Kirchhoff Satz

$$\Delta_r H = \left(\frac{\partial H}{\partial \xi}\right)_{T,p}$$

$$\left(\frac{\partial \Delta_r H}{\partial T}\right)_p = \left(\frac{\partial \left(\frac{\partial H}{\partial \xi}\right)_{T,p}}{\partial T}\right)_p = \left(\frac{\partial^2 H}{\partial \xi \, \partial T}\right)_p$$

$$= \left(\frac{\partial^2 H}{\partial T \, \partial \xi}\right)_p = \left(\frac{\partial \left(\frac{\partial H}{\partial T}\right)_p}{\partial \xi}\right)_T = \left(\frac{\partial C_p}{\partial \xi}\right)_{p,T} = \Delta_r C_p$$

$$\Delta_r C_p \qquad \Delta_r C_p = \sum_i \nu_i C_{p_i}$$

$\int$:

$$d\Delta_r H = \Delta_r C_p \cdot dT$$

$$\int_{\Delta_r H(T_0)}^{\Delta_r H(T_1)} d\Delta_r H = \int_{T_0}^{T_1} \Delta_r C_p \cdot dT$$

$\Delta_r C_p \neq f(T)$

$$\Delta_r H(T_1) - \Delta_r H(T_0) = \Delta_r C_p \cdot (T_1 - T_0)$$

T_0: Standard-Temperatur

$$\Delta_r H(T) = \underbrace{\Delta_r H(T_0)}_{\text{Bekannt}} + \Delta_r C_p (T - T_0)$$

(Kirchhoff'scher Satz)

Annahme: $\Delta_r C_p \neq f(T)$ i. A. oft erfüllt

Beispiel: $\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \longrightarrow \underbrace{NH_3(g)}$

o o

$\Delta_r H = -46.1 \frac{kJ}{mol}$

$$\Delta C_p = \sum_i \nu_i C_{p_i} = C_p(NH_3) - \frac{1}{2} C_p(N_2) - \frac{3}{2} C_p(H_2)$$

$$35 \frac{J}{K\,mol} - \frac{1}{2} 29.1 \frac{J}{K\,mol} - \frac{3}{2} \cdot 28{,}8 \frac{J}{K\,mol}$$

$$= \underline{-22.75} \frac{J}{K\,mol}$$

$$\rightarrow C_p = a + bT + \frac{c}{T^2}$$

$$C_p = A + BT + CT^2 + DT^3$$

$$C_p(NH_3) = \underset{a}{29.75} \frac{J}{K\,mol} + \underset{b}{25.1} \cdot 10^{-3} \frac{J}{K^2 mol} \cdot T - \underset{c}{1.55} \cdot 10^{-5} \frac{JK}{mol} \cdot \frac{1}{T^2}$$

$$A = 29.29 \frac{J}{K\,mol}$$

$$B = 0.011 \frac{J}{K^2 mol} \cancel{(T)}$$

$$C = 4.24 \cdot 10^{-5} \frac{J}{K^3 mol} \cdot \cancel{(-T^2)}$$

$$D = -2.77 \cdot 10^{-8} \frac{J}{K^4 mol}$$

Totale Differential dV

$$dH = \left(\frac{\partial H}{\partial p}\right)_{T,\xi} + \left(\frac{\partial H}{\partial T}\right)_{p,\xi} + \left(\frac{\partial H}{\partial \xi}\right)_{p,T}$$

$$(p,V,) \quad (p,T) \quad (V,T)$$

$$\boxed{dV = \underbrace{\left(\frac{\partial V}{\partial T}\right)_p}_{} dT + \underbrace{\left(\frac{\partial V}{\partial p}\right)_T}_{} dp}$$

$$\boxed{\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p} \qquad \boxed{\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T}$$

Thermische Ausdehnungskoeffizient — Kompressibilitäts-Koeffizient

$f(\alpha,\kappa) = ?$ $\quad \beta = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V$ Spannungskoeffizient

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

falls $dz = 0$

$$0 = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$\boxed{\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x}$$

$$x, y, z \longleftrightarrow p, T, V$$

$$\boxed{\left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_p \cdot \left(\frac{\partial p}{\partial V}\right)_T}$$

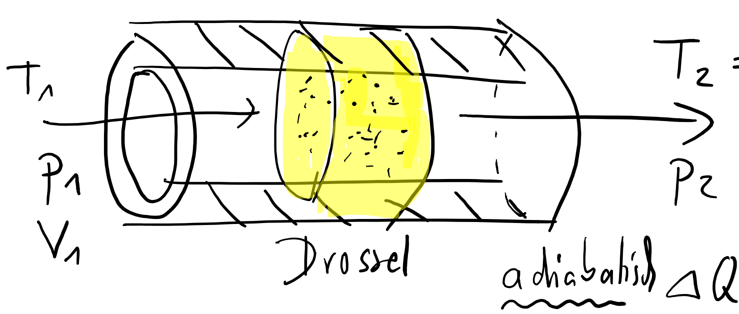
$$\underbrace{\partial T\Big)_V \qquad \partial T\Big)_p}$$

$$\beta \cdot p = -\frac{1}{V}(V\cdot\alpha) - \frac{1}{VK}$$

$$\hookrightarrow \boxed{K = \frac{1}{p}\cdot\frac{\alpha}{\beta}} \qquad \alpha,\beta \rightarrow K$$

	$\alpha\,[10^{-4}\,K^{-1}]$	$K\,[10^{-6}\,\frac{1}{bar}]$
Benzol	12.4	90.9
Wasser	2.1	49
Quecksilber	1.82	38.2
Diamant	0.030	0.185

Joule Thomson Effekt



$T_2 = ?$ $\boxed{T_2 \neq T_1}$ im Allgemeinen

$p_1 > p_2$

adiabatisch $\Delta Q = 0$ $W = -p \cdot V$

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

$$\underbrace{U_1 + p_1 \cdot V_1}_{H_1} = \underbrace{U_2 + p_2 V_2}_{H_2} \qquad \Delta H = 0$$

isenthalpisch
$\Delta H = 0$

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

isothermer Drosseleffekt

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

$$-\left(\frac{\partial H}{\partial T}\right)_p \cdot \left(\frac{\partial T}{\partial p}\right)_H = \left(\frac{\partial H}{\partial p}\right)_T$$

$$\boxed{\mu = \left(\frac{\partial T}{\partial p}\right)_H = \frac{-\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p} = -\frac{\epsilon}{C_{pK}}}$$

ideales Gas: $V = \frac{R \cdot T}{p}$, $\left(\frac{\partial H}{\partial p}\right)_T = 0$

$\hookrightarrow \mu = 0$

reales Gas (van der Waals)

$$\boxed{\mu = \frac{\frac{2a}{RT} - b}{C_p}}$$

T-abhängig!

a, b van der Waals-Parameter

$\mu = 0 \rightarrow$ keine T-Änderung bei Expans.

$$0 = \frac{\frac{2a}{RT_I} - b}{C_p}$$

$\boxed{T_I : \text{Inversions-Temperatur}}$

$$\frac{2a}{RT_I} = b$$

$$\boxed{T_I = \frac{2a}{Rb}}$$

Beispiele:

H_2 : $a = 0.2509 \, \frac{\ell^2 \, \text{bar}}{\text{mol}}$

$b = 2.661 \cdot 10^{-2} \, \frac{\ell}{\text{mol}}$

$\boxed{T_I = 227 K}$

$T = 300K \rightarrow H_2$ erwärmt sich

$T = 200K \rightarrow H_2$ abkühlen

$T_{exp} = 202K$

He : $\left.\begin{array}{l} a = 0.03503 \\ b = 2.37 \end{array}\right\}$ $T_I = 36K$

$T_{exp} = 40K$

CO_2 : $\underline{T_I = 1500K}$

Linde Verfahren

Carl Paul Gottfried Linde
(1842-1934)

Studium an Polytechnikum Zürich
Nach Studentenprotest zwangsexmatrikuliert
Ruf mit 26 Jahren an Polytechnische Schule München
Mit 37 Jahren Linde's Eismaschinen AG
Mit 55 Jahren in den Adelstand erhoben (Ritter von Linde)

Kältetechnikverfahren
Verflüssigung und Trennung von Luft
Erster Kühlschrank