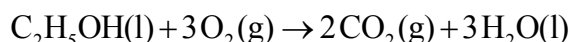


CHEM-A2250 Fysikaalinen kemia BioIT:lle
1. välikoe 22.10.2018
Ratkaisut

1.



V vakio \Rightarrow mitataan ΔU

Lämpöä kehittyi 90,447 kJ $\Rightarrow \Delta_r U^\circ(298\text{ K}) = -90447\text{ J}$

$$\Delta_r U_m^\circ(298\text{ K}) = \frac{\Delta U_R^\circ(298\text{ K})}{m_{\text{C}_2\text{H}_5\text{OH}} / M_{\text{C}_2\text{H}_5\text{OH}}} = \frac{-90447\text{ J}}{3,05\text{ g} / 46,1\text{ g mol}^{-1}} = -1367,1\text{ kJ mol}^{-1}$$

a)

$$\Delta_r H_m^\circ(298\text{ K}) = \Delta_r U_m^\circ(298\text{ K}) + RT \cdot \Delta \nu_g = -1367,1\text{ kJ mol}^{-1} + 8,314\text{ J K}^{-1}\text{ mol}^{-1} \cdot 298\text{ K} \cdot (2-3)$$

$$= -1370\text{ kJ mol}^{-1}$$

b)

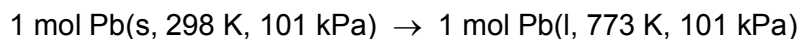
$$\Delta_r H_m^\circ = 2 \cdot \Delta_f H_m^\circ(\text{CO}_2, \text{g}) + 3 \cdot \Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l}) - \Delta_f H_m^\circ(\text{C}_2\text{H}_5\text{OH}, \text{l}) - 3 \cdot \Delta_f H_m^\circ(\text{O}_2, \text{g})$$

Taulukkotietojen avulla 298 K:ssä

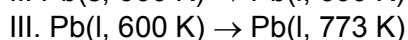
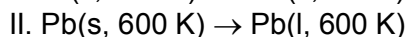
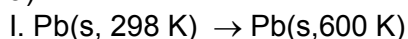
$$\Delta_r H_m^\circ(\text{C}_2\text{H}_5\text{OH}, \text{l}) = 2 \cdot \Delta_f H_m^\circ(\text{CO}_2, \text{g}) + 3 \cdot \Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l}) - 3 \cdot \Delta_f H_m^\circ(\text{O}_2, \text{g}) - \Delta_r H_m^\circ$$

$$= [2 \cdot (-393) + 3 \cdot (-285) - 3 \cdot 0 - (-1370)]\text{ kJ mol}^{-1} = -271\text{ kJ mol}^{-1}$$

2.



a)



$$\Delta S_m = \Delta S_{m,\text{I}} + \Delta S_{m,\text{II}} + \Delta S_{m,\text{III}}$$

$$\Delta S_m^\circ = \int_{298\text{ K}}^{600\text{ K}} \frac{C_{p,m}^\circ(\text{Pb}, \text{s}) dT}{T} + \frac{\Delta_{\text{fus}} H_m^\circ(\text{Pb})}{600\text{ K}} + \int_{600\text{ K}}^{773\text{ K}} \frac{C_{p,m}^\circ(\text{Pb}, \text{l}) dT}{T}$$

$$\Delta S_m^\circ = \int_{298\text{ K}}^{600\text{ K}} \frac{(23,6 + 0,01T) dT}{T} + \frac{4810\text{ J mol}^{-1}}{600\text{ K}} + \int_{600\text{ K}}^{773\text{ K}} \frac{32,4 dT}{T}$$

$$\Delta S_m^\circ = \left[23,6 \cdot \ln\left(\frac{600\text{ K}}{298\text{ K}}\right) + 0,01 \cdot (600 - 298) + \frac{4810}{600} + 32,4 \cdot \ln\left(\frac{773\text{ K}}{600\text{ K}}\right) \right] \text{ J K}^{-1}\text{ mol}^{-1}$$

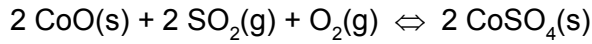
$$\Delta S_m^\circ = [16,52 + 3,02 + 8,02 + 8,21] \text{ J K}^{-1}\text{ mol}^{-1} = 35,8\text{ J K}^{-1}\text{ mol}^{-1}$$

b)

$$\Delta S_m^\circ = S_m^\circ(\text{Pb, l, 773 K, 101 kPa}) - S_m^\circ(\text{Pb, s, 298 K, 101 kPa})$$

$$S_m^\circ(\text{Pb, l, 773 K, 101 kPa}) = \Delta S_m^\circ + S_m^\circ(\text{Pb, s, 298 K, 101 kPa}) = (35,8 + 64,9) \text{ J K}^{-1} \text{ mol}^{-1} \\ = \mathbf{100,7 \text{ J K}^{-1} \text{ mol}^{-1}}$$

3.



a)

Taulukkotietojen avulla:

$$\Delta_r H_m^\circ(298 \text{ K}) = [2 \cdot (-888) - 2 \cdot (-238) - 2 \cdot (-297) - 0] \text{ kJ mol}^{-1} = -706 \text{ kJ mol}^{-1}$$

$$\Delta_r S_m^\circ(298 \text{ K}) = [2 \cdot 118 - 2 \cdot 53 - 2 \cdot 248 - 205] \text{ J K}^{-1} \text{ mol}^{-1} = -571 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta C_{p,m}^\circ(298 \text{ K}) = [2 \cdot 130 - 2 \cdot 55 - 2 \cdot 40 - 29] \text{ J K}^{-1} \text{ mol}^{-1} = 41 \text{ J K}^{-1} \text{ mol}^{-1} \quad \text{oletetaan vakioksi}$$

$$\Delta_r H_m^\circ(948 \text{ K}) = \Delta_r H_m^\circ(298 \text{ K}) + \Delta C_{p,m} \cdot (948 - 298) \text{ K}$$

$$\Delta_r H_m^\circ(948 \text{ K}) = -706 \text{ kJ mol}^{-1} + 41 \cdot 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \cdot (948 - 298) \text{ K} = \mathbf{-679 \text{ kJ mol}^{-1}}$$

$$\Delta_r S_m^\circ(948 \text{ K}) = \Delta_r S_m^\circ(298 \text{ K}) + \Delta C_{p,m} \cdot \ln\left(\frac{948 \text{ K}}{298 \text{ K}}\right)$$

$$\Delta_r S_m^\circ(948 \text{ K}) = -571 \text{ J K}^{-1} \text{ mol}^{-1} + 41 \text{ J K}^{-1} \text{ mol}^{-1} \cdot \ln\left(\frac{948 \text{ K}}{298 \text{ K}}\right) = \mathbf{-524 \text{ J K}^{-1} \text{ mol}^{-1}}$$

b)

$$\Delta_r G_m^\circ(T) = \Delta_r H_m^\circ(T) - T \cdot \Delta_r S_m^\circ(T)$$

$$\Delta_r G_m^\circ(948 \text{ K}) = -679 \text{ kJ mol}^{-1} - 948 \text{ K} \cdot (-524 \cdot 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) = \mathbf{-182 \text{ kJ mol}^{-1}}$$

$$K = \exp\left[\frac{-\Delta_r G_m^\circ(T)}{RT}\right]$$

$$K = \exp\left[\frac{-(-182000 \text{ J mol}^{-1})}{8,314 \text{ J K}^{-1} \text{ mol}^{-1} \cdot 948 \text{ K}}\right] = \mathbf{1,07 \cdot 10^{10}}$$

4.

a)

Kiinteä-höyrytasapaino, Clausius-Clapeyron: $\frac{dP}{dT} = \frac{P \cdot \Delta_{\text{sub}} H_m}{RT^2}$

$$\text{Integroidaan} \Rightarrow \ln \frac{P_f}{P_i} = -\frac{\Delta_{\text{sub}} H_m}{R} \left(\frac{1}{T_f} - \frac{1}{T_i} \right)$$

$$\Delta_{\text{sub}} H_m = \frac{-R \cdot \ln \frac{P_f}{P_i}}{\left(\frac{1}{T_f} - \frac{1}{T_i} \right)} = \frac{-8,314 \text{ J K}^{-1} \text{ mol}^{-1} \cdot \ln\left(\frac{517,973 \text{ kPa}}{101,325 \text{ kPa}}\right)}{\left(\frac{1}{216,55 \text{ K}} - \frac{1}{194,65 \text{ K}} \right)} = \mathbf{26,1 \text{ kJ mol}^{-1}}$$

b)

101,325 kPa < 517,973 kPa (kolmoispisteen paine)

Kolmoispisteen alapuolella olevassa paineessa nestefaasi ei ole stabiili.

⇒

101,325 kPa paineessa ainoastaan kiinteä faasi (s) voi esiintyä kaasufaasin (g) kanssa tasapainossa.

5.

Gibbsin isotermi: $\Gamma^\sigma = -\frac{c}{RT} \cdot \left(\frac{\partial \gamma}{\partial c}\right)$

$$\gamma = \gamma^* \cdot \left(1 - 0,1785 \cdot \ln\left(1 + \frac{c}{a}\right)\right) \Rightarrow \frac{\partial \gamma}{\partial c} = -\gamma^* \cdot 0,1785 \cdot \frac{1}{1 + \frac{c}{a}} \cdot \left(\frac{1}{a}\right)$$

$$\Gamma^\sigma = -\frac{c}{RT} \cdot \left(-\gamma^* \cdot 0,1785 \cdot \frac{1}{1 + \frac{c}{a}} \cdot \frac{1}{a}\right) = \frac{c \cdot \gamma^* \cdot 0,1785}{RT \cdot (a + c)}$$

Kun $c = 0,276 \text{ mol dm}^{-3}$

$$\Gamma^\sigma = \frac{0,276 \text{ mol dm}^{-3} \cdot 72,86 \cdot 10^{-3} \text{ N m}^{-1} \cdot 0,1785}{8,314 \text{ J K}^{-1} \text{ mol}^{-1} \cdot 291,15 \text{ K} \cdot (0,0510 + 0,276) \text{ mol dm}^{-3}} = 4,53 \cdot 10^{-6} \text{ mol m}^{-2} = \mathbf{4,53 \cdot 10^{-10} \text{ mol cm}^{-2}}$$