal/K}$$

$$\Delta S_{UNIV} = \Delta S_{Sistema} + \Delta S_{meio}$$

$$\Delta S_{UNIV} = -2{,}285 + 2{,}313$$

$$\mathbf{\Delta S_{UNIV} = +0{,}028 \text{ cal/K}}$$

Cu*(l)*: 1340K → Cu*(s)*: 1340K

$$\Delta G_{Cu} = ?$$

Soluções para **ΔG**:

- ✓ **$\Delta G = \Delta H - T\Delta S$**
- ✓ **Usando *loop* e $dG = VdP - SdT$**
- ✓ **Gibbs-Helmholtz para ΔG**

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Usando:

✓ $\Delta G = \Delta H - T\Delta S$

$$\Delta H_{Cu} = -3098{,}91 \ \text{cal/mol}$$
$$\Delta S_{Cu} = -2{,}285 \ \text{cal/K.mol}$$

$\Delta G_{Cu} = ?$

$$\Delta G = G_{final} - G_{inicial}$$
$$\Delta G = (H_f - TS_f) - (H_i - TS_i)$$
$$\Delta G = (H_f - H_i) - T(S_f - S_i)$$
$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G_{Cu} = \Delta H_{Cu} - T\Delta S_{Cu}$$
$$\Delta G_{Cu} = -3098{,}91 - 1340x(-2{,}285)$$
$$\mathbf{\Delta G_{Cu} = -37{,}01 cal/mol}$$

Com mais casas decimais, o valor se torna mais próximo dos outros métodos... (ver adiante)

$$\Delta G_{Cu} = \Delta H_{Cu} - T\Delta S_{Cu}$$

$$\Delta G_{Cu} = -3098{,}9120 - 1340x(-2{,}2853)$$

$$\mathbf{\Delta G_{Cu} = -36{,}61 cal/mol}$$

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✓ **Usando *loop* e dG = VdP – SdT**

$$\Delta G = \int_{1340}^{1356} dG_l + 0 + \int_{1356}^{1340} dG_s$$

$$\Delta G = \int_{1340}^{1356} (VdP - SdT)_l + \int_{1356}^{1340} (VdP - SdT)_s$$

$$\Delta G = \int_{1340}^{1356} (-SdT)_l + \int_{1340}^{1356} (SdT)_s$$

Termodinâmica do *loop*:

$\Delta G_{sistema}$ = ?

Cu(*l*): 1340K → Cu(*s*): 1340K

↓ ↑

Cu(*l*): 1356K → Cu(*s*): 1356K

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✓ **Usando *loop* e dG = VdP – SdT**

$$\Delta G = \int_{1340}^{1356} dG_l + 0 + \int_{1356}^{1340} dG_s$$

$$\Delta G = \int_{1340}^{1356} (VdP - SdT)_l + \int_{1356}^{1340} (VdP - SdT)_s$$

$$\boxed{\Delta G = \int_{1340}^{1356} (-SdT)_l + \int_{1340}^{1356} (SdT)_s}$$

$$\Delta G = \int_{1340}^{1356} (S_s - S_l)dT = \int_{1340}^{1356} (\Delta S_{l\to s})dT = \int_{1340}^{1356} [(\Delta S_{l\to s,1356} + \int_{1356}^{T} \frac{\Delta c_p}{T} dT)]dT$$

$$\Delta G = \int_{1340}^{1356} [\frac{-3100}{1356} + \int_{1356}^{T} (\frac{5{,}41 + 1{,}5x10^{-3}T - 7{,}5}{T})dT]dT$$

$$\Delta G = \int_{1340}^{1356} [-2{,}2861 + \int_{1356}^{T} (\frac{-2{,}09}{T} + 0{,}0015)dT]dT$$

$$\Delta G = \int_{1340}^{1356} [-2{,}2861 - 2{,}09(\ln T - \ln 1356) + 0{,}0015(T - 1356)]dT$$

$$\Delta G = \int_{1340}^{1356} [-2{,}2861 + 15{,}07 - 2{,}03 - 2{,}09 \ln T + 0{,}0015T]dT = \int_{1340}^{1356} [10{,}75 - 2{,}09 \ln T + 0{,}0015T]dT$$

$$\Delta G = 10{,}75(16) - 2{,}09[(1356 \ln 1356 - 1356) - (1340 \ln 1340 - 1340)] + \frac{0{,}0015}{2}(1356^2 - 1340^2)$$

$$\Delta G = 172{,}00 - 2{,}09[8423{,}87 - 8308{,}57] + 32{,}35 = 172{,}00 - 240{,}98 + 32{,}35$$

$$\Delta G = -36{,}63 \text{ cal/mol}$$

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Usando:

✓ **Gibbs-Helmholtz para ΔG, com $\Delta c_p = 0$**

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

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

$$\Delta G_{l\to s} = -T\int \frac{\Delta H_{l\to s,1356} + \int_{1356}^{1340}\Delta c_p dT}{T^2}dT$$

$$\Delta c_p = 0 \Rightarrow$$

$$\Delta G_{l\to s} = -T\int \frac{\Delta H_{l\to s,1356}}{T^2}dT = -T\int \frac{-3100}{T^2}dT$$

$$\Delta G_{l\to s} = 3100T\left(-\frac{1}{T} + cte\right)$$

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Usando:

✓ **Gibbs-Helmholtz para ΔG, com $\Delta c_p = 0$**

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

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

$$\Delta G_{l\to s} = -T\int \frac{\Delta H_{l\to s,1356} + \int_{1356}^{1340}\Delta c_P dT}{T^2}dT$$

$$\Delta c_P = 0 \Rightarrow$$

$$\Delta G_{l\to s} = -T\int \frac{\Delta H_{l\to s,1356}}{T^2}dT = -T\int \frac{-3100}{T^2}dT$$

$$\Delta G_{l\to s} = 3100T\left(-\frac{1}{T} + cte\right)$$

$$0 = 3100\text{x}1356\left(-\frac{1}{1356} + \text{cte}\right)$$

$$\text{cte} = 7{,}37\text{x}10^{-4}$$

$$\Delta G_{l\to s} = 3100T\left(-\frac{1}{T} + 7{,}37\text{x}10^{-4}\right)$$

$$\Delta G_{l\to s} = -3100 + 2{,}2861T$$

$$\Delta G_{l\to s,1340} = -36{,}63 \text{ cal/mol}$$

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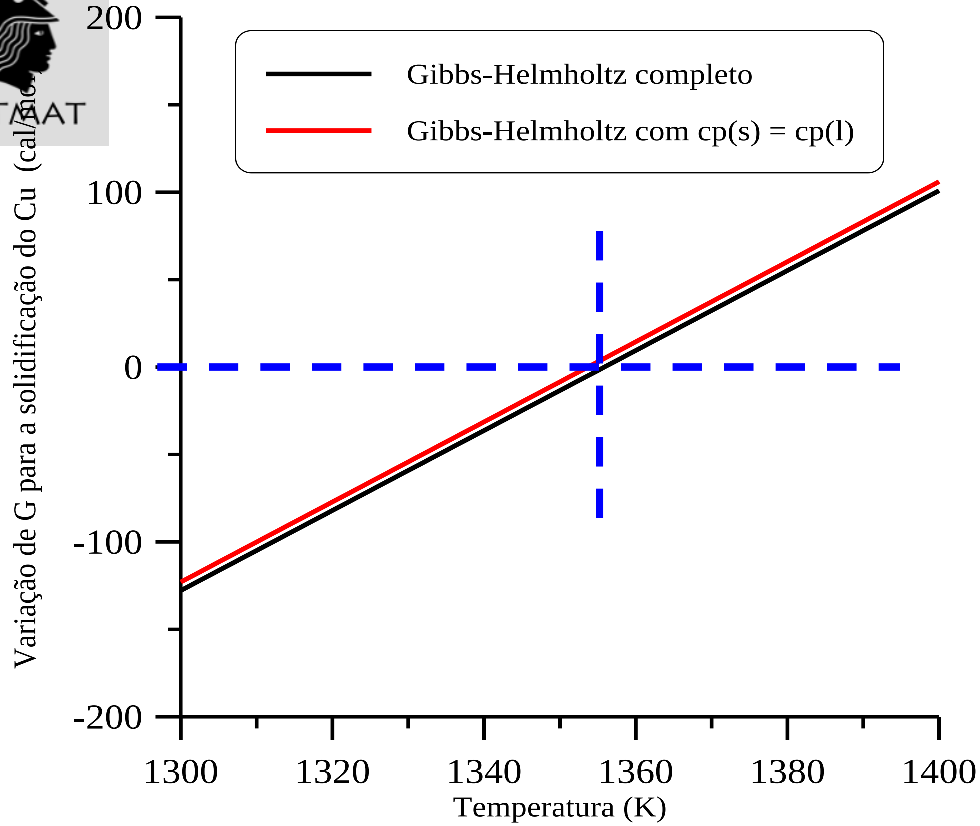
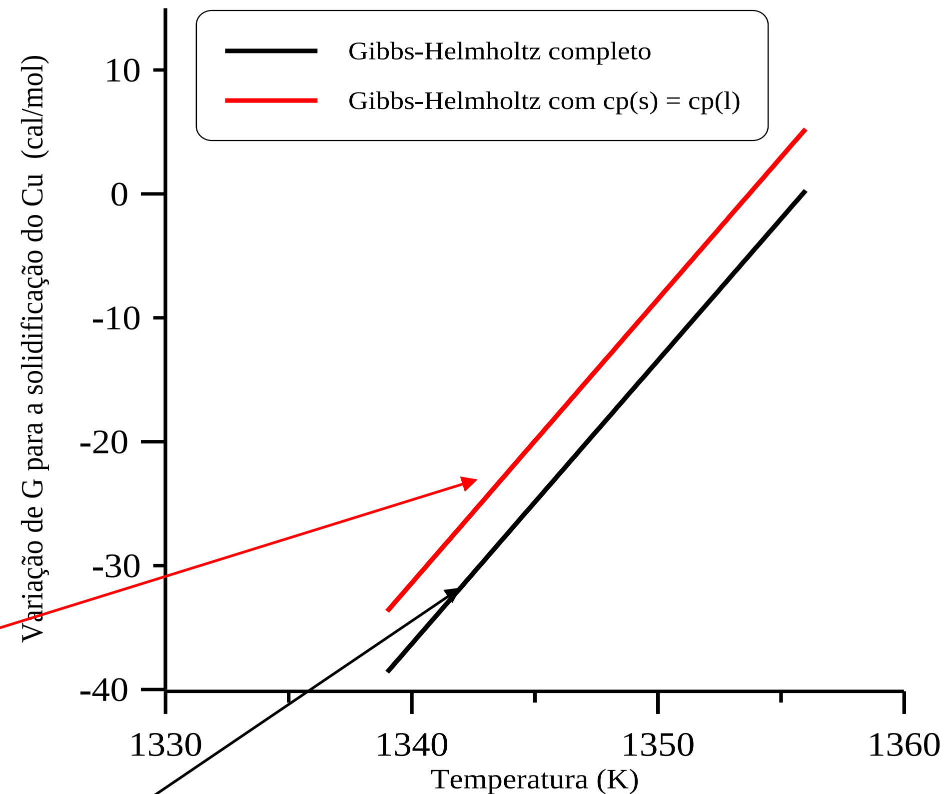
Soluções para **ΔG**:

- ✓ **$\Delta G = \Delta H - T\Delta S$ = -37,01 cal/mol**
- ✓ **Usando *loop* e $dG = VdP - SdT$ = -36,63 cal/mol**
- ✓ **Gibbs-Helmholtz: para ΔG = - 36,63 cal/mol com $\Delta c_P = 0$**
- ✓ **Gibbs-Helmholtz: completo: ΔG = - 36,63 cal/mol**



$\Delta G_{l \to s}$



$\Delta G = -3100 + 2{,}2861T$

$\Delta G = -0{,}75x10^{-3}T^2 + 2{,}09T\,lnT - 12{,}8436T - 1645{,}0120$