WdH

∘ ZS für HO

→ WK für Festkörper

$$H = \sum_{i=1}^{f} \frac{p_i^2}{2m} + \frac{1}{2}\, \underline{q}\, \underline{\underline{V}}\, \underline{q} = \sum_{i=1}^{f} \left(\frac{\tilde{p}_i^2}{2m} + \frac{1}{2} m \Omega_i^2 \tilde{q}_i^2 \right)$$

$$C_V = \sum_{i=1}^{f} C_V^{(i)}(\beta_i \Omega_i) = n \cdot C_V^{mol}$$

$\beta \cdot \Omega_i >> 1$ (tiefe T) ⇝ i-ter Osz. trägt nicht bei

$\beta \cdot \Omega_i << 1$ (hohe T) ⇝ Osz. trägt bei

$$\xrightarrow{T \to \infty} 3N \cdot k_B = \frac{R \cdot f}{R} k_B T$$

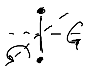
∘ WK mehratomiger idealer Gase

→ Freiheitsgrade zählen: Translation der Moleküle, Rotation ", Vibration "

2-atomiges Gas

$$C_V^{mol} \to \frac{3}{2} R \longrightarrow \frac{5}{2} R \longrightarrow \frac{7}{2} R$$

(nur Translation) (Translation + Rotation) (Transl., Rot., Vibr.)



∘ reale Gase

$$Z_C = \frac{1}{N!} \int e^{-\beta(H_{kin} + H_{pot})} \prod_{i=1}^{f} \frac{dq_i\, dp_i}{h} = Z_{kin}(\beta) \cdot Z_{pot}(\beta, V)$$

$$\boxed{p = \frac{1}{\beta} \partial_V \ln Z_C}$$

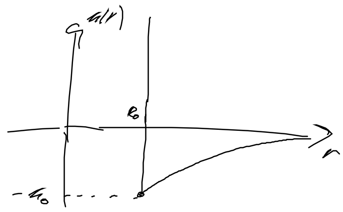
$$\boxed{\begin{aligned} \beta \cdot p &= \frac{N}{V} + C_2(\beta) \left(\frac{N}{V}\right)^2 + \dots \quad \text{WW-Potential} \\ C_2(\beta) &= -\frac{1}{2} \int_0^\infty 4\pi r^2 \left(e^{-\beta u(r)} - 1\right) dr \end{aligned}}$$

Virialgleichung

2.3.7. Van-der Waals Gleichung

Beispiel

$$u(r) = \begin{cases} \infty & r < R_0 \\ -u_0 \left(\frac{R_0}{r}\right)^6 & r > R_0 \end{cases}$$



=> Werte $C_2(\beta)$ aus

$$C_2(\beta) = \frac{1}{2}\cdot\frac{4\pi}{3}R_0^3 - \frac{1}{2}\int_{R_0}^{\infty}\underbrace{\left(e^{-\beta\cdot u(r)}-1\right)}_{\approx -\beta\cdot u(r)\ \text{(hohe Temp.)}}\cdot 4\pi r^2\,dr = \frac{2\pi}{3}R_0^3\left[1-\beta\cdot u_0\right]$$

~> in die ZGL eins.

$N\cdot R_0^3 \ll V$ $\qquad$ $\frac{1}{1-x}\overset{x\ll 1}{\approx} 1+x$

$$\beta\left(P+\frac{2\pi}{3}R_0^3\cdot u_0\frac{N^2}{V^2}\right) = \frac{N}{V}\left[1+\frac{2\pi}{3}R_0^3\left(\frac{N}{V}\right)\right] \simeq \frac{N/V}{1-\frac{2\pi}{3}R_0^3\frac{N}{V}}$$

$$\boxed{\left(P+\underbrace{\frac{2\pi}{3}R_0^3 u_0}_{a=b\cdot u_0}\cdot\frac{N^2}{V^2}\right)\left(V-N\cdot\underbrace{\frac{2\pi}{3}R_0^3}_{b}\right) = N\cdot k_B T}$$

Binnendruck
Kohäsionsdruck

Kovolumen

van-der Waals-Gleichung

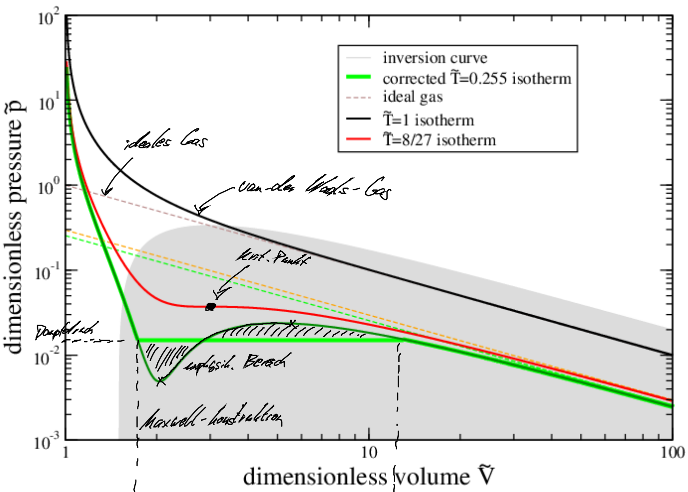
- ideales Gas: $a=0$ & $b=0$
- a & b werden gemessen

$\tilde T = \frac{a}{b}\cdot k_B T \qquad \tilde p = \frac{b^2}{a}p \qquad \tilde V = \frac{V}{N b}$ ~> dimensionslos

~> $$\boxed{\left(\tilde p+\frac{1}{\tilde V^2}\right)\left(\tilde V-1\right) = \tilde T}$$

dim.lose Gleichung

~> nach $\tilde p(\tilde V)$ auflösen



- löse $\left(\frac{\partial p}{\partial V}\right)_T = 0$ & $\left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0$

~> $\tilde T_c = \frac{8}{27}$

$\tilde V_c = 3$

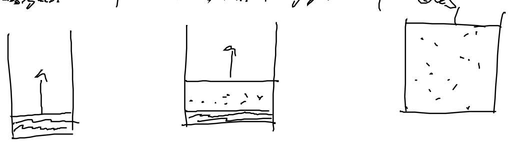
$\tilde p_c = \frac{1}{27}$

$\tilde V \gg 1$

$\tilde T \gg 1$

Konflikt

Flüssigkeit $\qquad$ koexistenz flüssig-gasf. $\qquad$ Gas



Energie & Entropie

~> $u = -\partial_\beta \ln Z_c$ $\longrightarrow u = \frac{3N}{2}k_B T - \frac{N^2}{V}\cdot\underbrace{\frac{2\pi}{3}\cdot R_0^3 u_0}_{a}$ ~> Absenkung d. inn. Energie

experimentell: a & b gemessen
$C_V(T)$ gemessen
$\supset p(T,V)$

$\Big\} \longrightarrow \underline{u(T,V)}$ geht auch abzulesen

$$\begin{array}{ccc} -S & u & V \\ H & & \boxed{F} \\ -p & G & T \end{array}$$

$dF = -S\cdot dT - p\cdot dV \qquad (dN=0)$

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

$\rightsquigarrow$ gemischte Ableitungen

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \text{"Maxwell-Relation"}$$

$$dU = T\,dS - p\,dV \qquad (dN = 0)$$

$$\Rightarrow \left(\frac{\partial U}{\partial T}\right)_V \cdot dT + \left(\frac{\partial U}{\partial V}\right)_T \cdot dV = T\left(\left(\frac{\partial S}{\partial T}\right)_V \cdot dT + \left(\frac{\partial S}{\partial V}\right)_T dV\right) - p \cdot dV$$

$$\Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P = T\cdot\left(\frac{\partial P}{\partial T}\right)_V - P \qquad P(T,V) \text{ ist bekannt}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = n \cdot C_V^{mol}$$

$$dU = n \cdot C_V^{mol} \cdot dT + \left[T \cdot \left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$$

brauchen $p(T,V)$ + $C_V^{mol}(T)$ $\rightsquigarrow$ $U(T,V)$

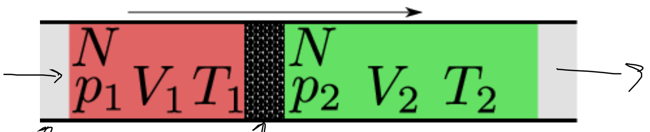
$$U = n \cdot C_V^{mol}(T - T_0) - \frac{a \cdot N^2}{V} + \frac{a N^2}{V_0}$$

Entropie: geht analog

Joule-Thomson Effekt

Lord Kelvin

- reales (van-der-Waals)-Gas zeigt Abkühlung beim Gay-Lussac Exp.
- technische Abkühlung realer Gase: Joule-Thomson-Prozess



Rohr

poröse Platte

Druckminderung $p_2 < p_1$

Frage: ist $T_2 < T_1$?

Antwort: hängt davon ab

Idealisiert: • Arbeit $\Delta W = \int_{V_1}^{0} p_1 \cdot dV + \int_{0}^{V_2} p_2 \cdot dV = p_2 \cdot V_2 - p_1 \cdot V_1$

• ad. abgeschl. $\Delta Q = 0$

$$0 = \Delta Q = \Delta U + \Delta W = U(T_2, V_2) - U(T_1, V_1) + p_2 V_2 - p_1 \cdot V_1 = 0$$

$\rightsquigarrow$ Enthalpie ist konstant $\quad U(T_1, V_1) + p_1 \cdot V_1 = U(T_2, V_2) + p_2 \cdot V_2$

$$\begin{matrix} -S & U & V \\ \boxed{H} & & F \\ -p & G & T \end{matrix}$$

$$0 = dH = T\,dS + V\,dp \qquad S(T,p)$$

$$= T\left(\left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp\right) + V\,dp$$

$$\rightsquigarrow \left(\frac{\partial T}{\partial p}\right)_H = -\frac{\left(\frac{\partial S}{\partial p}\right)_T + V}{T\left(\frac{\partial S}{\partial T}\right)_p} = \ldots = \boxed{\text{Joule-Thomson-Koeffiz.} \quad \mu = \frac{V}{C_p}\left(\alpha \cdot T - 1\right)}$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

- falls $\mu > 0$: $p_2 < p_1 \rightsquigarrow T_2 < T_1$
- falls $\mu < 0$: $p_2 < p_1 \rightsquigarrow T_2 > T_1$

Test: id. Gas: $V = \frac{N k_B T}{p}$

$$\alpha_{id} = \frac{N k_B}{p \cdot V} \rightsquigarrow \alpha_{id} \cdot T = 1$$

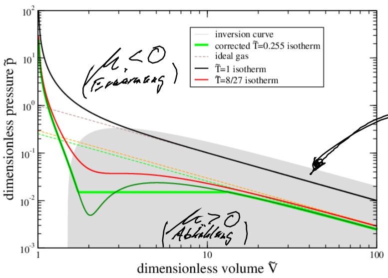
$$\rightsquigarrow \mu_{id} = 0$$

$\rightsquigarrow$ Best. von α über Ableitung der ZS

$$\left(\frac{\partial}{\partial T}\right)_p$$

$$T \cdot \alpha \left[p \cdot V - a\frac{N^2}{V^2}(V - 2 \cdot Nb)\right] = N \cdot k_B \cdot T = \left(p + a\frac{N^2}{V^2}\right)(V - Nb)$$

best. Kurve für welche $T \cdot \alpha = 1$



Inversionskurve

- Luft lässt sich kühlen
- He muss vorgekühlt werden

Abgabe Lehr-evaluation + entweder gleich hier
+ oder Fr. Klenz