1 22

a) +1P: dE   +1P: δ, nicht d

$$dE = \delta Q + \delta W$$

+1P: Q & W ③

b)

$$dS \geq \frac{\delta Q}{T}$$

+1P: dS   +1P   +1P: δQ nicht dQ   +1P: T^{-1}

$\geq$ nicht >, = ④

c) chemische Arbeit

$$dE = T\,dS \underbrace{- p\,dV}_{\text{mechanische Arbeit}} + \overbrace{\mu\,dN}^{\text{chemische Arbeit}}$$

+1P   +1P   +1P ③

d)

$$F = E - TS$$ ④

$$dF = dE - d(TS) = dE \underbrace{- T\,dS - S\,dT}$$

+1P   +1P   +1P $d(ab) = a\,db + da\,b$

$$= -S\,dT - p\,dV + \mu\,dN$$

+1P

e) Zu zeigen:

$$\left.\frac{\partial E}{\partial V}\right|_{T,N} = T\left.\frac{\partial p}{\partial T}\right|_{V,N} - p$$ ⑧

Für $E(S,V,N)$ gilt:

$$dE = T\,dS - p\,dV + \mu\,dN$$

Für $S(T,V,N)$ gilt:

+1P: $S(T,V,N)$ nötig

kann weggelassen werden

$$dS = \left.\frac{\partial S}{\partial T}\right|_{V,N} dT + \left.\frac{\partial S}{\partial V}\right|_{T,N} dV \left(+ \left.\frac{\partial S}{\partial N}\right|_{T,V} dN \right)$$

+1P: $df(x,y,z) = \partial_x f\,dx + \dots + \partial_z f\,dz$

Daraus folgt für das Differential von $E(T,V,N)$:

+1P: dS in dE einsetzen

$$dE = T \cdot \left.\frac{\partial S}{\partial T}\right|_{V,N} dT + \underbrace{T\left.\frac{\partial S}{\partial V}\right|_{T,N} dV - p\,dV} + T\left.\frac{\partial S}{\partial N}\right|_{T,V} dN + \mu\,dN$$

+1P: dT = 0, dN = 0 setzen

$$\Rightarrow \left.\frac{\partial E}{\partial V}\right|_{T,N} = T\left.\frac{\partial S}{\partial V}\right|_{T,N} - p$$

+1P: dE/dV erhalten

Aus Satz von Schwarz für F folgt.

$$\frac{\partial^2 F}{\partial T \partial V} = \frac{\partial^2 F}{\partial V \partial T}$$

✓ + 1P: Reihenfolge vertauschen

+1P: $p = -\partial_V F$

$$\Rightarrow \quad -\frac{\partial p}{\partial T}\Big|_V = -\frac{\partial S}{\partial V}\Big|_T$$

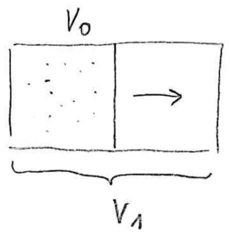
✓ +1P: $S = -\partial_T F$

$$\Rightarrow \quad \boxed{\frac{\partial E}{\partial V}\Big|_{T,N} = \frac{\partial p}{\partial T}\Big|_{V,N} - p}$$

q. e. d.

Kann auch ohne die Berücksichtigung der N-Abhängigkeit durchgerechnet werden.

2



30

(1) Adiabatisch reversibel

(13)

$$\delta Q = 0 \qquad dS = 0 \quad \Rightarrow \quad \boxed{\Delta S = 0}$$ ✓ +1P

$$dE = -p\,dV = -N k_B \frac{T}{V}\,dV$$ ✓ +1P: thermische Zst.Gl. $pV = Nk_BT$ eingesetzt

✓ +1P: dE mit dS=0

$T(V)$ wird aus der folgenden Relation bestimmt:

$$= \begin{cases} dE = -N k_B \frac{T}{V}\,dV \\ dE = \frac{3}{2} N k_B\,dT \end{cases} \Rightarrow \quad -\frac{T}{V}\,dV = \frac{3}{2}\,dT \qquad -\frac{dV}{V} = \frac{3}{2}\frac{dT}{T}$$

+1P: dE thermisch = dE kalorisch ✓

✓ +1P: Diff. von $E = \frac{3}{2}Nk_BT$ aus kalorischer Zst.Gl.

$$\Rightarrow \quad -\ln\frac{V}{V_0} = \frac{3}{2}\ln\frac{T}{T_0} \quad \Rightarrow \quad T(V) = T_0 \cdot \left(\frac{V_0}{V}\right)^{2/3}$$ ✓ +1P: aufgel. nach T(V)

Damit ergibt sich:

$$dE = -N k_B T_0 V_0^{2/3} \frac{1}{V^{5/3}}\,dV$$

alternativ gerechnet: $-\frac{N k_B T_0 V_0^{2/3}}{V^{5/3}}$ ✓ +1P ✓ +2P

$$\Delta E = -N k_B T_0 V_0^{2/3} \int_{V_0}^{V_1} \frac{1}{V^{5/3}}\,dV = \frac{3}{2} N k_B T_0 V_0^{2/3} \left[\frac{1}{V_1^{2/3}} - \frac{1}{V_0^{2/3}}\right]$$ ✓

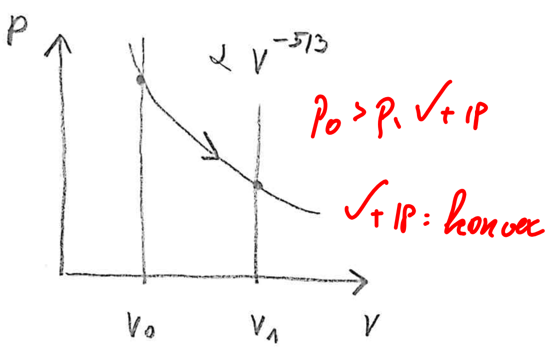
+1P: $\int x^n dx = \frac{1}{n+1} x^{n+1}$

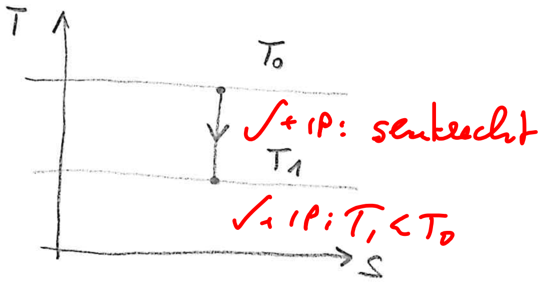
$$= \underbrace{\frac{3}{2} N k_B T_0 \left(\frac{V_0}{V_1}\right)^{2/3}}_{E_1} - \frac{3}{2} N k_B T_0$$

✓ +1P: E_1 identifiziert

$$\Rightarrow \quad \boxed{E_1 = \frac{3}{2} N k_B T_0 \left(\frac{V_0}{V_1}\right)^{2/3}} \qquad \boxed{T_1 = T_0 \left(\frac{V_0}{V_1}\right)^{2/3}}$$

✓ +1P: T_1 aus E_1 ermittelt





② Thermisch isoliert

⑨

$dT = 0 \Rightarrow dE = 0\ , \ \Delta E = 0$ ✓+1P

$\Rightarrow \boxed{E_1 = \frac{3}{2} N k_B T_0}$ $\boxed{T_1 = T_0}$

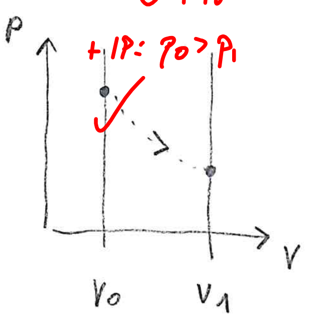
✓+1P: ΔE eingesetzt ✓+1P: T_1 aus E_1

Aus Sackur-Tetrode Gleichung:

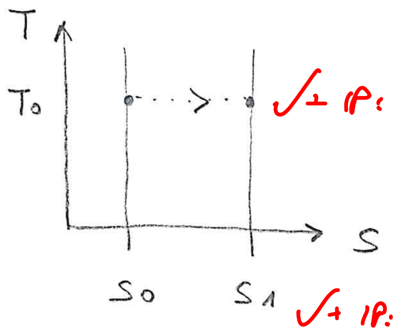
$\boxed{\Delta S = k_B N \left(\ln V_1 - \ln V_0 \right)}$ ✓+1P: aus S.T. oder hergeleitet

Da $\delta Q = 0$ aber $\Delta S > 0 \Rightarrow$ irreversibler Prozess

✓+1P ✓+1P



+1P: $p_0 > p_1$ ✓



✓+1P: horizontal

✓+1P: $S_1 > S_0$

③ Isobar reversibel

⑧ für Fall 3 nicht(c)

$p = N k_B \frac{T_0}{V_0} = N k_B \frac{T_1}{V_1} \Rightarrow \boxed{T_1 = T_0 \cdot \frac{V_1}{V_0}}$

✓+1P: T_1 aus thermischer Gl. $pV = Nk_BT$

$\boxed{E_1 = \frac{3}{2} N k_B T_0 \cdot \frac{V_1}{V_0}}$ ✓+1P: E_1 aus T_1

$$\Delta S = k_B N \left[\ln V_1 - \ln V_0 + \frac{3}{2} \ln \left(\frac{T_1}{T_0} \right) \right] =$$

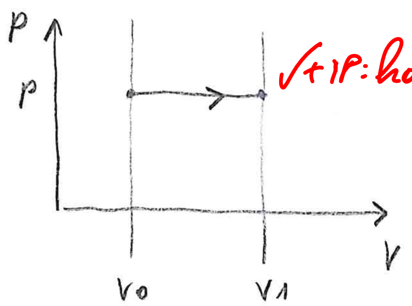
✓+1P: relevante Teile aus S.T.Gl.

$$= k_B N \left[\ln V - \ln V_0 + \frac{3}{2} \ln V_1 - \frac{3}{2} \ln V_0 \right]$$

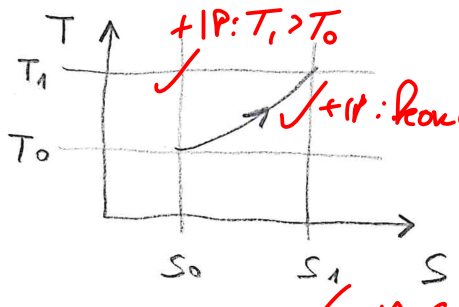
$\Rightarrow$

$\boxed{\Delta S = \frac{5}{2} k_B N \ln \frac{V_1}{V_0} > 0}$ ✓+1P

(trotzdem reversibel, da $\Delta Q > 0$)



✓+1P: horizontal



+1P: $T_1 > T_0$ ✓

✓+1P: konvex

✓+1P: $S_1 > S_0$

3

24

8

a) $S = k_B \ln \Omega$ ✓+1P: S aus Ω

$$S(V,N) = k_B \ln \frac{V!}{N!\,(V-N)!}$$

✓+1P: Binomialkoeff durch n!

Für $N \gg 1$, $V \gg 1$:
Mit Stirling-Formel: $\ln n! = n \ln n - n \Rightarrow$

$$S(V,N) = k_B \left[\underbrace{V \ln V - N \ln N - (V-N) \ln (V-N)}_{✓+1P} \right]$$

$$\ln (V-N) = \ln V \left(1 - \frac{N}{V}\right) = \ln V + \ln \left(1 - \frac{N}{V}\right)$$

✓+1P: umformen auf $\log(1+x)$ $x \ll 1$

Für $V \gg N \gg 1$:

Entwicklung von $\ln(1-x)$ um kleine x:

$$\ln(1-x) = -x + O(x^2) \Rightarrow$$

✓+1P: Entwicklung

$$\ln\left(1 - \frac{N}{V}\right) = -\frac{N}{V} + O\left(\frac{N^2}{V^2}\right) \Rightarrow$$

$$S(V,N) = k_B \left[\cancel{V \ln V} - N \ln N - \cancel{V \ln V} + N \ln V \right.$$

✓+1P: $V \log V$ fällt weg

+1P: $\frac{N^2}{V}$ Term

$$\left. - \underbrace{(V-N)\left(-\frac{N}{V}\right)}_{N - \frac{N^2}{V}} + \underbrace{(V-N)\, O\left(\frac{N^2}{V^2}\right)}_{O\left(\frac{N^2}{V}\right)} \right] \Rightarrow$$

✓+1P: N Term identifiziert

$$S(V,N) = + N k_B \left[\ln V - \ln N + 1 \right] + O\left(\frac{N^2}{V}\right) \Rightarrow$$

$$F(T,V,N) = - k_B T N \left[\ln V - \ln N + 1 \right] + O\left(\frac{N^2}{V}\right)$$

b) (6)

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N}$$

+1P: $F(T,V,N)$ ist richtiges Potential

$$\left.\frac{\partial p}{\partial V}\right|_{T,N} = -\left.\frac{\partial^2 F}{\partial^2 V}\right|_{T,N} = +k_B T N \frac{\partial^2}{\partial V^2}\ln V = -\frac{k_B T N}{V^2}$$

+1P: $\left(\frac{\partial V}{\partial p}\right)^{-1} = \frac{\partial p}{\partial V}$ +1P: $p = -\partial_V F$ +1P: F eingesetzt +1P: $(\log V)' = \frac{1}{V}$ +1P: $\left(\frac{1}{V}\right)' = -\frac{1}{V^2}$

$$\Rightarrow \kappa_T = +\frac{1}{V}\frac{V^2}{k_B T N} = \frac{V}{N k_B T}$$

c) (10)

$$C_V = T\left.\frac{\partial S}{\partial T}\right|_{V,N} = -T\left.\frac{\partial^2 F}{\partial T^2}\right|_{V,N} = 0$$

+1P +1P: $\partial_T F = -S$ +1P seltsam, richtig?

$$C_p = T\left.\frac{\partial S}{\partial T}\right|_{p,N} = -T\left.\frac{\partial^2 G}{\partial T^2}\right|_{p,N}$$

$G(T,p,N)$ richtiges Pot. +1P: und p const.

$$G(T,p,N) = F(T, V(T,p,N), N) + p\cdot V(T,p,N)$$

+1P: Legendre $F \mapsto G$

$$p = -\left.\frac{\partial F}{\partial V}\right|_{T,N} = \frac{k_B T N}{V} \Rightarrow V = \frac{k_B T\cdot N}{p}$$

+1P: p aus F +1P: umformen auf $V(T,p)$

$$G = -k_B T N\left[\ln\frac{k_B T\cdot N}{p} - \ln N + \cancel{1}\right] + \cancel{N k_B T}$$

+1P einsetzen V in $F + pV$

$$\left.\frac{\partial^2 G}{\partial T^2}\right|_{p,N} = \frac{\partial}{\partial T}\left[-k_B N \ln T - \frac{k_B T\cdot N}{k_B T\cdot N}\right] = -\frac{k_B N}{T}$$

+1P: erste Ableitung +1P: 2. Abl.

$$\Rightarrow \boxed{C_p = N k_B}$$

24

4 $H(\vec{q},\vec{p}) = \sqrt{(mc^2)^2 + (pc)^2}$

a) $$\Omega(E,V,1) = \underbrace{\frac{1}{h^3}}_{+1P} \underbrace{\int d^3q \int d^3p}_{+1P} \underbrace{\delta[H(\vec{q},\vec{p}) - E]}_{+1P}$$ 3

b) $$\Omega(E,V,1) = \frac{V}{h^3} 4\pi \int_{E \geq mc^2} dp\, p^2\, \delta\left(\sqrt{(mc^2)^2 + (pc)^2} - E\right)$$ 8

+1P: $\int d^3q = V$ +1P: $\int d^3p = \int_0^\infty 4\pi p^2 dp$

$$g(p) = \sqrt{(mc^2)^2 + (pc)^2} - E$$

Nullstellen:

✓+1P: $p_E \geq 0$ da $\int_0^\infty$

$$E^2 = (mc^2)^2 + (pc)^2 \Rightarrow p_E = \frac{1}{c}\left(+\sqrt{E^2 - (mc^2)^2}\right) \text{ für } E \geq mc^2$$

✓+1P: $p_E(E)$

$$g'(p) = \frac{1}{2} \frac{1}{\sqrt{(mc^2)^2 + (pc)^2}} 2 \cdot pc^2$$

✓+1P: innere Abl.

✓+1P: $(x^{1/2})' = \frac{1}{2}x^{-1/2}$

$$|g'(p_E)| = \frac{\sqrt{E^2 - (mc^2)^2} \cdot c}{\sqrt{(mc^2)^2 + E^2 - (mc^2)^2}} = \frac{\sqrt{E^2 - (mc^2)^2} \cdot c}{E}$$

✓+1P: p_E eingesetzt

✓+1P: $\int f\delta(g) = \sum_{p_E} \frac{f(p_E)}{|g'(p_E)|}$

$$\Omega = \frac{4\pi V}{h^3} \frac{\left(E^2 - (mc^2)^2\right)}{c^3} \frac{E}{\sqrt{E^2 - (mc^2)^2}} =$$

$$= \frac{4\pi V E}{h^3 c^3} \sqrt{E^2 - (mc^2)^2}$$

c)

13

$$S(E,V,N) = \underbrace{k_B \ln \phi(E,V,N)}_{+1P}$$

$dE = TdS - pdV + \mu dN$

$\Rightarrow dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN$ ✓ +1P

- $\left.\frac{\partial S}{\partial V}\right|_{E,N} = \frac{p}{T}$ ✓ +1P aus dS, gewußt OK

$$\left.\frac{\partial S}{\partial V}\right|_{E,N} = \frac{\partial}{\partial V}\left[k_B \underbrace{\ln V^N}_{\checkmark +1P}\right] = \frac{k_B N}{V} = \frac{p}{T}$$

+1P: $\log V^N = N \log V$

✓ +1P: V abhängiger Teil v. S

✓ +1P: $(\log V)' = \frac{1}{V}$

✓ +1P: Einsetzen in $\frac{\partial S}{\partial V} = \frac{p}{T}$

$\Rightarrow \boxed{pV = N k_B T}$ thermische Zustandsgleichung

✓ :-) wie ideales nicht-relativistisches Gas

- $\left.\frac{\partial S}{\partial E}\right|_{V,N} = \frac{1}{T}$ ✓ +1P: $\frac{\partial S}{\partial E} = \left(\frac{\partial E}{\partial S}\right)^{-1}$ $\quad \frac{\partial E}{\partial S} = T$ ✓ +1P

$$\left.\frac{\partial S}{\partial E}\right|_{V,N} = \frac{\partial}{\partial E}\left[k_B \ln E^{3N}\right] = 3N k_B \frac{1}{E} = \frac{1}{T}$$

✓ +1P $(\log E^{3N}) = 3N \log E$

✓ +1P. E abhängiger Teil

✓ +1P: $(\log E)' = \frac{1}{E}$

✓ +1P: Einsetz. in $\frac{\partial S}{\partial E} = \frac{1}{T}$

$\Rightarrow \boxed{E = 3N k_B T}$ kalorische Zustandsgleichung