工業反応装置特論

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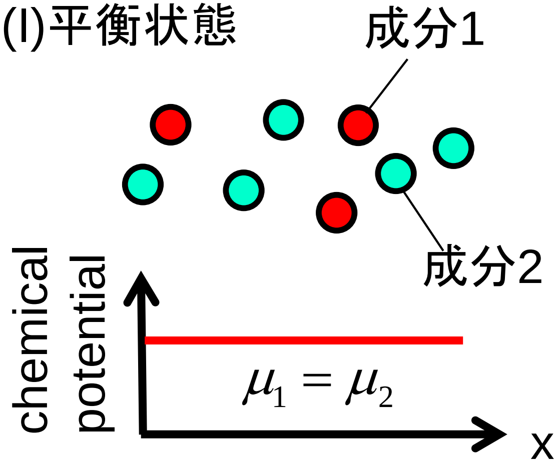
Chemical Potential (1)

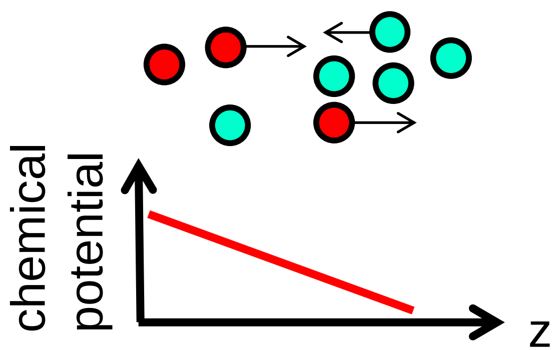
（例）成分1と成分2の混合物

(I)平衡状態



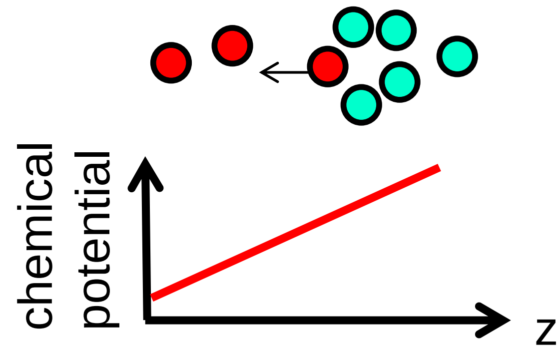
各成分の化学ポテンシャルは等しい

(II)化学ポテンシャル勾配あり
～非分離系～



化学ポテンシャルの低い方へ拡散
（濃度勾配に沿った拡散）

(II)化学ポテンシャル勾配あり
～相分離系～



化学ポテンシャルの低い方へ拡散
（濃度勾配とは逆向きの拡散）

（注）I,IIのみに着目して「拡散は濃度の低い方へ起こる」と書かれた書籍もあるが
case IIIでは正しくない

以下では成分間の相互作用パラメータが大きな場合にcase IIIが生じることを示そう

MASS FLUX (1)

成分1についての体積平均速度基準の質量流束は次式で定義される

$$j_1^{\neq} \equiv \rho_1 (v_1 - v^{\neq})$$

ただし体積平均速度は定義より

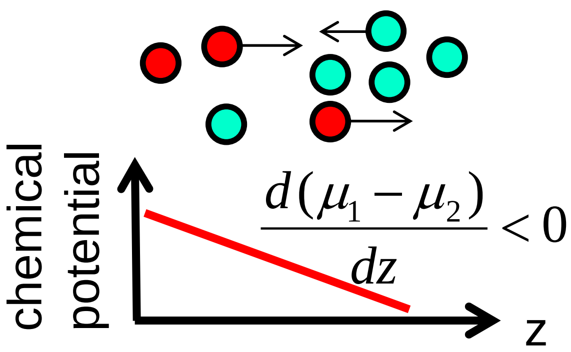
$$v^{\neq} \equiv \sum_{i=1}^{2} \phi_i v_i = \sum_{i=1}^{2} \rho_i \hat{V}_i v_i = \rho_1 \hat{V}_1 v_1 + \rho_2 \hat{V}_2 v_2$$

上の2式から体積平均速度を消去すると

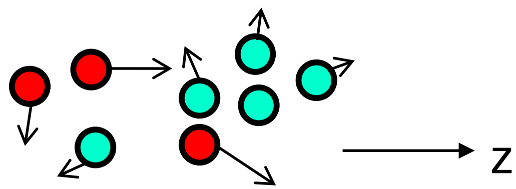
$$j_1^{\neq} \equiv \rho_1 (v_1 - \rho_1 \hat{V}_1 v_1 - \rho_2 \hat{V}_2 v_2) = \rho_1 \left\{ (1 - \rho_1 \hat{V}_1) v_1 - \rho_2 \hat{V}_2 v_2 \right\}$$

従って理想混合 $\rho_1 \hat{V}_1 + \rho_2 \hat{V}_2 = 1$ なら

$$j_1^{\neq} = \rho_1 \rho_2 \hat{V}_2 (v_1 - v_2) \quad (1)$$



FRICTION THEORY（1）



$$\nabla \mu_i \equiv \frac{d}{dz} \mu_i$$

(z方向に勾配がある場合）

化学ポテンシャル勾配に沿って拡散する分子を考える。
・隣接する分子との間に「摩擦」が作用
・隣接する分子との速度差は∇μの大きさと共に増加
・摩擦係数ζが増加すると、速度差は減少

Bearman理論(1961)によればN成分系中のある成分iのchemical potential勾配は摩擦係数ζ_{ij}を、質量濃度ρ(kg/m^3)、分子量M (kg/mol)、各成分の速度vを用いて

$$\nabla \mu_i = -\sum_{j=1}^{N} \frac{\rho_j}{M_j} \zeta_{ij} (v_i - v_j)$$

簡単のためN=2（2成分系）を考える。成分1と成分2の化学ポテンシャルは

$$\nabla \mu_1 = -\frac{\rho_2}{M_2} \zeta_{12} (v_1 - v_2) \quad (2)$$

$$\nabla \mu_2 = -\frac{\rho_1}{M_1} \zeta_{21} (v_2 - v_1) \quad (3)$$

FRICTION THEORY（2）

(1)-(2)の差をとれば

$$\nabla \mu_1 - \nabla \mu_2 = -\frac{\rho_2}{M_2}\zeta_{12}(v_1 - v_2) + \frac{\rho_1}{M_1}\zeta_{21}(v_2 - v_1)$$

$$= -\left(\frac{\rho_2}{M_2}\zeta_{12} + \frac{\rho_1}{M_1}\zeta_{21}\right)(v_1 - v_2)$$

$$\therefore \nabla(\mu_1 - \mu_2) = -\left(\frac{\rho_2}{M_2}\zeta_{12} + \frac{\rho_1}{M_1}\zeta_{21}\right)(v_1 - v_2) \quad (4)$$

2成分系なら互いの摩擦係数が等しく$\zeta_{21} = \zeta_{12}$が成り立つ。よって(4)より

$$v_1 - v_2 = -\frac{\nabla(\mu_1 - \mu_2)}{\left(\frac{\rho_2}{M_2} + \frac{\rho_1}{M_1}\right)\zeta_{12}} \quad (5)$$

MASS FLUX (2)

一般に、N成分系中の成分iの化学ポテンシャルの基準状態からの差は次式で定義される(Nauman&Balsara, 1989)。ただしΦiは成分iの体積分率である。

$$\frac{\mu_i - \mu^{\oplus}}{RT} \equiv \gamma + \frac{\partial \gamma}{\partial \phi_i} - \sum_{j=1}^{N} \phi_j \frac{\partial \gamma}{\partial \phi_j}$$

$$\text{ただし} \frac{\partial \gamma}{\partial \phi_i} = \frac{\partial}{\partial \phi_i}\left(\frac{G}{RT}\right) - \nabla \cdot \frac{\partial}{\partial \nabla \phi_i}\left(\frac{G}{RT}\right)$$

2成分系では

$$\frac{\mu_1 - \mu^{\oplus}}{RT} \equiv \gamma + \frac{\partial \gamma}{\partial \phi_1} - \left(\phi_1 \frac{\partial \gamma}{\partial \phi_1} + \phi_2 \frac{\partial \gamma}{\partial \phi_2}\right)$$

$$\frac{\mu_2 - \mu^{\oplus}}{RT} \equiv \gamma + \frac{\partial \gamma}{\partial \phi_2} - \left(\phi_1 \frac{\partial \gamma}{\partial \phi_1} + \phi_2 \frac{\partial \gamma}{\partial \phi_2}\right)$$

差をとると

$$\frac{\mu_1 - \mu_2}{RT} = \frac{\partial \gamma}{\partial \varphi_1} - \frac{\partial \gamma}{\partial \varphi_2}$$

$$= \left\{\frac{\partial}{\partial \varphi_1}\left(\frac{G}{RT}\right) - \nabla \cdot \frac{\partial}{\partial \nabla \varphi_1}\left(\frac{G}{RT}\right)\right\} - \left\{\frac{\partial}{\partial \varphi_2}\left(\frac{G}{RT}\right) - \nabla \cdot \frac{\partial}{\partial \nabla \varphi_2}\left(\frac{G}{RT}\right)\right\}$$

MASS FLUX (3)

特別な場合

Flory-Huggins式に従う界面を持たない2成分高分子ブレンドでは

$$\frac{G}{RT}=\frac{g}{RT}=\frac{\phi_1\ln\phi_1}{N_1}+\frac{\phi_2\ln\phi_2}{N_2}+\chi_{12}\phi_1\phi_2$$

ただし体積分率には$\phi_1+\phi_2=1$の関係が成り立つのでϕ_1のみの関数として

$$\frac{G(\phi_1)}{RT}=\frac{\phi_1\ln\phi_1}{N_1}+\frac{(1-\phi_1)\ln(1-\phi_1)}{N_2}+\chi_{12}\phi_1(1-\phi_1) \quad (6)$$

高分子が溶け合っているなら濃度勾配$\nabla\phi_i$はないので

$$\frac{\partial}{\partial\nabla\phi_i}\left(\frac{G}{RT}\right)=0 \quad ただし i=1,2$$

従って化学ポテンシャルの差は

$$\frac{\mu_1-\mu_2}{RT}=\frac{\partial}{\partial\phi_1}\left(\frac{g}{RT}\right)-\frac{\partial}{\partial\phi_2}\left(\frac{g}{RT}\right)=\frac{\partial}{\partial\phi_1}\left(\frac{g}{RT}\right)-0=\frac{\partial}{\partial\phi_1}\left(\frac{g}{RT}\right) \quad (7)$$

(注)$\frac{\partial g}{\partial\phi_1}=0$と満たすバイノーダル線上では$\mu_1=\mu_2$であり平衡状態

MASS FLUX (4)

(7)を(5)に代入すれば質量流束は

$$j_1^{\neq} = -\frac{\rho_1\rho_2 \hat{V}_2}{\left(\frac{\rho_2}{M_2}+\frac{\rho_1}{M_1}\right)\zeta_{12}} RT\nabla \frac{\partial}{\partial\phi_1}\left(\frac{g}{RT}\right)$$

(6)を微分すると

$$\frac{\partial}{\partial\phi_1}\left(\frac{g}{RT}\right) = \frac{\ln\phi_1}{N_1} + \frac{\phi_1}{N_1}\cdot\frac{1}{\phi_1} - \frac{\ln(1-\phi_1)}{N_2} - \frac{1-\phi_1}{N_2}\cdot\frac{1}{1-\phi_1} + \chi_{12}(1-2\phi_1)$$

$$= \frac{\ln\phi_1}{N_1} + \frac{1}{N_1} - \frac{\ln(1-\phi_1)}{N_2} - \frac{1}{N_2} + \chi_{12}(1-2\phi_1)$$

この勾配をとると

$$\nabla\frac{\partial}{\partial\phi_1}\left(\frac{g}{RT}\right) = \nabla\left[\frac{\ln\phi_1}{N_1} + \frac{1}{N_1} - \frac{\ln(1-\phi_1)}{N_2} - \frac{1}{N_2} + \chi_{12}(1-2\phi_1)\right]$$

$$= \frac{\nabla\phi_1}{N_1\phi_1} + \frac{\nabla\phi_1}{N_2(1-\phi_1)} - 2\chi_{12}\nabla\phi_1$$

MASS FLUX (5)

$$\therefore \nabla \frac{\partial}{\partial \phi_1}\left(\frac{g}{RT}\right)=\left\{\frac{1}{N_1\phi_1}+\frac{1}{N_2(1-\phi_1)}-2\chi_{12}\right\}\nabla\phi_1$$

従って

$$j_1^{\neq}=-\frac{\rho_1\rho_2\hat{V}_2}{\left(\frac{\rho_2}{M_2}+\frac{\rho_1}{M_1}\right)\zeta_{12}}RT\left\{\frac{1}{N_1\phi_1}+\frac{1}{N_2(1-\phi_1)}-2\chi_{12}\right\}\nabla\phi_1 \quad (8)$$

従って相互作用パラメータχ_{12}が大きく

$\frac{1}{N_1\phi_1}+\frac{1}{N_2(1-\phi_1)}-2\chi_{12}<0$の場合は

$j_1^{\neq}<0$となり濃度勾配$\nabla\phi_1$とは逆向きの拡散が生じる

MASS FLUX (6)

界面がある一般的な場合

混合の自由エネルギーが体積分率の勾配$\nabla\Phi_1$、$\nabla\Phi_2$の関数と考えてテーラー展開すると

$$\frac{G(\phi_1,\phi_2,\nabla\phi_1,\nabla\phi_2)}{RT}=\frac{g}{RT}+\kappa_{12}\nabla\phi_1\nabla\phi_2+\frac{\kappa_{11}}{2}(\nabla\phi_1)^2+\frac{\kappa_{22}}{2}(\nabla\phi_2)^2+\cdots \quad (9)$$

Flory-Huggins式
（界面なし）

界面が存在することによる
エネルギー増加分(Ginzburg-Landau式）

$\phi_2=1-\phi_1$を用いて書き直すと

$$\frac{G(\phi_1)}{RT}=\frac{g}{RT}+\frac{\kappa_{11}}{2}(\nabla\phi_1)^2+\frac{\kappa_{22}}{2}(\nabla(1-\phi_1))^2+\kappa_{12}\nabla\phi_1\nabla(1-\phi_1)$$

$$=\frac{g}{RT}+\frac{\kappa_{11}}{2}(\nabla\phi_1)^2+\frac{\kappa_{22}}{2}(-\nabla\phi_1)^2-\kappa_{12}(\nabla\phi_1)^2$$

$$=\frac{g}{RT}+\left(\frac{\kappa_{11}}{2}+\frac{\kappa_{22}}{2}-\kappa_{12}\right)(\nabla\phi_1)^2$$

$$=\frac{g}{RT}+\frac{\kappa_1}{2}(\nabla\phi_1)^2 \quad (10)$$ ただし$\frac{\kappa_1}{2}\equiv\frac{\kappa_{11}}{2}+\frac{\kappa_{22}}{2}-\kappa_{12}$

MASS FLUX (7)

微分すると

$$\frac{\partial}{\partial \nabla \phi_1}\left(\frac{G}{RT}\right) = 0 + \frac{\partial}{\partial \nabla \phi_1}\left\{\frac{\kappa_1}{2}\left(\nabla \phi_1\right)^2\right\} = \kappa_1 \nabla \phi_1 \quad (11),$$

$$\frac{\partial}{\partial \nabla \phi_2}\left(\frac{G}{RT}\right) = 0 + 0 = 0 \quad (12)$$

$$\frac{\partial}{\partial \phi_1}\left(\frac{G}{RT}\right) = \frac{\partial}{\partial \phi_1}\left(\frac{g}{RT}\right) = \frac{\ln \phi_1}{N_1} + \frac{1}{N_1} - \frac{\ln(1-\phi_1)}{N_2} - \frac{1}{N_2} + \chi_{12}(1-2\phi_1) \quad (13)$$

$$\frac{\partial}{\partial \phi_2}\left(\frac{G}{RT}\right) = \frac{\partial}{\partial \phi_2}\left(\frac{g}{RT}\right) = 0 \quad (14)$$

(11)–(14)を用いて整理すると成分1と成分2の化学ポテンシャルの差は

$$\frac{\mu_1 - \mu_2}{RT} \equiv \left[\frac{\partial}{\partial \phi_1}\left(\frac{g}{RT}\right) - \nabla(\kappa_1 \nabla \phi_1)\right] - (0-0) = \frac{\partial}{\partial \phi_1}\left(\frac{g}{RT}\right) - \kappa_1 \nabla^2 \phi_1 \quad (15)$$

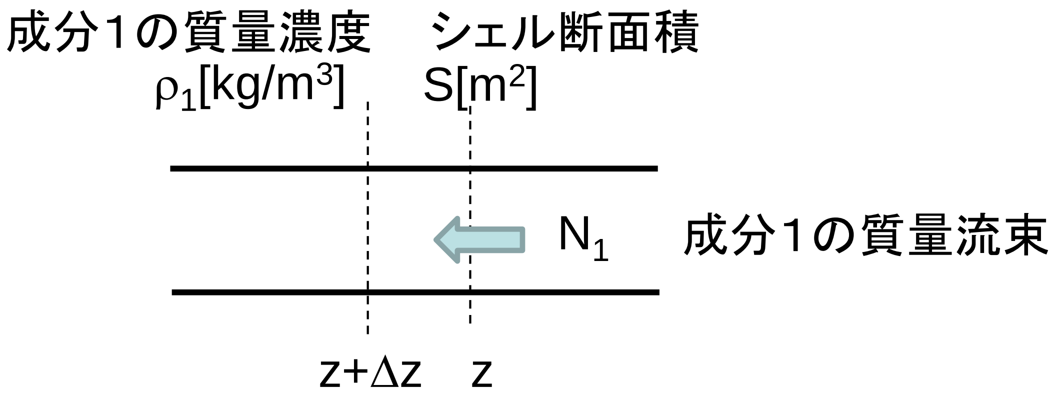
ただし$\nabla \phi_1 = \dfrac{\partial \phi_1}{\partial z}$

MASS FLUX (8)

(15)を(5)に代入すれば質量流束は

$$j_1^{\neq} = -\frac{\rho_1 \rho_2 \hat{V}_2}{\left(\frac{\rho_2}{M_2} + \frac{\rho_1}{M_1}\right)\zeta_{12}} RT \nabla \left\{ \frac{\partial}{\partial \varphi_1}\left(\frac{g}{RT}\right) - \kappa_1 \nabla^2 \varphi_1 \right\} \quad (16)$$

EQUATION OF CONTINUETY(1)



Δt間におけるシェル内の溶媒質量変化は

$$(\rho_1 S\Delta z)\big|_{t+\Delta t} - (\rho_1 S\Delta z)\big|_t \quad (kg/m^3)(m^2)(m) = kg$$

シェルへの流入質量は

$$N_1(z)S\Delta t \quad (kg/m^2 s)(m^2)(s) = kg$$

シェルからの流出質量は

$$N_1(z+\Delta z)S\Delta t \quad (kg/m^2 s)(m^2)(s) = kg$$

シェルバランスから

$$(\rho_1 S\Delta z)\big|_{t+\Delta t} - (\rho_1 S\Delta z)\big|_t = N_1(z)S\Delta t - N_1(z+\Delta z)S\Delta t$$

EQUATION OF CONTINUETY(2)

整理して

$$\frac{\rho_1\big|_{t+\Delta t} - \rho_1\big|_t}{\Delta t} = -\frac{N_1(z+\Delta z) - N_1(z)}{\Delta z}$$

$$\therefore \frac{d\rho_1}{dt} = -\frac{dN_1}{dz} \quad (17)$$

成分1の速度をv_1と書くと質量流束N_1の定義から$N_1 \equiv \rho_1 v_1$

一方で体積平均速度$v^{\neq}$に対する成分1の質量流束$j_1^{\neq}$は定義から

$$j_1^{\neq} \equiv \rho_1(v_1 - v^{\neq})$$

従って

$$j_1^{\neq} = N_1 - \rho_1 v^{\neq} \quad \therefore \quad N_1 = j_1^{\neq} + \rho_1 v^{\neq} \quad (18)$$

(18)を(17)に代入すると

$$\frac{d\rho_1}{dt} + \frac{d(\rho_1 v^{\neq})}{dz} = -\frac{dj_1^{\neq}}{dz} \quad (19)$$

流れがなければ$v^{\neq} = 0$なので

$$\frac{d\rho_1}{dt} = -\frac{dj_1^{\neq}}{dz} \quad (20)$$

EQUATION OF CONTINUETY(3)

(16)を(20)に代入すれば

$$\frac{d\rho_1}{dt} = -\frac{d}{dz}\left[-\frac{\rho_1 \rho_2 \hat{V}_2}{\left(\frac{\rho_2}{M_2} + \frac{\rho_1}{M_1}\right)\zeta_{12}} RT\nabla \left\{ \frac{\partial}{\partial \varphi_1}\left(\frac{g}{RT}\right) - \kappa_1 \nabla^2 \varphi_1 \right\} \right]$$

体積分率の定義から$\varphi_1 \equiv \rho_1 \hat{V}_1$なので両辺に$\hat{V}_1$を乗じて整理すれば

$$\frac{d\varphi_1}{dt} = \frac{d}{dz}\left[\frac{(\rho_1 \hat{V}_1)(\rho_2 \hat{V}_2)}{\left(\frac{\rho_2}{M_2} + \frac{\rho_1}{M_1}\right)\zeta_{12}} RT\nabla \left\{ \frac{\partial}{\partial \varphi_1}\left(\frac{g}{RT}\right) - \kappa_1 \nabla^2 \varphi_1 \right\} \right]$$

$\rho_2 \hat{V}_2 = 1 - \rho_1 \hat{V}_1 = 1 - \varphi_1$に注意し、$\nabla \equiv \frac{\partial}{\partial z}$と書き直せば解くべき式は

$$\frac{d\varphi_1}{dt} = \frac{\partial}{\partial z}\left[\frac{\varphi_1 (1-\varphi_1)}{\left(\frac{\rho_2}{M_2} + \frac{\rho_1}{M_1}\right)\zeta_{12}} RT \frac{\partial}{\partial z} \left\{ \frac{\partial}{\partial \varphi_1}\left(\frac{g}{RT}\right) - \kappa_1 \nabla^2 \varphi_1 \right\} \right] \quad (21)$$

(Cahn-Hilliard方程式）

Report 8 Derivation of Cahn-Hilliard Equation

氏名

Consider a phase-separating blend of polymer 1 and polymer 2. The free energy of mixing is given by Eq. (1). The second, third, and forth terms in right hand side of Eq. (1) represent the interfacial energies, which are expressed as a product of spatial gradient in polymer volume fractions. ϕ_i denotes the volume fraction of component i (I = 1,2), and κ_{ij} is the interaction parameter between component i and j. The spatial gradient of ϕ_i is expressed as $\nabla\phi_1 = d\phi_1/dz$ when molecules diffuse only in z-direction.

$$\frac{G(\phi_1,\phi_2)}{RT} = \frac{g}{RT} + \frac{\kappa_{11}}{2}(\nabla\phi_1)^2 + \frac{\kappa_{22}}{2}(\nabla\phi_2)^2 + \kappa_{12}\nabla\phi_1\nabla\phi_2 \quad (1)$$

Q1. Chemical potential difference between component 1 and 2 is given by

$$\frac{\mu_1-\mu_2}{RT} \equiv \left[\frac{\partial}{\partial\phi_1}\left(\frac{G}{RT}\right) - \nabla\left\{\frac{\partial}{\partial\nabla\phi_1}\left(\frac{G}{RT}\right)\right\}\right] - \left[\frac{\partial}{\partial\phi_2}\left(\frac{G}{RT}\right) - \nabla\left\{\frac{\partial}{\partial\nabla\phi_2}\left(\frac{G}{RT}\right)\right\}\right] \quad (2)$$

Derive Eq. (3) from Eqs. (1) and (2) where $\phi_1+\phi_2=1$ and $\frac{\kappa_1}{2} \equiv \frac{\kappa_{11}}{2} + \frac{\kappa_{22}}{2} - \kappa_{12}$

$$\frac{\mu_1-\mu_2}{RT} = \frac{\partial}{\partial\phi_1}\left(\frac{g}{RT}\right) - \kappa_1\nabla^2\phi_1 \quad (3)$$

Q2. Derive the equation of motion Eq. (4) where $v^{\neq}$ is the volume-averaged velocity and $j_1^{\neq}$ is the mass fraction of component 1 with respect to $v^{\neq}$, and ρ_1 is the mass concentration of component 1.

$$\frac{d\rho_1}{dt} + \frac{d(\rho_1 v^{\neq})}{dz} = -\frac{dj_1^{\neq}}{dz} \quad (4)$$

Q3. Based on Bearman friction theory (1961), the mass flux is expressed as Eq. (5). Derive the Cahn-Hilliard Equation (6) by combining Eqs. (3), (4) and (5) in case of $v^{\neq}=0$. $\hat{V}_1$ and $\hat{V}_2$ are the partial volume of component 1 and 2. The volume fraction is defined as $\phi_i \equiv \rho_i \hat{V}_i$.

$$j_1^{\neq} = -\frac{\rho_1\rho_2\hat{V}_2}{\left(\frac{\rho_2}{M_2}+\frac{\rho_1}{M_1}\right)\zeta_{12}}\frac{d}{dz}(\mu_1-\mu_2) \quad (5)$$

$$\frac{d\phi_1}{dt} = \frac{\partial}{\partial z}\left[M\frac{\partial}{\partial z}\left\{\frac{\partial}{\partial\phi_1}\left(\frac{g}{RT}\right) - \kappa_1\nabla^2\phi_1\right\}\right] \quad (6), \quad M \equiv \frac{\phi_1(1-\phi_1)}{\left(\frac{\rho_2}{M_2}+\frac{\rho_1}{M_1}\right)\zeta_{12}}RT$$