Physikalische Chemie VL 24.05.17

Wdh: Poissonsche Gleichung V,T

adiabat. rev. Exp. eines id. Gases

$dq = 0 \quad \underbrace{dU = dw = -pdV \; ; \; dU = C_V dT}$

$C_V dT = -pdV$

$\boxed{TV^{\gamma-1} = const} \qquad \gamma = \frac{\tilde{C}_p}{\tilde{C}_V}$

Poissonsche Gleichung p,V

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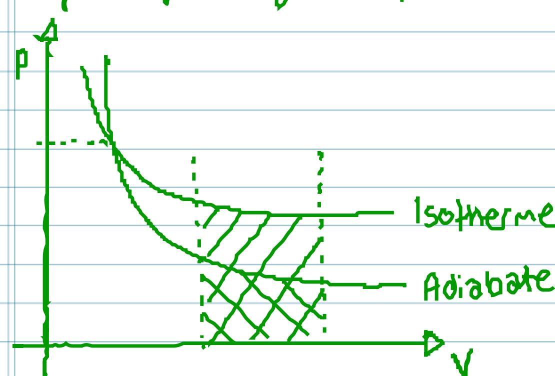
id. Gasges: $T = \frac{pV}{Rn} \rightarrow pV^{\gamma} = const$

$p_1V_1^{\gamma} = p_2V_2^{\gamma}$

$\tilde{C}_p > \tilde{C}_V \rightarrow \gamma = 1$ für alle Gase



→ max. Arbeit bei isoth. rev. Exp
↳ Wärmezufuhr vermindert p-Verlust

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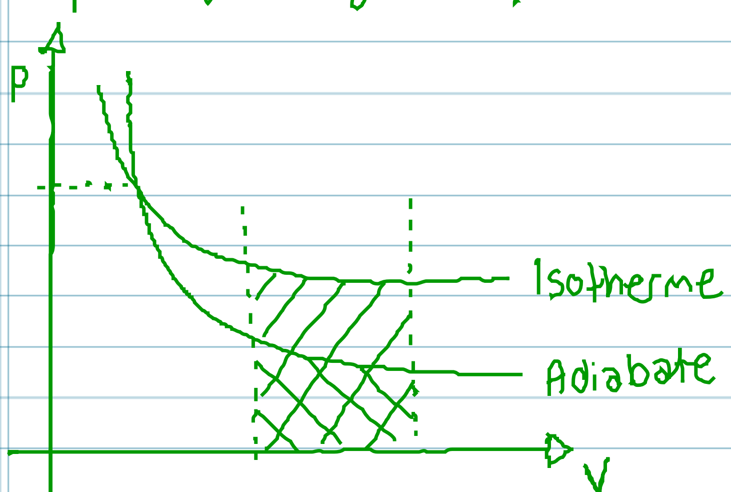

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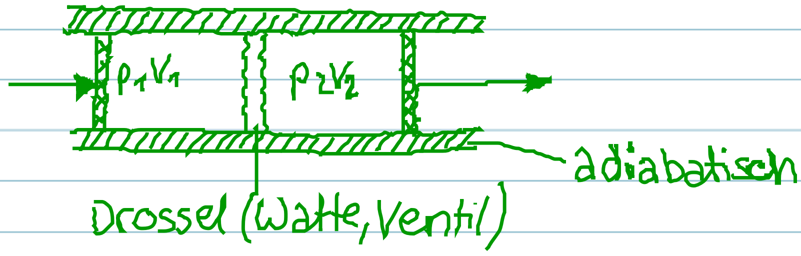
Poissonsche Gl p, T

$pV^\gamma = \text{const}$

id. Gasgesetz: $V = \frac{RnT}{p}$ $\rightarrow$ $\boxed{p^{1-\gamma} \; T^\gamma = \text{const}}$

6.3 Joule-Thomson-Effekt

„Adiabat. Entspannung eines realen Gases beim Durchströmen einer Drossel."



adiabat. $dq = 0$
$\hookrightarrow dU = dw$

$\Delta U = U_2 - U_1 = p_1 V_1 - p_2 V_2$

$$\boxed{U_1 + p_1 V_1 = U_2 + p_2 V_2 = H_2 = H_1}$$

$\hookrightarrow dH = 0$ isenthalpisch

Beobachtung: $T = 300\,K$

fast alle Gase $\rightarrow$ Abkühlung

H_2, He, Ne $\rightarrow$ Erwärmung

charakt. Temp. T_{inv} = Inversionstemp

$T < T_{inv}$: $\frac{dT}{dp} > 0$ Abkühl

$T > T_{inv}$: $\frac{dT}{dp} < 0$ Erwärmung

$\left(\frac{\partial T}{\partial p}\right)_H = \mu$ Joule-Thomson-Koeff.

Anwendung: Gasverflüssigung

Quant. Beschr. Ziel: $\left(\frac{\partial T}{\partial p}\right)_H = ?$

$$dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \underbrace{\left(\frac{\partial H}{\partial T}\right)_p}_{C_p} dT = 0$$

$$C_p dT = -\left(\frac{\partial H}{\partial p}\right)_T dp$$

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{-\left(\frac{\partial H}{\partial p}\right)_T}{C_p} \qquad \left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + V$$ (5. Üb, 3. Aufg)

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{\left(\frac{\partial V}{\partial T}\right)_p T - V}{C_p}$$

a) Id. Gas

$$pV = RnT \rightarrow V = \frac{RnT}{p} \qquad \left(\frac{\partial V}{\partial T}\right)_p = \frac{Rn}{p}$$

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{\frac{Rn}{p} \cdot T - V}{C_p} = 0$$

b) reales Gas

$$p \cdot V = RnT + B(T)\,pn \qquad V = \frac{RnT}{p} + B(T)\,n$$

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{RN}{p} + B'n$$

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{\cancel{\frac{Rn}{p}T} + B'nT - \cancel{\frac{RnT}{p}} - Bn}{C_p}$$

$$\boxed{\left(\frac{\partial T}{\partial p}\right)_H = \frac{(B'T - B)n}{C_p}}$$

V.d.Waals-Gas (kleine Drücke)

$$B = b - \frac{a}{RT} \rightarrow \text{2. Übung}$$

$$B' = \frac{a}{RT^2}$$

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{\left(\frac{a}{RT} - b + \frac{a}{RT}\right) n}{C_p}$$

$$\boxed{\left(\frac{\partial T}{\partial p}\right)_H = \frac{\left(\frac{2a}{RT} - b\right)n}{C_p}}$$

Inv. temp? $\frac{dT}{dp} = 0 \qquad \frac{2a}{RT_{inv}} - b = 0$

$\hookrightarrow T_{inv} = \frac{2a}{bR}$

Bsp: Entspannung von N_2 (id.) um 180 bar
200 bar $\rightarrow$ 20 bar ; $T = 300\,K$

$a = 0{,}137\ Pa\ \frac{m^6}{Mol^2} \qquad b = 3{,}96 \cdot 10^{-5}\ \frac{m^3}{Mol}$

$$\left(\frac{\partial T}{\partial p}\right)_H \approx \frac{\left(\frac{2a}{RT}\right) - b}{\tilde{C}_p}$$

$$\Delta T \approx \Delta p \, \frac{\frac{2a}{RT} - b}{\tilde{c}_p} = 180 \cdot 10^{-5}\ \text{Pa} \ldots / \tfrac{7}{2} R$$

$$\approx 43\ \text{K} \qquad T_{inv} = 832\ \text{K}$$