→ TOPLOTNE OSOBINE ČVRSTIH TELA I ADSORPCIJA GASOVA:

5.3.1) DEBAJEV MODEL KRISTALA:

$3N - 6 \approx 3N$ NORMALNIH MODOVA

$$g(\nu) = \frac{9N}{\nu_D^3} \cdot \nu^2$$

$\nu_D \to$ MAKSIMALNA DOZVOLJENA FREKVENCIJA (DEBAJEVA FREKVENCIJA)

$C_V = ?$

$$Q = \prod_{i=1}^{3N} \frac{e^{-\frac{1}{2}\beta h\nu_i}}{1 - e^{-\beta h\nu_i}} \Rightarrow \ln Q = \sum_{i=1}^{3N}\left[\ln e^{-\frac{1}{2}\beta h\nu_i} - \ln\left(1 - e^{-\beta h\nu_i}\right)\right] =$$

$$= \sum_{i=1}^{3N}\left[-\frac{1}{2}\beta h\nu_i - \ln\left(1 - e^{-\beta h\nu_i}\right)\right]$$

↳ ZBOG VELIKOG BROJA NORMALNIH MODOVA, SUMU MOŽEMO DA APROKSIMIRAMO INTEGRALOM

$$\sum_i f(\nu_i) \longrightarrow \int g(\nu) \cdot f(\nu)\, d\nu$$

$$\int_0^{\nu_D} g(\nu) \cdot \left(-\frac{1}{2}\beta h\nu - \ln\left(1 - e^{-\beta h\nu}\right)\right) d\nu \qquad \Rightarrow g(\nu) = ?$$

→ PRETPOSTAVIMO DA JE VIBRACIONO FONONSKO KRETANJE NEKAKAV STOJEĆI TALAS:

$$\vec{k} = \frac{\pi}{L}\left(n_x \vec{e}_x + n_y \vec{e}_y + n_z \vec{e}_z\right) \qquad n_x, n_y, n_z = 1, 2, 3, \ldots$$

$$\vec{k} \cdot \vec{k} = k^2 = \frac{\pi^2}{L^2}\left(n_x^2 + n_y^2 + n_z^2\right) \Rightarrow n_x^2 + n_y^2 + n_z^2 = \left(\frac{Lk}{\pi}\right)^2 \Rightarrow R = \frac{Lk}{\pi}$$

$$\Phi(k) = \frac{1}{8} V_{SFERE} = \frac{1}{8} \cdot \frac{4}{3} R^3 \pi = \frac{1}{\cancel{8}_2} \cdot \frac{\cancel{4}}{3} \pi \left(\frac{Lk}{\pi}\right)^3 = \frac{L^3 k^3}{6\pi^2} = \frac{Vk^3}{6\pi^2}$$

UKUPAN BR. STANJA

$$g(k) = \frac{d\Phi(k)}{dk} = \frac{\cancel{3}Vk^2}{\cancel{6}\pi^2} = \frac{k^2 V}{2\pi^2}$$

$\Rightarrow$ NAMA TREBA RASPODELA PO FREKVENCIJAMA

$$g(\nu)\, d\nu = g(k)\, dk$$

$$g(\nu) = g(k) \frac{dk}{d\nu}$$

$$\lambda \cdot \nu = v \Rightarrow \nu = \frac{v}{\lambda} \cdot \frac{2\pi}{2\pi} = \frac{vk}{2\pi} \Rightarrow k = \frac{2\pi\nu}{v} \qquad \frac{dk}{d\nu} = \frac{2\pi}{v}$$

v – BRZINA PROSTIRANJA STOJEĆEG TALASA

$$g(\nu) = g(k) \cdot \frac{2\pi}{v} = \frac{k^2 V}{\cancel{2}\pi^{\cancel{2}}} \cdot \frac{\cancel{2}\cancel{\pi}}{v} = \frac{k^2 V}{v\pi}$$

$$k = \frac{2\pi}{\lambda} = \frac{2\pi\nu}{v} \Rightarrow g(\nu) = \frac{4\pi^{\cancel{2}} V}{v^2 v \cancel{\pi}} \nu^2 = \frac{4\pi V}{v^3} \nu^2 \sim \nu^2$$

$\Rightarrow$ GUSTINA RASPODELE VIBRACIONIH FREKVENCIJA U OVOM SISTEMU

$$g(\nu) = \frac{4\pi V}{v^3}\nu^2$$ } JOŠ MALO ĆEMO DA KORIGUJEMO OVAJ IZRAZ

→ NA SVAKOJ FREKVENCIJI STOJEĆI TALAS U KRISTALU MOŽE DA SE „RAZBIJE" NA DVA TRANSFERZALNA I JEDAN LONGITUDINALNI TALAS:

$$g(\nu) = 2\,\frac{4\pi V}{v_T^3}\cdot\nu^2 + \frac{4\pi V}{v_L^3}\nu^2 = 4\pi V\nu^2\left(\frac{2}{v_T^3} + \frac{1}{v_L^3}\right)$$

JER TRANSFERZALNI TALAS MOŽE DA BUDE DVOSTRUKO POLARIZOVAN

→ POJEDNOSTAVLJENJE ⇒ APROKSIMIRAMO $v_T = v_L = v_0$

$$\boxed{g(\nu) = \frac{12\pi V}{v_0^3}\nu^2}$$ ⇒ MALO DA SREDIMO, KORISTIMO USLOV:

$$\int_0^\infty g(\nu)\,d\nu = 3N$$

↳ BROJ OSCILATORA

$$\int_0^{\infty = \nu_D} \frac{12\pi V}{v_0^3}\nu^2\,d\nu = \frac{12\pi V}{v_0^3}\cdot\frac{\nu_D^3}{3} = 3N \Rightarrow \boxed{\frac{12\pi V}{v_0^3} = \frac{9N}{\nu_D^3}}$$

↳ OVE FREKVENCIJE NE MOGU DA IDU DO ∞, NEGO DO MAKSIMALNE DOZVOLJENE FREKVENCIJE (ν_D)

$$\boxed{g(\nu) = 9N\frac{\nu^2}{\nu_D^3}}$$

$$\ln Q = \int_0^{\nu_D} g(\nu)\left[-\frac{1}{2}\beta h\nu - \ln\left(1 - e^{-\beta h\nu}\right)\right]d\nu =$$

$$= \int_0^{\nu_D}\frac{9N}{\nu_D^3}\cdot\nu^2\cdot\left[-\frac{1}{2}\beta h\nu - \ln\left(1 - e^{-\beta h\nu}\right)\right]d\nu = \frac{9N}{\nu_D^3}\int_0^{\nu_D}\left[-\frac{1}{2}\beta h\nu^3 - \nu^2\ln\left(1 - e^{-\beta h\nu}\right)\right]d\nu$$

$$\langle E\rangle = -\left(\frac{\partial \ln Q}{\partial\beta}\right) = \frac{9N}{\nu_D^3}\int_0^{\nu_D}\left[\frac{1}{2}h\nu^3 + \nu^2\frac{-e^{-\beta h\nu}}{1 - e^{-\beta h\nu}}(-h\nu)\right]d\nu$$

$$\langle E\rangle = \frac{9N}{\nu_D^3}\int_0^{\nu_D}\left[\frac{1}{2}h\nu^3 + \frac{h\nu^3}{e^{\beta h\nu} - 1}\right]d\nu$$

$$C_V = \left(\frac{\partial\langle E\rangle}{\partial T}\right)_{V,N} = \frac{9N}{\nu_D^3}\int_0^{\nu_D}\left(-\frac{h\nu^3\cdot e^{\frac{1}{kT}h\nu}}{\left(e^{\beta h\nu} - 1\right)^2}\cdot\left(-\frac{h\nu}{kT^2}\right)\right)d\nu =$$

$$= \frac{9N}{\nu_D^3}\cdot\frac{h^2}{kT^2}\cdot\int_0^{\nu_D}\frac{\nu^4\cdot e^{\beta h\nu}}{\left(e^{\beta h\nu} - 1\right)^2}d\nu = \frac{9Nk}{\nu_D^3}\cdot\frac{h^2}{k^2T^2}\cdot\int_0^{\nu_D}\frac{\nu^4 e^{\beta h\nu}}{\left(e^{\beta h\nu} - 1\right)^2}d\nu$$

$$C_V = \frac{9Nk}{\nu_D^3}(h\beta)^2\int_0^{\nu_D}\frac{\nu^4 e^{\beta h\nu}}{\left(e^{\beta h\nu} - 1\right)^2}d\nu =$$ { SMENA: $\beta h\nu = x \Rightarrow \nu = \frac{x}{\beta h} \Rightarrow d\nu = \frac{dx}{\beta h}$

$$C_V = \frac{9Nk}{\nu_D^3}(h\beta)^2\int_0^{\beta h\nu_D}\frac{x^4}{(\beta h)^4}\cdot\frac{e^x}{\left(e^x - 1\right)^2}\cdot\frac{dx}{\beta h}$$

$$\boxed{\Theta_D = \frac{h\nu_D}{k}}$$ → DEBAJEVA TEMPERATURA (ODGOVARA MAKSIMALNOJ DOZVOLJENOJ FREKVENCIJI ν_D)

$$C_V = \underbrace{\frac{9Nk}{\nu_D^3}\cdot \cancel{(h\beta)^2}\cdot \frac{1}{(h\beta)^{\cancel{5}}}} \int_0^{\beta h\nu_D} \frac{x^4 e^x}{(e^x-1)^2}\,dx \qquad \Rightarrow \frac{\Theta_D}{T} = \frac{h\nu_D}{kT} = \beta h \nu_D$$

$$\frac{9Nk}{\nu_D^3\cdot\beta^3\cdot h^3} = \frac{9Nk\,k^3\,T^3}{\nu_D^3\,h^3} = 9Nk\left(\frac{T}{\Theta_D}\right)^3$$

$$\boxed{C_V = 9Nk\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\frac{\Theta_D}{T}} \frac{x^4\cdot e^x}{(e^x-1)^2}\,dx}$$

→ OVAJ INTEGRAL NE MOŽEMO ANALITIČKI DA REŠIMO ALI MOŽEMO DA IZVRŠIMO APROKSIMACIJE (PRI NISKIM I PRI VISOKIM TEMPERATURAMA)

1) $T \to 0 \Rightarrow \frac{\Theta_D}{T} \to \infty$

$x \to \infty$

$$C_V = 9Nk\left(\frac{T}{\Theta_D}\right)^3 \underbrace{\int_0^{\frac{\Theta_D}{T}} \frac{x^4 e^x}{(e^x-1)^2}\,dx}_{\neq f(T)} \sim T^3$$

$$\boxed{T \to 0;\ C_V \sim T^3}$$

2) $T \to \infty \Rightarrow \frac{\Theta_D}{T} \to 0$

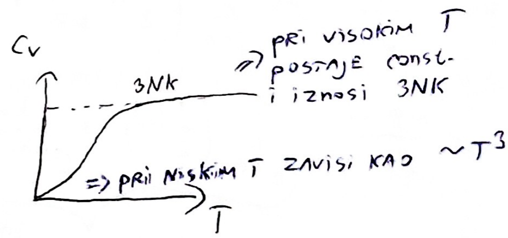
$x \to 0$

$$C_V = 9Nk\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\frac{\Theta_D}{T}} \frac{x^4(1+x+\ldots)\,dx}{(\cancel{1}+x+\ldots\cancel{-1})^2} \approx 9Nk\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\frac{\Theta_D}{T}} \frac{x^{\cancel{4}}}{\cancel{x^2}}\,dx \approx 9Nk\left(\frac{T}{\Theta_D}\right)^3 \frac{x^3}{3}\Big|_0^{\frac{\Theta_D}{T}} \approx$$

↳ SADA PODINTEGRALNA FUNKCIJA ZAVISI OD T ALI POŠTO $x \to 0$, ONDA OVO e^x MOŽEMO DA RAZVIJEMO U RED.

$$\approx {}^3\cancel{9}Nk\left(\frac{\cancel{T}}{\cancel{\Theta_D}}\right)^{\cancel{3}} \frac{1}{\cancel{3}}\left(\frac{\cancel{\Theta_D}}{\cancel{T}}\right)^{\cancel{3}} \Rightarrow \boxed{C_V \approx 3Nk}$$

→ EKSPERIMENTALNO JE POKAZANO DA C_V ZAVISI OD T OVAKO:



5.32 MI-GRINAJZEROVA J-NA:

$$p = -\frac{d\Phi}{dV} + \gamma\frac{U}{V}$$ U → UNUTRAŠNJA ENERGIJA VIBRACIONOG KRETANJA

→ DEBAJEVA J-NA NE DAJE ZAVISNOST OD V

$\Phi = \Phi(V)$ → POTENCIJALNA ENERGIJA KRISTALNE REŠETKE

→ GRINAJZEROVA PRETPOSTAVKA: FREKVENCIJE NORMALNIH MODOVA (FONONA) ZAVISE OD V:

$$\frac{d\ln\nu_j}{d\ln V} = -\gamma\ ;\ \gamma > 0$$

→ VIBRACIONI KVANTNI BROJEVI ZA SVAKI NORMALNI MOD

$$E(V) = \underbrace{\Phi(V)}_{\text{potencijalna energija kristalne rešetke}} + \underbrace{\sum_{j=1}^{3N}\left(n_j + \frac{1}{2}\right)h\nu_j(V)}_{\text{energije vibracija}}$$ → UKUPNA ENERGIJA KRISTALA

$$Q = \sum_i g_i e^{-\beta \varepsilon_i} = \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots\sum_{n_j=0}^{\infty} e^{-\frac{E_j}{kT}}$$

$g_i = 1$ => POŠTO SU VIBRACIONI NIVOI NEDEGENERISANI

$$Q = e^{-\frac{\Phi(V)}{kT}} \underbrace{\sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \sum_{n_j=0}^{\infty} e^{-\frac{(n_j+\frac{1}{2})h\nu_j(V)}{kT}}}_{q_{vib}}$$

$$Q = e^{-\frac{\Phi(V)}{kT}} \cdot q_{vib} = e^{-\frac{\Phi(V)}{kT}} \cdot \prod_{j=1}^{3N} \frac{e^{-\frac{1}{2}\beta h\nu_j}}{1-e^{-\beta h\nu_j}}$$

$$F = -kT\ln Q = +\cancel{kT}\cdot\frac{\Phi(V)}{\cancel{kT}} - kT\sum_{j=1}^{3N}\left[-\frac{1}{2}\frac{h\nu_j}{kT} - \ln\left(1-e^{-\frac{h\nu_j(V)}{kT}}\right)\right]$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = -\frac{d\Phi(V)}{dV} + \cancel{kT}\sum_{j=1}^{3N}\left[-\frac{1}{2}\frac{h}{\cancel{kT}}\frac{d\nu_j}{dV} - \frac{-e^{-\frac{h\nu_j}{kT}}\left(-\frac{h}{\cancel{kT}}\right)\frac{d\nu_j}{dV}}{1-e^{-\frac{h\nu_j}{kT}}}\right] =$$

$$= -\frac{d\Phi(V)}{dV} - \sum_{j=1}^{3N}\left(\frac{1}{2} h\frac{d\nu_j}{dV} + \frac{h\frac{d\nu_j}{dV}}{e^{\beta h\nu_j}-1}\right) =$$

$$= -\frac{d\Phi(V)}{dV} - \underbrace{\sum_{j=1}^{3N}\left(\frac{1}{2} h\nu_j + \frac{h\nu_j}{e^{\beta h\nu_j}-1}\right)}_{-\left(\frac{\partial\ln Q}{\partial\beta}\right) = \langle E\rangle = \sum_{j=1}^{3N}\langle E_j\rangle} \frac{1}{\nu_j}\frac{d\nu_j}{dV}$$

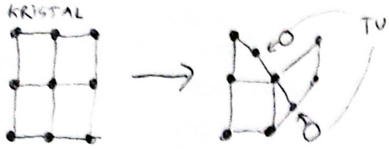
$$\to \frac{1}{\nu_j}\cdot\frac{d\nu_j}{dV} = \frac{V}{V}\cdot\frac{1}{\nu_j}\cdot\frac{d\nu_j}{dV} = \frac{1}{V}\cdot\frac{\frac{d\nu_j}{\nu_j}}{\frac{dV}{V}} = \frac{1}{V}\cdot\frac{d\ln\nu_j}{d\ln V} = -\gamma\frac{1}{V}$$

$$p = -\frac{d\Phi(V)}{dV} - \sum_{j=1}^{3N}\langle E_j\rangle\cdot\frac{1}{V}(-\gamma)$$

$$\boxed{p = -\frac{d\Phi(V)}{dV} + \gamma\frac{\langle E\rangle}{V}}$$ → Mi-GRINAJZEROVA j-NA

5.33 <u>FRENKELOVI DEFEKTI</u>:

IDEALAN KRISTAL



TU SU BILI

→ NEKI OD ATOMA SE IZMESTE U ŠUPLJINE IZMEĐU

n - br. defekata $\qquad 1 \ll n \ll N$ $\qquad$ w - ENERGIJA POTREBNA ZA IZMEŠTANJE JEDNOG ATOMA

N' - br. šupljina $\qquad N \simeq N'$

N - br. atoma

→ POKAZATI DA VAŽI: $n \simeq \sqrt{NN'} \cdot e^{-\frac{w}{2kT}}$ $\qquad$ AKO JE: 1) $kT \ll w$

2) IZMEŠTENI ATOMI NE INTERAGUJU

$n \cdot w$ → ENERGIJA ZA KOJU SE POVEĆAVA ENERGIJA KRISTALA

$$\Gamma(n) = \frac{N!}{n!(N-n)!} \cdot \frac{N'!}{n!(N'-n)!} \equiv \left(\begin{array}{l}\text{BROJ NAČINA DA SE} \\ n \text{ OD } N \text{ ATOMA IZMESTI} \\ \text{NA } N' \text{ ŠUPLJINA}\end{array}\right)$$

$$S(n) = k \ln \Gamma(n)$$

$$F = E(n) - TS(n) = wn - kT \ln \Gamma(n) \qquad \ln N! = N \ln N - N$$

$$\left(\frac{\partial F}{\partial n}\right)_{V,T,N,N'} = 0 \implies \text{RAVNOTEŽA}$$

$$F = wn - kT\left[\underline{N \ln N} - \cancel{N} + \underline{N' \ln N'} - \cancel{N'} - 2n \ln n + \cancel{2n} - (\underline{N}-n)\ln(N-n) + (\cancel{N} - \cancel{n}) - (\underline{N'}-n)\ln(N'-n) + \right.$$
$$\left. + (\cancel{N'} - \cancel{n})\right] =$$

$$= wn - kT\left[N \ln\left(\frac{N}{N-n}\right) + N' \ln\left(\frac{N'}{N'-n}\right) - n \ln\left(\frac{n^2}{(N-n)(N'-n)}\right)\right] \approx$$

$$\approx wn - kT\left[\underbrace{N \ln \frac{N}{N}}_{0} + \underbrace{N' \ln \frac{N'}{N'}}_{0} - n \ln\left(\frac{n^2}{NN'}\right)\right] = wn + nkT \ln\left(\frac{n^2}{NN'}\right) \Big/ \frac{\partial}{\partial n}$$

$$\left(\frac{\partial F}{\partial n}\right)_{N,N',V,T} = w + kT \ln\left(\frac{n^2}{NN'}\right) + nkT \cdot \frac{1}{\frac{n^2}{\cancel{NN'}}} \cdot \frac{2\cancel{n}}{\cancel{NN'}} = 0$$

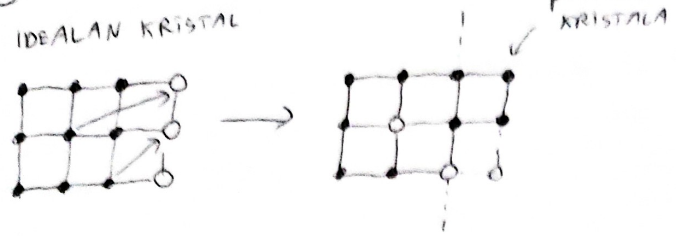
$$w + \cancel{n}kT \ln\left(\frac{n^2}{NN'}\right) + \cancel{n}kT \cdot \frac{2}{\cancel{n}} = 0 \quad /:2kT$$

$$\frac{w}{2kT} + \frac{1}{2}\ln\left(\frac{n^2}{NN'}\right) + 1 = 0 \implies \frac{w}{2kT} + \ln\left(\frac{n}{\sqrt{NN'}}\right) + 1 = 0$$

$$-\frac{w}{2kT} - 1 = \ln\left(\frac{n}{\sqrt{NN'}}\right) \implies \frac{n}{\sqrt{NN'}} = e^{-\left(\frac{w}{2kT}+1\right)} \implies n = \sqrt{NN'} \cdot e^{-\left(\frac{w}{2kT}+1\right)} \approx \sqrt{NN'} \cdot e^{-\frac{w}{2kT}}$$

→ BROJ DEFEKATA FRENKELOVOG TIPA: $\boxed{n = \sqrt{NN'} \cdot e^{-\frac{w}{2kT}}}$

5.34 ŠOTKIJEVI DEFEKTI:



→ NEKI OD ATOMA ČVRSTE FAZE KRISTALA SE IZVUKU NA POVRŠINU KRISTALA

n - br. defekata

N - br. atoma

W - ENERGIJA POTREBNA DA SE JEDAN ATOM IZMESTI NA POVRŠINU

$1 \ll n \ll N$

→ DOKAZATI DA VAŽI $n \simeq N e^{-\frac{W}{kT}}$ AKO JE: $kT \ll W$

$n \cdot w$ → ENERGIJA ZA KOJU SE POVEĆAVA ENERGIJA KRISTALA

$\Gamma(n) = \frac{(N+n)!}{N!\,n!} \equiv$ (BROJ NAČINA DA SE RASPOREDI N+n ŠUPLJINA i ATOMA)

$$\left(\frac{\partial F}{\partial n}\right)_{N,V,T} = 0 \qquad F = E - TS = wn - kT \ln \Gamma(n)$$

$$F = wn - kT\left[(N+n)\ln(N+n) - \cancel{(N+n)} - N\ln N + \cancel{N} - n\ln n + \cancel{n}\right] =$$

$$= wn - kT\left[N\ln(N+n) + n\ln(N+n) - N\ln N - n\ln n\right] =$$

$$= wn - kT\left[N\ln\left(\frac{N+n}{N}\right) + n\ln\left(\frac{N+n}{n}\right)\right] \approx wn - kT\left[\underbrace{N\ln\left(\frac{N}{N}\right)}_{=0} + n\ln\left(\frac{N}{n}\right)\right]$$

$$F = wn - nkT\ln\frac{N}{n} \quad \Big/ \frac{\partial}{\partial n}$$

$$\left(\frac{\partial F}{\partial n}\right)_{N,V,T} = w - kT\ln\frac{N}{n} + nkT\frac{1}{\frac{\cancel{N}}{\cancel{n}}}\cdot\frac{\cancel{N}}{n^2} = 0$$

$$w - kT\ln\frac{N}{n} + \cancel{n}kT\frac{1}{\cancel{n}} = 0 \quad /:kT \Rightarrow \frac{w}{kT} - \ln\frac{N}{n} + 1 = 0 \Rightarrow \frac{w}{kT} + \ln\frac{n}{N} + 1 = 0 \Rightarrow$$

$$\frac{n}{N} = e^{-\left(\frac{w}{kT}+1\right)} \Rightarrow n = N e^{-\left(\frac{w}{kT}+1\right)} \approx N e^{-\frac{w}{kT}}$$

→ BROJ DEFEKATA ŠOTKIJEVOG TIPA: $n \simeq N e^{-\frac{w}{kT}}$

5.35 $T = 300K$

$w = 1eV$

$n = ?$

$N = N_a = 6{,}022 \cdot 10^{23}$

$n = N_a \cdot e^{-\frac{w}{kT}}$

$n = 9{,}547 \cdot 10^{6}\ \frac{1}{mol}$

(5.36) NA NISKIM TEMPERATURAMA VAŽI:

$$C_V = \underbrace{\gamma T}_{\text{DOPRINOS ELEKTRONSKOG KRETANJA}} + \underbrace{AT^3}_{\text{DOPRINOS VIBRACIONOG KRETANJA}} \qquad C_V = C_V^{el} + C_V^{vib} \qquad \to \text{KRISTAL } N_2$$

$T_1 = 2K$ $\quad \gamma = \dfrac{\pi^2 N k}{2 T_F}$; $T_F = 3,7 \cdot 10^4 K$

$T_2 = 20K$

$$A = \frac{12\pi^4 N k}{5\,\Theta_D^3} \; ; \; \Theta_D = 150K$$

$C^{el}_{V,T_1} = 2,21785 \cdot 10^{-3} \frac{J}{mol K}$ $\quad C^{vib}_{V,T_1} = 103,6678 \frac{J}{mol K}$ $\Rightarrow$ ZA T_1: $\dfrac{C^{el}_{V,T_1}}{C^{vib}_{V,T_1}} = 2,1394 \cdot 10^{-5}$

$C^{el}_{V,T_2} = 2,21785 \cdot 10^{-2} \frac{J}{mol K}$ $\quad C^{vib}_{V,T_2} = 103,6678 \cdot 10^{3} \frac{J}{mol K}$ $\Rightarrow$ ZA T_2: $\dfrac{C^{el}_{V,T_2}}{C^{vib}_{V,T_2}} = 2,1394 \cdot 10^{-7}$

(5.37) LANGMIROVA ADSORPCIONA IZOTERMA:

→ KONSTANTA RAVNOTEŽE

→ PRITISAK

$$\Theta = \frac{K(T)\cdot p}{1 + K(T)\cdot p} \to \text{MONOSLOJNA ADSORPCIONA IZOTERMA}$$

→ ZAPOSEDNUTOST N ATOMA NA M ADSORPCIONIH MESTA

$$Q = \frac{N}{M} = \frac{K(T)\cdot p}{1 + K(T)\cdot p}$$

q^0_{vib} → VIBRACIONA PARTICIONA FUNKCIJA ADSORBOVANOG ATOMA U KOME JE OSNOVNI NIVO POSTAVLJEN NA NULU

ε_0 → ENERGIJA ADSORPCIJE ATOMA

---

1) (N,V,T) ANSAMBL

→ BIĆE MALO DRUGAČIJI ANSAMBL JER RAZMATRAMO ADSORPCIJU MOLEKULA

↳ UMESTO $(N,V,T) \longrightarrow (N,M,T)$ ANSAMBL

UMESTO V KORISTIMO BROJ ADSORPCIONIH MESTA (M JE ISTO EKSTENZIVNA VELIČINA KAO I V)

→ SADA TRAŽIMO PARTICIONU FUNKCIJU $Q = Q(M,N,T)$

$$Q = \underbrace{\frac{M!}{N!(M-N)!}}_{\text{NAČIN RASPOREĐIVANJA N ATOMA NA M ADSORPCIONIH MESTA}} \cdot \underbrace{q_{ads}^{N}}_{\text{PARTICIONA FUNKCIJA ADSORBOVANOG ATOMA (IMAMO IH N)}} \Rightarrow q_{ads} = q_{vib} \cdot q_{el} = q^0_{vib} \cdot e^{\beta\varepsilon_0}$$

PRAVA ENERGIJA ADSORPCIJE TOG ATOMA

$$Q = \underbrace{\frac{M!}{N!(M-N)!}}_{\text{ENTROPIJSKI DOPRINOS}} \cdot (q^0_{vib})^N \cdot \underbrace{(e^{\beta \varepsilon_0})^N}_{\text{ENERGIJSKI DOPRINOS}}$$

$$\ln Q = M\ln M - \cancel{M} - N\ln N + \cancel{N} - (M-N)\ln(M-N) + \cancel{M} - \cancel{N} + N\ln q_{ads}$$

$$F = -kT\ln Q = -kT\left[M\ln M - M\ln(M-N) + N\ln(M-N) + N\ln q_{ads} - N\ln N\right]$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{M,T} = -kT\left[-M\frac{-1}{M-N} + \ln(M-N) + N\cdot\frac{-1}{M-N} + \ln q_{ads} - \ln N - \cancel{N}\cdot\frac{1}{\cancel{N}}\right]$$

$$= -kT\left[+\frac{1}{\cancel{M-N}}\cancel{(M-N)} + \ln\left(\frac{M-N}{N}\right) + \ln q_{ads}\right] \Rightarrow \mu = kT\ln\left(\frac{N}{M-N}\right) - kT\ln q_{ads}$$

$$\ln\left(\frac{N}{M-N}\right) = \frac{\mu}{kT} + \ln q_{ads} \Rightarrow \frac{N}{M-N} = e^{\frac{\mu}{kT} + \ln q_{ads}}$$

$$\boxed{\theta = \frac{N}{M}}$$

$$e^{\frac{\mu}{kT} + \ln q_{ads}} = \frac{N}{M-N} = \frac{1}{\frac{M}{N} - 1} = \frac{1}{\frac{1}{\theta} - 1}$$

$$q_{ads}\cdot e^{\frac{\mu}{kT}} = \frac{1}{\frac{1}{\theta} - 1} \Rightarrow \frac{1}{\theta} = \frac{1}{q_{ads}\cdot e^{\frac{\mu}{kT}}} + 1 \Rightarrow \frac{1}{\theta} = \frac{q_{ads}\cdot e^{\frac{\mu}{kT}} + 1}{q_{ads}\cdot e^{\frac{\mu}{kT}}} \Rightarrow$$

$$\boxed{\theta = \frac{N}{M} = \frac{q_{ads}\cdot e^{\frac{\mu}{kT}}}{1 + q_{ads}e^{\frac{\mu}{kT}}}}$$

OVAJ HEMIJSKI POTENCIJAL SE ODNOSI NA ADSORBOVANI ATOM (μ_{ads})

$\mu = ?$ $\quad A_{(g)} \rightleftarrows A_{(ads)}$ $\Rightarrow$ POŠTO SU U RAVNOTEŽI, TO ZNAČI $\mu_{ads} = \mu_{gas}$

$$Q_{gas} = \frac{q^N}{N!} = \frac{1}{N!}\cdot q_{tr}^N = \frac{V^N}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}}$$

$$\mu_{gas} = \left(\frac{\partial F}{\partial N}\right) = -kT\frac{\partial}{\partial N}\left[\ln Q_{gas}\right]_{V,T} = -kT\frac{\partial}{\partial N}\left[N\ln V - N\ln N + N + \frac{3}{2}N\ln\left(\frac{2\pi mkT}{h^2}\right)\right]_{V,T}$$

$$\mu_{gas} = -kT\left[\ln V - \ln N - \cancel{N\frac{1}{N}} + \cancel{1} + \frac{3}{2}\ln\left(\frac{2\pi mkT}{h^2}\right)\right] \Rightarrow$$

$$\mu_{gas} = -kT\ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right] \qquad pV = NkT \Rightarrow \frac{V}{N} = \frac{kT}{p}$$

$$\boxed{\mu_{gas} = -kT\ln\left[\frac{kT}{p}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right]}$$

→ UVEŠĆEMO: $\lambda_T = \dfrac{h}{\sqrt{2\pi m k T}} \Rightarrow \dfrac{1}{\lambda_T^3} = \left(\dfrac{2\pi m k T}{h^2}\right)^{\frac{3}{2}}$

↳ DE BROLJEVA TALASNA DUŽINA

$$\mu_{gas} = \mu_{ads} = -kT\ln\left[\frac{kT}{p}\cdot\frac{1}{\lambda_T^3}\right] = kT\ln\left[\frac{\lambda_T^3}{kT}\cdot p\right]$$ ⇒ UBACIMO U $\theta = \dfrac{q_{ads}\cdot e^{\frac{\mu}{kT}}}{1+q_{ads}\cdot e^{\frac{\mu}{kT}}}$

$$\theta = \frac{q_{vib}^{0}\cdot e^{\beta\varepsilon_0}\cdot e^{+\ln\left(\frac{\lambda_T^3}{kT}\cdot p\right)}}{1+q_{vib}^{0}\cdot e^{\beta\varepsilon_0}\cdot e^{+\ln\left(\frac{\lambda_T^3}{kT}\cdot p\right)}} = \frac{q_{vib}^{0}\cdot e^{\beta\varepsilon_0}\cdot\frac{\lambda_T^3}{kT}\cdot p}{1+q_{vib}^{0}\cdot e^{\beta\varepsilon_0}\cdot\frac{\lambda_T^3}{kT}\cdot p} = \frac{k(T)\cdot p}{1+k(T)\cdot p}$$

↳ $k(T) = q_{vib}^{0}\, e^{\beta\varepsilon_0}\cdot\dfrac{\lambda_T^3}{kT}$

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b) (μ, M, T) ANSAMBL

$\lambda = e^{\beta\mu}$

$$\Xi = \Xi(\mu, M, T)$$

$$\Xi = \sum_{N=0}^{\infty}\sum_{i=1}^{\infty} e^{-\beta(\varepsilon_i - \mu N)} = \sum_{N=0}^{\infty}\sum_{i=1}^{\infty} e^{-\beta\varepsilon_i}\cdot e^{\beta\mu N} = \sum_{N=0}^{\infty} Q_N\lambda^N$$

$$Q_N = \frac{M!}{N!(M-N)!}\cdot q_{ads}^N$$

$$\Xi = \sum_{N=0}^{M}\frac{M!}{N!(M-N)!}(q_{ads}\cdot\lambda)^N\cdot 1^M = \sum_{N=0}^{M}\binom{M}{N}(q_{ads}\lambda)^N\cdot 1^M = (1+q_{ads}\lambda)^M$$

$\theta = ? \Rightarrow \langle N\rangle = ?$

$$\langle N\rangle = \left(\frac{\partial\ln\Xi}{\partial\beta\mu}\right)_{\beta,M} = \lambda\left(\frac{\partial\ln\Xi}{\partial\lambda}\right)_{\beta,M} = \lambda\cdot\frac{\partial}{\partial\lambda}\left[M\ln(1+q_{ads}\lambda)\right] = \lambda M\cdot\frac{q_{ads}}{1+q_{ads}\lambda}$$

↳ $\dfrac{\partial}{\partial\beta\mu} = \dfrac{\partial}{\partial\lambda}\cdot\dfrac{\partial\lambda}{\partial\beta\mu} = \dfrac{\partial}{\partial\lambda}\cdot\dfrac{\partial}{\partial\beta\mu}\left(e^{\beta\mu}\right) = e^{\beta\mu}\cdot\dfrac{\partial}{\partial\lambda} = \lambda\cdot\dfrac{\partial}{\partial\lambda}$

$$\theta = \frac{\langle N\rangle}{M} = \frac{\lambda q_{ads}}{1+\lambda q_{ads}} = \frac{q_{ads}\cdot e^{\frac{\mu}{kT}}}{1+q_{ads}e^{\frac{\mu}{kT}}}$$ $\mu = ?$

$\mu_{ads} = \mu_{gas}$ JER JE RAVNOTEŽA

$$\mu_{gas} = kT\ln\left[\frac{p}{kT}\,\frac{h^3}{(2\pi m kT)^{\frac{3}{2}}}\right] = kT\ln\left[\frac{\lambda_T^3}{kT}\cdot p\right]$$

$$\theta = \frac{q_{vib}^{0}\,e^{\beta\varepsilon_0}\cdot\frac{\lambda_T^3}{kT}\cdot p}{1+q_{vib}^{0}\,e^{\beta\varepsilon_0}\frac{\lambda_T^3}{kT}\cdot p} = \frac{k(T)\cdot p}{1+k(T)\cdot p}$$

$$k(T) = q_{vib}^{0}\,e^{\beta\varepsilon_0}\cdot\frac{\lambda_T^3}{kT}$$

5.38 Višeslojna adsorpcija. BET-ova izoterma

1) Veliki kanonski ansambl

M - br. adsorpcionih mesta

s - br. atoma koji mogu da se adsorbuju na jedno mesto

$0 < s < M$

N - br. atoma

a_s - adsorpciona mesta sa s adsorbovanih atoma

$$\sum_{s=0}^{M} a_s = a_0 + a_1 + \ldots + a_M = M \quad (1)$$

$$\sum_{s=0}^{M} s \cdot a_s = N \quad (2)$$

$q(s)$ - kanonska particiona f-ja za s adsorbovanih atoma na jednom mestu

$q(0) = 1$

$$Q_N = \sum_{a_0, a_1, \ldots, a_M} \frac{M!}{a_0!\, a_1! \ldots a_M!} q(0)^{a_0} q(1)^{a_1} q(2)^{a_2} \cdot \ldots \cdot q(M)^{a_M}$$

↳ Uslovi (1) i (2) prave problem

$\Rightarrow$ pomoć!

(μ, V, T) ansambl

→ permutacije sa ponavljanjem

$$\Xi = \sum_{N=0}^{M} Q_N \lambda^N = \sum_{a_0, a_1, \ldots, a_M} \frac{M!}{a_0!\, a_1! \ldots a_M!} \cdot q(0)^{a_0} \cdot q(1)^{a_1} \cdot \ldots \cdot q(M)^{a_M} \cdot \lambda^{\sum_{s=0}^{M} s \cdot a_s} =$$

$$= \sum_{a_0, a_1, \ldots, a_M} \frac{M!}{a_0! \cdot a_1! \cdot \ldots \cdot a_M!} \left(q(0) \cdot \lambda^0\right)^{a_0} \left(q(1) \lambda^1\right)^{a_1} \cdot \ldots \cdot \left(q(M) \lambda^M\right)^{a_M}$$

Razvoj multinoma

→ Ostao je jedan uslov (1)

$$\Xi = \left[q(0) + q(1)\lambda + q(2)\lambda^2 + \ldots + q(M)\lambda^M\right]^M = \xi^M$$

ξ - Velika kanonska particiona f-ja za jedno adsorpciono mesto

$$\xi = q(0) + q(1)\lambda + q(2)\lambda^2 + \ldots + q(M)\lambda^M$$

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2) BET-ova izoterma

$$\langle s \rangle = \frac{cx}{(1-x-cx)(1-x)}$$

→ Srednji broj adsorbovanih atoma na jednom mestu

$M \to \infty$ $\quad$ c - konstanta $\quad$ $x \sim p$ $\quad$ $\langle s \rangle = \frac{\langle N \rangle}{M}$

q_1 - particiona f-ja atoma u prvom adsorpcionom sloju

q_2 - particiona f-ja atoma u drugom i svim ostalim slojevima

$$q(s) = q_1 \cdot q_2 \cdot q_2 \cdot \ldots \cdot q_2 = q_1 q_2^{s-1}$$

→ IZ PRETHODNOG PRIMERA, IMAJUĆI U VIDU DA $M \to \infty$:

$$\xi = q(0) + q(1)\lambda + q(2)\lambda^2 + \dots$$

$$\xi = 1 + q_1\lambda + q_1 q_2 \lambda^2 + q_1 q_2^2 \lambda^3 + \dots \qquad \Xi = \xi^M$$

$$\langle N \rangle = \left(\frac{\partial \ln \Xi}{\partial(\beta\mu)}\right)_{M,\beta} = \lambda \frac{\partial}{\partial\lambda}\left[\ln \Xi\right]_{M,\beta} = M\lambda\left(\frac{\partial \ln \xi}{\partial \lambda}\right)_{M,\beta}$$

$$\frac{\langle N \rangle}{M} = \langle s \rangle = \lambda \cdot \frac{q_1 + 2q_1q_2\lambda + 3q_1q_2^2\lambda^2 + \dots}{1 + q_1\lambda + q_1q_2\lambda^2 + \dots} = \frac{\lambda q_1(1 + 2q_2\lambda + 3q_2^2\lambda^2 + \dots)}{1 + \lambda q_1(1 + q_2\lambda + q_2^2\lambda + \dots)} =$$

$$= \frac{\lambda q_1(1 + 2q_2\lambda + 3q_2^2\lambda^2 + \dots)}{1 + \lambda q_1 \cdot \frac{1}{1 - q_2\lambda}} = \frac{\lambda q_1(1 + 2q_2\lambda + 3q_2^2\lambda + \dots)(1 - q_2\lambda)}{1 - q_2\lambda + q_1\lambda} =$$

$$= \frac{\lambda q_1(1 + 2q_2\lambda + 3q_2^2\lambda^2 + \dots - q_2\lambda - 2q_2^2\lambda^2 - 3q_2^3\lambda^3 - \dots)}{1 - q_2\lambda + q_1\lambda} =$$

$$= \frac{\lambda q_1(1 + q_2\lambda + 2q_2^2\lambda^2 + \dots)}{1 - q_2\lambda + q_1\lambda} = \frac{q_1\lambda \cdot \frac{1}{1 - q_2\lambda}}{1 - q_2\lambda + q_1\lambda} = \frac{q_1\lambda}{(1 - q_2\lambda + q_1\lambda)(1 - q_2\lambda)} =$$

$$= \frac{\lambda q_2 \cdot \left(\frac{q_1}{q_2}\right)}{\left(1 - q_2\lambda + q_2\lambda\left(\frac{q_1}{q_2}\right)\right)(1 - q_2\lambda)} = \langle s \rangle$$

$$\frac{cX}{(1 - X - cX)(1 - X)} = \langle s \rangle \Rightarrow \boxed{c = \frac{q_1}{q_2}} \qquad X = q_2\lambda = q_2 e^{\beta\mu}$$

$$\mu = \mu_{gas} = \mu_{ads}$$

$$\mu_{gas} = -kT \ln\left[\frac{kT}{p}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right] =$$

$$= -kT \ln\left[\frac{kT}{p} \cdot \frac{1}{\lambda_T^3}\right] = kT \ln\left[\frac{\lambda_T^3}{kT} \cdot p\right]$$

$$X = q_2 \cdot e^{\frac{1}{\cancel{kT}} \cdot \cancel{kT} \ln\left[\frac{\lambda_T^3}{kT} \cdot p\right]}$$

$$\boxed{X = q_2 \cdot \frac{\lambda_T^3}{kT} \cdot p}$$

5.3) DISOCIJACIJA PRILIKOM ADSORPCIJE – KATALIZATOR

$$A_{2(g)} \rightleftarrows 2A_{(ads)}$$

$\theta = f(p) \Rightarrow$ Adsorpciona izoterma

$$q(A_2) = q_{tr}(A_2) \cdot q_v(A_2) = V \cdot \left(\frac{2\pi m kT}{h^2}\right)^{\frac{3}{2}} \cdot q_v(A_2)$$

$$\mu_{gas}(A_2) = -kT \ln\left[\frac{kT}{p}\left(\frac{2\pi m kT}{h^2}\right)^{\frac{3}{2}} \cdot q_v(A_2)\right] = -kT \ln\left[\frac{kT}{p} \cdot \frac{1}{\lambda_T^3} \cdot q_v(A_2)\right] =$$

$$= kT \ln\left[\frac{\lambda_T^3}{kT} \cdot q_v^{-1}(A_2) \cdot p\right]$$

$$\mu_{gas}(A_2) = 2 \cdot \mu_{ads}(A) \Rightarrow \mu_{ads}(A) = \frac{1}{2}\mu_{gas}(A_2) \Rightarrow \mu_{ads}(A) = kT \ln\left[\frac{\lambda_T^3}{kT} \cdot q_v^{-1}(A_2) \cdot p\right]^{\frac{1}{2}}$$

$\rightarrow$ Iz ZADATKA 37 $\Rightarrow$ $$\theta = \frac{q_{ads}\, e^{\mu_{ads}\beta}}{1 + q_{ads}\, e^{\beta\mu_{ads}}}$$

$$\theta = \frac{q_{ads} \cdot e^{\ln\left[\frac{\lambda_T^3}{kT} \cdot q_v^{-1}(A_2) \cdot p\right]^{\frac{1}{2}}}}{1 + q_{ads} \cdot e^{\ln\left[\frac{\lambda_T^3}{kT} \cdot q_v^{-1}(A_2) \cdot p\right]^{\frac{1}{2}}}} = \frac{q_{ads} \cdot \left(\frac{\lambda_T^3}{kT} \cdot q_v^{-1}(A_2)\right)^{\frac{1}{2}} \cdot p^{\frac{1}{2}}}{1 + q_{ads}\left(\frac{\lambda_T^3}{kT} \cdot q_v^{-1}(A_2)\right)^{\frac{1}{2}} \cdot p^{\frac{1}{2}}} = \frac{k(T) \cdot \sqrt{p}}{1 + k(T)\sqrt{p}}$$

$$\boxed{k(T) = q_{ads}\sqrt{\frac{\lambda_T^3}{kT\, q(A_2)}}}$$