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

1.

$$C_2H_5OH(l) + 3\,O_2(g) \rightarrow 2\,CO_2(g) + 3\,H_2O(l)$$

V vakio $\Rightarrow$ mitataan ΔU

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

$$\Delta_r U^\circ_m(298\,\mathrm{K}) = \frac{\Delta U^\circ_R(298\,\mathrm{K})}{m_{C_2H_5OH} / M_{C_2H_5OH}} = \frac{-90447\,\mathrm{J}}{3,05\,\mathrm{g} / 46,1\,\mathrm{g\,mol^{-1}}} = -1367,1\,\mathrm{kJ\,mol^{-1}}$$

a)

$$\Delta_r H^\circ_m(298\,\mathrm{K}) = \Delta_r U^\circ_m(298\,\mathrm{K}) + RT \cdot \Delta\nu_g = -1367,1\,\mathrm{kJ\ mol^{-1}} + 8,314\,\mathrm{J\,K^{-1}mol^{-1}} \cdot 298\,\mathrm{K} \cdot (2-3)$$

= – 1370 kJ mol^{-1}

b)

$$\Delta_r H^o_m = 2 \cdot \Delta_f H^o_m(CO_2,g) + 3 \cdot \Delta_f H^o_m(H_2O,l) - \Delta_f H^o_m(C_2H_5OH,l) - 3 \cdot \Delta_f H^o_m(O_2,g)$$

Taulukkotietojen avulla 298 K:ssä

$$\Delta_f H^o_m(C_2H_5OH,l) = 2 \cdot \Delta_f H^o_m(CO_2,g) + 3 \cdot \Delta_f H^o_m(H_2O,l) - 3 \cdot \Delta_f H^o_m(O_2,g) - \Delta_r H^o_m$$

= [2·(–393) + 3·(–285) – 3·0 –(–1370)] kJ mol^{-1} = **– 271 kJ mol^{-1}**

2.

1 mol Pb(s, 298 K, 101 kPa) $\rightarrow$ 1 mol Pb(l, 773 K, 101 kPa)

a)

I. Pb(s, 298 K) $\rightarrow$ Pb(s,600 K)
II. Pb(s, 600 K) $\rightarrow$ Pb(l, 600 K)
III. Pb(l, 600 K) $\rightarrow$ Pb(l, 773 K)

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

$$\Delta S^o_m = \int_{298K}^{600K} \frac{C^o_{p,m}(Pb,s)dT}{T} + \frac{\Delta_{fus}H^o_m(Pb)}{600K} + \int_{600K}^{773K} \frac{C^o_{p,m}(Pb,l)dT}{T}$$

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

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

ΔS°_m = [16,52 + 3,02 + 8,02 + 8,21] J K^{-1} mol^{-1} = **35,8 J K^{-1} mol^{-1}**

b)

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

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

= **100,7 JK^{-1}mol^{-1}**

3.

2 CoO(s) + 2 SO_2(g) + O_2(g) $\Leftrightarrow$ 2 $CoSO_4$(s)

a)

Taulukkotietojen avulla:

$\Delta_r H°_m$(298 K) = [2·(– 888) – 2·(–238) – 2·(–297) – 0] kJ mol^{-1} = – 706 kJ mol^{-1}

$\Delta_r S°_m$(298 K) = [2·118 – 2·53 – 2·248 – 205] J K^{-1} mol^{-1} = – 571 J K^{-1} mol^{-1}

$\Delta C_{P,m}$(298 K) = [2·130 – 2·55 – 2·40 – 29] J K^{-1} mol^{-1} = 41 J K^{-1} mol^{-1} oletetaan vakioksi

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

$\Delta_r H°_m$(948 K) = – 706 kJ mol^{-1} + 41·10^{-3} kJ K^{-1}mol^{-1}·(948 – 298) K = **– 679 kJ mol^{-1}**

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

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

b)

$$\Delta_r G_m^o(T) = \Delta_r H_m^0(T) - T \cdot \Delta_r S_m^o(T)$$

$\Delta_r G°_m$(948 K) = – 679 kJ mol^{-1} – 948 K · (– 524·10^{-3} kJ K^{-1} mol^{-1}) = **– 182 kJ mol^{-1}**

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

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

4.

a)

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

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

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

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

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

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

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