PC III   1.7.13

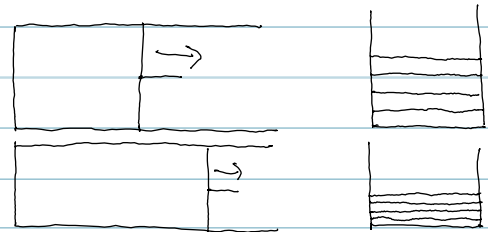## 8.4 Wärme und Arbeit

$$U = \langle E \rangle = \sum_j E_j(N,V) \cdot p_j(N,V,T)$$

$$dU = \sum_j d\left[E_j(N,V)\, p_j(N,V,T)\right]$$

$$= \sum_j E_j\, dp_j + \sum_j p_j\, dE_j$$

$$= \sum_j E_j\, dp_j + \sum_j p_j\left(\frac{\partial E_j}{\partial V}\right)_N dV$$

makroskopische Beschreibung von dU:

$$\boxed{dU = dq_{rev} + dw_{rev}}$$

$$dw_{rev} = -p\, dV$$

$$dw_{rev} = \sum_j p_j\left(\frac{\partial \bar{E}_j}{\partial V}\right)_N dV$$

reversibel ausgetauschte Arbeit resultiert aus einer
infinitesimalen Änderung der Energien des Systems

$$p = -\sum_j p_j\left(\frac{\partial E_j}{\partial V}\right)_N$$

$$p = -\left\langle \left(\frac{\partial E}{\partial V}\right)_N \right\rangle$$

$$\boxed{dq_{rev} = \sum E_j\, dp_j}$$

reversibel ausgetauschte Wärme resultiert aus einer
Änderung der Wahrscheinlichkeitsverteilung der Zustände des
Systems

8.5 Druck

$$\langle p \rangle = \sum_j P_j (N, V, T) \; p_j (N, V) = \sum_j P_j \left(-\frac{\partial E}{\partial V} \right)_N = -\sum_j \left(\frac{\partial E_j}{\partial V} \right)_N \frac{e^{-E_j/kT}}{Q}$$

Druck in Abhängigkeit von der Zustandssumme!

$$\left(\frac{\partial Q}{\partial V} \right)_{N,T} = -\frac{1}{kT} \sum_j \left(\frac{\partial E_j}{\partial V} \right)_N e^{-E_j/kT}$$

$$\frac{1}{Q} \left(\frac{\partial Q}{\partial V} \right)_{N,T} = \left(\frac{\partial \ln Q}{\partial V} \right)_{N,T} = -\frac{1}{kT} \sum_j \left(\frac{\partial E_j}{\partial V} \right)_N \frac{e^{-E_j/kT}}{Q}$$

$$\boxed{\langle p \rangle = kT \left(\frac{\partial \ln Q}{\partial V} \right)_{N,T}}$$ Druck in Abhängigkeit der Zustandssumme

z.B. 1-atomiges ideales Gas

$$Q = \frac{q^N}{N!} \qquad \ln Q = N \ln q - \ln N!$$

$$q = \left(\frac{2\pi m kT}{h^2} \right)^{\frac{3}{2}} V \; g_{e1}$$

$$\ln Q = N \cdot \frac{3}{2} \ln \left(\frac{2\pi m kT}{h^2} \right) + N \ln V + N \ln g_{e1} - \ln N!$$

$$\langle p \rangle = kT \frac{1}{V} N = \frac{NkT}{V} = \frac{nRT}{V} = P \quad \underline{\text{ideales Gasgesetz}}$$

Warum ist $\beta = \frac{1}{kT}$?

$$S_{ensemble} = k \ln W = k \ln \frac{A!}{\prod_j a_j} = k \ln A! - k \sum_j \ln a_j!$$

Stirling: $\ln x! \approx x \ln x - x$

$$S_{ensemble} = k \ln A - kA - k \sum_j a_j \ln a_j + k \sum_j a_j \qquad a_j = p_j A$$

$$= k A \ln A - k \sum_j p_j A \ln p_j A$$

$$= k A \ln A - k \sum_j p_j A \ln p_j - k \sum_j p_j A \ln A$$

$$S_{ensemble} = -k \sum_j p_j A \ln p_j$$

$$S_{System} = \frac{S_{ensemble}}{A} = -k \sum_j p_j \ln p_j$$

$$dS = -k \sum_j d(p_j \ln p_j) = -k \sum_j (\ln p_j \, dp_j + dp_j^{\nearrow 0})$$

$$p_j = \frac{e^{-E_j \beta}}{Q}$$

$$= -k \sum_j \ln p_j \, dp_j = -k \sum_j (-E_j \beta - \ln Q) dp_j$$

$$= -k \sum_j -E_j \beta \, dp_j + k \sum_j \ln Q^{\nearrow 0} \, dp_j$$

$$dS = k\beta \underbrace{\sum_j E_j \, dp_j}_{dq_{rev}}$$

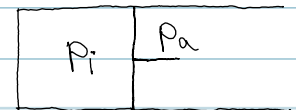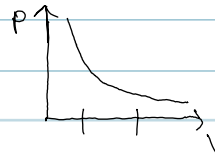$$\underline{dS = k\beta \cdot dq_{rev}} = \frac{dq_{rev}}{T}$$

$$\boxed{\beta = \frac{1}{kT}}$$

isotherme Expansion eines Gases (1-atomig, ideal)

Volumenarbeit
$$W_{rev} = -\int_{V_A}^{V_E} p \, dV = -\int_{V_A}^{V_E} \frac{RnT}{V} \, dV$$

$$= -RnT \int_{V_A}^{V_E} \frac{dV}{V} = -RnT \ln \frac{V_E}{V_A} = -NkT \ln \frac{V_E}{V_A}$$

$$R = k N_L$$
$$n = \frac{N}{N_L}$$

statistisch:
$$W_{rev} = -\int_{V_A}^{V_E} p \, dV = -\int_{V_A}^{V_E} kT \left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} dV = -kT \int_{V_A}^{V_E} \left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} dV$$

$$Q = \frac{q^N}{N!} \qquad \ln Q = N \ln q - \ln N!$$

$$q = \left(\frac{2\pi m kT}{h^2}\right)^{\frac{3}{2}} V \, q_{el} \qquad \left(\frac{\partial \ln Q}{\partial V}\right) = \frac{N}{V}$$

$$W_{rev} = -kT \int_{V_A}^{V_E} \frac{1}{V} \, dV = -NkT \ln \frac{V_E}{V_A}$$

Entropieänderung

isotherm: $dU = 0$

$dq_{rev} = -dw_{rev}$

$$dS = \frac{dq_{rev}}{T} = -\frac{dw_{rev}}{T}$$

$$\Delta S = nR \ln \frac{V_E}{V_A}$$

statistisch:

$$S = kT\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} + k \ln Q \qquad\qquad q = \left(\frac{2\pi m kT}{h^2}\right)^{\frac{3}{2}} V_{ges}$$

$$S_A = kT \frac{3}{2} N \frac{1}{T} + Nk \ln(qV_A)$$

$$S_E = kT \frac{3}{2} N \frac{1}{T} + Nk \ln(qV_E)$$

$$\Delta S = S_E - S_A = Nk \ln\left(\frac{V_E}{V_A}\right)$$

Bsp.: Enthalpie in Abhängigkeit von der Zustandssumme

$$H = U + pV = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} + kT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} \cdot V$$
$$= U + nRT$$

z.B.: 1-atomiges ideales Gas

$$H = kT^2 \frac{3}{2} N \frac{1}{T} + kT \frac{N}{V} V = \frac{3}{2} NkT + NkT = \frac{5}{2} NkT$$

1 Mol: $H_m = \frac{5}{2} RT$