Übungsaufgaben IV, von 15.05.2001

Musterlösungen

1. Euler-Kettenregel besagt:

$$\left(\frac{\partial p}{\partial T}\right)_V \cdot \left(\frac{\partial T}{\partial V}\right)_p \cdot \left(\frac{\partial V}{\partial p}\right)_T = -1 \quad ↵$$

$$\left(\frac{\partial p}{\partial T}\right)_V = -1 \cdot \frac{1}{\left(\frac{\partial T}{\partial V}\right)_p \cdot \left(\frac{\partial V}{\partial p}\right)_T} \quad ↵$$

$$= -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} = +\frac{\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p}{-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T} \quad ↵$$

$$= \frac{\alpha}{K}$$

Expansion coefficient $\alpha^{H_2O} = 2.1 \times 10^{-4}\,K^{-1}$

Isothermal Compressibility $K^{H_2O} = 49.6 \times 10^{-6}\,atm^{-1}$

$$\left(\frac{\partial p}{\partial T}\right)_V = 4.23 \quad atm\,K^{-1}$$

Expansion coefficient $\alpha^{C_6H_6} = 12.4 \times 10^{-4}\,K^{-1}$

Isothermal Compressibility $K^{C_6H_6} = 92.1 \times 10^{-6}\,atm^{-1}$

$$\left(\frac{\partial p}{\partial T}\right)_V = 13.46 \quad atm\,K^{-1}$$

2. Enthalpy ist eine Zustandsgröße, daher kann man das totale Differential schreiben

$$dH \stackrel{!}{=} C_p\left\{dT - \mu_{JT}dp\right\} = \left(\frac{\partial H}{\partial T}\right)_p \cdot dT + \left(\frac{\partial H}{\partial p}\right)_T \cdot dp \qquad \text{↵}$$

mit $\mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H$ und $C_p = \left(\frac{\partial H}{\partial T}\right)_p$

Euler Kettenregel besagt :

$$\underbrace{\left(\frac{\partial p}{\partial T}\right)_H}_{\frac{1}{\mu_{JT}}} \cdot \left(\frac{\partial H}{\partial p}\right)_T \cdot \underbrace{\left(\frac{\partial T}{\partial H}\right)_p}_{\frac{1}{C_p}} = -1$$

$$\Rightarrow \frac{1}{\mu_{JT}} \cdot \left(\frac{\partial H}{\partial p}\right)_T \cdot \frac{1}{C_p} = -1$$

$$\Rightarrow \left(\frac{\partial H}{\partial p}\right)_T = -\mu_{JT}C_p$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_p \cdot dT + \left(\frac{\partial H}{\partial p}\right)_T \cdot dp$$

$$dH = C_p dT + \left(-\mu_{JT}C_p dp\right) \qquad \text{↵}$$

$$dH = C_p\left\{dT - \mu_{JT}dp\right\}$$

3. a) Bildungsreaktion: $2C(s)+3H2(g)\rightarrow C2H6(g)$ $\Delta_B H^{\otimes}(298K)=-84{,}68 kJmol^{-1}$

b) Bestimmung von $\Delta_B H^{\otimes}(350K)$ mit Hilfe des Kirchhoff'schen Gesetzes:

$$T_2 = 350\ K\quad T_1 = 298\ K$$

$$\Delta_B H^{\otimes}(T_2)=\Delta_B H^{\otimes}(T_1)+\int_{T_1}^{T_2}\Delta_R C_P dT$$

$$\Delta_R C_P = \sum_J \nu_J C_{p,m}(J)=C_{p,m}(C_2H_6)-2C_{p,m}(C)-3C_{p,m}(H_2)$$

$$C_{p,m}(C_2H_6)(JK^{-1})=14{,}73+0{,}1272\times T$$

$$C_{p,m}(C_{(s)})(JK^{-1})=16{,}86+(4{,}77\times10^{-3})T-(\frac{8{,}54\times10^5}{T^2})$$

$$C_{p,m}(H_{2(g)})(JK^{-1})=27{,}28+(3{,}26\times10^{-3})T-(\frac{0{,}5\times10^5}{T^2})$$

+!!!

$$\Delta_R C_P(JK^{-1})=-100{,}83+(0{,}1079)T+(\frac{1{,}56\times10^6}{T^2})$$

$$\int_{T_1}^{T_2}\Delta_R C_P dT=-100{,}83\times(T_2-T_1)+\frac{1}{2}(0{,}1079)\times(T_2^2-T_1^2)-(1{,}56\times10^6)\times\left(\frac{1}{T_2}-\frac{1}{T_1}\right)=-2{,}65 kJmol^{-1}$$

$$\Delta_B H^{\otimes}(350K)=\Delta_B H^{\otimes}(298K)-2{,}65 kJ.mol^{-1}=-87{,}33 kJmol^{-1}$$

4. a) $H = U + pV = U + RT \rightarrow \Delta H = \Delta U + \Delta n_g RT$

Δn_g = Änderung der Stoffmenge in der Gasphase

$$C_3H_6(g) + \frac{9}{2}O_2(g) \rightarrow 3CO_2(g) + 3H_2O(l)$$

$$\Delta n_g = 3 - \frac{9}{2} - 1 = -\frac{5}{2}$$

$$RT = 2{,}478 \text{ kJmol}^{-1}$$

$$\Delta H = \Delta U - 6{,}195 \text{ kJ}$$

$$\Delta U = \Delta H + 6{,}195 \text{ kJ} = -2058 + 6{,}195 = -2051{,}8 \text{ kJ}$$

b) $\Delta H = \Delta U + P(V_w - V_G)$

V_w = Volumen von 1 mol weiss Zinn = 16,24 cm^3

V_G = Volumen von 1 mol grau Zinn = 20,65 cm^3

$$P(V_w - V_G) = -4{,}41 \text{ J} \rightarrow \Delta U = \Delta H + 4{,}41 \text{ J} = 6{,}51 \text{ J}$$