Thermodynamische Potentiale

$U(S,V,N) = TS - pV + \mu N$ | $dU = TdS - pdV + \mu dN$

$F(T,V,N) = U - TS = -pV + \mu N$ | $dF = -SdT - pdV + \mu dN$

$G(T,p,N) = F + pV = \mu N$ | $dG = -SdT + Vdp + \mu dN$

$H(S,p,N) = U + pV = TS + \mu N$ | $dH = TdS + Vdp + \mu dN$

$\Omega(T,V,\mu) = F - \mu N = -pV$ | $d\Omega = -SdT - pdV - Nd\mu$

konvex, konkav, linear
extensiv, intensiv, extensiv

$p \leftrightarrow -H$ (intensiv)

$(T,V) = $ const. $\Rightarrow$ F minimal, $(T,p) = $ const $\Rightarrow$ G minimal

Adiabatisch

$\delta Q = 0$

$p \propto T^{\gamma(\gamma-1)}$

$TV^{\gamma-1} = $ const.

$Tp^{-\alpha} = $ const.

$\kappa_S = -\frac{1}{V}\frac{\partial V}{\partial p}\Big|_S \geq 0$

Isochor

$\delta Q = C_V dT$

$p \propto T$

Isotherm

$U = $ const. (i. Gas)

$pV = $ const. (i. Gas)

$\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial p}\Big|_T > 0$

Ideales Gas

$pV = nRT = Nk_BT$

$\delta W = -pdV$

$U = \frac{3}{2}Nk_BT$

Innere Energie

$dU = \delta W + \delta Q$

$dU = C_V dT$ isochor

$dU = C_p dT$ isobar

$dU = 0$ isotherm

$dU = -pdV$ adiabat

$dU = C_M dT$ magn.-const.

$dU = C_V dT + [T\frac{\partial p}{\partial T}|_V - p]dV$

Isobar

$\delta Q = C_p dT$, $\alpha = \frac{1}{V}\frac{\partial V}{\partial T}\Big|_p$

$|\alpha_p| \leq \sqrt{\frac{c_p \kappa_T}{VT}}$

Photonengas

$U = aT^4V = 3pV \Rightarrow aT^4 = 3p$

$T^3V = $ const. (adiabat)

$S = \frac{4}{3}aT^3V$, $C_V = 4aVT^3$

Magn. Substanz

$\delta W = HdM$, $M = K\frac{H}{T}$ (Curie)

$dU = C_M dT$, $dU = 0$ (isotherm)

$C_M = \frac{\partial U}{\partial T}\Big|_M$, $C_H - C_M = -T\frac{\partial H}{\partial T}\Big|_M \frac{\partial M}{\partial T}\Big|_H$

$T = T_0 \exp\left(\frac{M^2 - M_0^2}{2KC_M}\right)$ (adiabat)

adiabat isotherm

$\chi_T = \frac{\partial M}{\partial H}\Big|_T$, $\chi_S = \frac{\partial M}{\partial H}\Big|_S$

Gibbs-Duhem

$SdT - Vdp + Nd\mu = 0$

Homogenitätsrelation

$S = \frac{1}{T}(U + pV - \mu N)$

Entropie

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

Zustandsgrösse

I. Hauptsatz $p \in P_S$

· $\sigma_1, \sigma_2 \in \Sigma_S$

$\exists p$ s.d. $\sigma_1 \xrightarrow{p} \sigma_2$

oder p' s.d. $\sigma_2 \xrightarrow{p'} \sigma_1$

· $W_S(p) = W_S(p')$

Van-der Waals $a, b > 0$

$(p + \frac{a}{V^2})(V - b) = RT$

$dU = C_V dT + \frac{a}{V^2}dV$

$\delta Q = C_V(T)dT + \frac{RT}{V-b}dV$

$\eta_C = 1 - \frac{T_K}{T_H}$, $\frac{C_V dT}{T dV} = -\frac{R}{V-b}$

Thermo square

T	G	-p
F		H
V	U	-S

Bsp. $T = \frac{\partial H}{\partial S}\Big|_p$

$-\frac{\partial S}{\partial p}\Big|_T = \frac{\partial V}{\partial T}\Big|_p$

Materialkonstanten

$C_V = \frac{\delta Q}{\partial T}\Big|_V = \frac{\partial U}{\partial T}\Big|_V = T\frac{\partial S}{\partial T}\Big|_V = -T\frac{\partial^2 F}{\partial T^2}\Big|_{N,V} > 0$

$C_p = \frac{\delta Q}{\partial T}\Big|_p = \frac{\partial U}{\partial T}\Big|_p + p\frac{\partial V}{\partial T}\Big|_p = T\frac{\partial S}{\partial T}\Big|_p = \frac{\partial H}{\partial T}\Big|_p > 0$

$C_p - C_V = \frac{TV\alpha_p^2}{\kappa_T}$, $\alpha_p = \frac{1}{V}\frac{\partial V}{\partial T}\Big|_p$, $\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial p}\Big|_T$

Effizienz

$\eta = \frac{W_{tot}}{Q_{in}} = 1 - \frac{Q_K}{Q_H} \leq 1 - \frac{T_K}{T_H}$

$COP = \frac{Q_{R_K}}{W_S} \leq \frac{1}{1 - \frac{T_{R_K}}{T_{R_H}}}$

II Hauptsatz $p \in P_{SVR}$

$W_S(p) \geq 0$

Chemische GGW

1.) Bestimme Permeabilität
2.) Bestimme GGW. bedingung
3.) Setze GGW
4.) Taylore $\tilde{\mu}_i^0$ meist in T oder p
5.)

Clausius Clapeyron

$\frac{dp_c}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{T(V_g - V_f)}$

Chemisches Potential

$\mu_i = \tilde{\mu}_i^0 + RT\log c_i \Rightarrow \log c_1 = -\sum_{i=2}^{r} c_i$ ($c_1 \approx 1$)

$\mu_i = u_i - Ts_i + pv_i = \frac{G_i}{N_i}$, $\frac{\partial \mu}{\partial p} = V$, $\frac{\partial \mu}{\partial T} = -S$

$c_i = \frac{N_i}{N}$

Mischentropie

$S = \frac{3}{2}nR\log\left(\frac{T}{T_0}\right) + nR\log\left(\frac{V_1 n_0}{V_0 n_1}\right)$

$S = \sum S_i - R\sum N_i \log\left(\frac{N_i}{N}\right)$

ideales Gas: ≥ 0 Mischentropie

Entropiesatz

$p \in P$ adiabat

insb. arbeitsprozesse

$S(\langle p]) \leq S([p\rangle)$

"=" falls reversibel

Extremalprinzip

$S(\sigma) = \max S_{S'}(\sigma') + S_{S''}(\sigma'')$

Entropie maximal im GGZ.

$\Rightarrow$ Konkavität

im GGZ: $S(z') + S(z'') = S(z' + z'')$

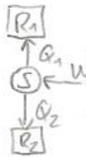
Clausius Theorem

i) $\sum_i \frac{Q_S(p_i)}{T_i} \leq 0$

ii) p rev $\Rightarrow$ "="

p nicht unbed. adiabatisch

Carnot



i) $-\frac{Q_{R_1}'}{Q_{R_2}'} \leq -\frac{Q_{R_1}}{Q_{R_2}}$

$\frac{T_1'}{T_2'} \leq \frac{T_1}{T_2}$

$-\frac{Q_1}{Q_2}$ hängt für rev. proz nicht von S ab

Henry-Gesetz

$c_S(T,p) = f(T)\cdot p$

T = const bedingung

Dalton

$p = \sum_i p_i$ einzeln erfüllen i. Gas Gesetz

Joule Thomson

$T\frac{\partial V}{\partial T}\Big|_p - V = 0$

(inversionskurve)

">" 0 bei Abkühlung

$\frac{\partial T}{\partial p}\Big|_H > 0 \rightsquigarrow$ Abk.

Massenwirkungsgesetz

$\sum \nu_i \log\left(\frac{N_i}{N}\right) = $ const.

$\prod_{i=1}^{r} c_i^{\nu_i} = \exp\left(-\frac{1}{RT}\sum_i \nu_i \mu_i^0\right) = K$

$= \exp\left(-\frac{\Delta G}{RT}\right)$

$\Delta G = \nu_1 G_{1,P} + \nu_2 G_{2,pt} - \dots - \nu_3 G_{1,E}$

Gas flüssig Gemisch

$G = G^{gas} + G^{flüss}$

GGW $\rightleftarrows$

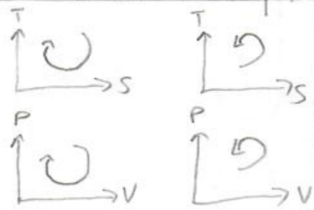
$\frac{\partial G}{\partial n_i} = 0$ für i. Gas

$(T,p) = $ const.

Kritische Punkt

$\frac{\partial p}{\partial V}\Big|_T = \frac{\partial^2 p}{\partial V^2}\Big|_T = 0$

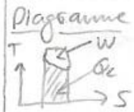
Konkavität von F



Motor $W_S < 0$

Wärmepumpe/Kühlschrank $W_S > 0$

Diagramme

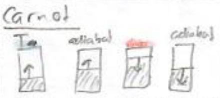


W: ausgetauschte Arbeit

Q_c: Wärmeaustausch mit Umwelt/R_K

W: Netto verrichtete Arbeit

Carnot



$dV < 0$, $\delta Q = 0$, $dV > 0$, $\delta Q = 0$

$\delta Q < 0$, $\delta Q > 0$

$dU = 0$, $dU = 0$

Abs. Temp

$T(R_1, R_2) = -\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$

Endotherm/Exotherm

$H_1 \longrightarrow H_2$

$\Delta H = H_2 - H_1$

$H_1 < H_2$: endotherm

$H_1 > H_2$: exotherm

τ

· $\tau(R_1, R_2) = \frac{1}{\tau(R_2, R_1)}$

· transitiv

· reflexiv

$\tau(R,R) = 1$

$\Rightarrow$ 0. Hauptsatz

B. $T_1 = T_2$

Phasenübergänge 2. ordn.

$\Delta S = 0$, $\Delta V = 0$

$\Delta c_p = \frac{dp}{dT}VT\Delta\alpha$

$\Delta\alpha = \frac{dp}{dT}\cdot\Delta\kappa_T$

Clausius Clapeyron Magnet:

$\frac{dH_c}{dT} = -\frac{S_2 - S_1}{M_2 - M_1}$

Osmose

$p - p_1 = \frac{RT\sum_{i=2}^{r} c_i}{V_1}$

Volumenänderung

$\Delta V = N(\tilde{v} - \bar{v})$

Ideale Mischung

$\Delta U = 0$, rev. und adiabat.

$\sum U_i = U$

GGW der Konz.

Bsp. $-H_2 + 2H = 0$

$\nu_{H_2} = -2$, $\nu_H = 2$ } prod. positiv

$\nu_{H_2}\mu_{H_2} + \nu_H\mu_H \stackrel{!}{=} 0$

Bsp.

Finde ν_i, berechne G,
Nutze Formel (MWG)
Finde K, setze $K = \prod c_i^{\nu_i}$.
Ansatz da rechts $\rightarrow$
Finde λ, bestimme physikalische lösung.

Verunreinigung

1.) GGZ bestimmen
2.) Gibbs-Duhem
3.) Potential Taylorn
4.) ① Nutzen

$\Rightarrow RTc_2 = (\tilde{v}_1 - v_1)\Delta p - (\tilde{s}_1 - s_1)\Delta T$

$c_i^0 = \frac{N_i^0}{N}$

Brute Force Potentiale

$\rightarrow$ alle identitäten
$\rightsquigarrow$ Maxwell relation
$\rightarrow$ Zustand als diff. quotient
$\rightsquigarrow$ Ableitung machen
Produktregel
$w(x_i, y)$ finden

GGW konz bestimmen

$N_i = N_i^0 + \nu_i\lambda$

$c_i = c_i^0 + \frac{\nu_i\lambda}{N}$

$K \stackrel{!}{=} c_1^{\nu_1}\cdot c_2^{\nu_2} c_3^{\nu_3}$

Ableiten

$$\frac{\partial x}{\partial y}\Big|_z = \left(\frac{\partial y}{\partial x}\Big|_z\right)^{-1} \qquad \frac{\partial x}{\partial y}\Big|_z = -\frac{\frac{\partial z}{\partial y}\big|_x}{\frac{\partial z}{\partial x}\big|_y}$$

$$\frac{\partial x}{\partial w}\Big|_z = \frac{\partial x}{\partial y}\Big|_z \frac{\partial y}{\partial w}\Big|_z \qquad \frac{\partial x}{\partial z}\Big|_w = \frac{\partial x}{\partial y}\Big|_w \frac{\partial y}{\partial z}\Big|_w$$

$$\frac{\partial x}{\partial y}\Big|_z = \frac{\partial x}{\partial y}\Big|_w + \frac{\partial x}{\partial w}\Big|_y \frac{\partial w}{\partial y}\Big|_z$$

Legendre

1) Ableitung $= p$
2) nach x auflösen
3) $f^* = xp - f(x)$, $x(p)$

i) p immer konvex
ii) konstante wechseln, konkav $\leftrightarrow$ konvex
iii) Beachte Minus in Def

Stirling

$$N! = N^N \frac{1}{e^N}\sqrt{2\pi N}$$

$$\log N! = N\log N - N$$

$$\log\left(\binom{n}{k}\right) = n\log n - k\log k - (n-k)\log(n-k) = -k\log\left(\frac{k}{n}\right) - (n-k)\log\left(\frac{n-k}{n}\right)$$

Gauss Integral

$$\int dx\, e^{-ax^2+bx+c} = \sqrt{\frac{\pi}{a}}\, e^{\frac{b^2}{4a}+c}$$

Lagrange

$$\tilde f(\lambda, x_i) = f(x_i) - \lambda\,(\overbrace{\text{Nebenbed}}^{=0})$$

$$\langle (N-\langle N\rangle)^2\rangle = \langle N^2\rangle - \langle N\rangle^2$$

Neg. semidef

konkav: $\frac{\partial S}{\partial u} \le 0$, $\det \partial^2 S \ge 0$

Kombinatorik

	wichtig RW	$n>k$ R.u.W
mZL	n^k	$\binom{n-1+k}{k}$
o.Z.L	$\frac{n!}{(n-k)!\,k!}$	$\binom{n}{k} = \binom{n}{n-k}$

Trigonometrie

$$\sin(x) = \frac{e^{ix}-e^{-ix}}{2i} \qquad \cosh z = \frac{e^z+e^{-z}}{2}$$

$$\cos(x) = \frac{e^{ix}+e^{-ix}}{2} \qquad S = SC \pm CS$$

$$\sinh(z) = \frac{e^z - e^{-z}}{2} \qquad C = CC \mp SS$$

Kugel

$$H(x) = \frac{1}{2m}\sum_{i=1}^N p_i^2 + x_i^2$$

$$\iint_{H\le E} d^N x\, d^N p = C_{2N}(\underbrace{2mE}_{R})^{N/2} \cong 2IE$$

$$C_{2N} = \frac{\pi^N}{N!}$$

Separation

$$H = \sum H_0(q_i, p_i) \Rightarrow Z_N = (Z_1)^N$$

Σ	U,V,N	S
Z	N,V	F
Ξ	V	Ω

Σ

$\Sigma = \#$ Mikrozustände

$$\phi = \int_{H\le E} d^{3N}q\, d^{3N}p$$

$$\frac{\partial\phi}{\partial E} = \Sigma$$

$$S = k_B \log\Sigma \overset{N\to\infty}{=} k_B\log\phi$$

$$= \frac{1}{h^{3N}N!}\log\Sigma$$ falls ununterscheidbar und Quanten

$$w_E = \frac{1}{\Sigma(E)}\delta(H(x)-E)$$

Z_N

$$Z_N = \sum e^{-\beta H} = \int dE\, e^{-\beta H}\Sigma(E) = \int_{\mathbb{R}^6} d^{3N}q\, d^{3N}p\, e^{-\beta H}$$

$$F = -k_B T\log Z_N$$

$$U = -\frac{\partial \log Z_N}{\partial\beta}\Big|_{V,N}$$

$$w(x) = \frac{1}{Z_N}e^{-\beta H},$$

Ξ

$$\Xi = \sum_{N=0}^\infty e^{\beta\mu N} Z_N(\beta)$$

$$\Xi = \sum_{N=0}^\infty \int_{\Gamma_N} dx\, e^{-\beta(H(x)-\mu N)}$$

$$\Omega = -k_B\log\Xi$$

$$w(N,x) = \frac{e^{-\beta(H(x)-\mu N)}}{\Xi(\beta,\mu)}$$

$$\langle N\rangle = \frac{1}{\Xi}\sum_{N=0}^\infty\int_{\Gamma_N} dx\, N e^{-\beta(H-\mu N)} = \frac{1}{\Xi}\frac{1}{\beta}\frac{\partial}{\partial\mu}\Xi$$

Gibbs

$E, N = \text{fix} \Rightarrow$ GGZ: S maximal

III. Hauptsatz

Für jedes System strebt die Entropie für $T\to 0$ gegen einen von anderen Zustandsvariablen unabhängigen endlichen Wert.

Ergodenhypothese

Das einzige unter φ_t invariante Mass auf Γ_N ist die mikrokanonische Gesamtheit.

Avogadro $N \sim 10^{23}\cdot 6$

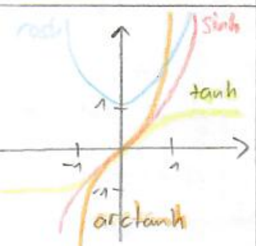
Gleichverteilungssatz

$$\langle x_i \frac{\partial H}{\partial x_j}\rangle = \delta_{ij}k_B T$$

$$c_V = \frac{f}{2}k_B,\quad \frac{C_V}{N} = c_V$$

$$\langle H\rangle = \frac{f}{2}Nk_B T$$

$$f = f_{trans} + f_{rot} + 2f_{vib}$$



Freiheitsgrade

Teile dann :2

	f_{trans}	f_{rot}	f_{vib}	tot
1 atom	3	0	0	3
2 atom	3	2	1	7
3 atom linear	3	2	4	13
3 atom gewinkelt	3	3	3	12

Taylor

$$\sin x = x - \frac{1}{6}x^3 \qquad \sinh x = x + \frac{x^3}{6}$$

$$\cos x = 1 - \frac{1}{2}x^2 \qquad \cosh x = 1 + \frac{x^2}{2}$$

$$\tan x = 1 + \frac{1}{3}x^3 \qquad \tanh x = x - \frac{1}{3}x^3$$

$$\cot x = 1 - \frac{1}{3}x^3 \qquad \coth x = \frac{1}{x} + \frac{x}{3}$$

Freie Energie

$T\to 0$, minimiere $U \rightsquigarrow$ Festkörper

$T\to\infty$, maximiere $S \rightsquigarrow$ Gasphase

Carnot