2. ispit Kem. TD – K1 (16.02.2011)

računske z.

(2.50) 1.) $dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV^{\to 0} = \left(\frac{\partial P}{\partial T}\right)_V dT \Rightarrow \Delta P \approx \left(\frac{\partial P}{\partial T}\right)_V \Delta T = \frac{\alpha}{\beta}\Delta T = \frac{1{'}8\cdot 10^{-4}\,K^{-1}}{3{'}9\cdot 10^{-6}\,bar^{-1}}\cdot 2K = 92{'}3\,bar \Rightarrow P_2 = P_1 + \Delta P = 93{'}3\,bar$ 0'5 0'5 0'5 0'5 0'5

(2.50) 2.) $\Delta U = q^{=0} + w \Rightarrow C_V\cdot(T_2 - T_1) = -P_2\cdot(V_2 - V_1) \Rightarrow n C_{V,m}\cdot(T_2 - T_1) = -P_2\cdot\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right) \Rightarrow T_2 = T_1\cdot\frac{C_{V,m} + R\frac{P_2}{P_1}}{C_{V,m} + R}$ 0'5 0'5 0'5 0'5

$T_2 = 298{'}15K\left(\frac{4{'}95 + 1{'}9872\,\frac{10}{30}}{4{'}95 + 1{'}9872}\right) = 241K = -31{'}9\,°C$ 0'5

(2.50) 3.) $\frac{dP}{dT} = \frac{\Delta S°}{\Delta V°} = \frac{\Delta H°}{T\Delta V°}$; $\Delta V° = V°_{tek} - V°_{trd} = M\cdot\left(\frac{1}{\rho_{tek}} - \frac{1}{\rho_{trd}}\right)$; $dP = \frac{\Delta H°}{\Delta V°}\, d\ln T \Rightarrow \underbrace{P_2 - P_1}_{\Delta P} = \frac{M\cdot\Delta H_{tal}}{M\cdot\left(\frac{1}{\rho_{tek}} - \frac{1}{\rho_{trd}}\right)}\cdot\ln\frac{T_2}{T_1}$ 0'5 0'5 0'5

$\ln\frac{T_2}{T_1} = \frac{\Delta P\cdot\left(\frac{1}{\rho_{tek}} - \frac{1}{\rho_{trd}}\right)}{\Delta H_{tal}} = \frac{(99\,atm)\cdot\frac{760\,Pa}{750\,atm}\cdot 10^5\cdot\left(\frac{10^{-6}}{10\,g\,m^{-3}} - \frac{10^{-6}}{9{'}673\,g\,m^{-3}}\right)}{52{'}89\,J\,g^{-1}} = -6{'}412\cdot 10^{-4}$ 0'5

$T_2 = T_1\cdot e^{\ln\frac{T_2}{T_1}} = 544{'}1K = 270{'}95\,°C$ 0'5

(2.50) 4.) $\Delta G°_T = -RT\ln K_a = -RT\ln\frac{a_{CaO}\cdot a_{CO_2}}{a_{CaCO_3}} = -RT\ln a_{CO_2} \approx -RT\ln\frac{P_{CO_2}}{P^\ominus}$; $P^\ominus = 1\,atm \Rightarrow P_{CO_2} = P^\ominus e^{-\frac{\Delta G°_T}{RT}}$ 0'25 0'25 0'25 0'25 0'25

$\Delta G°_{T_1} = 130{'}4\,kJ\,mol^{-1}$

$\Delta G°_{T_2} \Leftarrow \left[\frac{\partial\frac{\Delta G°}{T}}{\partial T}\right]_P = -\frac{\Delta H°}{T^2} \Rightarrow d\left(\frac{\Delta G°}{T}\right) = -\frac{\Delta H°}{T^2}dT \Rightarrow \frac{\Delta G°_{T_2}}{T_2} - \frac{\Delta G°_{T_1}}{T_1} = \frac{\Delta H°}{1}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \Rightarrow \Delta G°_{T_2} = \Delta G°_{T_1}\frac{T_2}{T_1} + \Delta H°\left(1 - \frac{T_2}{T_1}\right)$ 0'5

$\Delta G°_{T_2} = 1{'}553\,kJ\,mol^{-1} \Rightarrow P_{CO_2}(T_1) = 1{'}424\cdot 10^{-23}\,Atm = 1{'}44\cdot 10^{-18}\,Pa$ $P_{CO_2}(T_2) = 0{'}841\,atm = 85{'}2\,kPa$ 0'25 0'25 0'25

teoretske z.

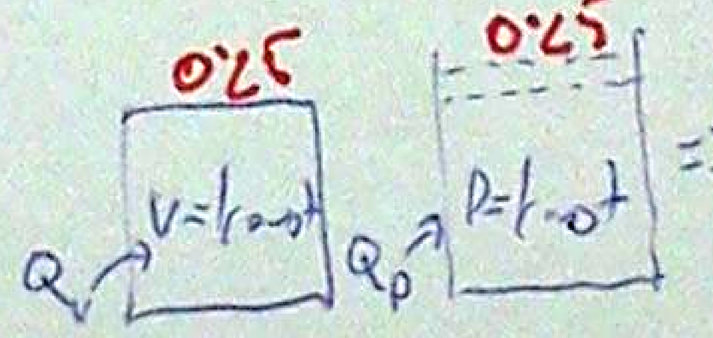
(2.50) 1.) $\underbrace{\left(P + a\frac{n^2}{V^2}\right)}_{P_{id}}\cdot\underbrace{(V - nb)}_{V_{id}} = nRT$ 1'00

privlačne int. $\left(a\frac{n^2}{V^2}\right)$ 0'25 0'25

odbojne int. (isključ. volumen; nb) ⇒ dimenzija molekul 0'25 0'25

– ukapljivanje plina pri srednjim tlakovima (→100 bar) – kritično ukapljiv. 0'25 0'25

(2.50) 2.) $C_p = \frac{dQ_p}{dT} = \left(\frac{\partial H}{\partial T}\right)_p$; $C_V = \frac{dQ_V}{dT} = \left(\frac{\partial U}{\partial T}\right)_V$; 0'25 0'25



0'25 0'25

za isti ΔT je $Q_p > Q_V \Rightarrow C_p > C_V$ 0'25

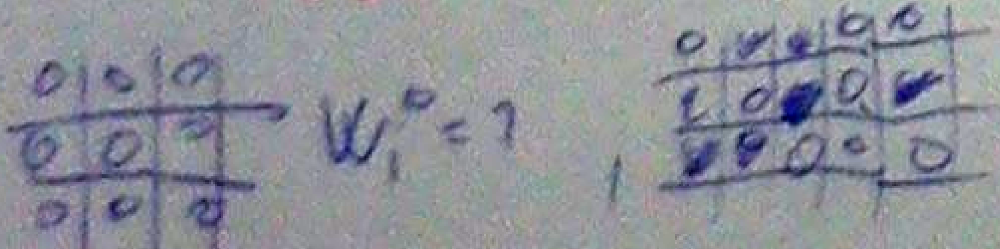
⇒ p = konst dio topline za rad protiv unutrašnjih privlačnih i vanjskih sila

$C_p - C_V = \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_p = T\left(\frac{\partial P}{\partial T}\right)_V\cdot\left(\frac{\partial V}{\partial T}\right)_p = \frac{TV\alpha^2}{\beta}$; $T, V, \alpha^2, \beta > 0 \Rightarrow C_p - C_V > 0$ 0'5 0'25 0'25 0'25

unutr. tlak

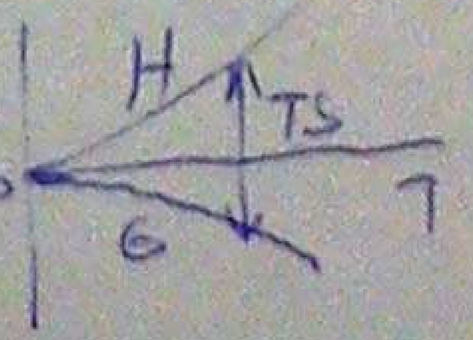
(2.50) 3.) $dS = \frac{dQ_{rev}}{T}$ (TD) ; $S = k\ln W$ (stat.) ; izolirani ($dQ, dW = 0$) ⇒ $dU = dQ + dW = 0 \Rightarrow U = konst$; $dV = 0 \Rightarrow V = konst$ 0'25 0'25 0'25 0'25

$(dS)_{U,V} \geq 0$ > spontano, = ravnoteža ; $\Delta S_m = -R\sum_i n_i\ln x_i$; $\Delta S_m = k\ln W_r = k\ln\frac{N_0!}{N_1!N_2!\ldots} > 0$ 0'5 0'5 0'25



$W_1° = 1$, $W_r \gg 1$ 0'25

(2.50) 4.) $dG = -SdT + VdP \Rightarrow \left(\frac{\partial G}{\partial T}\right)_p = -S = \frac{G - H}{T} \Rightarrow \frac{\left(\frac{\partial G}{\partial T}\right)_p T - G}{T^2} = -\frac{H}{T^2} \Rightarrow \left(\frac{\partial\frac{G}{T}}{\partial T}\right)_p = -\frac{H}{T^2}$ Gibbs–Helmholz 0'25 0'25 0'5



– ovisnost G o T 0'25

Debye-va zraka ($C_p = aT^3 \Rightarrow C_{p,0} = 0$; III. zak. TD: $S_0 = 0 \Rightarrow G_0 = H_0$)

$\left(\frac{\partial G}{\partial P}\right)_T = V \Rightarrow G = G_0 + \int_{P_0}^{P} VdP$; id. plin $G = G_0 + nRT\ln\frac{P}{P_0}$ 0'25 0'5 0'25