EKB. Teoretisk fysikk ID
Lunsdag 26. mai 1972
kl. 9-14

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①

Løsning.

I

a/ σ må være positiv, $\underline{\sigma \geq 0}$.

b

Gen. strømmer og krefter:

$\underline{J_1 = J}$ $\quad$ $\underline{J_2 = I}$

$\underline{X_1 = \Delta p/T}$ $\quad$ $\underline{X_2 = \Delta\varphi/T}$

Fenomenologiske likninger:

$$J = L_{11}\,\Delta p/T + L_{12}\,\Delta\varphi/T$$
$$I = L_{21}\,\Delta p/T + L_{22}\,\Delta\varphi/T$$

c/

$$J = L_{11}\,\Delta p/T + L_{12}\,\Delta\varphi/T$$
$$0 = L_{21}\,\Delta p/T + L_{22}\,\Delta\varphi/T$$

$$\Delta p = -\frac{L_{22}}{L_{21}}\Delta\varphi \qquad J = \left(-L_{11}\frac{L_{22}}{L_{21}} + L_{12}\right)\Delta\varphi/T$$

$$A = \left(\frac{\Delta\varphi}{J}\right)_{I=0} = \underline{-\frac{L_{21}\,T}{L_{11}L_{22} - L_{12}L_{21}}}$$

$$J = L_{22}\,\Delta\varphi \qquad B = \left(J/\Delta\varphi\right)_{\Delta p=0} = \underline{L_{12}/T}$$

$$0 = L_{11}\,\Delta p + L_{12}\,\Delta\varphi \qquad \Delta\varphi = -\frac{L_{11}}{L_{12}}\Delta p$$

$$I = L_{21}\,\Delta p + L_{22}\,\Delta\varphi = \left(L_{21} - L_{22}\frac{L_{11}}{L_{12}}\right)\Delta p/T$$

$$C = \left(\frac{\Delta p}{I}\right)_{J=0} = \underline{-\frac{L_{12}\,T}{L_{11}L_{22} - L_{12}L_{21}}}$$

$$I = L_{21}\,\Delta p \qquad D = \left(I/\Delta p\right)_{\Delta\varphi=0} = \underline{L_{21}/T}$$

Resiprositetsrelasjonen for dette systemet

$$L_{12} = L_{21}$$

Dette gir sammenhengen:

$$A = C \qquad B = D$$

II

a) Likevektsbetingelsene er at

p, T og μ_i $(i = 1, 2, \cdots, c)$ er konstante over systemet.

Ideell blanding.

i) Ingen volumendring ved blanding (konst p og T): $V = \sum_i N_i v_i^0 = V_0$

ii) Ingen energiendring — " — $U = \sum_i N_i u_i^0 = U_0$

iii) Blandingsentropi som ved ideelle gasser: $S = \sum_i N_i (s_i^0 - k \ln x_i)$

$$G = U + pV - ST = U_0 + pV_0 - S_0 T + kT \sum_i N_i \ln x_i$$

$$= G_0 + kT \sum_i N_i \ln x_i$$

$$\mu_n = \left(\frac{\partial G}{\partial N_n}\right)_{p,T,N_{i\neq n}} = \mu_n^0 + kT \ln x_n + \sum_i N_i \cdot \frac{\partial}{\partial N_n}(\ln N_i - \ln N)$$

$$= \mu_n^0 + kT \ln x_n + \sum_i \left(\delta_{in} - \frac{N_i}{N}\right) = \mu_n^0 + kT \ln x_n$$

b/

$$G^{ex} = N\left[\sum_{i=1}^{s} f_i x_i + \frac{1}{2}\sum_{i,j=1}^{s} f_{ij} x_i x_j + \cdots\right]$$

$$= \sum_{i=1}^{s} f_i N_i + \frac{1}{2}\sum_{i,j=1}^{s} f_{ij}\frac{N_i N_j}{N} + \cdots$$

$$\mu_0^{ex} = \frac{\partial G^{ex}}{\partial N_0} = -\frac{1}{2}\sum_{i,j=1}^{s} f_{ij}\frac{N_i N_j}{N^2} + \cdots = \underline{-\frac{1}{2}\sum_{i,j=1}^{s} f_{ij} x_i x_j + \cdots}$$

$$\mu_k^{ex} = \frac{\partial G^{ex}}{\partial N_k} = f_k + \frac{1}{2}\sum_{i=1}^{s}(f_{ik}+f_{ki})\frac{N_i}{N} - \frac{1}{2}\sum_{i,j=1}^{s} f_{ij}\frac{N_i N_j}{N^2} + \cdots$$

$$= \underline{f_k + \sum_{i=1}^{s} f_{ik} x_i - \frac{1}{2}\sum_{i,j=1}^{s} f_{ij} x_i x_j + \cdots} \qquad k = 1,2,\cdots,s$$

(med $f_{ik} = f_{ki}$)

Svak oppløsning:

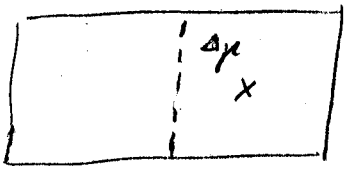
Oppløst stoff ($k = 1,2,\cdots,s$):

$$\underline{\mu_k^{ex} = f_k}$$

Oppløsningsmiddel:

$$\underline{\mu_0^{ex} = 0}$$

c/



Likevekt er gitt ved at det kjemiske potensial for oppløsningsmiddlet er det samme på begge sider av membranen

$$\mu^\circ(p) = \mu(p+\Delta p, x) = \mu^\circ(p+\Delta p) + kT\ln(1-x)$$

$$\mu^\circ(p+\Delta p) = \mu^\circ(p) + \int_p^{p+\Delta p}\frac{\partial \mu^\circ(p)}{\partial p}dp = \mu^\circ(p) + \int_p^{p+\Delta p} v^\circ dp = \mu^\circ(p) + v^\circ \Delta p$$

$$\mu^0(p) = \mu^0(p) + v^0 \Delta p + kT \ln(1-x)$$

Osmotisk trykk: $\Delta p = \underline{\underline{- \frac{kT}{v^0} \ln(1-x)}}$

For små x:

$$\Delta p \approx \frac{kT}{v^0} x = \frac{kT N x}{N v^0} =$$

$$\approx \frac{N_S kT}{V} = n \frac{N_A kT}{V} = \underline{\underline{n \frac{RT}{V}}} \qquad \left(V = N_S v_S + N_0 v^0 = N(x v_S + (1-x) v^0) \approx N v^0 \right)$$

d)

Molekylvekt:

$12 \cdot 12 =$	144
$22 \cdot 1 =$	22
$11 \cdot 16 =$	176
	342

$$n = \frac{100\,g}{342\,g/mol} = \frac{100}{342}\,mol$$

$$\Delta p = \frac{100}{342}\,mol \cdot \frac{8{,}32\,J/deg\,mol \cdot 293\,deg}{10^{-3}\,m^3} = \underline{\underline{7{,}13 \cdot 10^5\,J/m^3}}$$

$$\approx \underline{\underline{7\,atm}}$$

$$\left(J/m^3 = \frac{N m}{m^3} \approx 10^{-1}\,\frac{kp}{m^2} = 10^{-5}\,kp/cm^2 \approx 10^{-5}\,atm \right)$$