$p = 1\ bar$

$T = 25°C = 298{,}15\ K$

$\Delta G^\ominus = 2{,}84\ kJ$

Ali je reakcija pretvorbe grafita v diamant pri $p = 1$ bar in $T = 25°C$ spontana?

$dG = -SdT + Vdp$; $T = konst.$

$\underline{dG = Vdp}$

$dG_G = V_G dp$

$dG_D = V_D dp$

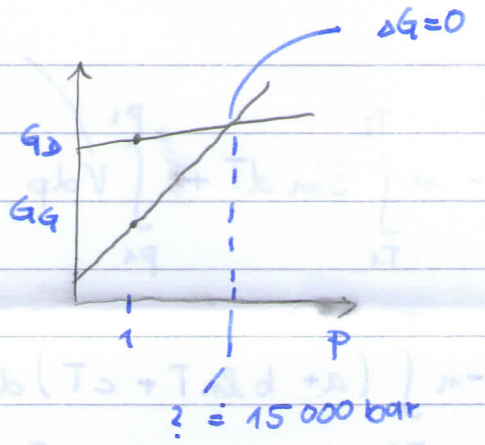
$\rho_D = 3{,}51\ g/cm^3$

$\rho_G = 2{,}25\ g/cm^3$

$m = 12\ g$

$V_D = \frac{12\ g}{3{,}51\ g\ cm^3} = 3{,}42\ cm^3$ $\Big\}$ $\Delta V = -1{,}91\ cm^3$

$V_G = 5{,}33\ cm^3$



$dG_D - dG_G = Vdp - V_G dp$

$\int_{\Delta G^\ominus}^{\Delta G} d\Delta G = \int_{p^\ominus}^{p} \Delta V\, dp$

$\Delta G - \Delta G^\ominus = \Delta V (p - p^\ominus)$

ΔG = 0, saj je to spontan proces

$-\Delta G^\ominus = \Delta V (p - p^\ominus)$

$p = \frac{-\Delta G^\ominus}{\Delta V} + p^\ominus = \frac{-2{,}84 \cdot 10^3\ J \cdot 10^{-5}}{-1{,}91 \cdot 10^{-6}\ cm^3} + 1\ bar = 1{,}49 \cdot 10^4\ bar =$

$= \underline{15\,000\ bar}$

Spontan proces bo pri $T = 25°C$, $p = 15\,000$ bar.

Gledamo T: $\Delta S^\ominus = -3{,}31\ J/K$ $\Delta G = -SdT + Vdp$ $p = konst.$

$d\Delta G = -\Delta S dT \Rightarrow \frac{\partial \Delta G}{\partial T} = -\Delta S^\ominus > 0$, če bi T višali; proces pretvorbe G v D bi bil manj spontan

$n = 1\ mol$
$p_1 = 1\ atm$
$T_1 = 300K$

$\Rightarrow$

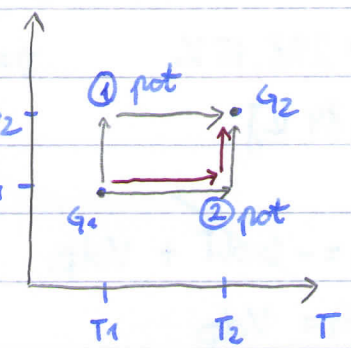
$p_2 = 2\ atm$
$T_2 = 400K$

$\Delta G = ?$

$a = 82{,}65\ J/molK$

$b = 29{,}26\ J/molK$

$c = 4{,}18 \cdot 10^{-3}\ J/molK^2$



$dG = -SdT + Vdp$

$S_m(p=1\ atm) = a + b \cdot \ln T(K) + c \cdot T$

$dG = -n \cdot S_m dT + Vdp$

① - vedeti bi morali $S_m(p=2atm) =$ ne vemo

② - vemo podatek $S_m(p=1atm) = ?$

$\frac{nRT_2}{p}$ - premo po ② poti

i) $p = konst.$

$$\Delta G = -n\int_{T_1}^{T_2} S_m\,dT + \int_{p_1}^{p_2} V\,dp$$

$$\Delta G = -n\int_{T_1}^{T_2} (a + b\ln T + cT)\,dT + nRT_2 \ln\frac{p_2}{p_1} =$$

$$= -n\left[a(T_2 - T_1) + b\int_{T_1}^{T_2} \ln T\,dT + \frac{c(T_2^2 - T_1^2)}{2} - RT_2 \ln\frac{p_2}{p_1}\right]$$

posebej:

$$\int \ln T\,dT$$

$$\int u\,dv = uv - \int v\,du$$

$u = \ln T \quad dv = dT$

$du = \frac{1}{T} \quad v = T$

$$= \ln T \cdot T\Big|_{T_1}^{T_2} - \int_{T_1}^{T_2} T \cdot \frac{1}{T}\,dT = \ln T \cdot T\Big|_{T_1}^{T_2} - \int_{T_1}^{T_2} dT =$$

$$= T_2 \ln T_2 - T_2 - (T_1 \ln T_1 - T_1)$$

$$\Delta G = -n\left[a(T_2-T_1) + b\left(T_2 \ln T_2 - T_2 - (T_1 \ln T_1 - T_1)\right) + \frac{c}{2}(T_2^2 - T_1^2) - R\underbrace{T_2}_{400K} \ln \frac{p_2}{p_1}\right] =$$

$$\underline{\Delta G = -23{,}24\ kJ}$$

Ali so proteini v vodni raztl. stabilni, če jih pomešamo z Ak, iz katerih nastanejo?

$$H_3N^{\oplus}CH_2CONHCH_2COO^{\ominus}(aq) + H_2O(l) \rightarrow 2\,H_3N^{\oplus}CH_2COO^{\ominus}(aq)$$
$$G_g \qquad\qquad\qquad\qquad\qquad G$$

$\Delta_{tv}G^{\ominus}_{G_g} = -377{,}69\ kJ/mol$

$\Delta_{tv}G^{\ominus}_{G_g} = -490{,}57\ kJ/mol$

$\Delta_{tv}G^{\ominus}_{H_2O} = -237{,}19\ kJ/mol$

pri $T = 25°C$

$$\Delta G^{\ominus} = 2\cdot \Delta_{tv}G^{\ominus}_{G} - \left(\Delta_{tv}G^{\ominus}_{G_g} + \Delta_{tv}G^{\ominus}_{H_2O}\right)$$

$$\underline{\Delta G^{\ominus} = -27{,}62\ kJ}$$

Spontano reagirajo v Ak, vendar ta reakcija teče počasi.

Zdaj poglejmo v naše telo:

$T = 37°C$

$$\left(\frac{\partial}{\partial T}\frac{\Delta G^{\ominus}}{T}\right)_p = -\frac{\Delta H^{\ominus}}{T^2}$$

$$\int_{\frac{\Delta G^{\ominus}(T_1)}{T_1}}^{\frac{\Delta G^{\ominus}(T_2)}{T_2}} d\frac{\Delta G^{\ominus}}{T} = \int_{T_1}^{T_2}\frac{\Delta H^{\ominus}}{T^2}\,dT$$

$$\frac{\Delta G^{\ominus}(T_2)}{T_2} = \frac{\Delta G^{\ominus}(T_1)}{T_1} - \int_{T_1}^{T_2}\frac{\Delta H^{\ominus}}{T^2}\,dT$$

$$\frac{\Delta G^{\ominus}(T)}{T} = \frac{\Delta G^{\ominus}(298K)}{298K} - \int_{298K}^{T}\frac{\Delta H^{\ominus}}{T^2}\,dT$$

$\Delta H^{\ominus}$: sprememba iz 25°C na 37°C ni znatna

$$\frac{\Delta G^\circ(310K)}{310K} = \frac{\Delta G^\circ(298K)}{298K} - \Delta H^\circ(298K)\left[-\left(\frac{1}{310K} - \frac{1}{298K}\right)\right]$$

$$\Delta H^\circ = 2\,\Delta_{tv}H^\circ_G - (\Delta_{tv}H^\circ_{Gq} + \Delta_{tv}H^\circ_{H_2O}) = -43{,}32\,kJ$$

iz tabel pri 25°C

$\Delta G^\circ(310K) = -26{,}99\,kJ > -43{,}32\,kJ \Rightarrow$ reakcija je manj spontana pri 37°C kot pri 25°C

Izračunaj ΔS pri izotermni kompresiji etana (2 mol) z 20 L na V = 2 L.
T = 400 K.

$n = 2\,mol$

$V_1 = 20\,L$

$V_2 = 2\,L$

$T = 400K$

a) realni plin: $b = 6{,}5144 \cdot 10^{-2}\,dm^3/mol$

b) idealni plin

$dA = -SdT - pdV$

$\left(\frac{dS}{dV}\right)_T = \left(\frac{dp}{dT}\right)_V$

$dS = \left(\frac{dp}{dT}\right)_V dV$

$V = n \cdot V_m$

$dV = n\,dV_m$

$dS = \left(\frac{dp}{dT}\right)_{V_m} n \cdot dV_m$

Van der Waals:

$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$

$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$

$\left(\frac{dp}{dT}\right)_{V_m} = \frac{R}{V_m - b}$

$$\Delta S = n\int_{V_{m1}}^{V_{m2}} \frac{dp}{dT} \cdot dV_m = n\int_{V_{m1}}^{V_{m2}} \frac{R}{V_m - b}\,dV_m =$$

$$= nR\,\ln\left(\frac{1}{V_{m2} - b} \Big/ \frac{1}{V_{m1} - b}\right) =$$

$$= nR\,\ln\frac{V_{m2} - b}{V_{m1} - b} = 2\,mol \cdot 8{,}314\,\frac{J}{mol\,K} \cdots$$

$V_{m1} = \frac{V_1}{n} = 10\ L/mol$

$V_{m2} = \frac{V_2}{n} = 1\ L/mol$

$\Delta S = 2\ mol \cdot 8{,}314 \frac{J}{mol\,K} \cdot \ln \frac{1 - 6{,}5144 \cdot 10^{-2}}{10 - 6{,}5144 \cdot 10^{-2}} = \underline{\underline{-39{,}3\ J/K}}$

b) $\Delta S = nR \ln \frac{V_2}{V_{m1}} = 2\ mol \cdot 8{,}314 \frac{J}{mol\,K} \cdot \ln \frac{1}{10} = \underline{\underline{-38{,}3\ J/K}}$