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Lappeenranta University of Technology

Department of Chemical Technology
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BJ20A1801 Chemical Engineering Unit Operations II

Membrane Separation

Osmotic pressure

Definition
$$\Pi = -\frac{R_g T}{V_1} \ln(\gamma_1 x_1) \quad (1)$$

van't Hoff
$$\Pi = c R_g T \quad (2)$$

Permeability and selectivity

Permeate flux
$$J_m = A(\Delta p - \Delta \Pi) \quad (3)$$

Observed rejection
$$R_m = 1 - \frac{c_p}{c_b} \quad (4)$$

True rejection
$$R = 1 - \frac{c_p}{c_w} \quad (5)$$

Mass transfer inside the membrane

Statistical-mechanical theory

$$\sum_{j=1}^N \frac{c_j}{c D_{ij}} (u_i - u_j) + \frac{u_i}{D_{iM}} = -\frac{l}{R_g T} (\nabla_T \mu_i - F_i) - \frac{\alpha_i B_0}{\eta_m D_{iM}} (\nabla p - cF) - \sum_{j=1}^N \frac{c_j}{c D_{ij}} D_{ij}^T \nabla \ln T \quad (6)$$

$$R = \frac{\sigma(e^{Pe} - 1)}{e^{Pe} - \sigma} \quad (7)$$

$$J_v = \left(\frac{L_p}{\Delta z} \right) [\Delta p - \sigma R_g T (c_w - c_p)] \quad (8)$$

$$Pe = \frac{(1 - \sigma) J_v}{P} \quad (9)$$

$$P = \frac{\omega R_g T}{\Delta z} \quad (10)$$

$$\frac{I}{R} = \frac{P}{\sigma} \frac{I}{J_v} + \frac{(I + \sigma)}{2\sigma} + K_1 J_v + K_2 J_v^2 + \dots \quad (11)$$

The solution-diffusion model

$$J_i = -L_{ii} \nabla \mu_i \quad (12)$$

$$\nabla \mu_i = RT \nabla \ln a_{iM} + V_{iM} \nabla p \quad (13)$$

$$J_A = -D_{AM} \frac{\Delta c_{AM}}{\delta} \quad (14)$$

$$R_w = \frac{I}{I + \frac{D_{AM} K_A R T c_{Bp}}{D_{BM} c_{BM} V_{BM} (p_w - p_p - \Pi_w + \Pi_p)}} \quad (15)$$

The finely porous model

$$R = I - \left[A_1 - (I - A_1) e^{\left(-A_2 \frac{J_v}{D_{sw}} \right)} \right]^{-1} \quad (16)$$

$$J_v = \frac{\Delta p_m}{B_1 c_p + B_2 \eta} \quad (17)$$

Mass transfer at the membrane interface

$$J_v = \frac{\Delta X}{\eta R_{tot}} \quad (18)$$

The film theory

$$\frac{\partial c}{\partial t} + J_v \frac{\partial c}{\partial y} = D_{sw} \frac{\partial^2 c}{\partial y^2} \quad (19)$$

$$\frac{c_w - c_p}{c_b - c_p} = \exp\left(\frac{J_v}{k}\right) \quad (20)$$

Tubular modules

Mass transfer correlations for tubular flow
- turbulent flow

$$Sh = 0.04 Re^{0.75} Sc^{0.33} \quad (21)$$

or

$$Sh = 0.023 Re^{0.88} Sc^{0.25} \quad (22)$$

- laminar flow

$$Sh = \left(3.66^3 + 1.61^3 Re Sc \frac{d}{L} \right)^{0.33} \quad (23)$$

Plate and frame modules

Mass transfer correlation for plate and frame narrow channel

$$Sh = \left(3.66^3 + 1.61^3 Re Sc \frac{h}{W} \right)^{0.33} \quad (24)$$

Where dimensionless numbers are

$$Sh = kd/D \quad (25)$$

$$Re = \rho dv/\eta \quad (26)$$

$$Sc = \eta/(\rho D) \quad (27)$$

Hollow fiber modules

Mass transfer correlations

$$Sh = 0.61 Re^{0.5} Sc^{0.33} \quad (Re > 40) \quad (28)$$

$$Sh Sc^{-0.3} = 0.35 + 0.56 Re^{0.52} \quad (1 < Re < 10000) \quad (29)$$

Performance of a hollow fiber module

$$n_A \frac{\pi}{4} d_e^2 = S_v \frac{d_e}{4} = 1 - \varepsilon \quad (30)$$

$$\dot{V}_{pi} = \frac{\pi d_e}{H} A (p_b - p_{pw} - R_m b c_b) \frac{\tanh(HL)}{1 + H l_s \tanh(HL)} \quad (31)$$

$$H = \sqrt{\frac{128 \eta d_e A}{d_i^4}} \quad (32)$$

Spiral wound module

Mass transfer correlation for spiral wound module

$$Sh = 1.065 \left(\frac{h_i \eta_{SP,i}}{L_{SP,i} (2 - \eta_{SP,i})} \right)^{0.5} Re^{0.5} Sc^{0.33} \quad (33)$$

Performance of a spiral wound module

- pressure drop at the feed side is negligible

Permeate recovery (volumetric flow rate of the permeate/volumetric flow rate of the feed)

$$\phi = (1 - \Pi_3^+) \left\{ 1 - \exp \left[\frac{\beta_1}{\Pi_3^+} \left(\frac{\phi}{\varphi_1} - 1 \right) \right] \right\} \quad (34)$$

$$\Pi_3^+ = \frac{\frac{A_M \rho b}{B_M} - 1}{\frac{A_M \rho b}{B_M}} \frac{\rho b c_{F0}}{p_{F0}} \frac{1}{1 - \frac{p_{PW}}{p_{F0}}} \quad (35)$$

$$\beta_1 = \varphi_1 \left(1 - \frac{p_{PW}}{p_{F0}} \right) \kappa \quad (36)$$

$$\varphi_1 = \frac{2 A_M p_{F0} \varepsilon_F}{v_{F0}} \frac{L}{h_F} \quad (37)$$

$$\kappa = \frac{\tanh \sqrt{\frac{C_p \eta A_M \varepsilon_F^2 W^2}{4 \varepsilon_p^2 h_p^3}}}{\sqrt{\frac{C_p \eta A_M \varepsilon_F^2 W^2}{4 \varepsilon_p^2 h_p^3}}} \quad (38)$$

- Osmotic pressure of the feed solution is negligible ($\Pi_3^+ \rightarrow 0$)

- permeate recovery (volumetric flow rate of the permeate/volumetric flow rate of the feed)

$$\phi = 1 - \left(\cosh \sqrt{\beta_2} - \frac{\beta_1}{\sqrt{\beta_2}} \sinh \sqrt{\beta_2} \right) \quad (39)$$

$$\beta_2 = \frac{A_M L^2 C_F \eta}{4 h_F^3 \varepsilon_F} \kappa \quad (40)$$

Process design

Volumetric concentration ratio

$$VCR = \frac{\dot{V}_F}{\dot{V}_R} \quad (41)$$

$$c_R = c_F (VCR)^R \quad (42)$$

Batch process

$$-\frac{dV}{dt} = A J_v \quad (43)$$

$$-\frac{d(Vc)}{dt} = A J_v c_p = A J_v c_w (1 - R) \quad (44)$$

$$J_v = f(t); R = g(t) \quad (45)$$

Continuous processes

- feed and bleed
- multi stage recycle

with equal concentration ratios of each recycle stage

$$VCR_i = \sqrt[N]{VCR} \quad (46)$$

With equal permeate flow rates of each recycle stage

Cost estimation

Investment

$$C_I = C_A A \left(\frac{A}{A_{ref}} \right)^b \quad (47)$$

$$C_{a,I} = \frac{r(1+r)^a}{(1+r)^a - 1} C_I \quad (48)$$

Operating costs (annually)

- membranes

$$C_{mbr} = \frac{C_m A}{a_m} \quad (49)$$

- power consumption

$$C_{pwr} = C_e P_T t_a \quad (50)$$

$$P_T = \sum_{i=0}^n P_i \quad (51)$$

$$P_i = \frac{\dot{V} \Delta p}{\eta} \quad (52)$$

- cleaning

$$C_{cln} = C_c A n_c t_d \quad (53)$$

- maintenance

$$C_{mtn} \approx 0.03 C_I \quad (54)$$

- labour

to be estimated by the required annual man-hours and the price per man-hour

Industrial Crystallization

Solubility

van't Hoff equation:

Ideal solution:
$$\ln x = \frac{\Delta H_f}{R} \left(\frac{1}{T_{fus}} - \frac{1}{T} \right) \quad (1)$$

Non-ideal solution:
$$\ln x = \ln \frac{1}{\gamma} + \frac{\Delta H_f}{R} \left(\frac{1}{T_{fus}} - \frac{1}{T} \right) \quad (2)$$

Nucleation rate

$$B = A \exp \left[- \frac{16\pi\gamma^3 v^2}{3k^3 T^3 (\ln S)^2} \right] \quad (3)$$

$$B = \frac{4\alpha_v}{k_v G^3 t_{ind}^4} \quad (4)$$

Crystal growth rate

Surface nucleation based birth and spread (B+S) mechanism:

$$G_{B+S} = A_{B+S} (S-1)^{5/6} \exp[-B_{B+S}/(S-1)] \quad (5)$$

Screw dislocation mechanism described by Burton, Cabrera and Frank (BCF):

$$G_{BCF} = A_{BCF} \left[(S-1)^2 / B_{BCF} \right] \tanh[-B_{BCF}/(S-1)] \quad (6)$$

MSMPR theory (Mixed Suspension Mixed Product Removal)

Population density

$$n = \frac{m_i}{\alpha \rho_c \bar{L}_i^3 V \Delta L_i} \quad (7)$$

MSMPR crystallization

$$n = n_0 \exp\left(-\frac{L}{G\tau}\right) \quad \text{or} \quad \ln \frac{n}{n_0} = -\frac{L}{G\tau} \quad (8)$$

Total number of crystals, i.e. the zeroth moment of the distribution

$$N_T = \int_0^\infty n_0 \exp\left(-\frac{L}{G\tau}\right) dL = n_0 G\tau \left[\frac{\text{particles}}{m^3 \text{ suspension}} \right] \quad (9)$$

Cumulative length of crystals, i.e. the first moment

$$L_T = \int_0^\infty L n_0 \exp\left(-\frac{L}{G\tau}\right) dL = n_0 (G\tau)^2 \left[\frac{\text{particles}}{m^3 \text{ suspension}} \right] \quad (10)$$

Total crystal surface, i.e. the second moment

$$A_T = \beta \int_0^\infty L^2 n_0 \exp\left(-\frac{L}{G\tau}\right) dL = 2\beta n_0 (G\tau)^3 \left[\frac{m_{crystal\ surface}^2}{m_{suspension}^3} \right] \quad (11)$$

where β is the surface shape factor. The suspension density, i.e. total mass of crystals per unit volume (the third moment of size distribution multiplied by crystal density):

$$M_T = \alpha \rho_c \int_0^\infty L^3 n_0 \exp\left(-\frac{L}{G\tau}\right) dL = 6\alpha \rho_c n_0 (G\tau)^4 \left[\frac{kg_{crystals}}{m^3_{suspension}} \right] \quad (12)$$

where α is the volume shape factor and ρ_c the crystal density.

Volume flow rate of feed or product stream in continuous process, Q

$$Q = \frac{P}{M_T} \quad (13)$$

where P is the production capacity, [kg crystals/s]. The median size L_M

$$\frac{\int_0^{L_M} L^3 n_0 \exp(-L/G\tau) dL}{\int_0^\infty L^3 n_0 \exp(-L/G\tau) dL} = 0.5 \quad (14)$$

yields

$$L_M = 3.67 G\tau \quad (15)$$

Dominating crystal size, mode, L_D

$$L_D = 3 G\tau \quad (16)$$

Nucleation rate is defined from equation, as $B=B_0$, when $L=0$

$$B_0 = \frac{dN_0}{dt} = \frac{dN_0}{dL} \frac{dL}{dt} = n_0 G \quad (17)$$

Substituting Eq. (24) and $n_0=B_0/G$ into Eq. (21) gives to suspension density an expression where the crystal size is expressed by the median:

$$M_T = \frac{\alpha \rho_c B L_M^4}{30G} \quad (18)$$

and substituting Eq. (25) including modal crystal size gives

$$M_T = \frac{2\alpha \rho_c B L_D^4}{27G} \quad (19)$$

When nucleation rate is expressed by $B_0 = k_N G^j M_T^j$ and $j=1$, from Eqs (24) and (25) is obtained:

$$G = \left[\frac{30}{\alpha \rho_c k_N L_M^4} \right]^{\frac{1}{i-1}} \quad (20)$$

$$G = \left[\frac{27}{2\alpha\rho_c k_N L_D^4} \right]^{\frac{1}{i-1}} \quad (21)$$

The dependence of nucleation rate on different variables:

$$B = k'_N M_T^j N^b \Delta C^n \quad (22)$$

where secondary nucleation usually $1 < n < 2,5$

$$B = k'_N G^i M_T^j N^k \quad (23)$$

Generally the influence of mixing is usually expressed by the mixing power/unit mass term, ($[\varepsilon]=W/kg$), which gives

$$B = k'_N G^i M_T^j \varepsilon^l \quad (24)$$

Crystal growth rate on crystal size can be expressed by ASL model (Abegg-Stephan-Larson)

$$G = G_0 \left(1 + \frac{L}{G_0 \tau} \right)^b \quad (25)$$

Population density:

$$n = n_0 \left(1 + \frac{L}{G_0 \tau} \right)^{-b} \exp \left[\frac{1 - (1 + L/G_0 \tau)^{1-b}}{1-b} \right] \quad (26)$$

Clear-liquor Advance Operation

The overflow liquid is continuously removed from the tank. This overflow is not actually clear but contains small crystals that did not settle in the overflow section. The removal rate R :

$$R = \frac{\dot{V}_p + \dot{V}_c}{\dot{V}_p} \quad (27)$$

Since the mixing intensity is constant, nucleation rate is

$$B = k'_N G^i M_T^j \quad (28)$$

Dominating crystal size is

$$\frac{L_{d2}}{L_{d1}} = \left(\frac{\dot{V}_p + \dot{V}_c}{\dot{V}_p} \right)^{(i-1)/(i+3)} = R^{(i-1)/(i+3)} \quad (29)$$

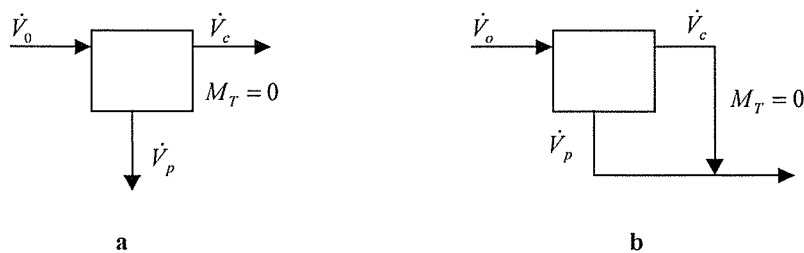


Figure 2. Clear-liquor Advance Operation

Fines Destruction with Solute Recycle

If the nucleus size to be dissolved is small compared to dominating size, the dissolving time t_{dis} is

$$t_{dis} = \frac{L_n^2 c_c}{8cD_{AB} \ln[c/(c-c^*)]} \quad (30)$$

The ratio of volume flow rates flowing to fines destruction and that of product stream, R , is determined

$$R = \frac{\tau_p}{\tau_F} = \frac{\dot{V}_p + \dot{V}_0}{\dot{V}_p} \quad (31)$$

Population density of fines destruction with solute recycle for MSMPR crystallization is

$$n = n_0 \exp\left(-\frac{RL_F}{G\tau}\right) \exp\left(-\frac{L-L_F}{G\tau}\right) \quad (32)$$

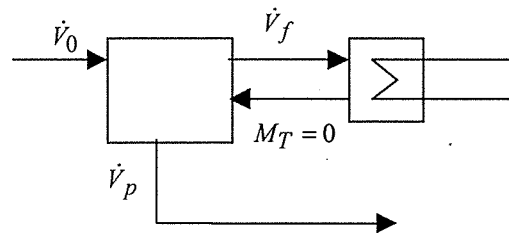


Figure 3. Fines Destruction.

Classified Product Removal

Population densities:

$$n = k_2 \exp\left(-\frac{L}{G_2 \tau}\right) \quad \text{for } L < L_c \quad (33)$$

$$n' = k_2' \exp\left(-\frac{zL}{G_2 \tau}\right) \quad \text{for } L > L_c \quad (34)$$

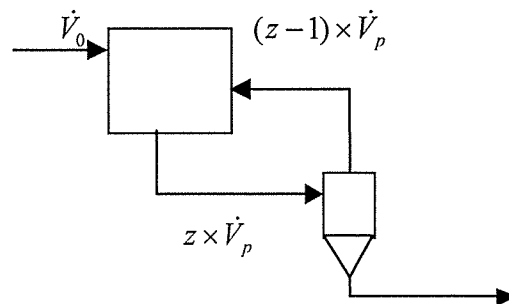


Figure 4. Classified Product Removal

Classified Product Removal With Fines Destruction

$$n = n_0 \exp\left(-\frac{RL}{G\tau}\right) \text{ for } L < L_F \quad (35)$$

$$n = n_0 \exp\left[-(R-1)\frac{L_F}{G\tau}\right] \exp\left(-\frac{L}{G\tau}\right) \text{ for } L_F < L < L_c \quad (36)$$

$$n = n_0 \exp\left[(z-1)\frac{L_c}{G\tau} - (R-1)\frac{L_F}{G\tau}\right] \exp\left(-\frac{zL}{G\tau}\right) \text{ for } L > L_c \quad (37)$$

Batch crystallization

Optimal cooling profile:

$$T = T_0 - (T_0 - T_f)(t/\tau)^n, \quad (38)$$

where T , T_0 ja T_f are the actual temperature at time t , the initial and final temperature, and τ the residence time, respectively. Mayrhofer ja Nyvlt derived optimal temperature profile with and without seeding:

$$\frac{T_0 - T}{T_0 - T_f} = \left[1 - K\left(1 - \frac{t}{\tau}\right)\right] \left(\frac{t}{\tau}\right)^3 \quad (39)$$

where K is the parametry, $K=(1+4N_s/B\tau)$, varying from 0 (no nucleation) to 1 (no seeding), N_s the number of seed crystals per unit solvent volume and B the nucleation rate.

Programmed cooling for seeded crystallization (Mullin & Nyvlt)

$$T = T_0 - XY(t/\tau) \left(1 + Y\frac{t}{\tau} + \frac{1}{3}Y^2\left(\frac{t}{\tau}\right)^2\right) \quad (40)$$

where

$$X = \frac{3w_s}{dc^*/dT} \quad (41)$$

$$Y = \frac{L_p - L_s}{L_s} \quad (42)$$

$$\frac{dc^*}{dT} \approx \frac{c_0 - c_f}{T_0 - T_f} \quad (43)$$

where w_s is the mass fraction of seed crystals (kg crystals/kg solvent), L_p the crystal size of the product and L_s the crystal size of seed crystals, c_0 and c_f are the initial and final concentrations (kg/kg solvent).

Programmed cooling for unseeded crystallization (Mullin & Nyvlt)

$$T = T_0 - \frac{w_s + w_Y}{dc^*/dT} \left(\frac{t}{\tau}\right)^4 \quad (44)$$

where w_Y is the mass fraction of crystals and solvent.

Natural cooling curve can be expressed by the function as follows

$$T = T_c + (T_0 - T_c)\exp(-Kt) \quad (45)$$

where T_c is the coolant temperature

$$K_i = \frac{1}{\tau} \ln \frac{T_0 - T_c}{T_f - T_c} \quad (46)$$

The product crystal size for seeded crystallization

$$L_P = \left(\frac{w_S + w_Y}{w_S} \right)^{\frac{1}{3}} L_S \quad (47)$$

Multicomponent mass transfer

Below are a few notes on the conventions used in this book. You may want to look back at this list occasionally while you are reading the book; do not expect to understand every detail on first reading.

- (1) In the drawings and sketches, the **positive direction is from left to right**. Velocities and fluxes in that direction are also positive.
- (2) A **force is directed down a potential gradient**. Examples are:

$$F_1 = - \frac{d\mu_1}{dz} \quad (48)$$

or

$$F_1 = F_{z_i} \frac{\Delta\phi}{\Delta z} \quad (49)$$

This convention holds both for differential and for difference equations.

- (3) When **computing a difference**, we **begin with the value at the most positive position (the right hand value) and subtract the other**:

$$\Delta x_2 = x_{2\beta} - x_{2\alpha} \quad (50)$$

- (4) Examples may consider compositions in many positions; these are denoted by Greek subscripts. If the problem considers different phases, these are distinguished by accents (Figure 1.1).

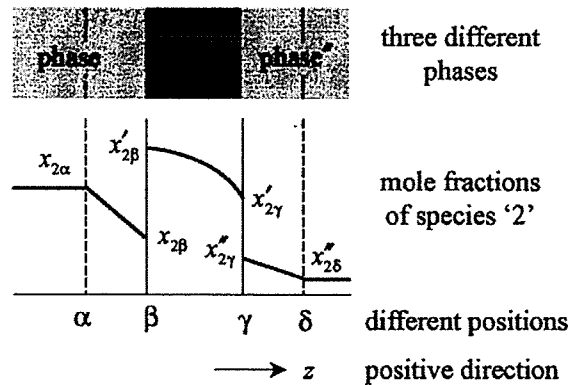


Fig. 1. Three different phases

(4) Two different forms of equations, binary mixtures

$$-\frac{\Delta a_1}{a_1} = \frac{1}{k_{1,2}} \bar{x}_2 (\bar{u}_1 - \bar{u}_2) \cdot \frac{\bar{c}x}{c} \quad (51)$$

$$\rightarrow \boxed{-x \frac{\Delta a_1}{a_1} = \frac{1}{k_{1,2}c} (\bar{x}_2 N_1 - \bar{x}_1 N_2)} \quad (52)$$

(5) Difference equation in velocity and flux forms

$$-\frac{\Delta a_i}{a_i} = \sum_{j \neq i} x_j \frac{\bar{u}_i - \bar{u}_j}{k_{i,j}} \quad (53)$$

$$-x_i \frac{\Delta a_i}{a_i} = \sum_{j \neq i} \frac{(\bar{x}_j N_i - \bar{x}_i N_j)}{k_{i,j}c} \quad (54)$$

for ideal solutions use driving force $-\Delta x_i$

(6) from binary to ternary and quaternary equations

$$\boxed{-\Delta x_1 = \frac{\bar{x}_2 N_1 - \bar{x}_1 N_2}{k_{1,2}c} + \frac{\bar{x}_3 N_1 - \bar{x}_1 N_3}{k_{2,3}c} + \dots} \quad (55)$$

$$\boxed{-\Delta x_2 = \frac{\bar{x}_1 N_2 - \bar{x}_2 N_1}{k_{1,2}c} + \frac{\bar{x}_3 N_2 - \bar{x}_2 N_3}{k_{2,3}c} + \dots} \quad (56)$$

(7) There is a number of different bootstrap relations.

- 1) membrane stagnant $u_M = 0$
- 2) bulk stagnant (absorption) $N_2 = 0$
- 3) trace stagnant (polarisation) $u_1 = 0$
- 4) equimolar exchange (distillation) $N_1 + N_2 = 0$
- 5) interface determined (vaporisation) $\frac{N_1}{N_2} = \frac{y_1}{y_2}$
- 6) reaction stoichiometry $\frac{N_1}{\nu_1} = \frac{N_2}{\nu_2}$

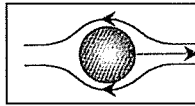
Empirical diffusion coefficient correlation of gases at ambient conditions:

$$\mathfrak{D}_{1,2} = 3.16 \times 10^{-8} \frac{T^{1.75}}{p(\nu_1^{1/3} + \nu_2^{1/3})^2} \times \left(\frac{1}{M_1} + \frac{1}{M_2}\right)^{1/2}$$

where

| | | | | | |
|--|----------------|----------------|-----------------|-----------------|------------------|
| $\frac{\nu_1}{10^{-6} \text{ m}^3 \text{ mol}^{-1}}$ | H ₂ | N ₂ | CO ₂ | NH ₃ | H ₂ O |
| | 7.07 | 17.9 | 26.9 | 14.9 | 12.7 |

Diffusivity of a dilute spherical species in a liquid:



this 'constant' varies with the ratio of the species.

$$\mathfrak{D}_{1,2} = \frac{RT}{2\pi A \eta_2 d_1^2 / d_2} \approx 10^{-9} \text{ m}^2 \text{ s}^{-1}$$

