Mótsögn Gibbs $\Leftrightarrow$ óaðgreinanleiki

fyrir klassískt kjörgas fékkst jafna Sackur-Tetrode

$$S = Nk_B\left\{\frac{5}{2} - \ln\left(n\lambda_{th}^3\right)\right\}$$

Skoðum Joule þenslu

þéttleiki gassins helmingast

$$\Delta S = S_f - S_i = Nk_B\left\{-\ln\left(\frac{n}{2}\lambda_{th}^3\right) + \ln\left(n\lambda_{th}^3\right)\right\}$$

$$= Nk_B \ln 2$$

Rétt eins og áður, útþenslan er eingengt ferli

útþensla tveggja mismunandi gastegunda

$$\longrightarrow \quad \Delta S = 2\{N k_B \ln 2\}$$

en, sama gastegund

samkvæmt sígildri eðlisfræði hefði mátt búast við $\Delta S = 2\{N k_B \ln 2\}$

óaðgreinanlegar sameindir $\longrightarrow$ engin breyting

$$\longrightarrow \quad \Delta S = 0$$

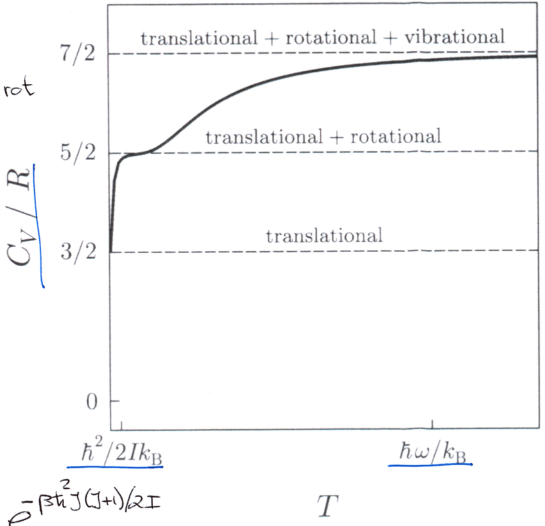
$\Updownarrow$

$\boxed{\text{óaðgreinanleiki}}$ $\longleftarrow$ skammtahugmynd

Varmarýmd tvíatóma gass

$$Z = Z_{trans} Z_{vib} Z_{rot}$$

$$Z_{trans} = \frac{V}{\lambda_{th}^3}$$



$$Z_{vib} = \frac{e^{-\frac{\beta\hbar}{2}}}{1-e^{-\beta\hbar\omega}}$$

$$Z_{rot} = \sum_{j=0}^{\infty} (2j+1)\, e^{-\beta\hbar^2 j(j+1)/2I}$$

$$U = -\frac{d\ln Z}{d\beta}$$

summa þáttanna tran, vib., rot.,
$\rightarrow$ C_v er einnig summa þeirra

Efnamætti

Þurfum að fjalla um kerfi með breytilegum fjölda einda, t.d.

$$2H_2 + O_2 \longrightarrow 2H_2O$$

Færum okkur frá kórsafninu yfir í stóra kórsafnið

Endurbætum 1. lögmálið

$$dU = TdS - pdV + \mu dN$$

ef engin breyting á S og V

orkan breytist ef eind er bætt við, eða hún er tekin úr kerfinu

Efnamættið er mælikvarði á hve mikla orku þarf til að breyta eindafjölda

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

Endurbætum varmafræðilegu mættin

$$F = U - TS, \quad G = U + pV - TS$$

$$\rightarrow \quad dF = -p\,dV - S\,dT + \mu\,dN$$
$$dG = V\,dp - S\,dT + \mu\,dN$$

$$\rightarrow \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{V,T}$$

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{p,T}$$

Merking μ

$$S = S(U,V,N)$$

S eykst eða stendur í stað í ferli

$$\rightarrow \quad dS = \left(\frac{\partial S}{\partial U}\right)_{N,V} dU + \left(\frac{\partial S}{\partial V}\right)_{N,U} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN$$

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

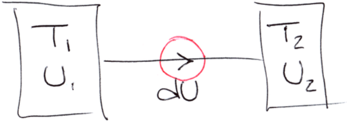
$$\rightarrow \quad dS = \frac{dU}{T} + \frac{p\,dV}{T} - \frac{\mu\,dN}{T}$$

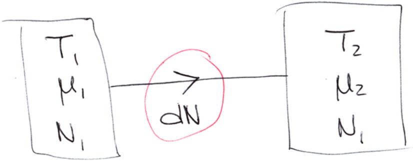
$$\rightarrow \quad \left(\frac{\partial S}{\partial U}\right)_{N,V} = \frac{1}{T}$$

$$\left(\frac{\partial S}{\partial V}\right)_{N,U} = \frac{p}{T}$$

$$\left(\frac{\partial S}{\partial N}\right)_{U,V} = -\frac{\mu}{T}$$

Varmaleiðni milli kerfa





$$dS = \left(\frac{\partial S_1}{\partial U_1}\right)_{N,V} dU_1 + \left(\frac{\partial S_2}{\partial U_2}\right)_{N,V} dU_2$$

$$= \left(\frac{\partial S_1}{\partial U_1}\right)_{N,V} (-dU) + \left(\frac{\partial S_2}{\partial U_2}\right) dU$$

$$= \underbrace{\left\{-\frac{1}{T_1} + \frac{1}{T_2}\right\} dU \geq 0}$$

2. lögmálið

hér verður $T_1 \geq T_2$ og jafnvægi næst þegar $T_1 = T_2$

$$dS = \left(\frac{\partial S_1}{\partial N_1}\right)_{U,V} dN_1 + \left(\frac{\partial S_2}{\partial N_2}\right)_{U,V} dN_2$$

$$= \left(\frac{\partial S_1}{\partial N_1}\right)_{U,V} (-dN) + \left(\frac{\partial S_2}{\partial N_2}\right)_{U,V} dN$$

$$= \left\{\frac{\mu_1}{N_1} - \frac{\mu_2}{N_2}\right\} dN \geq 0$$

Ef $T_1 = T_2$ og $dN > 0$

$\rightarrow$ eindir flæða frá 1 yfir í 2 þegar $\mu_1 > \mu_2$

jafnvægi þegar $\mu_1 = \mu_2$

Efnamættið fyrir kjörgas

Höfum að

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T}$$

og áður að

$$F = Nk_BT\left\{\ln(n\lambda_{th}^3) - 1\right\}$$

og $n = \frac{N}{V}$

$$\mu = k_BT\left\{\ln(n\lambda_{th}^3) - 1\right\} + Nk_BT\frac{1}{N}$$

$$= k_BT\ln(n\lambda_{th}^3)$$

Áður fékkst fyrir kjörgasið

$$G = Nk_BT\ln(n\lambda_{th}^3)$$

því fæst hér að

$$\mu = \frac{G}{N}$$

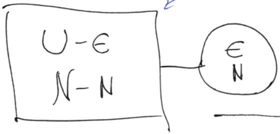
sjáum bráðlega að sú jafna helur víðari skírskotun

Stóra Kórsumman

Hugsum okkur lítið kerfi sem er opið fyrir orku og agna flutningi

óreiða geymis

$U \gg \epsilon \qquad \mathcal{N} \gg N$



$$S(U-\epsilon, \mathcal{N}-N) = S(U,\mathcal{N}) - \epsilon\left(\frac{\partial S}{\partial U}\right)_{\mathcal{N},V} - N\left(\frac{\partial S}{\partial \mathcal{N}}\right)_{U,V}$$

$$= S(U,\mathcal{N}) - \frac{\epsilon}{T} + \frac{N\mu}{T}$$

$$= S(U,\mathcal{N}) - \frac{1}{T}(\epsilon - \mu N)$$

$P(\epsilon, N)$ líkindi á stórsæju ástandi kerfis er í réttu hlutfalli við Ω, fjölda smásæja ástandi í stórsæja ástandinu

$$S = k_B \ln \Omega$$

$$P(\epsilon, N) \sim \exp\left\{\frac{S(U-\epsilon, \mathcal{N}-N)}{k_B}\right\} \sim \exp\{\beta(\mu N - \epsilon)\}$$

Dreifing Gibbs fyrir stóra kórsafnið

$$\boxed{P_i = \frac{e^{\beta(\mu N_i - E_i)}}{\mathcal{Z}}}$$

með stóru kórsummunna

$$\boxed{\mathcal{Z} = \sum_i e^{\beta(\mu N_i - E_i)}}$$

Hægt er að sýna að

$$N = \sum_i N_i P_i = k_B T \left(\frac{\partial \ln \mathcal{Z}}{\partial \mu}\right)_\beta$$

$$U = \sum_i E_i P_i = -\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right)_\mu + \mu N$$

$$S = -k_B \sum_i P_i \ln P_i$$

$$= \frac{U - \mu N + k_B T \ln \mathcal{Z}}{T}$$

Höfum kynnt

Litla kórsafnið

Orkan U föst

$$\Omega = e^{\beta T S}$$

$$S = k_B \ln \Omega$$

Kórsafnið

varmaskipti við geymi

$$Z = e^{-\beta F}$$

$$F = -k_B T \ln Z$$

Stóra kórsafnið

varma og einda skipti við geymi

$$\mathcal{Z} = e^{-\beta \Phi_G}$$

nýtt

Varmafræðilega mætti Gibbs

$$\boxed{\Phi_G = -k_B T \ln \mathcal{Z}}$$

höfðum áður

$$S = \frac{U - \mu N - k_B T \ln \mathcal{Z}}{T}$$

$$\rightarrow \quad -k_B T \ln \mathcal{Z} = U - TS - \mu N$$

$$\rightarrow \quad \boxed{\Phi_G = U - TS - \mu N = F - \mu N}$$

Afleiðan er

$$d\Phi_G = \underbrace{dF - \mu dN}_{} - N d\mu$$

$$= \overbrace{-SdT - pdV}^{} - N d\mu$$

Berum saman við

$$d\Phi_G = \left(\frac{\partial \Phi_G}{\partial T}\right)_{V,\mu} dT + \left(\frac{\partial \Phi_G}{\partial V}\right)_{T,\mu} dV + \left(\frac{\partial \Phi_G}{\partial \mu}\right)_{TV} d\mu$$

og sjáum að

$$S = -\left(\frac{\partial \Phi_G}{\partial T}\right)_{V,\mu}$$

$$p = -\left(\frac{\partial \Phi_G}{\partial V}\right)_{T,\mu}$$

$$N = -\left(\frac{\partial \Phi_G}{\partial \mu}\right)_{T,V}$$

finnum Φ_G fyrir kjörgas

Höfum

$$F = Nk_BT\left\{\ln(n\lambda_{th}^3) - 1\right\}$$

og

$$\mu = k_BT\ln(n\lambda_{th}^3)$$

og ástandsjöfnuna

$$pV = Nk_BT$$

$$\rightarrow \Phi_G = F - \mu N =$$

$$Nk_BT\left\{\ln(n\lambda_{th}^3) - 1\right\}$$

$$- Nk_BT\ln(n\lambda_{th}^3) = -Nk_BT$$

eða

$$\boxed{\Phi_G = -pV}$$

reynum

$$\left(\frac{\partial\Phi_G}{\partial\mu}\right)_{T,V} = \underbrace{\left(\frac{\partial\Phi_G}{\partial N}\right)_{T,V}}_{-k_BT}\underbrace{\left(\frac{\partial N}{\partial\mu}\right)_{T,V}}_{\frac{N}{k_BT}}$$

$$\hookrightarrow \left(\frac{\partial\Phi_G}{\partial\mu}\right)_{T,V} = -N$$

eins og sást áður

$$\left(\frac{\partial \Phi_G}{\partial V}\right)_{T,\mu} = -\left(\frac{\partial \Phi_G}{\partial \mu}\right)_{T,V}\left(\frac{\partial \mu}{\partial V}\right)_{T,\Phi_G} = N \left(\frac{\partial \mu}{\partial V}\right)_{\underbrace{T,\Phi_G}}$$

$\Phi_G = -N k_B T$

$\to$ fast T og N

notum $N = nV$

$$\left(\frac{\partial \mu}{\partial V}\right)_{T,N} = k_B T \left\{ \frac{\partial \ln (N \lambda_{th}^3 / V)}{\partial V} \right\}_{T,N}$$

$$= -\frac{k_B T}{V}$$

$$\to \left(\frac{\partial \Phi_G}{\partial V}\right)_{T,\mu} = -\frac{N k_B T}{V} = -p$$