Übungsaufgaben VIII, von 12.06.2001

Musterlösungen

1.

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

$$\left(p + \frac{a}{V^2}\right)\cdot(V-b) = R\cdot T$$

$$\Rightarrow p = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\Rightarrow \left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V-b} = \left(\frac{\partial S}{\partial V}\right)_T ; \quad \text{für ein reales Gas}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial}{\partial T}\left(\frac{RT}{V}\right)\right)_V = \frac{R}{V}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{R}{V} ; \quad \text{für ein ideales Gas}$$

da $b \geq 0$

$$\frac{R}{V} \geq \frac{R}{V-b}$$

größere Entropieänderung bei realen Gas

2.

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,p} ;\text{Definition}$$

Für eine reine Substanz ist $G = n \cdot G_m$

$$\rightarrow \mu = \left(\frac{\partial n G_m}{\partial n}\right)_{T,p} = G_m$$

Es gilt: $dG = -S \cdot dT + V \cdot dp$

Für konstante Temperatur $\rightarrow$ $dT=0$

$$\rightarrow \qquad \Delta G = \int_{p_1}^{p_2} V \cdot dp$$

$$\text{ideales Gas} \rightarrow \Delta G = \int_{p_1}^{p_2} \frac{n \cdot R \cdot T}{p} \cdot dp = n \cdot R \cdot T \cdot \ln\left(\frac{p_2}{p_1}\right)$$

$$\Delta G_m = R \cdot T \cdot \ln\left(\frac{p_2}{p_1}\right)$$

$\rightarrow$ Änderung von μ bei Druckerhöhung + konstante Temperatur

$$\Delta\mu = \Delta G_m = R \cdot T \cdot \ln\left(\frac{p_2}{p_1}\right)$$

$$\Rightarrow \Delta\mu = 8.314 \cdot \tfrac{J}{K \cdot mol} \cdot 478.15 \cdot K \cdot \ln\left(\frac{85\ kPa}{45\ kPa}\right)$$

$$= 2.528 kJ / mol$$

3.

Wenn Reaktionen addiert werden, werden die Gleichgewichtskonstanten multipliziert.

$Fe_2O_3(s) + 3CO(g) = 2Fe(s) + 3CO_2(g)$ $\quad K = 0{,}0467$

=> $2Fe_2O_3(s) + 6CO(g) = 4Fe(s) + 6CO_2(g)$ (1) $K = (0{,}0467)^2 = 2{,}19 \times 10^{-3}$

$2CO_2(g) = 2CO(g) + O_2(g)$ $\quad K = 1{,}4 \times 10^{-12}$

=> $6CO_2(g) = 6CO(g) + 3O_2(g)$ (2) $K = (1{,}4 \times 10^{-12})^3 = 2{,}74 \times 10^{-36}$

(1) + (2) => $2\ Fe_2O_3(s) = 4Fe(s) + 3O_2(g)$ => $K = (2{,}19 \times 10^{-3})\ (2{,}74 \times 10^{-36})$

$$K = 6{,}01 \times 10^{-39} = \left(\frac{P_{O_2}}{P}\right)^3 \Rightarrow P_{O_2} = 1{,}82 \times 10^{-13}\ \text{bar}$$

4.

$$\text{a)}\ G = \underset{i}{} n_i \mu_i$$

$$G_A = 2mol \times \left(\mu_{H_2} + RT\ln 2\right) + 4mol \times \left(\mu_{N_2} + RT\ln 3\right)$$

$$G_E = 2mol \times \left(\mu_{H_2} + RT\ln\frac{p_{H_2}}{p}\right) + 4mol \times \left(\mu_{N_2} + RT\ln\frac{p_{N_2}}{p}\right)$$

$$\text{Gesamtvolumen: } V = V_{H_2} + V_{N_2} = \frac{2mol \times RT}{2atm} + \frac{4mol \times RT}{3atm} = \frac{7}{3}RT$$

$$\text{Partielle Drücke: } p_{H_2} = \frac{n_{H_2}RT}{V} = \frac{2RT}{\frac{7}{3}RT} = 0{,}86\,atm$$

$$p_{N_2} = \frac{n_{N_2}RT}{V} = \frac{4RT}{\frac{7}{3}RT} = 1{,}71\,atm$$

$$G_E - G_A = \Delta G_M = -3{,}94RT$$

$$\text{b) Maxwell Relation: } \left(\frac{\partial G}{\partial T}\right)_{p,n} = -S \Rightarrow \Delta S_M = -\left(\frac{\partial \Delta G_M}{\partial T}\right)_{p,n_{H_2},n_{N_2}} = -\frac{\partial}{\partial T}(-3{,}94RT)$$

$$\Delta S_M = 3{,}94R = 32{,}7JK^{-1}$$

$$\text{c)}\ \Delta G_M = -3{,}94RT = -9{,}8\ kJ$$