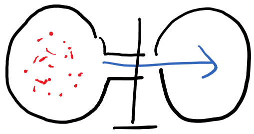
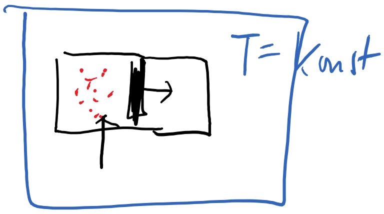
Irreversible Prozesse



$\Delta T = 0 \rightarrow \Delta U = 0$

$\Delta Q = 0 \rightarrow \cancel{\Delta S = \frac{\Delta Q}{T} = 0}$ da irreversibel!

Rev. Ersatz-Prozess



$$\Delta Q_{rev} = n \cdot R \cdot T \cdot \ln\left(\frac{V_2}{V_1}\right)$$

$$\hookrightarrow \Delta S_S = n \cdot R \cdot \ln\left(\frac{V_2}{V_1}\right) > 0$$

reversibel $\Delta S_R = - n \cdot R \cdot \ln\left(\frac{V_2}{V_1}\right)$

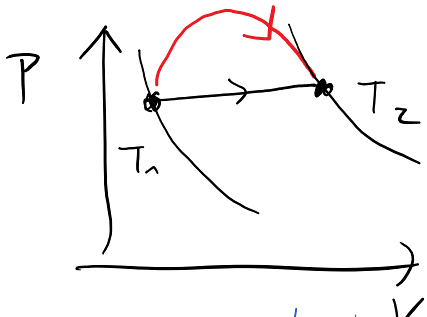
$$\boxed{\Delta S_G = \Delta S_S + \Delta S_R = 0}$$ reversibler Ersatzprozess

irrev. Prozess (Joule Exp)

$\Delta Q = 0, \Delta W = 0 \rightarrow \Delta S_R = 0$

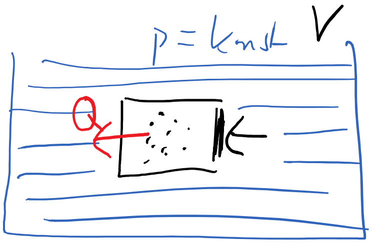
$$\boxed{\Delta S_G = \Delta S_S > 0}$$

2) Isobare (Erwärmung von T_1 nach T_2 bei konst. Druck



irreversibler Prozess

ΔS?



$$dQ_{rev} = n \cdot c_p \cdot dT$$

$$dS = \frac{dQ_{rev}}{T}$$

$$\Delta S = \int_{T_1}^{T_2} \frac{dQ_{rev}}{T} = n \int_{T_1}^{T_2} \frac{c_p}{T} \, dT$$

$c_p \neq f(T) \Rightarrow$ $$\boxed{\Delta S = n \cdot c_p \ln\left(\frac{T_2}{T_1}\right)}$$

T_1 T_1

$$c_p \neq f(T) \quad \Rightarrow \quad \boxed{\Delta S = n \cdot c_p \ln\left(\frac{T_2}{T_1}\right)}$$

Reaktions-Entropie

Gleiche Definition wie $\Delta_r U$, $\Delta_r H$:

$$\Delta_r S = \sum_i \nu_i S_i$$

S_i = Standard-Entropien der Stoffe

<u>T-Abhängigkeit von $\Delta_r S$</u>

$$\Delta_r S(T) = \Delta_r S(T_S) + \int_{T_S}^{T} \frac{\Delta C_p}{T} dT$$

$$\Delta C_p = \sum_i \nu_i C_p^i$$

falls näherungsweise $\Delta C_p \neq f(T)$

$$\Delta_r S(T) = \Delta_r S(T_S) + \Delta C_p \cdot \ln\left(\frac{T}{T_S}\right)$$

Beispiele

1) $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O$

S_i: $131 + 205 \quad 70 \quad \frac{J}{K\,mol}$ bei 298K

$$\Delta_r S = -131 - \frac{1}{2} \cdot 205 + 70 = -163.5 \frac{J}{K\,mol}$$

H_i: $0 \quad 0 \quad -286$

$$\Delta_r H = -286 \frac{kJ}{mol}$$

2) $H_2(g) \xrightarrow{1000K} 2H(g)$

S: $131 \quad 115 \quad \frac{J}{K\,mol}$ bei 298K

$$\Delta_r S(298) = 2 \cdot 115 - 131 = 99 \frac{J}{mol\,K}$$

$$\Delta_r S(1000K) = \Delta_r S(298) + \Delta c_p \cdot \ln\left(\frac{1000}{298}\right)$$

$$c_p(H_2) = 28.8 \frac{J}{K\,mol} \quad c_p(H) = 20.8 \frac{J}{mol\,K}$$

$$\Delta_r S(1000K) = 114 \frac{J}{K\,mol} \quad \left\{ \text{exp: } 113.5 \frac{J}{K\,mol} \right\}$$

Phasenübergänge $I \to II$ reversibel bei $T = T_p$

$T = T_p \qquad \Delta Q_{rev} = \Delta_p H$

$$\Delta_p S = \int_I^{II} \frac{dQ_{rev}}{T_p} = \frac{1}{T_p}\int_I^{II} dQ_{rev} = \frac{1}{T_p}\Delta_p H$$

Beispiel: H_2O 273K

$$\Delta_m H = 6\,\frac{kJ}{mol} \longrightarrow \Delta_m S = \frac{6}{273}\,\frac{kJ}{mol\,K}$$

Beispiel: Kristallisation von unterkühltem Wasser (−10°C)

Reversibel nur bei $T_m = 273\,K$

① Erwärme Flüssigkeit von 263K → 273K $\quad \Delta_1 S = \int_{263}^{273} \frac{C_p(l)}{T}\,dT$

② Phasenübergang $l \to s$ (273K) $\quad \Delta_2 S = \frac{-\Delta_m H}{T}$

③ Abkühlen von Festsoff von 273–263K $\quad \Delta_3 S = \int_{273}^{263} \frac{C_p(s)}{T}\,dT$

$$C_p(l) = 75.3\,\frac{J}{K\,mol} \qquad C_p(s) = 35.9\,\frac{J}{K\,mol}$$

$$\Delta_m H = \frac{6\,kJ}{mol} \qquad \Delta C_p = C_p(l) - C_p(s)$$

$$\Delta S_{Wasser} = \Delta C_p \cdot \ln\left(\frac{273}{263}\right) - \frac{\Delta_m H}{273\,K} = -20.5\,\frac{J}{K}$$

$$\Delta S_{Reservoir} = \frac{\Delta Q}{263\,K} = -\frac{\Delta_m H(263\,K)}{263\,K}$$

$$\Delta_m H(263\,K) = \Delta_m H(273\,K) + \Delta C_p \cdot \Delta T$$

$$\Delta_m H(263K) = \Delta_m H(273K) + \Delta C_p \cdot \Delta T$$

$$\Delta S_{Reservoir} = +21.3 \frac{J}{K}$$

$$\Delta S_{Gesamt} = \Delta S_{Wasser} + \Delta S_{Reservoir} = +0.8 \frac{J}{K}$$