

# 工業反応装置特論

講義時間:6限

場所 :8-1A

担当 :山村

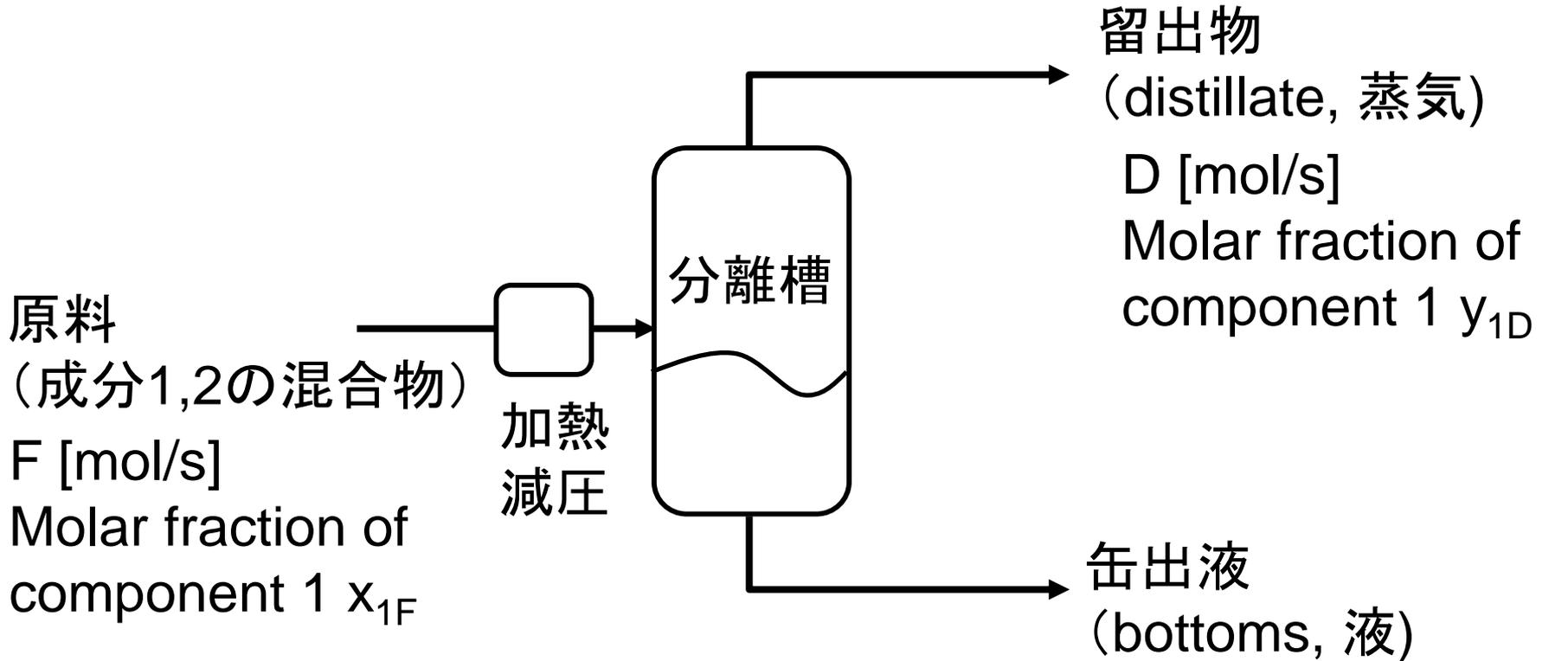
次回講義 2/4(火)

# 状態方程式

1 molの純成分気体について

理想気体	$P = \frac{RT}{V}$	
Van der Waals (VDW, 1873)	$P = \frac{RT}{V-b} - \frac{a}{V^2}$	分子間引力と 分子体積を考慮
Redlich-Kwong (RK)	$P = \frac{RT}{V-b} - \frac{a}{V^2} \cdot \frac{V}{(V+b)\sqrt{T}}$	VDW式中の定数aの 温度依存性を考慮
Soave-Redlich-Kwong (SRK, 1972)	$P = \frac{RT}{V-b} - \frac{a(T, \omega)}{V^2} \cdot \frac{V}{V+b}$	$\omega$ は分子形状の 影響を表す偏心因子
<b>Peng-Robinson</b> (PR, 1976)	$P = \frac{RT}{V-b} - \frac{a(T, \omega)}{V^2} \cdot \left\{ \frac{V}{(V+b) + b(V-b)/V} \right\}$	

# 連続単蒸留 (Flash蒸留)(1)



物質収支 (6変数)

$$\text{全体} \quad F = D + W \quad (1)$$

$$\text{成分1} \quad x_{1F}F = y_{1D}D + x_{1W}W \quad (2)$$

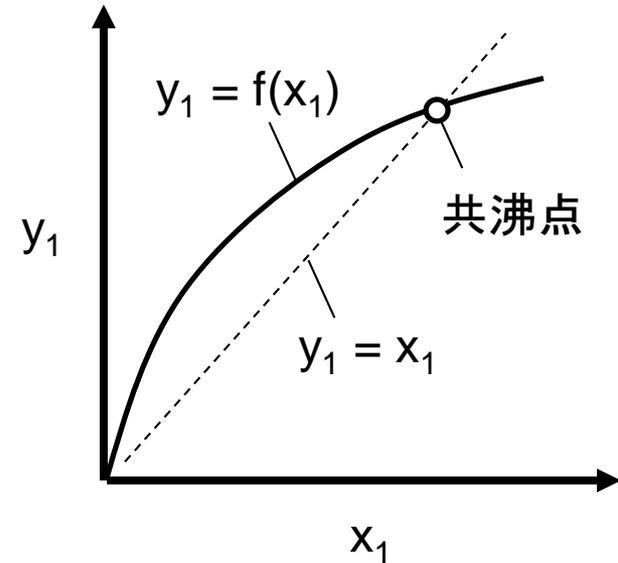
# 連続単蒸留(2)

$$\text{気液平衡 } y_{1D} = f(x_{1W}) \quad (3)$$

xy線図(右図)

圧力一定で液中の低沸点成分のモル分率を横軸に、蒸気中の同成分のモル分率を縦軸にとる

(注) 温度一定でも類似の図が書ける



例えば  $D$ (蒸気製品量)、 $W$ (液製品量)、 $x_{1F}$ (原料組成)が既知なら、式(1)-(3)から全変数が決まる

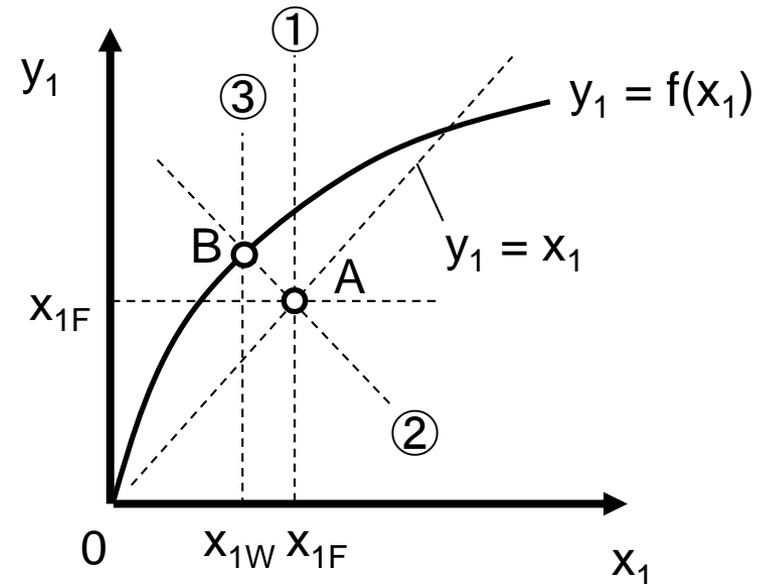
# 連続単蒸留(3)図解法

(1)(2)よりFを消去すると

$$x_{1F}(D+W) = y_{1D}D + x_{1W}W$$

$$(x_{1F} - y_{1D})D = (x_{1W} - x_{1F})W$$

$$\therefore -\frac{W}{D} = \frac{y_{1D} - x_{1F}}{x_{1W} - x_{1F}} \quad (4)$$



手順 (D, W,  $x_{1F}$ が既知の場合)

1. 原料組成 $x_{1F}$  (既知)を通る線①を引き、点Aを決定
2. 点Aを通り傾き $-W/D$  (既知)の直線②を引き、点Bを決定
3. 点Bを通る線③を引き、液製品組成 $x_{1W}$ を決定

# 理想溶液のxy線図(1)

純成分の蒸気圧(Antoine式)

$$\ln P_i^* [Pa] = A_i - \frac{B_i}{C_i + T[K]}$$

溶媒	$A_i$	$B_i$	$C_i$
toluene	20.9065	3096.52	-53.67
benzene	20.7936	2788.51	-52.36

理想溶液の蒸気圧(Raoult則)

$$P_1 = P_1^* x_1 \quad (1), \quad P_2 = P_2^* x_2 \quad (2)$$

全圧( $P_t$ )と蒸気中の成分1のモル分率

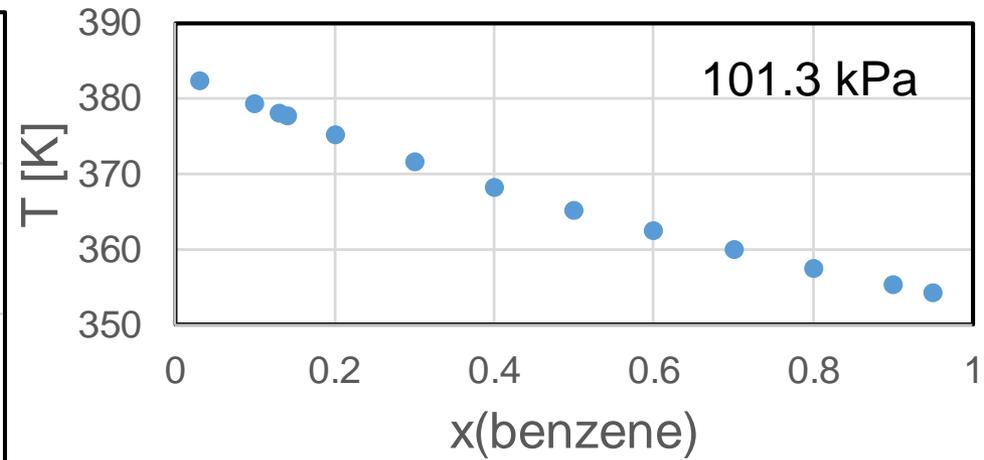
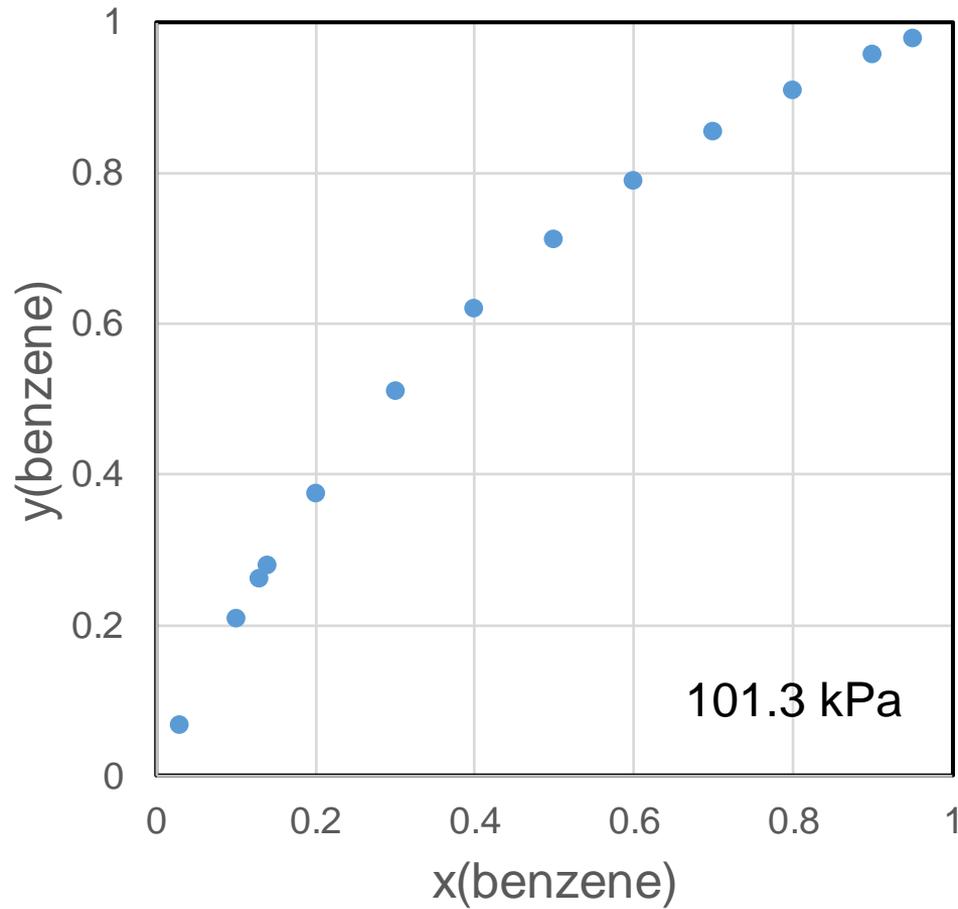
$$P_t \equiv P_1^*(T)x_1 + P_2^*(T)x_2 = P_1^*(T)x_1 + P_2^*(T)(1-x_1) \quad (3)$$

$$y_1 \equiv \frac{P_1}{P_1 + P_2} = \frac{P_1^*(T)}{P_t} x_1 \quad (4)$$

手順

1.  $x_1$ を与え、式(3)から全圧 $P_t$ が所定値となる絶対温度 $T[K]$ を決定
2. 式(4)から蒸気組成 $y_1$ を決定

# 理想溶液のxy線図(2)



# 気液平衡の推算法

van Laar (1906)

van der Waals式の拡張

Wilson(1964)

均相系に限定/多成分系

NRTL(Non-Random Two Liquids, 1968)

2相系に適用可/多成分系

UNIQUAC (Universal Quasi Chemical, 1975)

分子の大きさ/形と、分子間相互作用の効果をそれぞれ表現

UNIFAC(Universal Functional Group Activity Coefficient)

分子を構成する原子団にUNIQUACを応用(原子団寄与法)

詳しくは例えば大江, 分離のための相平衡の理論と計算, 講談社(2012)

# Wilson式の導出－非理想溶液－(1)

2成分系(成分*i*=1,2)を考える。同種分子、異種分子間の相互作用によって微視的にみると分子は不均一に存在すると考える。

均一分布



$$\gamma_{11} = \gamma_{12} = \gamma_{21} = \gamma_{22} = 0$$

不均一分布



成分*i*の周囲に存在する成分*j*の存在モル数  $\bar{n}_{ij}$  を考える  
巨視的に見たときの成分*j*の平均モル数を  $\bar{n}_j$  とする。  
理想溶液では分布は均一なので  $\bar{n}_{ij} = \bar{n}_j$

# Wilson式の導出(2)



$$\bar{n}_{11} < \bar{n}_1, \quad \bar{n}_{12} < \bar{n}_2$$

一般式として次の関数を考える。

$$\bar{n}_{ij} = \bar{n}_j \exp\left(-\frac{\gamma_{ij}}{RT}\right)$$



ならば  $\gamma_{11} > 0$



ならば  $\gamma_{12} > 0$

ある範囲に存在する局所的なモル数は

$$\bar{n}_{11} = \bar{n}_1 \exp\left(-\frac{\gamma_{11}}{RT}\right), \quad \bar{n}_{12} = \bar{n}_2 \exp\left(-\frac{\gamma_{12}}{RT}\right),$$

$$\bar{n}_{21} = \bar{n}_1 \exp\left(-\frac{\gamma_{21}}{RT}\right), \quad \bar{n}_{22} = \bar{n}_2 \exp\left(-\frac{\gamma_{22}}{RT}\right)$$

理想溶液なら

$$\gamma_{11} = \gamma_{12} = \gamma_{21} = \gamma_{22} = 0$$

# Wilson式の導出(3)

成分*i*のモル比体積を  $\hat{v}_i$  [m<sup>3</sup>/mol]と書けば

成分1の分子の周りにおける成分1と成分2の分子が占める体積はそれぞれ  $\bar{n}_{11}\hat{v}_1$ ,  $\bar{n}_{12}\hat{v}_2$

従って成分1分子の局所的な体積分率は

$$\xi_1 \equiv \frac{\bar{n}_{11}\hat{v}_1}{\bar{n}_{11}\hat{v}_1 + \bar{n}_{12}\hat{v}_2} = \frac{\bar{x}_1 \exp\left(-\frac{\gamma_{11}}{RT}\right)\hat{v}_1}{\bar{x}_1 \exp\left(-\frac{\gamma_{11}}{RT}\right)\hat{v}_1 + \bar{x}_2 \exp\left(-\frac{\gamma_{12}}{RT}\right)\hat{v}_2}$$

成分2も同様に

$$\xi_2 \equiv \frac{\bar{n}_{22}\hat{v}_2}{\bar{n}_{21}\hat{v}_1 + \bar{n}_{22}\hat{v}_2} = \frac{\bar{x}_2 \exp\left(-\frac{\gamma_{22}}{RT}\right)\hat{v}_2}{\bar{x}_1 \exp\left(-\frac{\gamma_{21}}{RT}\right)\hat{v}_1 + \bar{x}_2 \exp\left(-\frac{\gamma_{22}}{RT}\right)\hat{v}_2}$$

変形すると

$$\xi_1^{-1} = 1 + \frac{\bar{x}_2\hat{v}_2}{\bar{x}_1\hat{v}_1} \exp\left(-\frac{\gamma_{12} - \gamma_{11}}{RT}\right) = 1 + \frac{\bar{x}_2}{\bar{x}_1} \Lambda_{12}$$

$$\xi_2^{-1} = 1 + \frac{\bar{x}_1\hat{v}_1}{\bar{x}_2\hat{v}_2} \exp\left(-\frac{\gamma_{21} - \gamma_{22}}{RT}\right) = 1 + \frac{\bar{x}_1}{\bar{x}_2} \Lambda_{21}$$

ただし

$$\Lambda_{12} \equiv \frac{\hat{v}_2}{\hat{v}_1} \exp\left(-\frac{\gamma_{12} - \gamma_{11}}{RT}\right), \Lambda_{21} \equiv \frac{\hat{v}_1}{\hat{v}_2} \exp\left(-\frac{\gamma_{21} - \gamma_{22}}{RT}\right)$$

# Wilson式の導出(4)

書き直せば

$$\bar{x}_1 \xi_1^{-1} = \bar{x}_1 + \bar{x}_2 \Lambda_{12} \quad (1)$$

$$\bar{x}_2 \xi_2^{-1} = \bar{x}_2 + \bar{x}_1 \Lambda_{21} \quad (2)$$

この混合物の混合自由エネルギー $g$ と、理想溶液における混合自由エネルギー $g^I$ の差で定義される過剰Gibbs自由エネルギー $g^E$ が式(4)で表されると仮定する

$$g^E \equiv g - g^I \quad (3)$$

$$\frac{g^E}{RT} = -\bar{x}_1 \ln \bar{x}_1 \xi_1^{-1} - \bar{x}_2 \ln \bar{x}_2 \xi_2^{-1} \quad (4)$$

$$\frac{g^I}{RT} = \bar{x}_1 \ln \bar{x}_1 + \bar{x}_2 \ln \bar{x}_2 \quad (5) \quad (\text{理想溶液})$$

特別な場合  $\Lambda_{12} = \Lambda_{21} = 1$

$$(1)(2) \text{より} \quad \bar{x}_1 \xi_1^{-1} = \bar{x}_2 \xi_2^{-1} = 1$$

$$(4) \text{より} \quad \frac{g^E}{RT} = 0$$

$$(3) \text{より} \quad g = g^I \quad \text{であり理想溶液}$$

(注)  $\bar{x}_1 = \bar{x}_2 = 0.5$ で均一混合の場合  
体積分率は $\xi_1 = \xi_2 = 0.5$ なので

$$\begin{aligned} \frac{g^E}{RT} &= -\bar{x}_1 \ln \bar{x}_1 \xi_1^{-1} - \bar{x}_2 \ln \bar{x}_2 \xi_2^{-1} \\ &= -0.5 \ln\{(0.5)(2)\} - 0.5 \ln\{(0.5)(2)\} = 0 \end{aligned}$$

となり過剰Gibbs自由エネルギーは零

# Wilson式の導出(5)

$\Lambda_{12} \neq 1, \Lambda_{21} \neq 1$  の場合を考える

式(1)(2)を式(4)に代入すると

$$\frac{g^E}{RT} = -\bar{x}_1 \ln(\bar{x}_1 + \Lambda_{12}\bar{x}_2) - \bar{x}_2 \ln(\bar{x}_2 + \Lambda_{21}\bar{x}_1) \quad (6)$$

蒸気圧と関連づけるため

$$\frac{g^E}{RT} + \bar{x}_2 \frac{\partial}{\partial \bar{x}_1} \left( \frac{g^E}{RT} \right)$$

を考える。まず  $\frac{\partial}{\partial \bar{x}_1} \left( \frac{g^E}{RT} \right)$  は

$$\frac{\partial}{\partial \bar{x}_1} \left( \frac{g^E}{RT} \right) = -\ln(\bar{x}_1 + \Lambda_{12}\bar{x}_2) - \bar{x}_1 \frac{\partial \ln X}{\partial \bar{x}_1} + \ln(\bar{x}_2 + \Lambda_{21}\bar{x}_1) - \bar{x}_2 \frac{\partial \ln Y}{\partial \bar{x}_1}$$

# Wilson式の導出(6)

$$X \equiv \bar{x}_1 + \Lambda_{12}\bar{x}_2 = \bar{x}_1 + \Lambda_{12}(1 - \bar{x}_1)$$

$$Y \equiv \bar{x}_2 + \Lambda_{21}\bar{x}_1 = (1 - \bar{x}_1) + \Lambda_{21}\bar{x}_1 \quad \text{とおくと}$$

$$\frac{\partial \ln X}{\partial \bar{x}_1} = \frac{\partial X}{\partial \bar{x}_1} \frac{\partial \ln X}{\partial X} = \frac{1 - \Lambda_{12}}{\bar{x}_1 + \Lambda_{12}\bar{x}_2}$$

$$\frac{\partial \ln Y}{\partial \bar{x}_1} = \frac{\partial Y}{\partial \bar{x}_1} \frac{\partial \ln Y}{\partial Y} = \frac{-1 + \Lambda_{21}}{\bar{x}_2 + \Lambda_{21}\bar{x}_1} \quad \text{が成り立つので}$$

$$\begin{aligned} \frac{\partial}{\partial \bar{x}_1} \left( \frac{g^E}{RT} \right) &= -\ln(\bar{x}_1 + \Lambda_{12}\bar{x}_2) - \bar{x}_1 \frac{1 - \Lambda_{12}}{\bar{x}_1 + \Lambda_{12}\bar{x}_2} + \ln(\bar{x}_2 + \Lambda_{21}\bar{x}_1) - \bar{x}_2 \frac{-1 + \Lambda_{21}}{\bar{x}_2 + \Lambda_{21}\bar{x}_1} \\ &= -\ln(\bar{x}_1 + \Lambda_{12}\bar{x}_2) + \ln(\bar{x}_2 + \Lambda_{21}\bar{x}_1) + \left( \frac{\Lambda_{12}}{\bar{x}_1 + \Lambda_{12}\bar{x}_2} - \frac{\Lambda_{21}}{\bar{x}_2 + \Lambda_{21}\bar{x}_1} \right) \end{aligned}$$

$$\because -\bar{x}_1 \frac{1 - \Lambda_{12}}{\bar{x}_1 + \Lambda_{12}\bar{x}_2} = \frac{-\bar{x}_1 + \bar{x}_1\Lambda_{12}}{\bar{x}_1 + \Lambda_{12}\bar{x}_2} = \frac{-\bar{x}_1 + (1 - \bar{x}_2)\Lambda_{12}}{\bar{x}_1 + \Lambda_{12}\bar{x}_2} = \frac{\Lambda_{12} - (\bar{x}_1 + \bar{x}_2\Lambda_{12})}{\bar{x}_1 + \Lambda_{12}\bar{x}_2} = \frac{\Lambda_{12}}{\bar{x}_1 + \Lambda_{12}\bar{x}_2} - 1$$

$$-\bar{x}_2 \frac{-1 + \Lambda_{21}}{\bar{x}_2 + \Lambda_{21}\bar{x}_1} = -\frac{\Lambda_{21}}{\bar{x}_2 + \Lambda_{21}\bar{x}_1} + 1$$

# Wilson式の導出(7)

従って

$$\begin{aligned} \frac{g^E}{RT} + \bar{x}_2 \frac{\partial}{\partial \bar{x}_1} \left( \frac{g^E}{RT} \right) &= -\bar{x}_1 \ln(\bar{x}_1 + \Lambda_{12}\bar{x}_2) - \bar{x}_2 \ln(\bar{x}_2 + \Lambda_{21}\bar{x}_1) \\ &+ \bar{x}_2 \left\{ -\ln(\bar{x}_1 + \Lambda_{12}\bar{x}_2) + \ln(\bar{x}_2 + \Lambda_{21}\bar{x}_1) + \frac{\Lambda_{12}}{\bar{x}_1 + \Lambda_{12}\bar{x}_2} - \frac{\Lambda_{21}}{\bar{x}_2 + \Lambda_{21}\bar{x}_1} \right\} \\ &= -\ln(\bar{x}_1 + \Lambda_{12}\bar{x}_2) + \bar{x}_2 \left( \frac{\Lambda_{12}}{\bar{x}_1 + \Lambda_{12}\bar{x}_2} - \frac{\Lambda_{21}}{\bar{x}_2 + \Lambda_{21}\bar{x}_1} \right) \quad (7) \end{aligned}$$

一方、理想溶液の項は  $\frac{g^I}{RT} = \bar{x}_1 \ln \bar{x}_1 + (1 - \bar{x}_1) \ln(1 - \bar{x}_1)$  より

$$\frac{\partial}{\partial \bar{x}_1} \left( \frac{g^I}{RT} \right) = \ln \bar{x}_1 - \ln(1 - \bar{x}_1)$$

$$\therefore \frac{g^I}{RT} + \bar{x}_2 \frac{\partial}{\partial \bar{x}_1} \left( \frac{g^I}{RT} \right) = \ln \bar{x}_1 \quad (8)$$

# Wilson式の導出(8)

式(7)(8)を式(3)と組み合わせれば、混合物の混合自由エネルギーについて次式が成り立つ

$$\begin{aligned} \frac{g}{RT} + \bar{x}_2 \frac{\partial}{\partial \bar{x}_1} \left( \frac{g}{RT} \right) &= \left\{ \frac{g^E}{RT} + \bar{x}_2 \frac{\partial}{\partial \bar{x}_1} \left( \frac{g^E}{RT} \right) \right\} + \left\{ \frac{g^I}{RT} + \bar{x}_2 \frac{\partial}{\partial \bar{x}_1} \left( \frac{g^I}{RT} \right) \right\} \\ &= -\ln(\bar{x}_1 + \Lambda_{12}\bar{x}_2) + \bar{x}_2 \left( \frac{\Lambda_{12}}{\bar{x}_1 + \Lambda_{12}\bar{x}_2} - \frac{\Lambda_{21}}{\bar{x}_2 + \Lambda_{21}\bar{x}_1} \right) + \ln \bar{x}_1 \quad (9) \end{aligned}$$

式(9)の左辺は蒸気を理想気体と見なした場合の成分1の活量 $a_1$ に等しい

$$\frac{g}{RT} + \bar{x}_2 \frac{\partial}{\partial \bar{x}_1} \left( \frac{g}{RT} \right) = \ln a_1 \quad (10)$$

活量係数の定義から

$$a_1 = P_{1i} / P_1^* \equiv \gamma_1 \bar{x}_1 \quad (11)$$

# Wilson式の導出(9)

式(9)-(11)より、成分1の活量係数は次式で表される

$$\ln \gamma_1 = -\ln(\bar{x}_1 + \Lambda_{12}\bar{x}_2) + \bar{x}_2 \left( \frac{\Lambda_{12}}{\bar{x}_1 + \Lambda_{12}\bar{x}_2} - \frac{\Lambda_{21}}{\bar{x}_2 + \Lambda_{21}\bar{x}_1} \right) \quad (12)$$

同様に成分2について次式が成り立つ。式(12)(13)をWilsonの式と呼ぶ

$$\ln \gamma_2 = -\ln(\bar{x}_2 + \Lambda_{21}\bar{x}_1) + \bar{x}_1 \left( \frac{\Lambda_{21}}{\bar{x}_2 + \Lambda_{21}\bar{x}_1} - \frac{\Lambda_{12}}{\bar{x}_1 + \Lambda_{12}\bar{x}_2} \right) \quad (13)$$

例) Ethanol (1)-Toluene (2) \*

$$\Lambda_{12} = 0.192$$

$$\Lambda_{21} = 0.413$$

•Nagata I., Journal of Chemical Engineering of Japan, 6 (1973) 18

$\bar{x}_1 = 0.67$ の場合

$$\begin{aligned} \ln \gamma_1 &= -\ln(0.67 + 0.192 \times 0.33) + 0.33 \left( \frac{0.192}{0.67 + 0.192 \times 0.33} - \frac{0.413}{0.413 \times 0.67 + 0.33} \right) \\ &= 0.143 \end{aligned}$$

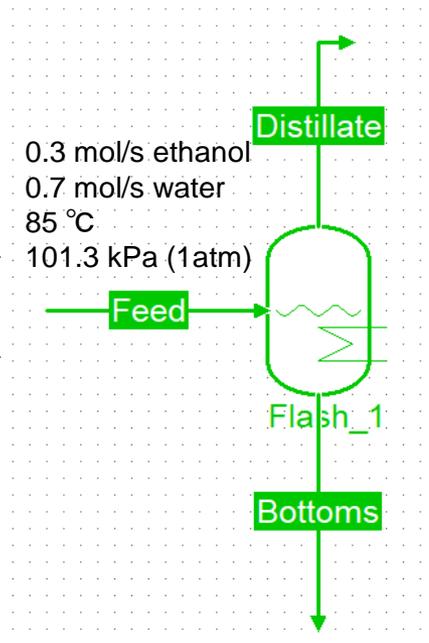
$$\therefore \gamma_1 = 1.15$$

Design a separator to separate ethanol and water from their mixture at 85 °C and 1 atm.

Q1. Following the procedure shown below, determine the composition in distillate/bottom streams.

Stream	1	2	3
From	<FEED>	Flash_1	Flash_1
To	Flash_1	<PRODUCT>	<PRODUCT>
Temperature	85	85	84.9927
Pressure	0.1013	0.1013	0.1013
Mole frac water	0.7	0.515502	0.866527
Mole frac ethanol	0.3	0.484498	0.133473
Flow rate	1	0.474402	0.525598

Q2. Use Wilson model instead of VanLaar model to separate the same feed. Compare the compositions of the products to discuss how the vapor-liquid equilibrium data influence the separation process.



### 1. Material selection

setting-property packages-add-ChemSep-select-New-component-find water-add-find ethanol-add

### 2. Vapor-liquid equilibrium model

properties-K-value(平衡定数)-DECHEMA-activity coefficient(活量係数)-VanLaar-Vapour pressure-Extended Antoine-Enthalpy-ideal-Enter thermodynamic model parameters-Van laar-load-vanlaar-load-Extended Antoine-load-antoine-load (close window, do you want to?Yes)

### 2. Flash distillator selection

Insert Unit Operations-Separators-Flash-select-Edit unit operation

### 3. Feed

Insert stream-Edit/view streams-0.1013 MPa-85 °C-Compound flows-Water-0.7 mol/s-ethanol-0.3 mol/s (check Overall properties-bublePointTemperature)

### 4. Distillate

Insert stream-Edit/view streams-connect to port Vapor

### 5. Bottoms

Insert stream- -Edit/view streams

### 6. solve(F5)