(10) a) 1^{er} orden

$dQ = L\,dn''$

$L = h'' - h'$

$L = T(s'' - s')$

$\mu' = \mu''$

$$\Longrightarrow \frac{dp}{dT} = \frac{s''-s'}{v''-v'} = \frac{L}{T(v''-v')}$$

Ecuac de Clapeyron

$s \cdot v$, $L \cdot v$

$$\frac{d\ln p}{dT} = \frac{L}{RT^2}$$

Eq met.

$$ds = \frac{c_p}{T}dT - \alpha v\,dp$$

$$\frac{dL}{dT} = c_p'' - c_p' + \frac{L}{T}\left(1 + T\frac{\alpha' v' - \alpha'' v''}{v'' - v'}\right) = T\left(\frac{ds}{dT}\right)_{SAT} = C_{SAT}$$

$$\frac{dL}{dT} = c_p^{V} - c_p^{l}$$

$L = T\,dS$

$$c_{SAT}^{V} = c_p^{V} - T\alpha v\left(\frac{dp}{dT}\right)_{SAT}$$

Rango coexistencia

T. de fase

$L\,v\,dm = m\,c^{l}_{SAT}\,dT$ (extr. vapor líquido)

AM	1a)
1	7
	9
	10
	12)

cubo
cojo
atmósfera - vacío

(TA1)

Molaridad $c = \frac{n_2}{V}$ V/dm^3

Molalidad $m = \frac{n_2}{m_1}$

T. másica $w_2 = \frac{m_2}{m_1 + m_2} \cdot 100$

$$c = \frac{\rho x_2}{x_2 (M_2 - M_1) + M_1}$$ M (g/mol)

$$m = \frac{1000\, x_2}{M_1 (1 - x_2)}$$

$F = \sum n_i f_i$

$$\sum n_i\, df_i = \left(\frac{\partial F}{\partial T}\right)_{p,n_j} dT + \left(\frac{\partial F}{\partial p}\right)_{T,n_j} dp$$

$$v_2 = \left(\frac{\partial V}{\partial c}\right)\left(\frac{\partial c}{\partial n_2}\right)_{T,p,n_1} \Rightarrow V = \frac{n_1 M_1 + n_2 M_2}{\rho} \rightarrow \rho(c)_{T,p}$$

V Map. $\Phi = \frac{V - n_1 v_1^0}{n_2} = \Phi(n_2)_{T,p,n_1}$

$$\hookrightarrow v_2 = \Phi + n_2 \left(\frac{\partial \Phi}{\partial n_2}\right)_{T,p,n_1}$$

$F^M = F'' - F'$

$$h_i^M = \left(\frac{\partial H^M}{\partial n_i}\right)_{T,p,n_j} \qquad H^M = Q \qquad h_i^M = h_i - h_i^0$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j}$$

Mod. ideales $\rightarrow \mu_{1\,(T,p,x_1)} = \mu_1^0(T,p) + RT \ln x_1$

No " $\rightarrow \mu_1(T,p,x_1) = \mu_1^0(T,p) + RT \ln \underbrace{\gamma_1 x_1}_{a_1} \rightarrow ?$ $\lim_{x_1 \to 1} \gamma_1 = 1$

$$d \ln \gamma_1 = -\frac{n_2}{n_1} d \ln \gamma_2$$

Ref. asimé:

$$\lim_{x_1\to 1} \gamma_2^a = 1 \quad \vee \quad \lim_{x_2\to 0} \gamma_2^a = 1$$

$$\mu_2(T,p,x_2) = \mu_2(T,p,x_2^*) + RT\ln \gamma_2^a x_2 \qquad x_2^* \to \gamma_2^a x_2^* = 1$$

c $\quad \mu_2^{*c}(T,p) + RT\ln \gamma^{(c)} c$

m

$$\lim_{x_2\to 0} \gamma^{(x)} = 1$$

$\gamma^{(c)m}$

$c \to 0$

Dis. diluidas

$$\mu_2^{*x}(T,p) - \mu_2^{*m}(T,p) = RT\ln \frac{1000}{M_1}$$

$$\frac{\gamma^{(x)}}{\gamma^{(m)}} = \frac{M_1 m}{1000 x_1} = \frac{1}{1-x_1}$$

$$G^M = G'' - G' = RT\left(\sum n_i \ln \gamma_i x_i\right)$$

$$V = \left(\frac{\partial G}{\partial p}\right)_{T,n_i} \qquad \frac{H}{T^2} = -\left(\frac{\partial (G/T)}{\partial T}\right)_{p,n_i}$$

$$V^M = RT\sum n_i \left(\frac{\partial \ln \gamma_i x_i}{\partial p}\right)_{T,n_i}$$

$$H^M = -RT^2 \sum n_i \left(\frac{\partial \ln \gamma_i x_i}{\partial T}\right)$$

$$X^E = X^M - X^{M\,id} \to \gamma_i = 1 \text{ siempre}$$

ideal $\Rightarrow V^{M\,id} = 0,\ H^{M\,id} = 0 \to V^E = V^M,\ H^E = H^M$

$$G^E = RT\sum n_i \ln \gamma_i$$

$$V^E = RT\sum n_i \left(\frac{\partial \ln \gamma_i}{\partial p}\right)_{T,n}$$

$$H^E = -RT^2 \sum n_i \left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{p,n_i}$$

Si ... ideal ... $\Delta G \cdot T\Delta S$

$S^M = -R\sum n_i \ln \gamma_i x_i \longrightarrow G'''$ ... 1 atm

25°C juntos 1 atm

compri. $\to G''$ ... 1 atm juntos

$\ldots G''' - G'' - G' = (G'' - G^M) \ldots$

S^M

(12)

$A_i = \mu_i' - \mu_i''$ $\quad >0 \ \mathrm{I} \to \mathrm{II}$; $< \ \mathrm{II} \to \mathrm{I}$

$A_i = -\Delta\mu_i^0 + RT \ln \frac{a_i'}{a_i''}$

$d\left(\frac{A_i}{T}\right) = \frac{\Delta h_i^0}{T^2} dT - \frac{\Delta v_i^0}{T} dp + R\, d\ln \frac{a_i'}{a_i''}$

$A_i = 0$
$\to d \ln \frac{a_i''}{a_i'} = \frac{\Delta h_i^0}{RT^2} dT - \frac{\Delta v_i^0}{RT} dp$

Líquidos $\to$ $dp = 0$ $\quad a_i' = 1$ $\quad a_i'' = a_i$

$d \ln a_i = \frac{\Delta h_i^0 \, dT}{RT^2}$

Diluido
$\to \Theta_c \approx \frac{R(T_1^0)^2 M_1}{1000 \Delta h_1^0} \cdot m$

L - V

$d \ln \frac{x_i^V}{a_i} = \frac{\Delta h_i^0}{RT^2} dT$ $\quad$ s. no volát. $a_1 \approx x_1$ $\to$ $\Theta_e = \frac{R T_1^{0\,2} M_1}{1000 \Delta h_1} m$

Δ L - V
$a_i'' = x_i^V$
$a_i' = a_i$ $\quad \to \quad x_i^V p = a_i p_i^0$

$\to p_i = a_i p_i^0$ presión parcial

$p_i = x_i^V p$

$p_i = a_i^L p_i^0 = x_i^V p$

$\to$ Diluidas $\quad p_1 = x_1 p_1^0$ Ley de Raoult (soluto)
$\gamma_1 = 1$
$\gamma_2^0 = 1$ $\quad p_2 = x_2 K_2$ " " Henry (disolv.)

$\cancel{p_2} = a_2 p_2^0 = x_2 p_2^0 \to K_2 = p_2^0$

$\to$ No diluidas
$p_2 = x_2 \gamma_2^a K_2$ $\quad | \quad x_B^V p = \gamma_B^S \cdot x_B^L p_B^0$ Sim
$x_B^V p = \gamma_B^a \cdot x_B^L K$ Asim

Regla de las fases $\quad W = 2 + K - \emptyset - r$

Ley de Nernst $\to \frac{a_3''}{a_3'} = K$ $\xrightarrow{\text{diluidas}} K = \frac{x_3''}{x_3}$

Presión osmótica $\quad \Pi = p'' - p'$ $\quad | \mu_1'' = \mu_1^0 + \mu_1^{0} \ldots$

$\ln a_1 = -\frac{\Pi v_1^0}{RT}$ $\xrightarrow{\text{diluida}}$ $\Pi = RTC$ $\quad A_1 = v_1[(p'' - p') - \Pi] <$

$a_1 \approx x_1$
$\ln x_1 \approx -x_2 \approx x_1/0.0$

13

$dn_i = \nu_i d\xi \longrightarrow n_i - n_i^0 = \nu_i \xi$

$dG = \sum \nu_i \mu_i d\xi$

$A = -\sum \nu_i \mu_i \qquad \left(\frac{\partial G}{\partial \xi}\right) = -A$

<u>Gas</u>

$\sum \nu_i \mu_i^* = -RT \sum \nu_i \ln p_i = -RT \ln K$

$K = \prod p_i^{\nu_i} = p^{\sum \nu} \prod_{1-k} x_i^{\nu_i}$

$Q = \sum \nu_i h_i^0$

$\frac{d \ln K}{dT} = \frac{Q}{RT^2} \longrightarrow$ Ecua de Van't Hoff

<u>Disolución</u>

$\sum \nu_i \mu_i^* = -RT \sum \nu_i \ln a_i$

$K_a = \prod_{1-k} a_i^{\nu_i}$

$A_{\nu_+} B_{\nu_-} \longrightarrow A^{z_+} + B^{z_-}$

$\nu_+ z_+ + \nu_- z_- = 0$

$n_2 \longrightarrow \begin{array}{l} n_+ = \nu_+ n_2 \\ n_- = \nu_- n_2 \end{array}$

$\tilde{\mu}_i = \left(\frac{\partial G}{\partial n_i}\right)_{n_1, n_j} \qquad i \neq j = +, -$

$\hookrightarrow \mu_i = \mu_i^*$
$\hookrightarrow \tilde{\mu}_i = \tilde{\mu}_i \longrightarrow \mu_2 = \nu_+ \tilde{\mu}_+ + \nu_- \tilde{\mu}_-$

$\nu = \nu_+ + \nu_-$

$\mu_2 = \mu_2^* + \nu RT \ln a_2$

$\hookrightarrow$ iones a partir electrolito

Pilas

$\Delta \tilde{\mu}_e = \tilde{\mu}_e^{\omega} - \tilde{\mu}_{e\alpha}$

$dW_{NE} = -F \Delta \psi \, dn_e$

$dG = (\tilde{\mu}_e^{\alpha} - \mu_e^{\omega}) \, dn_e$

$\Delta \tilde{\mu}_e = -F \Delta \psi$

Acumulador

$\Delta \psi = \dfrac{A}{nF}$ n = 2 plomo

Daniell

$\Delta \psi = \dfrac{A - \Delta \mu_{SO_4^{2-}}}{2F}$ $= \tilde{\mu}^{\delta}_{SO_4^{2-}} - \tilde{\mu}^{\gamma}_{SO_4^{2-}}$

$Q^* = nF \left[T \left(\dfrac{\partial \Delta \psi}{\partial T} \right)_{p, n_1, \dots n_k} - \Delta \psi \right]$

$Q = Q^* - \sum \nu_c h_i^M$

INTERFASE LÍQUIDO-VAPOR

(14)

$$dW = p\,dV - \sigma\, d\Sigma$$

$$dU = T\,dS - p\,dV + \sigma\, d\Sigma \qquad \sigma = \frac{F}{\ell}$$

$$dF = -S\,dT + \sigma\, d\Sigma - \mu\, dn \quad (V \text{ cte})$$

σ? $-\sigma d\Sigma$ Para Gibbs

Ley de Laplace

(I) ^{II}) $$p' - p'' = \frac{2\sigma}{r}$$

$$\sigma = \sigma^0 \left(1 - \frac{T}{T_c}\right)^{\gamma}$$

σ^0 de (...)

$T_{crít}$ $\gamma = 1{,}22 \pm 0{,}02$ Buff-Lovett

↓

desaparece interfase

γ_R?

$p^L - p^V = 2\sigma/r$

V / L $r > 0$ V / L $r < 0$

$$\ln \frac{(p^V)_r}{(p^V)_\infty} = \frac{2\sigma v^L}{RTr}$$ Ecuación de Kelvin

TERMODINÁMICA TÉCNICA

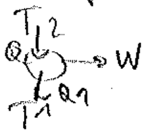
entender ciclos

$\Delta U = Q - W$

Ciclo $\rightarrow W = Q$

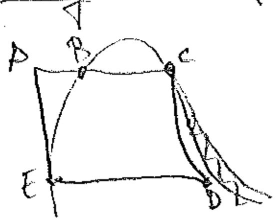
Máquinas térmicas

2 focos



$$\eta = \frac{W}{Q_2} < 1$$

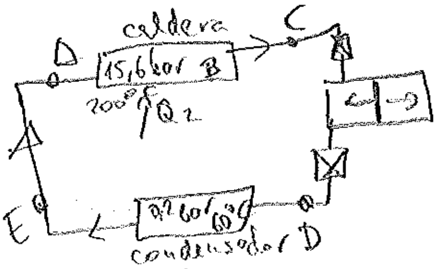
Máquina vapor - Ciclo Rankine



$W = h_C - h_D$

$Q_2 = h_C - h_A$

$$\eta = \frac{h_C - h_D}{h_C - h_A} \quad 27\%$$



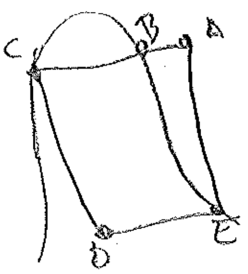
$$X_D = \frac{S_D - S_E}{S_F - S_E}$$

$EA \rightarrow dh = v\,dp \rightarrow AB \quad dS = \frac{C_p\,dT}{T}$

(...)

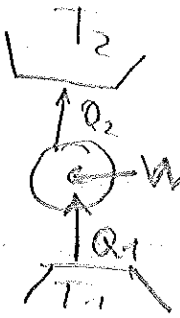
Máq. frigorífica

$$\eta = \frac{Q_1}{|W|} \gtrless 1$$

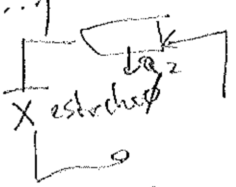


DC iso h

EA adiab.



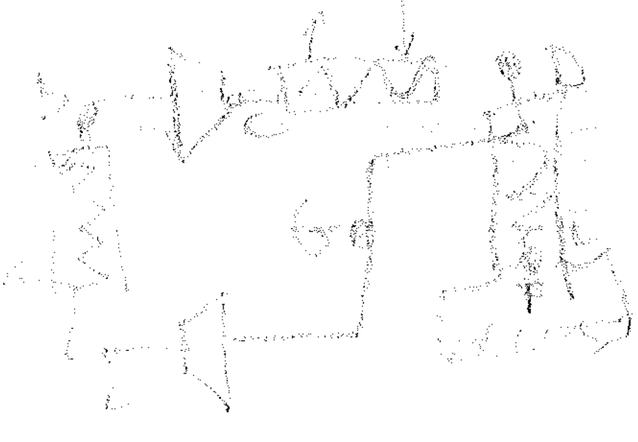
(...)



Pa1

bomba calor $\eta = \frac{Q_2}{W}$

Linde gases



PROCESOS IRREVERSIBLES

$\vec{J}^z \quad z = 1,2,\dots k, U = f(\vec{\nabla}T, \vec{\nabla}p, \vec{\nabla}\mu_i, \vec{j}, \lambda_i)$

$d^2 Z = \vec{J}^z \, d\vec{A} \, dt$

$\vec{J}^z = \lambda_{zT} \vec{\nabla}T + \lambda_{zp} \vec{\nabla}p + \lambda_{zc} \vec{\nabla}c_z + \lambda_{zj} \vec{j}$ $\qquad \vec{\nabla} = 0$, $\lambda \neq 0 \Rightarrow \cancel{\vec{\nabla}}$

$\lambda_{zi}(T, p, c_z)$ límite validez cerca $\vec{\nabla}$

L no de $\vec{\nabla}$

$\vec{J}^z \rightarrow$ flujos termodinámicos

$\vec{\nabla} \rightarrow$ fuerza "

$\lambda_{zi} \rightarrow$ coeficientes fenomenológicos o de transporte

→ " ecu. NS " "

Procesos termoeléctricos

e: carga e^- !!

Hilo conductor

$I, \frac{dI}{dx}$ V ind.

Obs → $I, T, \Delta\psi$

Rel → $J_U, \frac{d\tilde{\mu}_e}{dx}$

S: coeficiente de Seebeck / pot. termoeléctrico

σ: conductividad eléctrica

π: coef. de Peltier

$\Delta J_U = J_U^{II} - J_U^{I}$

J_Q

Estac. → $\Delta J_U = J_Q$

$\Delta\psi = \psi^{II} - \psi^{I}$

$\tilde{\mu}_e$ / partícula

$\mu = N_A \tilde{\mu}$ mol → 6,022·10²³

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

$$\boxed{\begin{aligned} J_U &= K A \frac{dT}{dx} + \left(\pi - \frac{\tilde{\mu}_e}{e}\right) I \\ \frac{d\tilde{\mu}_e/e}{dx} &= S \frac{dT}{dx} - \frac{I}{\sigma A} \end{aligned}}$$

1) L. Fourier $\quad I = 0, \frac{dT}{dx} \neq 0 \quad J_U = K A \frac{dT}{dx}$
Cond. calor sólido

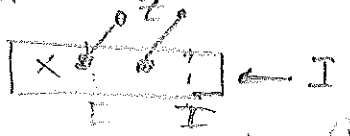
2) Efecto Joule $\quad I \neq 0, \frac{dT}{dx} = 0 \quad \Delta J_U = -\frac{\tilde{\mu}_e}{e} I = I\Delta\psi = W_{el} = J_Q$

3) Efecto Peltier $\quad I \neq 0 \quad \frac{dT}{dx} \neq 0 \quad (\pi_y - \pi_x)\frac{I}{A} = K_x \left(\frac{dT}{dx}\right)_x - K_y \left(\frac{dT}{dx}\right)_y$

J_Q? $\boxed{x \,|\, y \,|\, x}$ $J_Q < 0 \rightarrow \frac{dT}{dx}$ J_U

4) Ley Ohm $\quad \frac{dT}{dx} = 0, I \neq 0 \rightarrow \Delta\psi = \underbrace{\frac{\Delta x}{\sigma A}}_{R} I$

5) Efecto Seebeck $\quad \Delta\psi \neq 0, I = 0, \frac{dT}{dx} \neq 0 \rightarrow \Delta\psi = \int_{T_I}^{T_{II}} \underbrace{(S_z - S_x)}_{\text{pot. termoeléctrico}} dT + IR$



6) Coeficiente de Thomson $\quad S_{o}, T$ de

$A\left[K A \frac{dT}{dx}\right] + I \int_{T'}^{T''} \tau \, dT + I \Delta\psi = J_Q$

$\tau(\pi) = \left(\frac{d\pi}{dT} - S\right)$

Formula M.E.

$$J_U = KA\frac{dT}{dx} + \left(\Pi - \frac{\tilde{\mu}_e}{e}\right) I$$

$$d\tilde{\mu}_e \cdot S\frac{dT}{dx} \cdot \frac{I}{\sigma A}$$

$$T\theta = \psi = J_s\frac{dT}{dx} + I'\left(-\frac{d(\tilde{\mu}_e/e)}{dx}\right)$$

Flujos — F. termodinámicas

θ = producción de entropía

λ, reversi. $\theta = 0$

irrever. $\theta \neq 0$

$$T J_s = J_U + I\left(\frac{\tilde{\mu}_e}{e}\right)$$

$$Q = \Delta U + W$$

$$J_s = L_{11}\frac{dT}{dx} + L_{12}\left(-\frac{d(\tilde{\mu}_e/e)}{dx}\right)$$

$$I = L_{21}\frac{dT}{dx} + L_{22}\left(-\frac{d(\tilde{\mu}_e/e)}{dx}\right)$$

$L_{ij} = f(T)$

límite validez

$\vec{\nabla} \gg \rightarrow 2^{o}$ orden

$$\begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \quad L_{21} = L_{12}$$

Relac. de reciprocid. de Onsager $\rightarrow \Pi = T S'$

$$(\Pi_x - \Pi_y) = T(S_x - S_y)$$

$$K = \frac{1}{A}\left(L_{11} - \frac{L_{21}L_{12}}{L_{22}}\right)$$

$$\Pi = T\frac{L_{12}}{L_{22}} \qquad S' = \frac{L_{21}}{L_{22}} \qquad \sigma = \frac{L_{22}}{A}$$

Electrodifusión

B/B^{z-} $\quad B \rightarrow B^{z-} + z_- e$

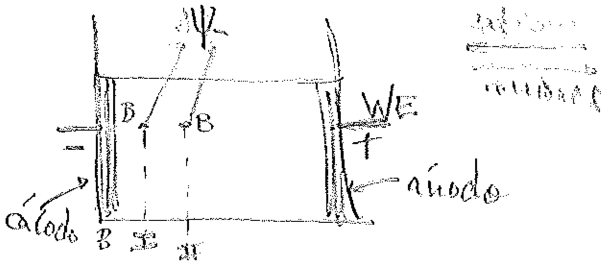
1: disolvente

2: soluto $A_{\nu_+}B_{\nu_-} \rightarrow A^{z+}/B^{z-}$

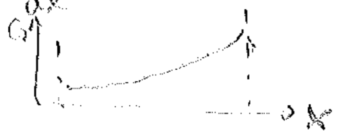
J_1, J_+, J_-, $\Delta\psi_- = \frac{\Delta\mu_-}{z_- F}$ $\rightarrow$ observable

$\rightarrow \Delta\tilde{\mu}_e = -\Delta\tilde{\mu}_-$

$$\Delta\psi = -\frac{\Delta\tilde{\mu}_e}{F} = \frac{\Delta\mu_-}{z_- F}$$



$\overline{\Delta T, p} \rightarrow \frac{dc_2}{dx}, I \rightarrow$ v. ind



ec. fenomenológ.:

$$\begin{cases} J_1 = D_1 A\frac{dc_2}{dx} + \frac{\tau_1}{F} I \\ \frac{J_+}{\nu_+} = D_2 A\frac{dc_2}{dx} + \frac{t_+}{\nu_+ z_+ F} \end{cases}$$

D_i: c. difusión

τ_i: nº transferc.

t_i: nº transporte

$I = 0 \rightarrow$ Difusión simple $\rightarrow \frac{J_+}{\nu_+} = \frac{J_-}{\nu_-} = J_2$

$\frac{dc_2}{dx} = 0 \rightarrow$ Proceso simple conducc. eléctrica $\rightarrow$ no difusión J_2

$t = 0$

$t = \infty$

Cond. eléctrica simple

formulario!

$\frac{dc_2}{dx} = 0$

$J_+ = \frac{t_+}{z_+ F} I$ — $t_+ = \frac{z_+ F J_+}{I}$, $t_- = \frac{z_- F J_-}{I}$ $\quad t_+ + t_- = 1$

$\nu_1 J_1 + \nu_2 \frac{J_+}{\nu_+} + \frac{\nu_B}{z_- F} I = 0 \qquad D_1 = -\frac{\nu_2}{\nu_1} D_2$

$z_1 = \frac{\nu - \nu_B - \nu_2 t_+}{\nu_+ z_+ \nu_1}$

$\psi = J_1 \frac{d\mu_1}{dx} + J_+ \frac{d\tilde{\mu}_+}{dx} + J_- \frac{d\tilde{\mu}_-}{dx} = J_1 \frac{d\mu_1}{dx} + \frac{J_+}{\nu_+} \frac{d\mu_2}{dx} + I \frac{d\psi_-}{dx}$

$\frac{J_+'}{\nu_+} = \frac{J_+}{\nu_+} - \left(\frac{c_2}{c_1}\right) J_1 \qquad \mathbb{L} = \mathbb{L}^T$

$\begin{pmatrix} J'_+ \\ I \end{pmatrix} = \mathbb{L} \begin{pmatrix} d\mu_2/dx \\ d\psi_-/dx \end{pmatrix}$

$L_{12} = L_{21}$

$\frac{L_{12}}{L_{22}} = \frac{t_+^1}{\nu_+ z_+ F}$

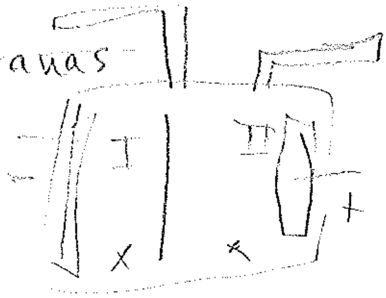
$\frac{d\psi}{dx} = \alpha_- \frac{dc_2}{dx} + \frac{I}{\sigma A}$

$\alpha_- = \frac{t_1'}{\nu_+ z_+ F} \frac{d\mu_2}{dc_2}$

$t_+^1 = -\nu_+ z_+ F \left(\frac{d\psi}{d\mu_2}\right)_{I=0}$

M_{B+}

Electrodifusión en membranas



T, p cte

$\Delta C_2, I, \frac{dC_2}{dt}$

$J_1 = P_1 \Delta C_2 + \frac{\xi_1}{F} I$

$\frac{J_+}{\nu_+} = P_2 A \Delta C_2 + \frac{t_+}{z_+ \nu_+ F} I$

$t_+ + t_- = 1$

$\Delta\psi_- = \Delta\tilde{\mu}_- / z_- F = \delta_- \Delta C_2 + R I$

$\Delta\tilde{\mu}_- = z_- F \Delta\psi_-$

$\Delta\tilde{\mu}_+ = \frac{\Delta\mu_2}{\nu_+} + z_+ F \Delta\psi_-$

$\psi = J_1 \Delta\mu_1 + \frac{J_+}{\nu_+} \Delta\mu_2 + I \Delta\psi = \frac{J_+'}{\nu_+} \Delta\mu_2 + I \Delta\psi_-$

$\frac{J_+'}{\nu^+} = \frac{J_+}{\nu_+} \nu_- \frac{C_2}{C_1} J_1$

$\begin{pmatrix} \frac{J'_+}{\nu_+} \\ I \end{pmatrix} = \rho \begin{pmatrix} \Delta\mu_2 \\ \Delta\psi_- \end{pmatrix}$

$\rho_{12} = \rho_{21}$

$\frac{\rho_{12}}{\rho_{22}} = \frac{t_+'}{\nu_+ z_+ F}$

$t_+ = \frac{\nu_+ z_+ F \Delta\psi_-}{\Delta\mu_2}$

Electrodiálisis

Membrana $\begin{cases} K & t_+^K \approx 1 \\ A & t_-^A \approx 1 \end{cases}$

$\Rightarrow \quad J_1^K - J_1^A$

$J_2 = (J_+^K - J_+^A) / \nu_+$

$\Delta C_2 = C_2^{II} - C_2^{I}$

$P_1 = P_1^K + P_1^A$

$P_2 = P_2^K + P_2^A$

$\begin{pmatrix} J_1 \\ J_2 \end{pmatrix} = \begin{matrix} P_1 A \Delta C_2 + \frac{\Delta \xi_1}{F} I \\ P_2 A \Delta C_2 + \frac{\Delta t_+}{\nu_+ z_+ F} I \end{matrix}$

$\Delta \xi_1 = \xi_1^K - \xi_1^A$

$\Delta t_+ = t_+^K - t_+^A$