Übungen zur Physikalischen Chemie für Mikrosystemtechnik WS2007/2008

Übungsblatt 8 – Lösungen

A 8.1:

Mit Gl. 4–13 a erhalten wir

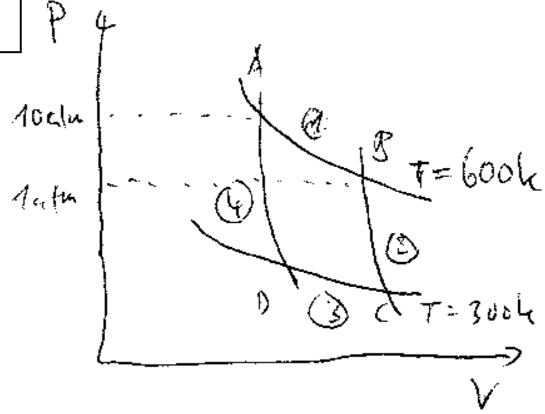
$$\Delta S_{\mathrm{m}} = \int_{T_1}^{T_2} \frac{C_{p,\mathrm{m}}\,\mathrm{d}T}{T} = \int_{T_1}^{T_2} \left(\frac{a + b\,T}{T}\right) \mathrm{d}T = a\,\ln\left(\frac{T_2}{T_1}\right) + b\,(T_2 - T_1)$$

$a = 91.47\ \mathrm{J\ K^{-1}\ mol^{-1}}$ $\qquad$ $b = 7.5 \times 10^{-2}\ \mathrm{J\ K^{-2}\ mol^{-1}}$

$$\Delta S_{\mathrm{m}}^{\ominus} = (91.47\ \mathrm{J\ K^{-1}\ mol^{-1}}) \cdot \ln\left(\frac{300\ \mathrm{K}}{273\ \mathrm{K}}\right) + (0.075\ \mathrm{J\ K^{-2}\ mol^{-1}}) \cdot (27\ \mathrm{K}) = 10.\overline{7}\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

Für 1 mol ist also $\boxed{\Delta S = +11\ \mathrm{J\ K^{-1}}}$

A 8.2:



1 mol id Gas

	q / kJ mol⁻¹	w / kJ mol⁻¹	ΔU / kJ mol⁻¹	ΔH / kJ mol⁻¹	ΔS_s / J K⁻¹ mol⁻¹	ΔS_u / J K⁻¹ mol⁻¹
①	+11.49	−11.49	0	0	19.14	−19.14
②	0	−3.741	−3.741	−6.236	0	0
③	−5.743	5.743	0	0	−19.14	+19.14
④	0	+3.741	+3.741	+6.236	0	0
∮	+5.747	−5.747	0	0	0	0

$\hookrightarrow \eta = \frac{+5.747}{11.49} = 0.5 = \frac{\Delta T}{T_h} = \frac{300}{600}$ ✓

① isotherme Expansion (rev)

$$w = -RT \ln\frac{V_B}{V_A} = -RT \ln\frac{p_A}{p_B} = -8.314 \cdot 600 \cdot \ln 10 \quad \text{J K}^{-1}\text{mol}^{-1}\cdot\text{K}$$

$pV = \text{const} \Rightarrow p \propto \frac{1}{V}$

$$= -11.49 \text{ kJ mol}^{-1}$$

$\Delta U = 0 \Rightarrow q = -w$

$\Delta H = \Delta U + nR\Delta T = 0$

$$\Delta S_s = \frac{q_{rev}}{T} = \frac{11.490 \text{ J mol}}{600\text{K}} = 19.14 \text{ J K}^{-1}\text{mol}^{-1}$$

$$\Delta S_u = \frac{-q_{rev}}{T}$$

(2) adiabat. rev. Expansion

$q = 0 \quad \Delta U = w = C_{V,m} \cdot n \cdot \Delta T = -\frac{3}{2} 8.314 \cdot 300 \quad \frac{J \cdot mol \cdot K}{K \cdot mol^2} =$

$= -3.741 \text{ kJ mol}^{-1}$

$\Delta H = \Delta U + nR\Delta T = -3.741 + 8.314 \cdot (-300) \text{ J mol}^{-1} = -6.236 \text{ kJ mol}^{-1}$

(3) isotherm. rev. Kompr.

Adiabate $P_B \cdot V_B^{\gamma} = P_C V_C^{\gamma} \qquad V = \frac{nRT}{P}$

$(nR)^{\gamma} \frac{P_B \cdot (RT)^{\gamma}}{P_B^{\gamma}} = \frac{(nR)^{\gamma} P_C \cdot T^{\gamma}}{P_C^{\gamma}}$

$P_B^{1-\gamma} T_B^{\gamma} = P_C^{1-\gamma} T_C^{\gamma}$

$P_C^{1-\gamma} = \left(\frac{T_B}{T_C}\right)^{\gamma} P_B^{1-\gamma} \quad \Big| \frac{1}{1-\gamma}$

$P_C = \left(\frac{T_B}{T_C}\right)^{\frac{\gamma}{1-\gamma}} P_B \qquad \gamma = \frac{C_{p,m}}{C_{V,m}} = \frac{5/2R}{3/2R} = \frac{5}{3}$

$1 - \gamma = -\frac{2}{3}$

$\frac{\gamma}{1-\gamma} = -\frac{5 \cdot 3}{3 \cdot 2} = -\frac{5}{2}$

$\Rightarrow P_C = 2^{-5/2} P_B = 0.1768 \cdot P_B = 0.1768 \text{ atm}$

$P_D = 2^{-5/2} P_A = 0.1768 P_A = 1.768$

$w = -RT \ln \frac{P_C}{P_D} = -300 \cdot 8.314 \ln \frac{0.1768}{1.768} = +300 \cdot 8.314 \ln 10 =$

$= +5.174 \text{ kJ mol}^{-1}$

$\Delta S_S = \frac{q_{rev}}{T} = \frac{-5740 \text{ J mol}^{-1}}{300 K} = -19.14 \text{ JK}^{-1} \text{mol}^{-1} \qquad \Delta U = \Delta H = 0$

(4) $q_{rev} = 0 = \Delta S_S = \Delta S_u \; ; \; w = \Delta U = C_V \cdot \Delta T = C_V (+300 K) = +3.741 \text{ kJ mol}^{-1}$

A 8.3:

3 mmol $N_2(g)$ $T = 300\,K$ $V = 36\,cm^3 \rightarrow V = 60\,cm^3$

$\Delta G = ?$

$$dG = \underbrace{\left(\frac{\partial G}{\partial p}\right)_T}_{V} dp + \underbrace{\left(\frac{\partial G}{\partial T}\right)_p}_{-S} dT$$

$T = const$

$$dG = V dp = G_2 - G_1 = \int_{p_1}^{p_2} V dp = nRT \int_{p_1}^{p_2} \frac{1}{p} dp = nRT \ln \frac{p_2}{p_1}$$

$$\Rightarrow \Delta G = nRT \ln \frac{p_2}{p_1} = nRT \ln\left(\frac{nRT \cdot V_1}{V_2 \cdot nRT}\right) = nRT \ln\left(\frac{V_1}{V_2}\right)$$

$$\Delta G = 3 \cdot 10^{-3}\,mol \cdot 8.314\,J\,K^{-1}\,mol^{-1} \cdot 300\,K \cdot \underbrace{\ln\left(\frac{36}{60}\right)}_{-0.5108} =$$

$$= -3.82\,J$$

A 8.4:

$H_2O(l) \rightarrow H_2O(g)$ $\quad T = 25\,°C; \; p = 0{,}1\,MPa$

$$\Delta\mu = \Delta G_m = \Delta G^{\ominus}_{B,m}(H_2O, g) - \Delta G^{\ominus}_{B,m}(H_2O, l) =$$

$$= -(228.57 - 237.13)\ kJ\,mol^{-1} =$$

$$= +8.56\ kJ\,mol^{-1}$$

$H_2O(g)$ hat ein höheres chem. Potential als Wasser

$\Rightarrow$ Wasserdampf ist chemisch reaktiver als $H_2O(l)$!

~~$\mu^{\ominus}(H_2O, g) = G^{\ominus}_{B,m}$~~

$$\mu = \mu^{\ominus} + RT \ln \frac{p}{p^{\ominus}} \Rightarrow \Delta\mu = \mu - \mu^{\ominus} = RT \ln \frac{p}{p^{\ominus}} =$$

$$= 2.48\ kJ\,mol^{-1} \cdot \ln 10 =$$

$$= 2.48 \cdot 2.3026\ kJ\,mol^{-1}$$

$$= 5.71\ kJ\,mol^{-1}$$

bei Druckerhöhung wird Wasserdampf noch reaktiver