Excess Properties

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I. Behavior of Excess Properties

- 1. Excess Gibbs energy, Excess enthalpy, Excess entropy are related by

❶ $$g^E = h^E - Ts^E$$

❷ $$\frac{g^E}{RT} = \frac{h^E}{RT} - \frac{s^E}{R}$$

❸ $$\frac{h^E}{RT} = -T\left(\frac{\partial(g^E/RT)}{\partial T}\right)_{P,X}$$

Definitions of Regions on the $\hat{g}$ vs. $\hat{h}$ Diagram

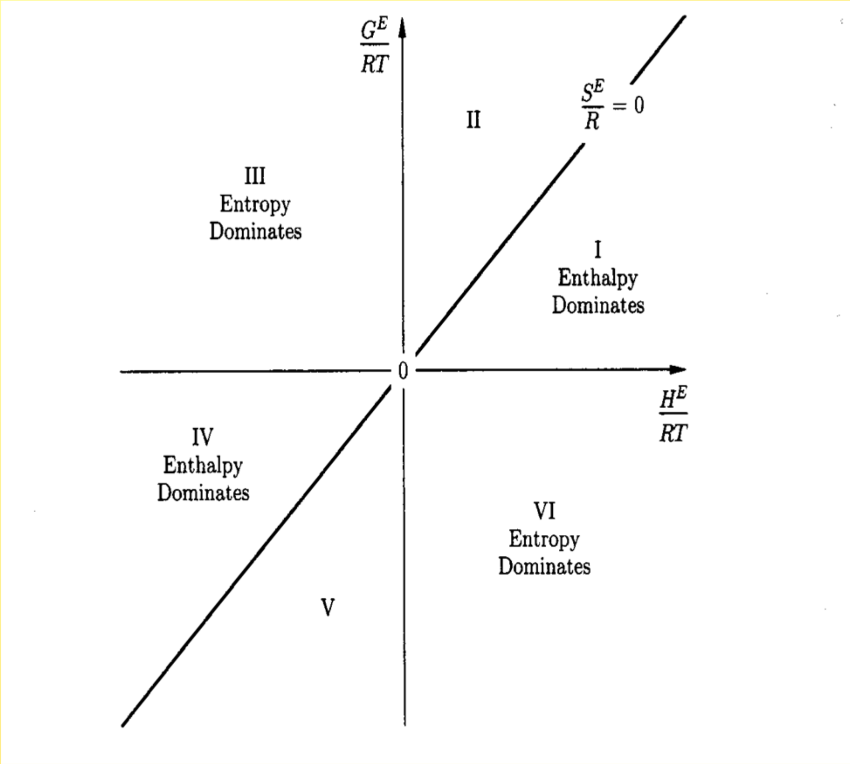
For convenience,

$$\left.\begin{aligned} \hat{g} &\equiv g^E / RT \\ \hat{h} &\equiv h^E / RT \\ \hat{s} &\equiv s^E / R \\ \hat{c} &\equiv c_P{}^E / R \end{aligned}\right] \quad \text{at} \quad x_1 = x_2 = 0.5$$

- 액체혼합물의 과잉물성과 상대적 크기들은 공학적 목적이나 관찰된 용액의 거동을 근거로 분자현상을 규명하는데 유용하게 쓰인다.

Definitions of Regions(I~VI)

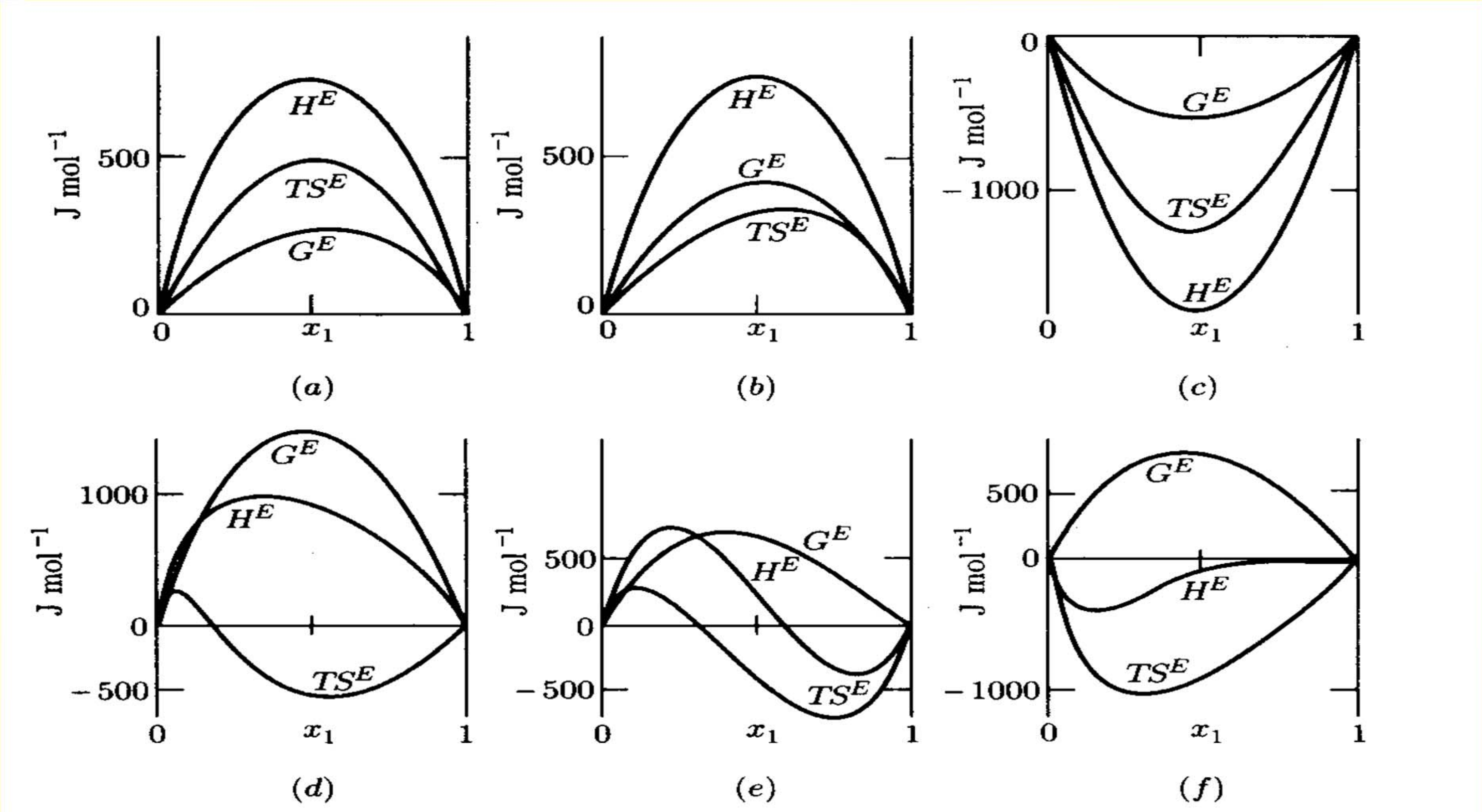
- Definitions of Regions on the $\hat{g}$ vs. $\hat{h}$ Diagram



Region	Sign G^E	Sign H^E	Sign S^E
I	+	+	+
II	+	+	−
III	+	−	−
IV	−	−	−
V	−	−	+
VI	−	+	+

50°C 의 6성분계 과잉물성

(a) 클로로포름(1)/n-헵탄(2)
(b) 아세톤(1)/메탄올(2)
(c) 아세톤(1)/ 클로로포름(1)
(d) 에탄올(1)/ n-헵탄(2)
(e) 에탄올(1)/ 클로로포름(2)
(f) 에탄올(1)/ 물(2)



Trends for equimolar mixtures
(298K의 2성분계)

[그림설명]

○: NP/NP 혼합물

●: NA/NP 혼합물

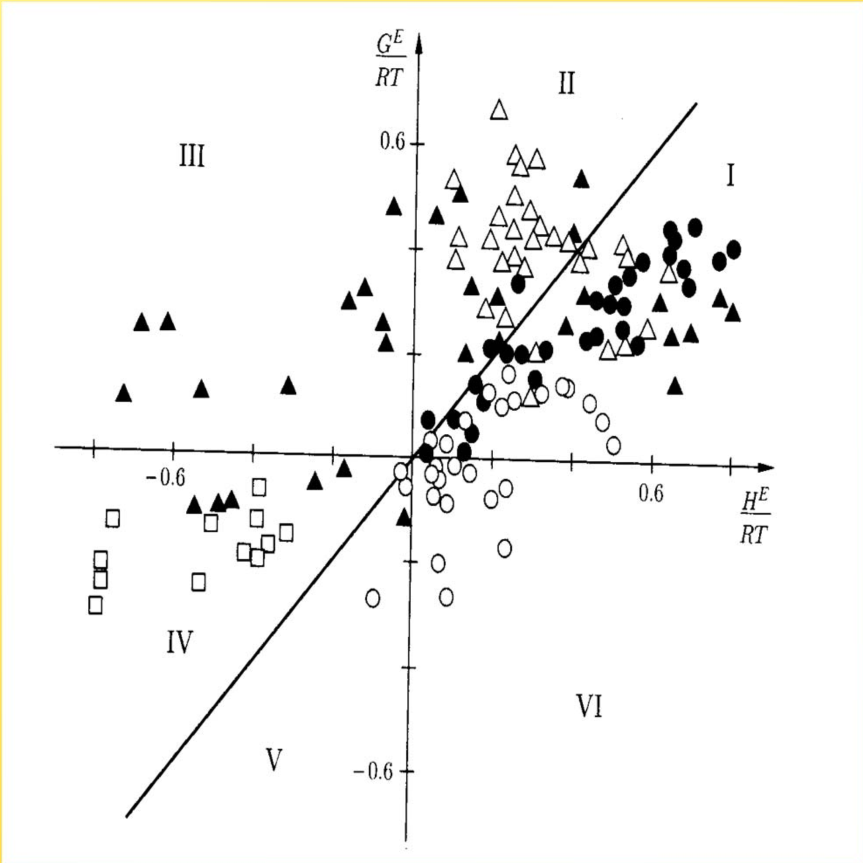
△: AS/NP 혼합물

▲: AS/NA 혼합물과

AS/AS 혼합물

□: 용매화 NA/NA

혼합물



II. Wohl's Expansion for the Excess Gibbs Energy

- Wohl's Expansion

$$\frac{g^E}{RT(x_1q_1+x_2q_2)} = 2a_{12}z_1z_2 + 3a_{112}z_1{}^2z_2$$

$$+3a_{122}z_1z_2{}^2 + 4a_{1112}z_1{}^3z_2 + 4a_{1222}z_1z_2{}^3 + 6a_{1122}z_1{}^2z_2{}^2$$

$$z_1 = \frac{x_1q_1}{x_1q_1+x_2q_2}, z_2 = \frac{x_2q_2}{x_1q_1+x_2q_2}$$

❶ van Laar Equation

$$\frac{g^E}{RT} = \frac{2a_{12}x_1x_2q_1q_2}{x_1q_1+x_2q_2}$$

Wohl's Expansion

❷ Margules Equation

$$\ln\gamma_1 = A' x_2^2 + B' x_2^3 + C' x_2^4$$

$$\ln\gamma_2 = (A' + \frac{3}{2}B' + 2C')x^2 - (B' + \frac{8}{3}C')x_1^3 + C' x_1^4$$

❸ Scatchard-Hamer Equation

$$\ln\gamma_1 = A' z_2^2 + B' z_2^3$$

$$\ln\gamma_2 = (A' + \frac{3}{2}B')(\frac{v_2}{v_1})z_1^2 - B'(\frac{v_2}{v_1})z_1^3$$

III. Wilson, NRTL, and UNIQUAC Equations

(1) Wilson Equation

* 개념 ... 각 성분 분자 주위의 국부적 환경이 용액 내의 거시적인 몰용액의 특성과 다름

* 완전 혼합 용액에서 적용 가능

$$\frac{g^E}{RT} = -x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(x_2 + \Lambda_{21}x_1)$$

$$\ln\gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right)$$

$$\ln\gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right)$$

$$\Lambda_{12} = \frac{\upsilon_2}{\upsilon_1}\exp\left(-\frac{\lambda_{12} - \lambda_{11}}{RT}\right) \qquad \Lambda_{21} = \frac{\upsilon_1}{\upsilon_{12}}\exp\left(-\frac{\lambda_{21} - \lambda_{22}}{RT}\right)$$

(2) NRTL Equation

* 완전한 혼합 성계와 불완전한 혼합의 적용

$$\frac{g^E}{RT} = x_1 x_2 \left(\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right)$$

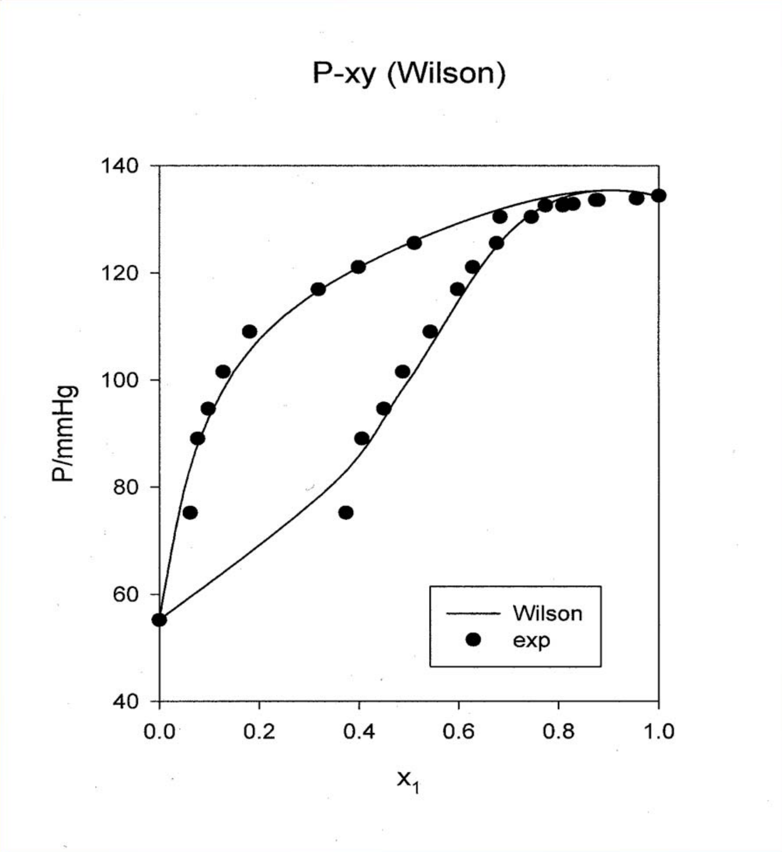
$$\tau_{12} = \frac{g_{12} - g_{22}}{RT} \qquad \tau_{21} = \frac{g_{21} - g_{11}}{RT}$$

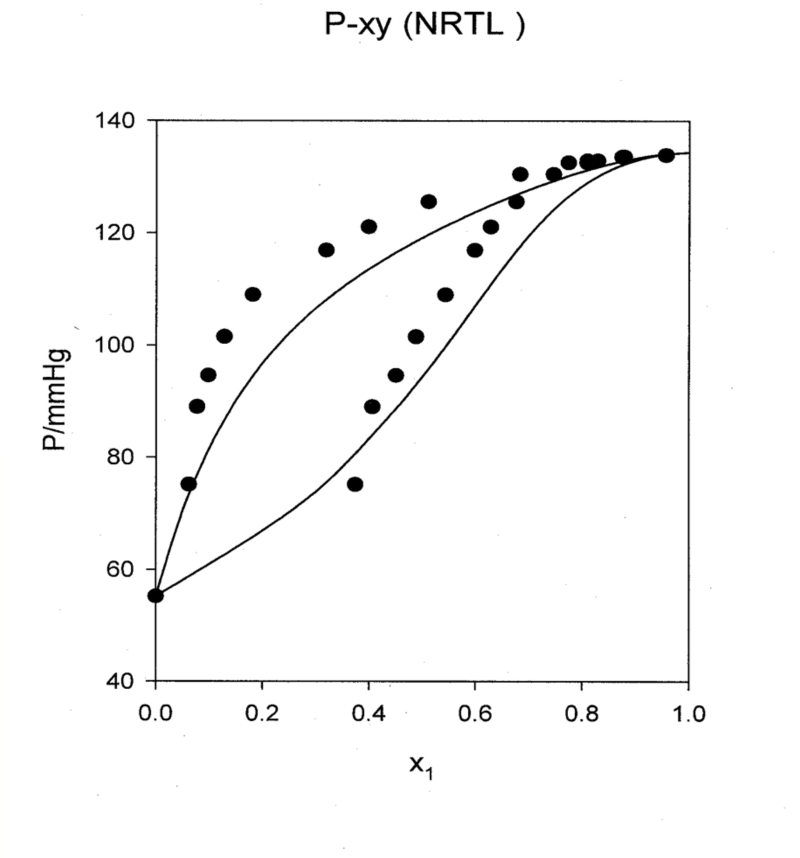
$$G_{12} = \exp(-\alpha_{12} \tau_{12}) \qquad G_{21} = \exp(-\alpha_{12} \tau_{21})$$

$$\ln \gamma_1 = x_2^2 \left(\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right)$$

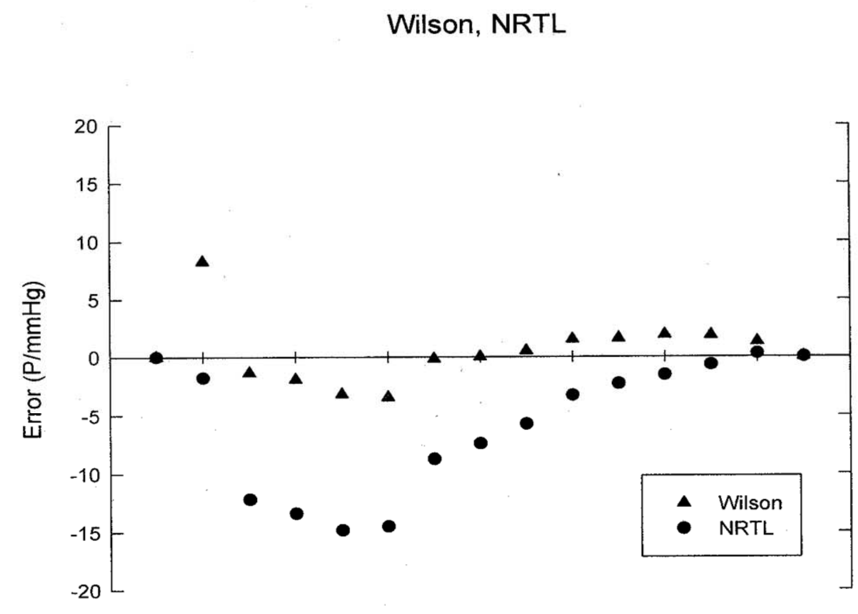
$$\ln \gamma_2 = x_1^2 \left(\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right)$$

Wilson Equation과 NRTL Equation의 비교
[system : ethanol(1) / water(2)]



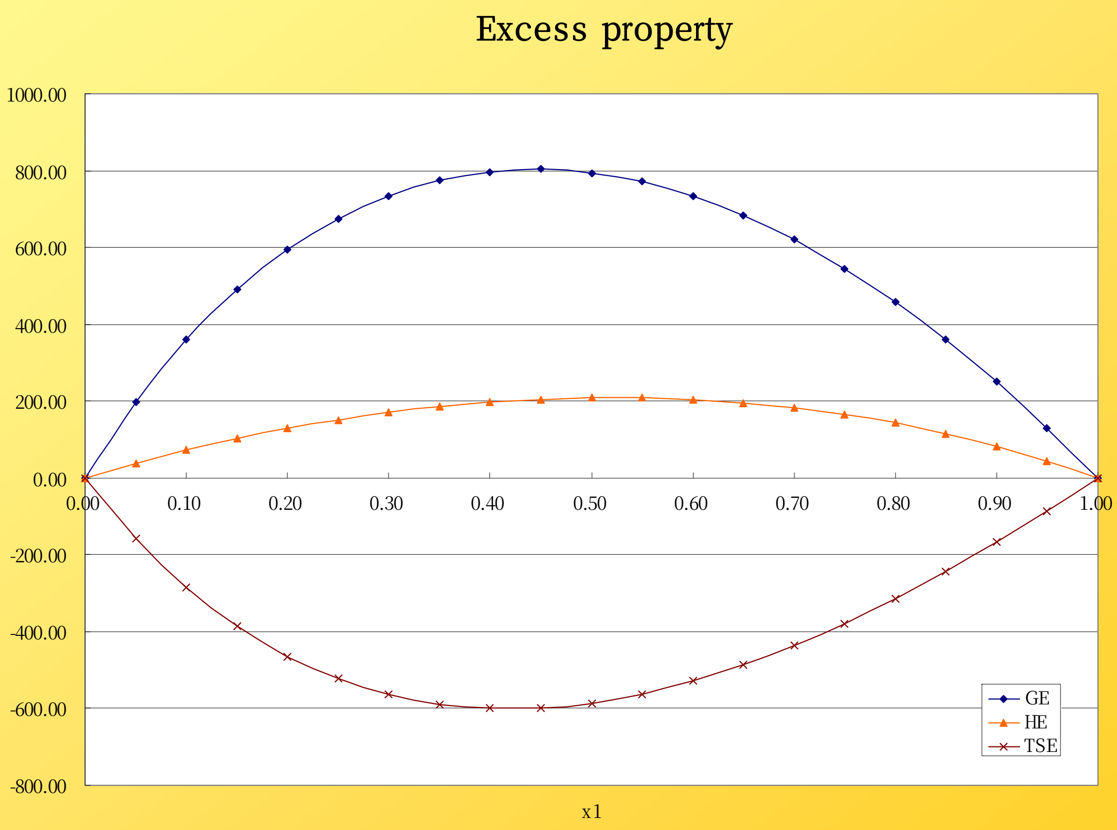


Wilson Equation과 NRTL Equation의 비교

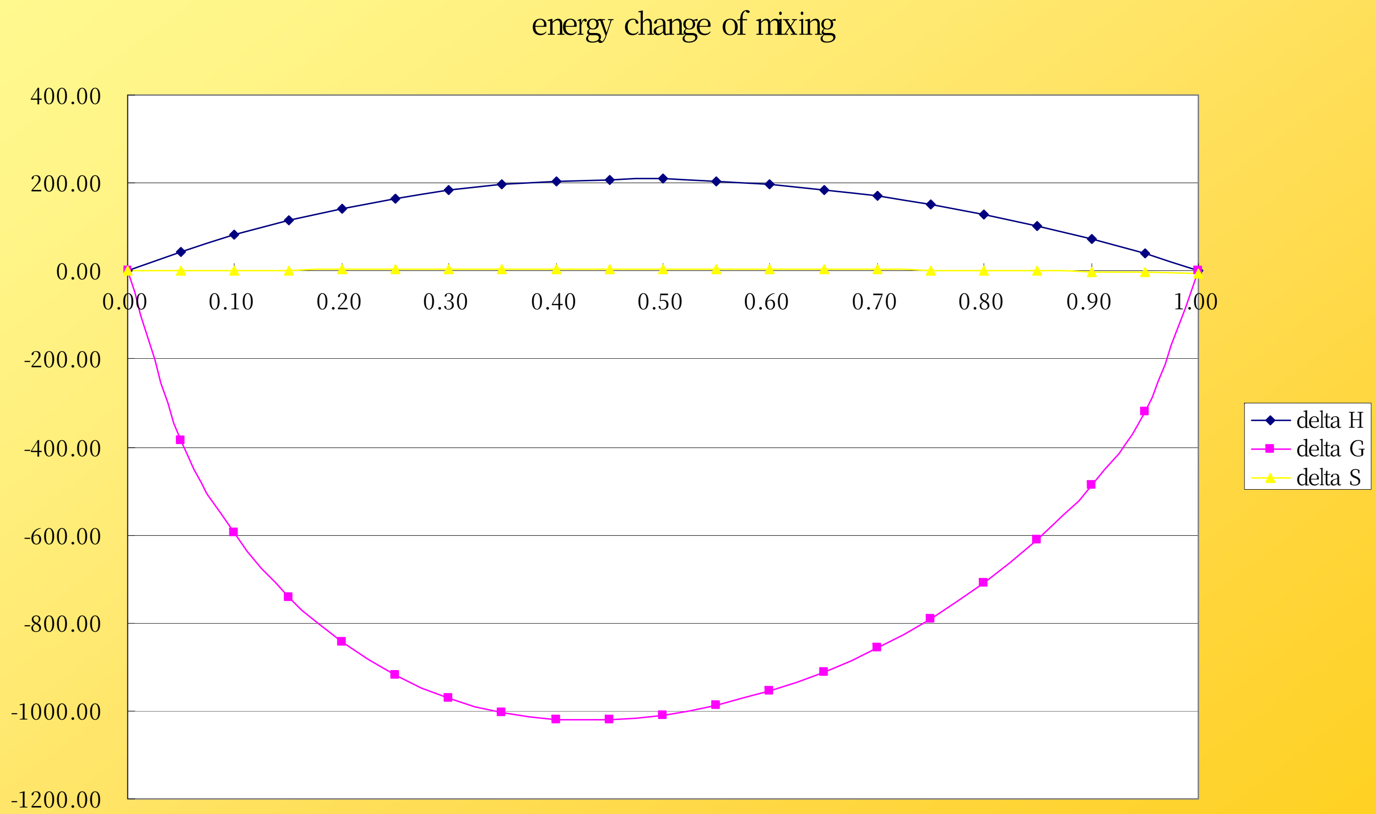


* NRTL 식은 parameter가 3개임에도 불구하고 Wilson식이 더 오차가 적은 것을 볼 수 있다.

Wilson Equation과 NRTL Equation의 비교



Wilson Equation과 NRTL Equation의 비교



(3) UNIQUAC Equation

* 극성 , 무극성 , partial miscible mixture에서도 적용
* 단지 2개의 ajustable parameter만으로도 대부분의 경우에 잘 만족시킴

$$\frac{g^E}{RT} = \left(\frac{g^E}{RT}\right)_{combinatorial} + \left(\frac{g^E}{RT}\right)_{residual}$$

$$\left(\frac{g^E}{RT}\right)_{combinatorial} = x_1 \ln\frac{\Phi_1^*}{x_1} + x_2 \ln\frac{\Phi_2^*}{x_2} + \frac{z}{2}\left(x_1 q_1 \ln\frac{\theta_1}{\Phi_1^*} + x_2 q_2 \ln\frac{\theta_2}{\Phi_2^*}\right)$$

$$\left(\frac{g^E}{RT}\right)_{residual} = -x_1 q_1' \ln(\theta_1' + \theta_2' \tau_{21}) - x_2 q_2' \ln(\theta_2' + \theta_1' \tau_{12})$$

[The definitions of parameters]

$$\Phi_1^* = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2} \qquad \Phi_2^* = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2}$$

$$\theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2} \qquad \theta_2 = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2}$$

$$\theta_1^{'} = \frac{x_1 q_1^{'}}{x_1 q_1^{'} + x_2 q_2^{'}} \qquad \theta_2^{'} = \frac{x_2 q_2^{'}}{x_1 q_1^{'} + x_2 q_2^{'}}$$

$$\tau_{12} = \exp(-\frac{\Delta u_{12}}{RT}) \equiv \exp(-\frac{a_{12}}{T}) \qquad \tau_{21} = \exp(-\frac{\Delta u_{21}}{RT}) \equiv \exp(-\frac{a_{21}}{T})$$

UNIQUAC Equation

$$\ln\gamma_1 = \ln\frac{\Phi_1^*}{x_1} + \frac{z}{2}q_1\ln\frac{\theta_1}{\Phi_1^*} + \Phi_2^*\left(l_1 - \frac{r_1}{r_2}l_2\right) - q_1^{'}\ln(\theta_1^{'} + \theta_2^{'}\tau_{21}) + \theta_2^{'}q_1^{'}\left(\frac{\tau_{21}}{\theta_1^{'} + \theta_2^{'}\tau_{21}} - \frac{\tau_{12}}{\theta_2^{'} + \theta_1^{'}\tau_{12}}\right)$$

$$\ln\gamma_2 = \ln\frac{\Phi_2^*}{x_2} + \frac{z}{2}q_2\ln\frac{\theta_2}{\Phi_2^*} + \Phi_2^*\left(l_2 - \frac{r_2}{r_1}l_1\right) - q_2^{'}\ln(\theta_2^{'} + \theta_1^{'}\tau_{12}) + \theta_1^{'}q_2^{'}\left(\frac{\tau_{12}}{\theta_2^{'} + \theta_1^{'}\tau_{12}} - \frac{\tau_{21}}{\theta_1^{'} + \theta_2^{'}\tau_{21}}\right)$$

$$l_1 = \frac{z}{2}(r_1 - q_1) - (r_1 - 1) \qquad l_2 = \frac{z}{2}(r_2 - q_2) - (r_2 - 1)$$

[Merits of UNIQUAC Equation] ... ❶ (relative) simplicity

❷ only two ajustable parameter

❸ wide range of applicability

[참고] Activity models

Equations of State

Pen-Robinson property package option은 PR.Sour PR, PRSV입니다.
Soave-Redlich-Kwong equation of state option은 SRK.Sour SRK, KD, ZJ입니다.

Activity Models

Application	Margules	van Laar	Wilson	NRTL	UNIQUAC
Binary Systems	A	A	A	A	A
Multicomponent System	LA	LA	A	A	A
Azeotropic Systems	A	A	A	A	A
Liquid-Liquid Equilibria	A	A	N/A	A	A
Dilute Systems	?	?	A	A	A
Self-Associating Systems	?	?	A	A	A
Polymers	N/A	N/A	N/A	N/A	A
Extrapolating	?	?	G	G	G

- A = Application
- N/A = Not Application
- ? = Questionable
- G = Good
- LA = Limited Application