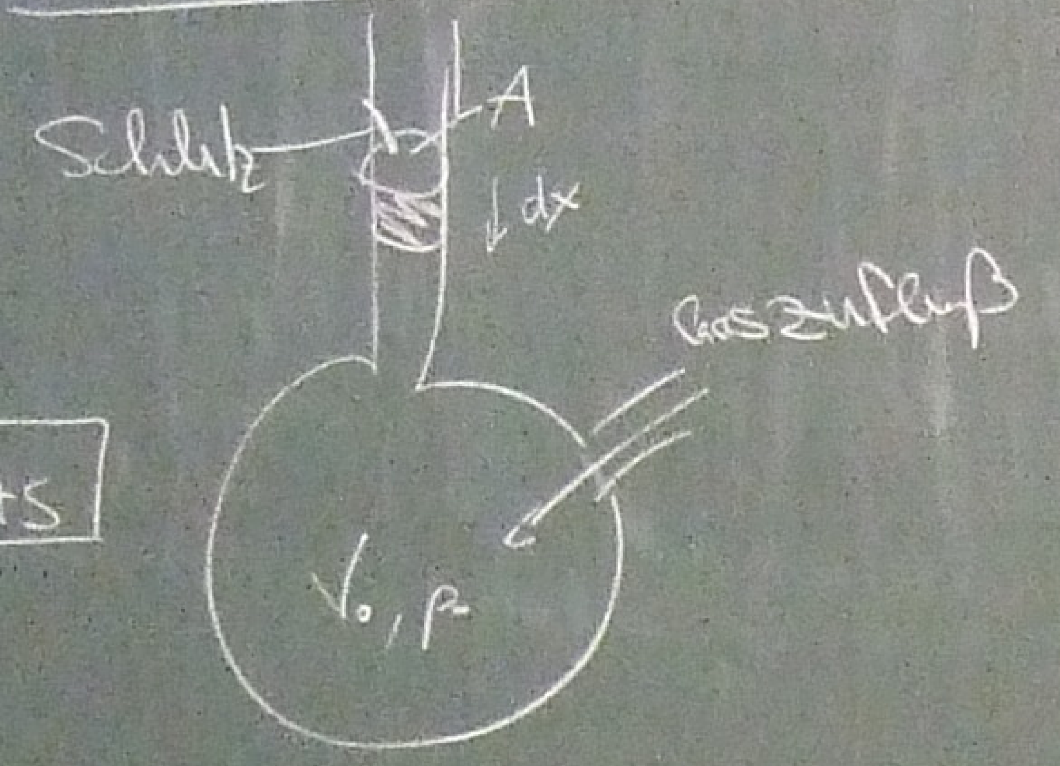
Rückert Gasoszillator



$$\boxed{T = 0{,}347\,s}$$

Federkonstante

$$dF = A\,dp \cdot 1$$
$$= A\,dp \cdot \frac{A\,dx}{dV}$$
$$= -D\,dx$$

Federkonstante

$$D = -A^2 \frac{dp}{dV}(V_0, p_0) = A^2 \frac{c_p}{c_v}\frac{p_0}{V_0}$$

Adiabatisch

$$pV^{c_p/c_v} = \text{const}$$
$$\frac{\partial p}{\partial V} = -\frac{c_p}{c_v}\cdot\frac{p_0}{V_0}$$

Periodendauer $T = 2\pi\sqrt{\frac{m}{D}}$

$$D = \frac{4\pi^2 m}{T^2}$$

$$K = \frac{c_p}{c_v} = \frac{D\,V_0}{A^2 p_0} = \frac{4\pi^2 m V_0}{A^2 p_0 T^2} = \boxed{\frac{64\, m V_0}{d^4 p_0 T^2} = \frac{c_p}{c_v}}$$

$$A = \frac{\pi d^2}{4} = \pi\left(\frac{d}{2}\right)^2$$

Thermod. Potentiale

$U(S,V) = \text{const}$, $S = \text{const}$ $(dS = 0)$
$V = \text{const}$ $(dV = 0)$

$$dU = 0$$
$$= TdS - pdV$$

Großkanonisches Potential

$$\Theta = G - \mu N = 0 \qquad G = \mu N$$

$$\Theta = G - \mu N = \underbrace{U + pV - TS}_{G} - \mu N = 0$$

$$dU + pdV + Vdp - TdS - SdT - \mu dN - Nd\mu = 0$$

mit $dU = TdS - pdV + \mu dN$ (Fund.rel.)

$$\boxed{Vdp - SdT - Nd\mu = 0}$$ Gibbs-Duhem Relation

Verwendung Δ, d, δ, (∂)

- keine Allg. Nomenklatur
- Δ: finite Unterschiede $\Delta U = \ldots$

  d: infinitesimale Unterschiede

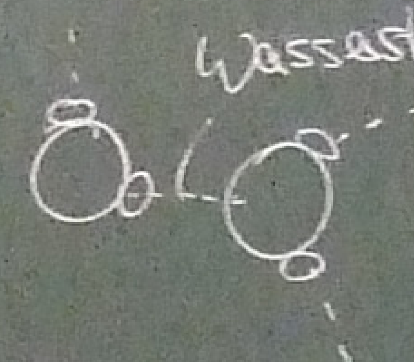
  δ: sehr ungewöhnlich, nur in TD

  „Folklore" Sinnvoller: ∂

Freiheitsgrade 3atomiges „Gas"

a) Wasser als Lösung $\quad c_V = 4{,}2 \frac{J}{gK}$, $m_W = 18 \frac{g}{mol}$

$$C_V = 76 \frac{J}{molK} \approx 9R \stackrel{!}{=} \frac{f}{2} R \rightsquigarrow f = 18$$



3 Atome im „Kristall"

$f = 3 \cdot 6 \approx 18$

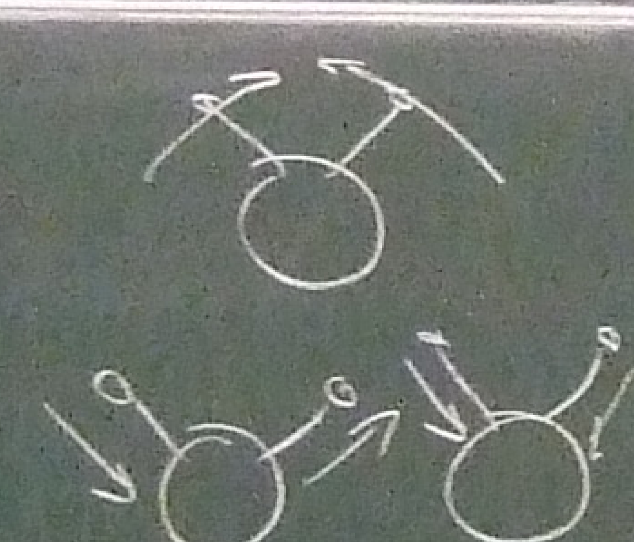
↳ 3 Schwingungen

b) Wasserdampf

3 Translation

3 Rotation

3 (6) Schwingungsf. (s. Animation)



$$C_p = \frac{\partial H}{\partial T} = \frac{(f+2)}{2} R + f(T)$$

$f = 12$

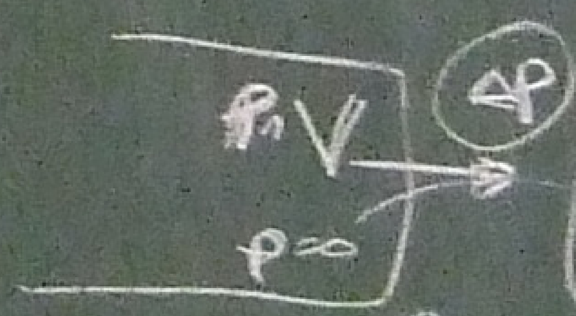
$c_V = 1{,}84 \frac{J}{gK}$

$C_V = 4R \rightsquigarrow f = 8$

$$dU = \cancel{\delta Q} + \delta W = -pdV = \frac{f}{2} Nk\, dT$$

$$dH = \ldots \quad V\Delta p = \frac{f+2}{2} Nk\, dT = 0$$

$$0 = (U_2 - U_1) - (p_2 V_2 - p_1 V_1)$$



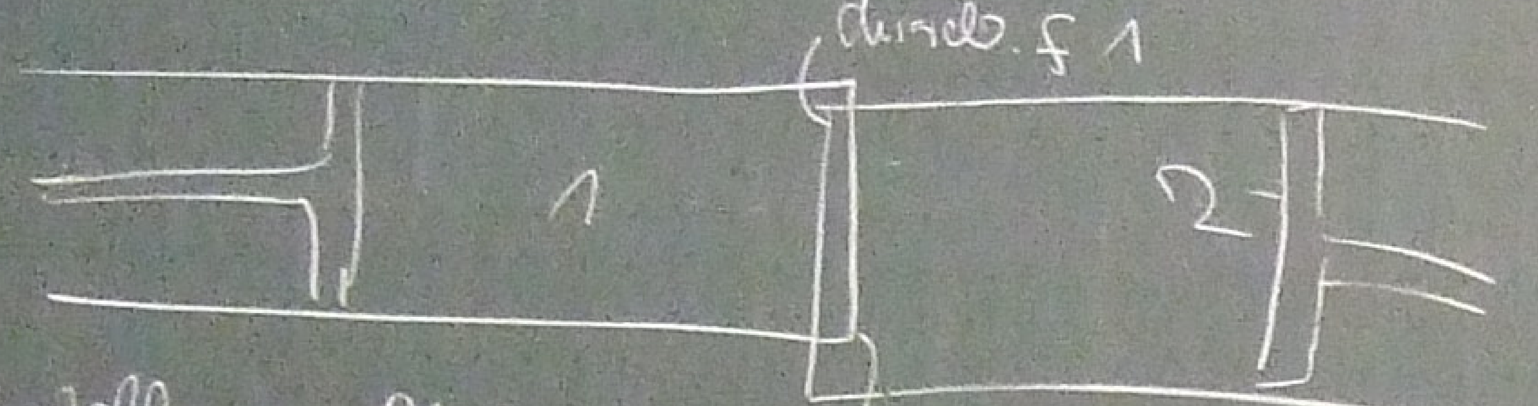
$$U_1 + p_1 V_1 = U_2 + p_2 V_2$$

$$\Rightarrow T_1 = T_2$$

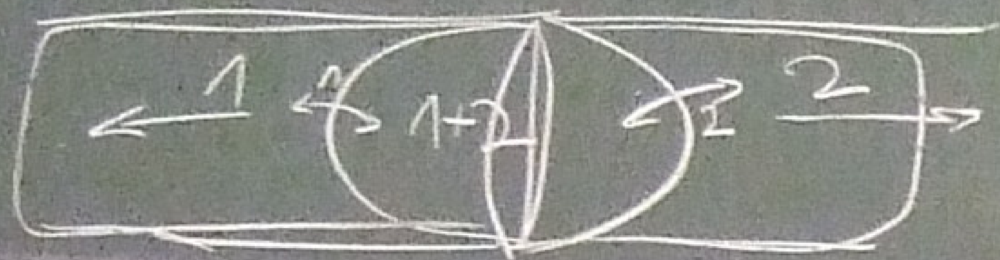
$$\Delta W_1 = \int \delta W = \int_0^{V_1} p_1 \, dV_1 = p_1 \int_0^{V_1} dV_1 = p_1 V_1$$

$p_1 V_1 - p_2 V_2$

Reversible Mischung v. Gasen



Vorstellung: flexible Membran



... reversibel geführt

$\downarrow K \sim \frac{1}{T^2}\nearrow$

ΔK

Leider undef. Begriff,

global (makr) reversibel $\longleftrightarrow$ $dS = 0 = \frac{\delta Q_{rev}}{T} = 0$

Überspitzt: „Es gibt keine reversiblen Prozesse"

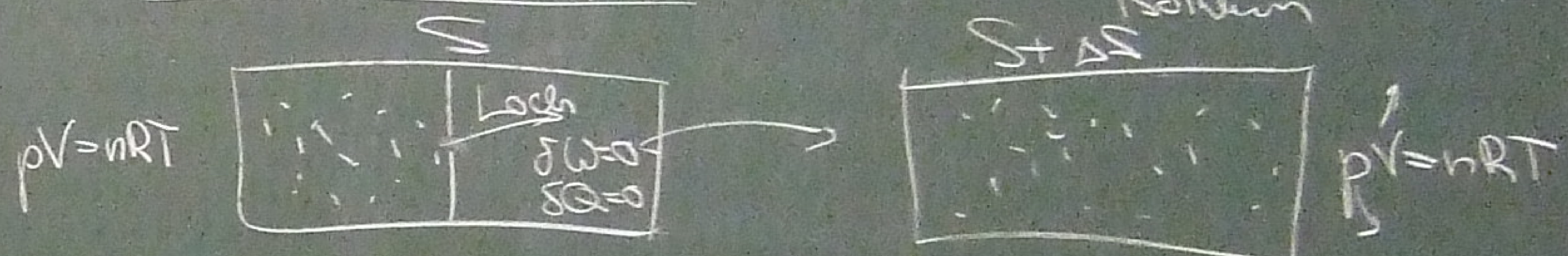
Besser: ◦ Quasistatische Prozesse

„Prozessführungszeit" $\gg$ Equilibrierungszeit

„langsam genug"

Kolben langsamer als Schallgeschw.

Klassische Beispiel



$dS = \frac{\delta Q_{rev}}{T}$ (isotherme Expansion)

„0" $\rightsquigarrow \Delta S$

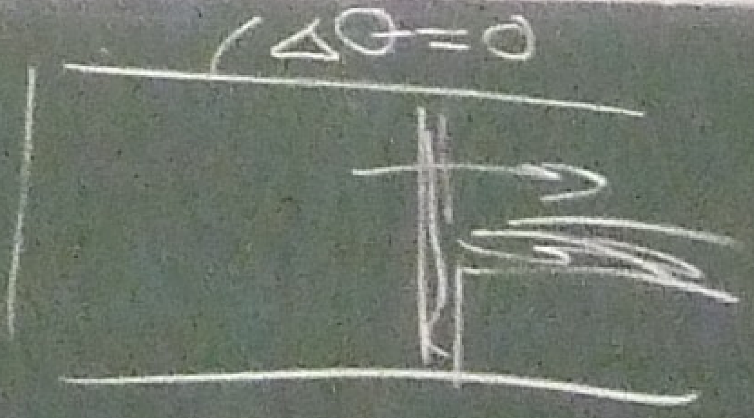
$\boxed{\Delta S\text{-const}}$ $dS \geq \frac{\delta Q}{T}$ ↘ nicht rev. geführt: δQ sinkt

Umdrehen: $\frac{\delta Q}{T} \leq dS$,

$$dS = \frac{\delta Q_{rev}}{T} - \frac{\delta Q_{irr}}{T}$$

$$dU = TdS - pdV$$

$$H = U + pV$$

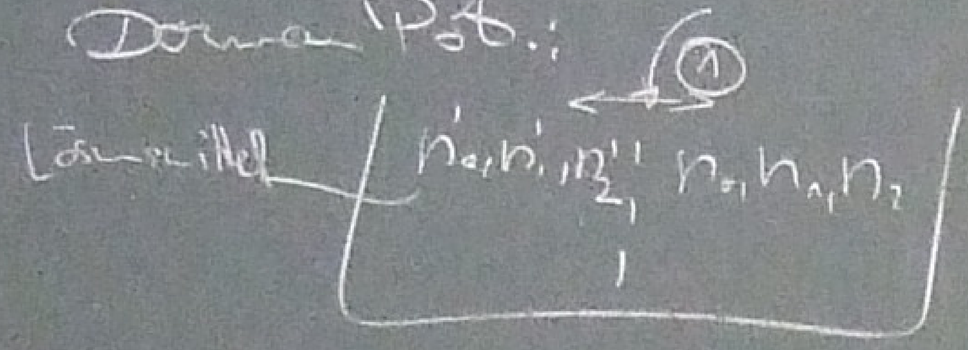


$T^{c_V/R}\, V = \text{const}$

$T\downarrow \quad V\uparrow$

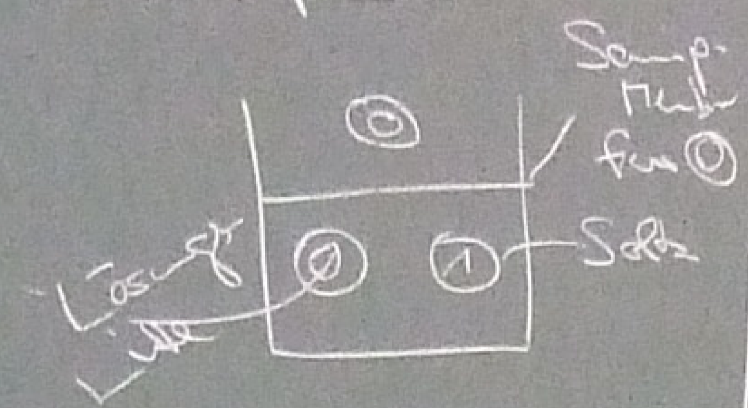
chemischen Potentiale

Donnan Pot.:



$\mu_1' = \mu_1$ „Minoritätenteilchen"

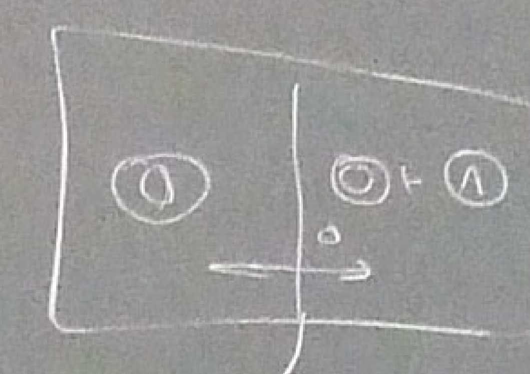
Siedepunkt



$\mu_0^{Misch} = \mu_0^{Gas}$

Majoritäten

Osm. Druck



$\mu_0 = \mu_0^{Misch}$

Knudsen ausfällich

$(n u_m)_1 = (n u_m)_2$

$p = nkT = \frac{N}{V}kT \rightsquigarrow n = \frac{p}{kT} \sim \frac{p}{T}$

$u_m \propto \sqrt{kT} \sim \sqrt{T}$

$\frac{p_1}{T_1}\sqrt{T_1} = \frac{p_2}{T_2}\sqrt{T_2} \rightsquigarrow \frac{p_1}{p_2} = \sqrt{\frac{T_1}{T_2}}$

DNA-Aufgabe

$\mu_i = \mu_i^{(0)} + kT \ln \frac{N_i}{N_0}$ ← Lösungsmittel-Teilchen

↑ Minoritätenteilchen

$\Delta G = 0 = \sum_i \mu_i N_i = 0 \rightsquigarrow \mu_A + \mu_B = \mu_{AB}$

$dS = 0 \neq \frac{\delta Q_{rev}}{T}$ $\quad \sum_i \mu_i dN_i = 0$

$dS_1 + dS_2 = 0$ $\quad dS = -\frac{Q_{rev}}{T}$

$\mu_A^{(0)} + kT\ln\frac{N_A}{N_0} + \mu_B^{(0)} + kT\ln\frac{N_B}{N_0} = \mu_{AB}^{(0)} + kT\ln\frac{N_{AB}}{N_0}$

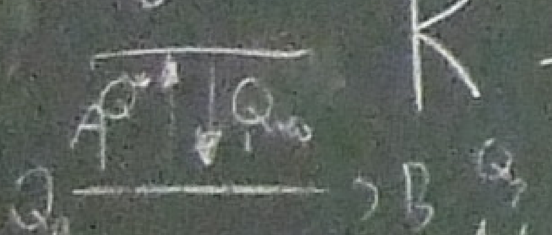
mit $-\frac{\Delta G^{(0)}}{N_{Avog}} = \mu_A^{(0)} + \mu_B^{(0)} - \mu_{AB}^{(0)}$

$-\Delta G^{(0)} = RT\left[\ln\frac{N_{AB}}{N_0} - \ln\frac{N_A}{N_0} - \ln\frac{N_B}{N_0}\right]$

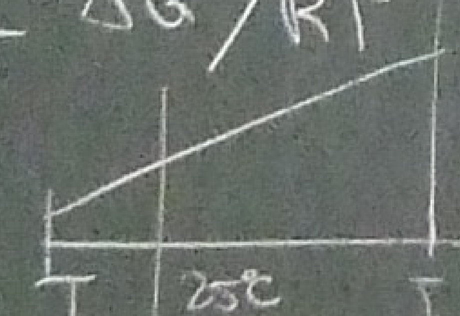
$= RT \ln \frac{N_{AB} N_0 N_0}{\cancel{N_0} N_A N_B}$

$\frac{Q - Q_{irr}}{T}$

$dU = \delta Q + \delta W$



$K = \frac{N_{AB} N_0}{N_A N_B} = e^{-\Delta G^{(0)}/RT}$ mit $\Delta G^{(0)} = \Delta H^{(0)} - T\Delta S^{(0)}$



$x_{AB} = \frac{N_{AB}}{N_0}, \quad x_A = \frac{N_A}{N_0}, \quad x_B = \frac{N_B}{N_0}$

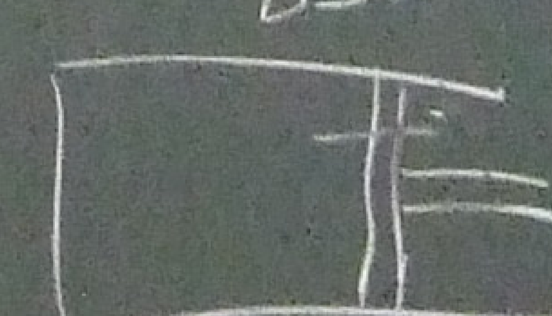
$N_{AB} = x_{AB} \cdot N_0$

$1 = K = \frac{x_{AB} \cdot N_0 \cdot N_0}{x_A N_0 \cdot x_B N_0} = e^{-\Delta G^{(0)}/RT}$

$\boxed{Q_{rev} = Q_{irr} + X}$

$A + B \rightleftharpoons AB$

$\Delta S > 0$



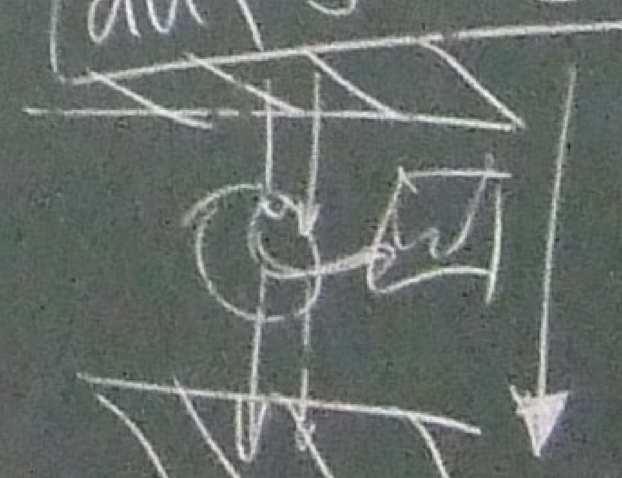
$T_m = \frac{\Delta H^{(0)}}{\Delta S^{(0)}}$

$\Delta S_H = \frac{\pm \Delta Q_H}{T_H}$ $\quad \boxed{dS = 0}$ $\quad dU = \delta Q + \delta W$

$\Delta S = \frac{\pm Q_{rev}}{T_m}$

$\boxed{dU \neq \delta W + \delta Q}$

$\Delta S > 0$



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