1a) Wärme-Ü 4

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$$dp = \left(\frac{\partial p}{\partial T}\right)_S dT + \left(\frac{\partial p}{\partial S}\right)_T dS$$

$$T(p,V) \Rightarrow dT = \left(\frac{\partial T}{\partial p}\right)_V dp + \left(\frac{\partial T}{\partial V}\right)_p dV$$

$$S(T,V) = S(T(p,V),V) =$$

$$= S(p,V) \Rightarrow dS = \left(\frac{\partial S}{\partial p}\right)_V dp + \left(\frac{\partial S}{\partial V}\right)_p dV$$

$\Rightarrow$

$$\frac{dp}{dp} = 1 = \left(\frac{\partial p}{\partial T}\right)_S \left\{\left(\frac{\partial T}{\partial p}\right)_V \frac{dp}{dp} + \left(\frac{\partial T}{\partial V}\right)_p \frac{dV}{dp}\right\} + \left(\frac{\partial p}{\partial S}\right)_T \left\{\left(\frac{\partial S}{\partial p}\right)_V \frac{dp}{dp} + \left(\frac{\partial S}{\partial V}\right)_V \frac{dV}{dp}\right\}$$

$$= \left\{\underbrace{\left(\frac{\partial p}{\partial T}\right)_S \left(\frac{\partial T}{\partial V}\right)_p + \left(\frac{\partial p}{\partial S}\right)_T \left(\frac{\partial S}{\partial V}\right)_p}_{=0\ \boxed{\text{Maxwell}}}\right\} \frac{dV}{dp} + \left(\frac{\partial p}{\partial T}\right)_S \underbrace{\left(\frac{\partial T}{\partial p}\right)_V}_{\substack{\text{Maxwell} \\ = \left(\frac{\partial V}{\partial S}\right)_T \\ F}} + \left(\frac{\partial p}{\partial S}\right)_T \underbrace{\left(\frac{\partial S}{\partial p}\right)_V}_{\substack{= -\left(\frac{\partial V}{\partial T}\right)_S \\ U}}$$

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

Schaun an.

1b)

$$W = \iint dp\, dV = \iint \underbrace{\frac{\partial(p,V)}{\partial(T,S)}}_{(a) \Rightarrow 1} \cdot dT\, dS = \iint dT\, dS = Q$$

Also sind die Definitionen äquivalent.

2.) $V = V_1 + V_2$; $dF = -S dT - p dV$; bilde Ableitungen:

$$F(T,V) = F_1(T_1,V_1) + F_2(T_2,V_2) = F_1(T_1,V_1) + F_2(T_2, V-V_1)$$

$$\Rightarrow \frac{\partial F}{\partial V_1} = \frac{\partial F_1}{\partial V_1} + \frac{\partial(V-V_1)}{\partial V_1} \frac{\partial F_2(T_2,V_2)}{\partial V_2} = -(-P_1 - P_2) = 0 \Rightarrow$$

$$\frac{\partial^2 F}{\partial V_1^2} = \frac{\partial P_2}{\partial V_1} - \frac{\partial P_1}{\partial V_1} = -\frac{\partial P_1}{\partial V_1} + \frac{\partial P_2}{\partial V_2}\underbrace{\frac{\partial V_2}{\partial V_1}}_{=-1}$$

$$= -\Big(\underbrace{\frac{\partial P_1}{\partial V_1}}_{<0} + \underbrace{\frac{\partial P_2}{\partial V_2}}_{<0}\Big) => 0$$

Aha.
ist also ein Minimum!

3.) $p = \frac{RT}{V-b} - \frac{a}{V^2}$ $\leadsto p' = \frac{-RT}{(V-b)^2} + \frac{2a}{V^3} \overset{!}{=} 0$
$\leadsto p'' = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4} \overset{!}{=} 0$ } gls...

... $\frac{4a}{V^3(V-b)} = \frac{6a}{V^4} \Rightarrow \frac{2}{V-b} = \frac{3}{V} \Rightarrow \underline{\underline{V_{kr} = 3b}}$, einsetzen in p' ...

... $RT_{kr} = \frac{2a}{27b^3}(2b)^3 = \underline{\underline{\frac{8a}{27b}}}$, einsetzen in p ...

... $p_{kr} = \frac{\frac{8}{27}\frac{a}{b}}{2b} - \frac{a}{9b^2} = \underline{\underline{\frac{a}{27b^2}}}$, alle 3 zusammen:

$$\frac{RT_{kr}}{V_{kr}p_{kr}} = \frac{\frac{8}{27}\frac{a}{b}}{3b\,\frac{a}{27b^2}} = \underline{\frac{8}{3}} \approx 2{,}7$$ Tada!

Experimentell findet man z.B. für

Wasserstoff : $\frac{RT}{Vp} \approx 2{,}6$

Stickstoff : $\approx 2{,}6$

Sauerstoff : $\approx 2{,}7$

sind die Abweichungen nicht größer?

✓

Ulrich