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Occupational Safety & Health Research Institute

Prediction of Flash Point for Binary Mixtures

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O C C U P A T I O N A L   S A F E T Y   &   H E A L T H   R E S E A R C H   I N S T I T U T E

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1. MSDS상의 혼합물 인화점
2. Prediction of Flash Point
3. Ideal vs. non-ideal solution
4. Procedure to estimate FP
5. FP of water-ethanol mixture
6. Conclusions

KOSHANET

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□ 구성성분 물질의 자료이용

5. 폭발 · 화재시 대처방법

구 분	제 품	벤 젠	톨 루 엔	나프탈렌
인 화 점	-2℃	-11	4	79
발 화 점	-	538	480	526
폭발범위 (상)	-	8.0%	7.1%	-
(공기중) (하)	-	1.5%	1.3%	-

하는 것이다.

혼합물의 물질안전보건자료(MSDS)는 혼합물 자체의 유해위험성이 시험(실험)을 거쳐

Prediction of flash point(1)

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Question1

Octane
FP: 15℃

+

Heptane
FP: -5℃

혼합물의 인화점은?

예 상 대 로

Flash Point between Individual Componetns

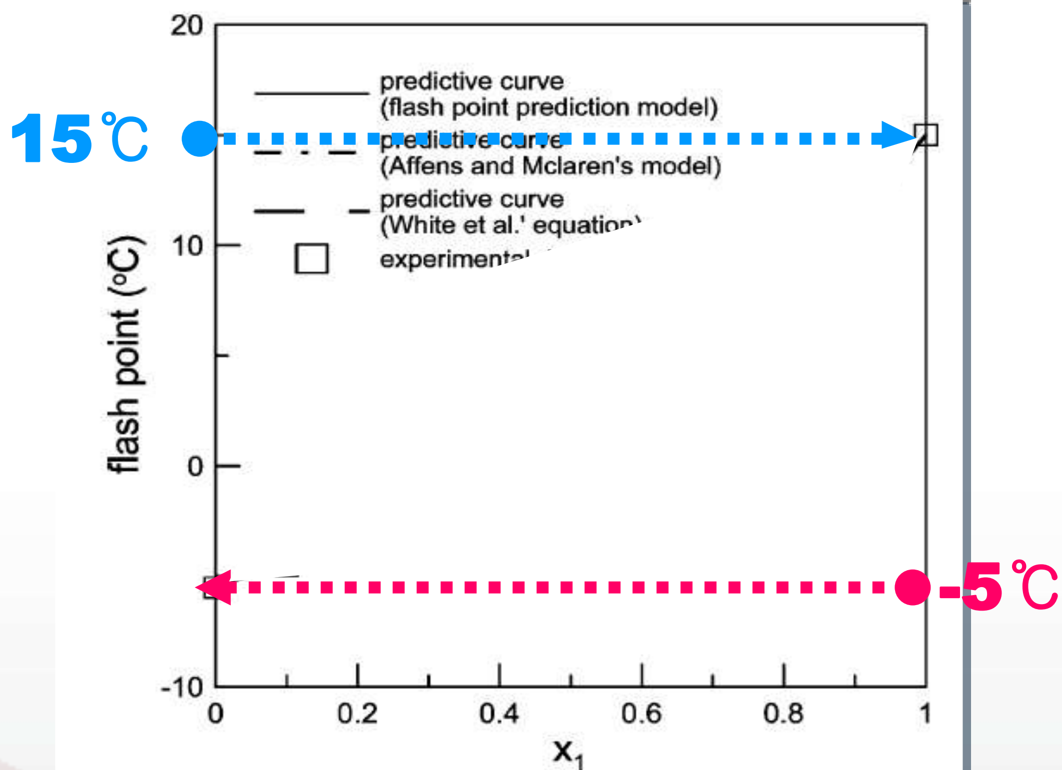

Fig. 1. Comparison of the flash point-prediction curves with experimentally-derived data for octane (1) + heptane (2) solution.

Horng-Jang Liaw, "A mathematical model for predicting the flash point of binary solutions"

Prediction of flash point(2)

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Question2

Octane
FP: 15℃

+

Ethanol
FP: 13℃

혼합물의 인화점은?

Min. 5℃

Minimum Flash Point Behavior

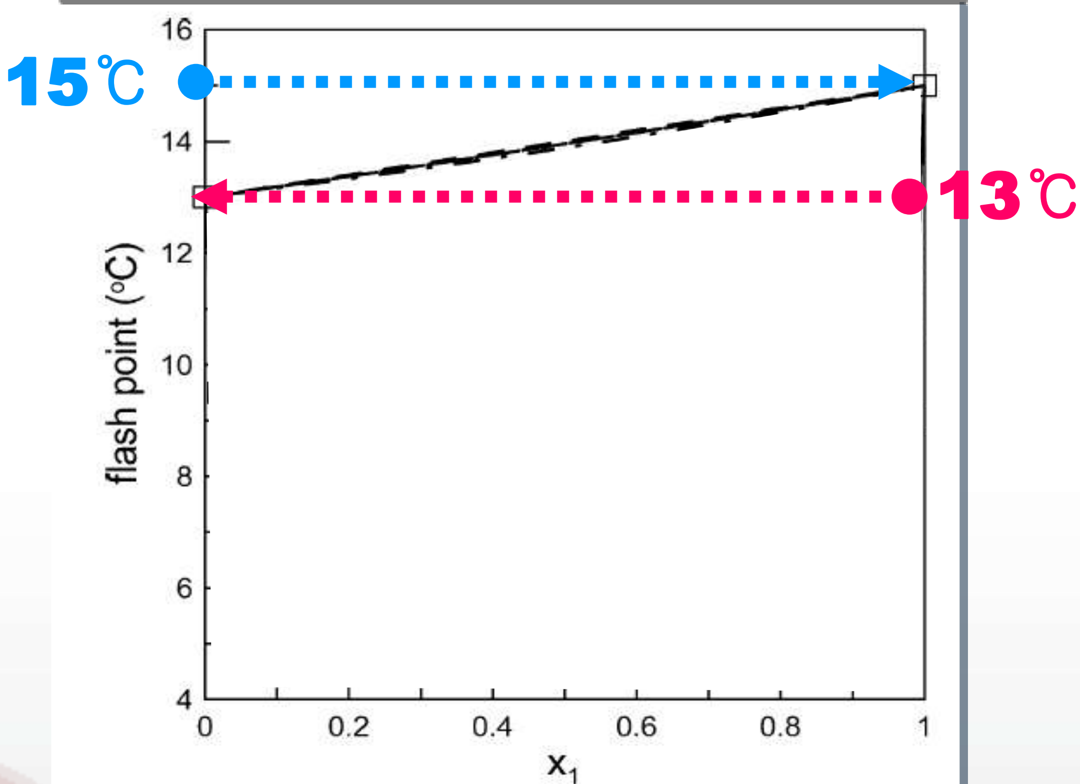


Fig. 5. Comparison of the flash point-prediction curves with experimentally-derived data for octane (1) + ethanol (2) solution.

Horng-Jang Liaw, "A mathematical model for predicting the flash point of binary solutions"

Prediction of flash point(3)

Question3

Phenol
FP: 83℃

+

Acetophenone
FP: 81℃

혼합물의 인화점은?

Max. 89℃

Maximum Flash Point Behavior

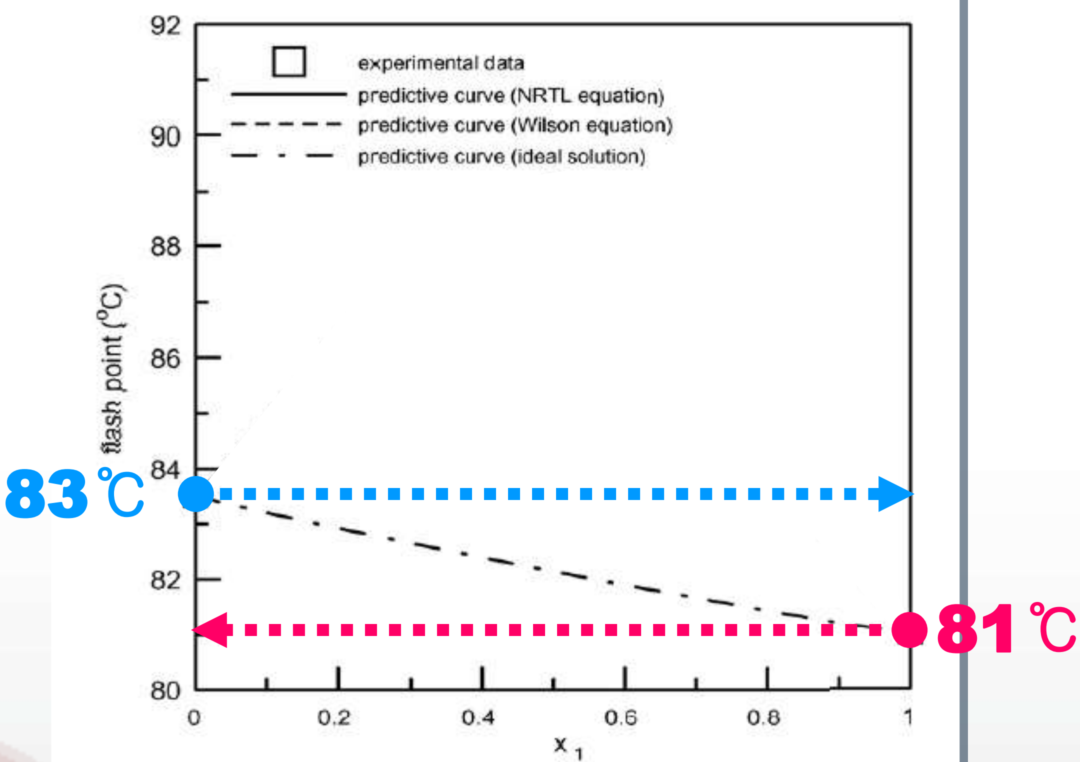


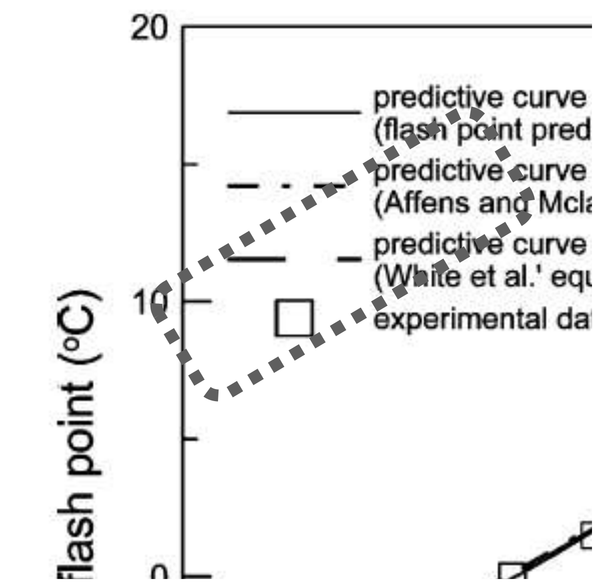
Fig. 5. Variation of flash point with composition for phenol (1) + acetophenone (2).

Horng-Jang Liaw, "Binary mixtures exhibiting maximum flash-point behavior"

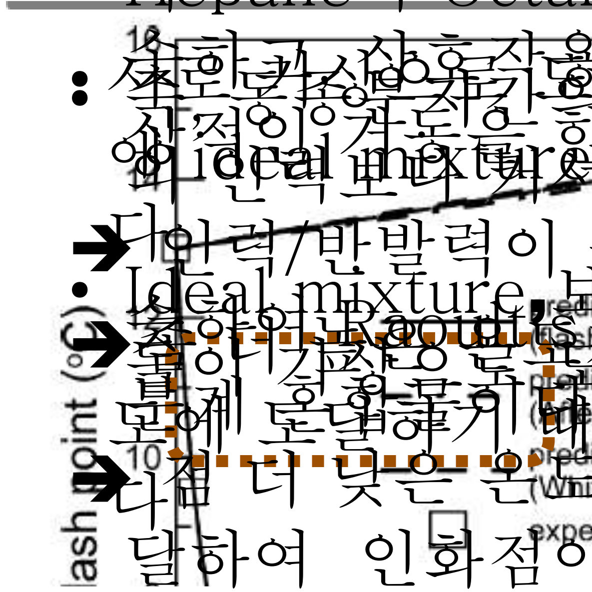
Max. FPB vs. Min. FPB

이렇게 물질에 따라 혼합할 때 인화점이 다른 이유는?

Max. nor min. Flash Point Behavior



Minimum Flash Point Behavior



Maximum Flash Point Behavior

- Hydrocarbon과 Alcohol은 극성이 다르기 때문에 상호작용이 매우 상이
- Heptane과 Octane은 분자구조가 비슷하고 상호작용을 비슷하게 가지며 이상적인 거동을 한다
- 동종분자간인력보다 이종분자간인력이 강해 ideal mixture 보다 증기압이 낮아진다

→ 인력/반발력이 동종/이종분자간 비슷

- Ideal mixture, Raoult's Law에 잘 부합

→ 증기압이 높아 혼합물이 가볍게 휘발하기 때문에

→ 조금 더 낮은 온도에서 폭발하한에 도달하여 인화점이 낮아진다

폭발하한 농도에 도달하기 때문에 인화점이 높아진다

Ideal Solution

2성분계에서 두 물질이 아주 이상적인 거동

Ideal Solution

3.2. Reduced model under an ideal solution assumption

For the ideal solution, the activity coefficients of the liquid phase are equal to unity, and the flash point-prediction model may be reduced to a simpler form. Under this condition, the vapor-liquid equilibrium equation, Eq. (5), was able to be reduced to Raoult's law for this study, this being described as:

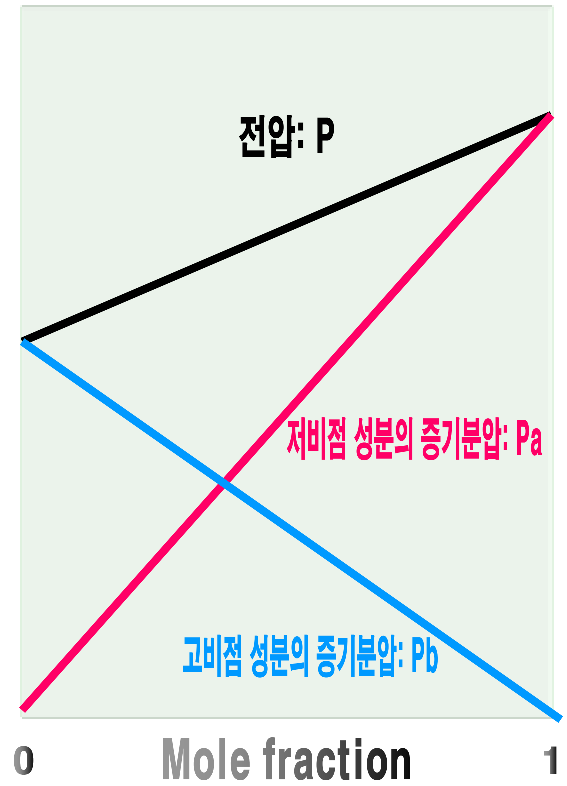
$$y_i = \frac{x_i P_i^{sat}}{P} \tag{8}$$

Therefore, the modified equation of Le Chatelier, Eq. (6), was reduced to:

$$1 = \sum \frac{x_i P_i^{sat}}{P_{i,fp}^{sat}} = \frac{x_1 P_1^{sat}}{P_{1,fp}^{sat}} + \frac{x_2 P_2^{sat}}{P_{2,fp}^{sat}} \tag{9}$$

this being the equation used by White et al. (1997) to estimate the flash point of aviation-fuel mixtures, JP-4/JP-8 and JP-5/JP-8. The Antoine equation, Eq. (7), was still deemed by us to be useful to estimate P_i^{sat} and $P_{i,fp}^{sat}$ for this reduced model. Therefore, the reduced

이상용액의 증기압 곡선



Horng-Jang Liaw, "A mathematical model for predicting the flash point of binary solutions"

Non-ideal Solution

$$y_i = \frac{x_i \gamma_i p_i^{sat}}{P}$$

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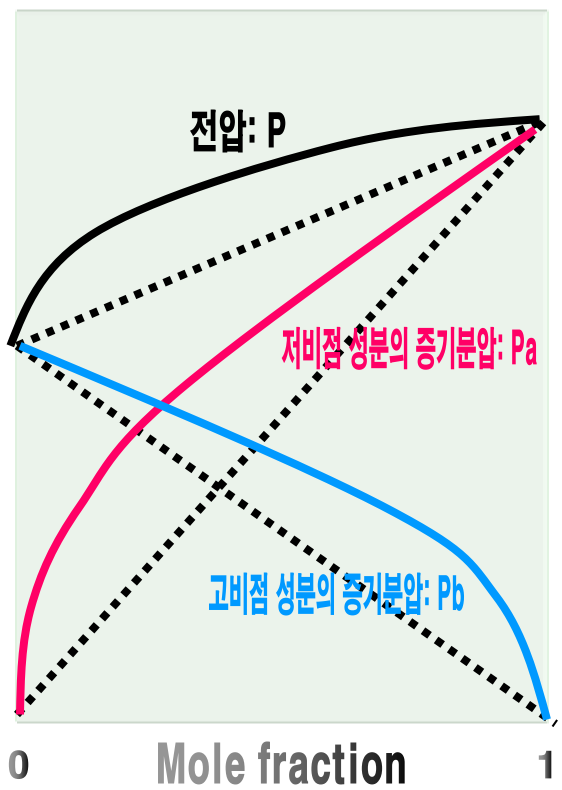
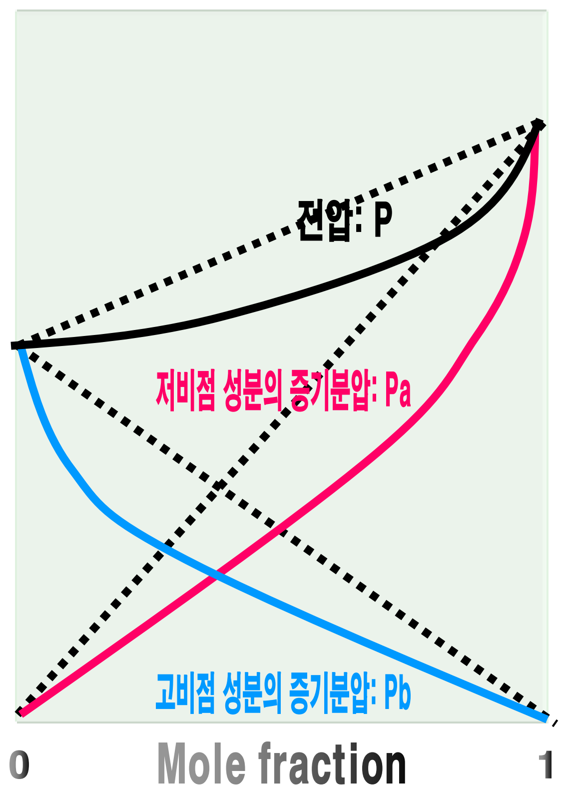
2성분계 비이상적인 거동

Positive Deviation(정편차)-증기압↑



Negative Deviation(부편차)-증기압↓



Comparison of Ideal & non-ideal Sol'n

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	Positive Deviation(정편차)-증기압↑	Ideal Solution과 유사	Negative Deviation(부편차)-증기압↓
증 기 압	이상용액에 비해 크게 나타남	이상용액과 비슷 or 크게 벗어나지 않음	이상용액에 비해 작게 나타남
인 력	동종분자간 인력 〉 이종분자간 인력	구조가 비슷하여 동종/이종 인력이 비슷	동종분자간 인력 〈 이종분자간 인력
활동도계수	$\gamma_A > 1, \gamma_B > 1$	$\gamma_A = 1, \gamma_B = 1$	$\gamma_A < 1, \gamma_B < 1$
2성분계	Octane-Ethanol Water-Ethanol Ethanol-Benzene Acetone-CS2계	Octane-Heptane Benzene-Toluene Methanol-Ethanol Methane-Ethane	Phenol-Acetophenone Acetone-Chloroform Water-염산 Water-황산

$$y_i = \frac{x_i \gamma_i P_i^{sat}}{P}$$

Procedure to estimate

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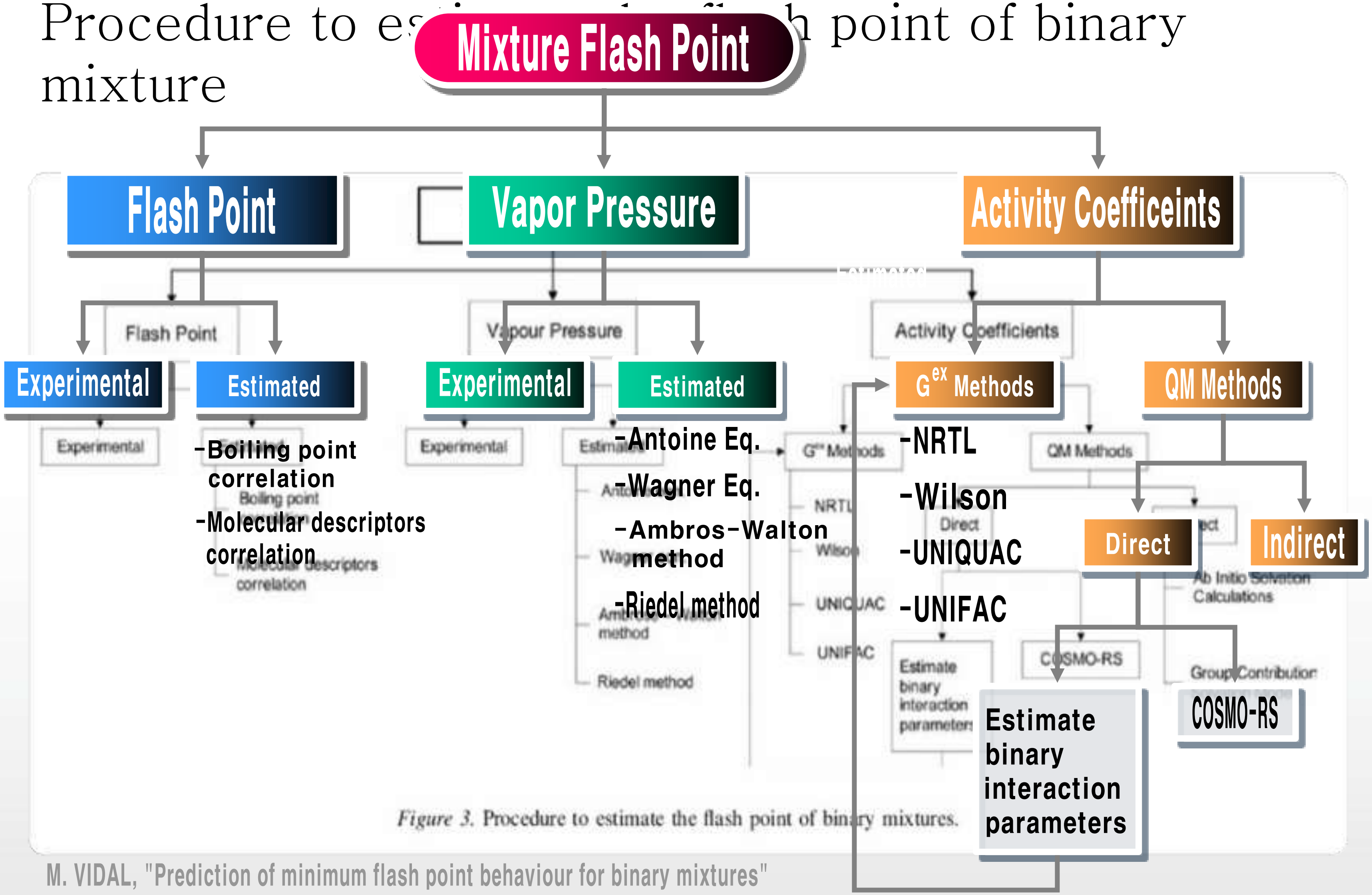
Procedure to es… h point of binary mixture



M. VIDAL, "Prediction of minimum flash point behaviour for binary mixtures"

인화성 액체와 물의 혼합물인 경우

한쪽은 불에 타는 물질이고 한쪽은 불에 타지 않는 물질

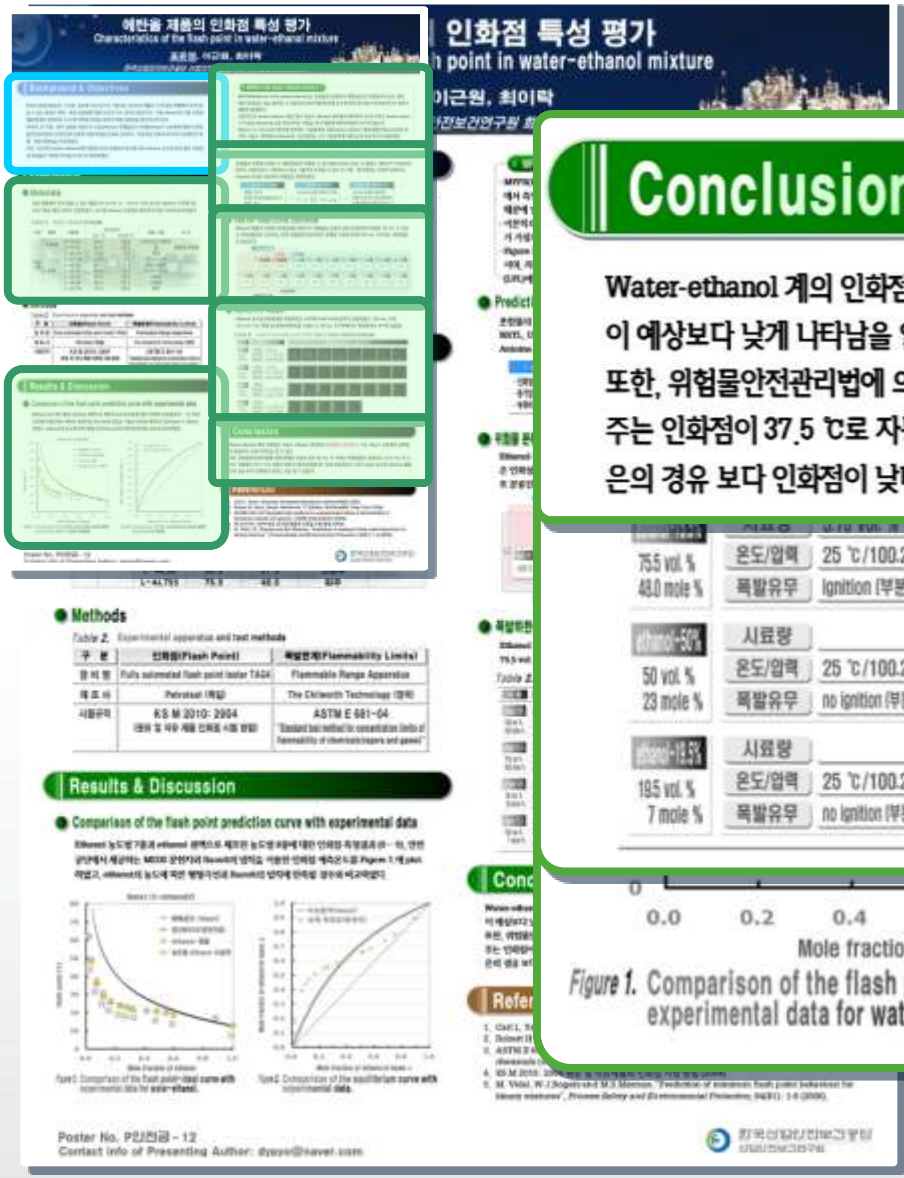
Ethanol-Water 계

물과 에탄올 모두 positive deviation(정편차)이 보이므로 실제로는 증기압이 더 커지지만...

➔물이 불연성이므로 기상으로 증발한 물분자는 기상의 에탄올 농도를 희석시키는 역할을 하기 때문에

➔Min. FPB 현상은 보이지 않으나, Raoul't law에 의한 예상치 보다 낮은 인화점을 갖게 된다.

Characteristics of the flash point in water-ethanol mixture



Conclusion

Water-ethanol 계의 인화점은 저농도 ethanol 영역에서 인화점이 낮아지고, 이는 저농도 주류에서 인화점이 예상보다 낮게 나타남을 알 수 있다.

또한, 위험물안전관리법에 의해 완제품 주류의 경우 62 vol. % 이하는 비위험물로 분류되나, 19.5 vol. % 소주는 인화점이 37.5 ℃로 자동차 연료인 경유(인화점 38 ℃)와 비슷하므로 이보다 높은 농도의 ethanol 제품은의 경유 보다 인화점이 낮다는 것을 알 수 있었다.

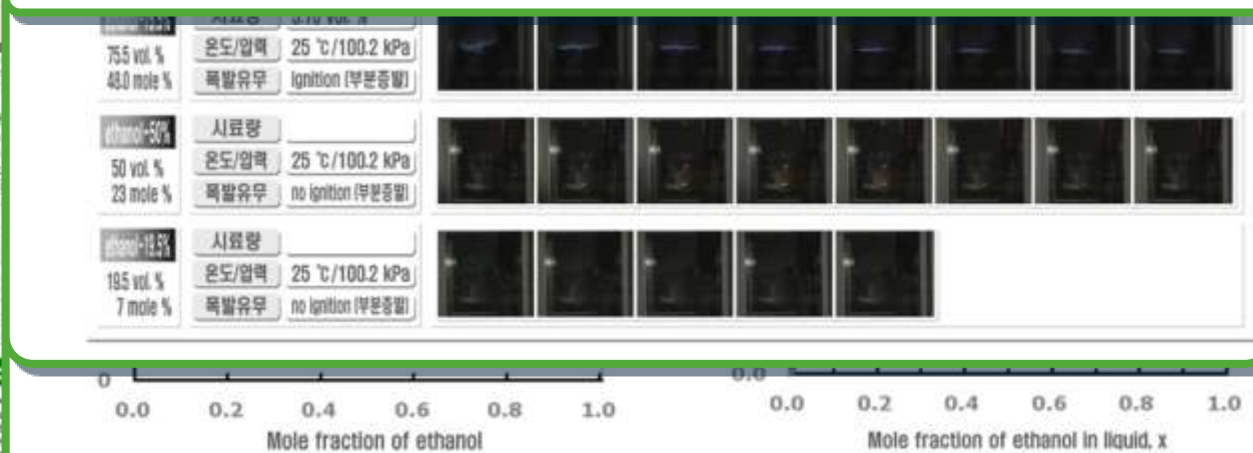


Figure 1. Comparison of the flash point-ideal curve with experimental data for water-ethanol.

Figure 2. Comparison of the equilibrium curve with experimental data.

Assumptions can be dangerous

Question

Can we treat mixtures as pure compounds and use the available methodologies to evaluate the risks associated with them?

Answer

The answer to this question is generally NO.

The behavior of mixtures can be extremely different compared to the behavior of the individual components, and making such assumptions can be very dangerous.

감사합니다!!!

A correlation of FP for organics…

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The flash point values of the individual mixture components can be obtained from experimental measurements or from correlations with boiling point or with molecular descriptors. A correlation of the flash point for organics compounds with their boiling points was developed by Satyanarayana and Rao (1992) and is presented in equation (7).

$$T_f = a + \frac{b(c/T_b)^2 e^{-c/T_b}}{(1 - e^{-c/T_b})^2} \tag{7}$$

where T_f is the flash point temperature (K), a, b, and c are constants provided in Satyanarayana and Rao (1992), and T_b is the boiling point temperature (K).

The equation was fit for over 1200 compounds with less than 1% absolute error with experimental data (based on K). The larger deviations, of approximately 10°C, were found for the phosphorous chemical group. A comparison of this correlation with other correlations is presented (Satyanarayana and Rao, 1992).

Mode

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Table 1
Models of activity coefficients and their composition effect in binary systems

Wilson equation	
$\ln\gamma_1$ and $\ln\gamma_2$	$\ln\gamma_1 = -\ln(x_1+\Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1+\Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1+x_2}\right)$, $\ln\gamma_2 = -\ln(x_2+\Lambda_{21}x_1) - x_1\left(\frac{\Lambda_{12}}{x_1+\Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1+x_2}\right)$, where $\Lambda_{12} = \frac{v_2^L}{v_1^L}\exp\left(-\frac{\lambda_{12}-\lambda_{11}}{RT}\right)$, $\Lambda_{21} = \frac{v_1^L}{v_2^L}\exp\left(-\frac{\lambda_{21}-\lambda_{22}}{RT}\right)$
$\left(\frac{\partial\gamma_1}{\partial x_1}\right)_T$ and $\left(\frac{\partial\gamma_2}{\partial x_1}\right)_T$	$\left(\frac{\partial\gamma_1}{\partial x_1}\right)_T = \gamma_1\left\{-\frac{1-\Lambda_{12}}{x_1-\Lambda_{12}x_2} - \left(\frac{\Lambda_{12}}{x_1+\Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1+x_2}\right) + x_2\left[-\frac{\Lambda_{12}}{(x_1+\Lambda_{12}x_2)^2}(1-\Lambda_{12}) + \frac{\Lambda_{21}}{(\Lambda_{21}x_1+x_2)^2}(\Lambda_{21}-1)\right]\right\}$, $\left(\frac{\partial\gamma_2}{\partial x_1}\right)_T = \gamma_2\left\{\frac{1-\Lambda_{21}}{x_2+\Lambda_{21}x_1} - \left(\frac{\Lambda_{12}}{x_1+\Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1+x_2}\right) + x_1\left[\frac{\Lambda_{12}}{(x_1+\Lambda_{12}x_2)^2}(1-\Lambda_{12}) - \frac{\Lambda_{21}}{(\Lambda_{21}x_1+x_2)^2}(\Lambda_{21}-1)\right]\right\}$
γ_1^∞ and γ_2^∞	$\gamma_1^\infty = \frac{1}{\Lambda_{12}}\exp(1-\Lambda_{21})$, $\gamma_2^\infty = \frac{1}{\Lambda_{21}}\exp(1-\Lambda_{12})$
NRTL equation	
$\ln\gamma_1$ and $\ln\gamma_2$	$\ln\gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1+x_2G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2+x_1G_{12})^2}\right]$, $\ln\gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2+x_1G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1+x_2G_{21})^2}\right]$, where $\tau_{12} = \frac{g_{12}-g_{22}}{RT}$, $\tau_{21} = \frac{g_{21}-g_{11}}{RT}$, $\ln G_{12} = -\alpha_{12}\tau_{12}$, $\ln G_{21} = -\alpha_{12}\tau_{21}$
$\left(\frac{\partial\gamma_1}{\partial x_1}\right)_T$ and $\left(\frac{\partial\gamma_2}{\partial x_1}\right)_T$	$\left(\frac{\partial\gamma_1}{\partial x_1}\right)_T = \gamma_1\left\{-2x_2\left[\tau_{21}\left(\frac{G_{21}}{x_1+x_2G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2+x_1G_{12})^2}\right] + x_2^2\left[-2\tau_{21}\frac{G_{21}^2}{(x_1+x_2G_{21})^3}(1-G_{21}) + \frac{2\tau_{12}G_{12}}{(x_2+x_1G_{12})^3}(1-G_{12})\right]\right\}$, $\left(\frac{\partial\gamma_2}{\partial x_1}\right)_T = \gamma_2\left\{2x_1\left[\tau_{12}\left(\frac{G_{12}}{x_2+x_1G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1+x_2G_{21})^2}\right] + x_1^2\left[2\tau_{12}\frac{G_{12}^2}{(x_2+x_1G_{12})^3}(1-G_{12}) - \frac{2\tau_{21}G_{21}}{(x_1+x_2G_{21})^3}(1-G_{21})\right]\right\}$
γ_1^∞ and γ_2^∞	$\gamma_1^\infty = \exp(\tau_{21}+\tau_{12}G_{12})$, $\gamma_2^\infty = \exp(\tau_{12}+\tau_{21}G_{21})$
UNIQUAC equation	
$\ln\gamma_1$ and $\ln\gamma_2$	$\ln\gamma_1 = \ln\frac{\Phi_1}{x_1} + \frac{z}{2}q_1\ln\frac{\theta_1}{\Phi_1} + \Phi_2\left(l_1 - \frac{r_1}{r_2}l_2\right) - q_1\ln(\theta_1+\theta_2\tau_{21}) + \theta_2 q_1\left(\frac{\tau_{21}}{\theta_1+\theta_2\tau_{21}} - \frac{\tau_{12}}{\theta_2+\theta_1\tau_{12}}\right)$, $\ln\gamma_2 = \ln\frac{\Phi_2}{x_2} + \frac{z}{2}q_2\ln\frac{\theta_2}{\Phi_2} + \Phi_1\left(l_2 - \frac{r_2}{r_1}l_1\right) - q_2\ln(\theta_2+\theta_1\tau_{12}) + \theta_1 q_2\left(\frac{\tau_{12}}{\theta_2+\theta_1\tau_{12}} - \frac{\tau_{21}}{\theta_1+\theta_2\tau_{21}}\right)$, where $\ln\tau_{12} = -\frac{u_{12}-u_{22}}{RT}$, $\ln\tau_{21} = -\frac{u_{21}-u_{11}}{RT}$, $\Phi_1 = \frac{x_1r_1}{x_1r_1+x_2r_2}$, $\Phi_2 = \frac{x_2r_2}{x_1r_1+x_2r_2}$, $\theta_1 = \frac{x_1q_1}{x_1q_1+x_2q_2}$, $\theta_2 = \frac{x_2q_2}{x_1q_1+x_2q_2}$, $l_1 = \frac{z}{2}(r_1-q_1)-(r_1-1)$, $l_2 = \frac{z}{2}(r_2-q_2)-(r_2-1)$, $z = 10$
$\left(\frac{\partial\gamma_1}{\partial x_1}\right)_T$ and $\left(\frac{\partial\gamma_2}{\partial x_1}\right)_T$	$\left(\frac{\partial\gamma_1}{\partial x_1}\right)_T = \gamma_1\left\{\frac{1}{\Phi_1}\frac{d\Phi_1}{dx_1} - \frac{1}{x_1} + \frac{z}{2}q_1\left(\frac{1}{\theta_1}\frac{d\theta_1}{dx_1} - \frac{1}{\Phi_1}\frac{d\Phi_1}{dx_1}\right) + \left(l_1 - \frac{r_1}{r_2}l_2\right)\frac{d\Phi_2}{dx_1} - \frac{q_1}{\theta_1+\theta_2\tau_{21}}\left(\frac{d\theta_1}{dx_1} + \tau_{21}\frac{d\theta_2}{dx_1}\right) + q_1\frac{d\theta_2}{dx_1}\left(\frac{\tau_{21}}{\theta_1+\theta_2\tau_{21}} - \frac{\tau_{12}}{\theta_2+\theta_1\tau_{12}}\right) + \theta_2q_1\left[\frac{\tau_{12}}{(\theta_2+\theta_1\tau_{12})^2}\left(\frac{d\theta_2}{dx_1} + \tau_{12}\frac{d\theta_1}{dx_1}\right) - \frac{\tau_{21}}{(\theta_1+\theta_2\tau_{21})^2}\left(\frac{d\theta_1}{dx_1} + \tau_{21}\frac{d\theta_2}{dx_1}\right)\right]\right\}$, $\left(\frac{\partial\gamma_2}{\partial x_1}\right)_T = \gamma_2\left\{\frac{1}{\Phi_2}\frac{d\Phi_2}{dx_1} + \frac{1}{x_2} + \frac{z}{2}q_2\left(\frac{1}{\theta_2}\frac{d\theta_2}{dx_1} - \frac{1}{\Phi_2}\frac{d\Phi_2}{dx_1}\right) + \left(l_2 - \frac{r_2}{r_1}l_1\right)\frac{d\Phi_1}{dx_1} - \frac{q_2}{\theta_2+\theta_1\tau_{12}}\left(\frac{d\theta_2}{dx_1} + \tau_{12}\frac{d\theta_1}{dx_1}\right) + q_2\frac{d\theta_1}{dx_1}\left(\frac{\tau_{12}}{\theta_2+\theta_1\tau_{12}} - \frac{\tau_{21}}{\theta_1+\theta_2\tau_{21}}\right) + \theta_1q_2\left[\frac{\tau_{21}}{(\theta_1+\theta_2\tau_{21})^2}\left(\frac{d\theta_1}{dx_1} + \tau_{21}\frac{d\theta_2}{dx_1}\right) - \frac{\tau_{12}}{(\theta_2+\theta_1\tau_{12})^2}\left(\frac{d\theta_2}{dx_1} + \tau_{12}\frac{d\theta_1}{dx_1}\right)\right]\right\}$, where $\frac{d\Phi_1}{dx_1} = \frac{r_1r_2}{(x_1r_1+x_2r_2)^2}$, $\frac{d\Phi_2}{dx_1} = -\frac{r_1r_2}{(x_1r_1+x_2r_2)^2}$, $\frac{d\theta_1}{dx_1} = \frac{q_1q_2}{(x_1q_1+x_2q_2)^2}$, $\frac{d\theta_2}{dx_1} = -\frac{q_1q_2}{(x_1q_1+x_2q_2)^2}$
γ_1^∞ and γ_2^∞	$\ln\gamma_1^\infty = \ln\frac{r_1}{r_2} + \frac{z}{2}q_1\ln\frac{r_2q_1}{r_1q_2} + \left(l_1 - \frac{r_1}{r_2}l_2\right) - q_1\ln\tau_{21} + q_1(1-\tau_{12})$, $\ln\gamma_2^\infty = \ln\frac{r_2}{r_1} + \frac{z}{2}q_2\ln\frac{r_1q_2}{r_2q_1} + \left(l_2 - \frac{r_2}{r_1}l_1\right) - q_2\ln\tau_{12} + q_2(1-\tau_{21})$

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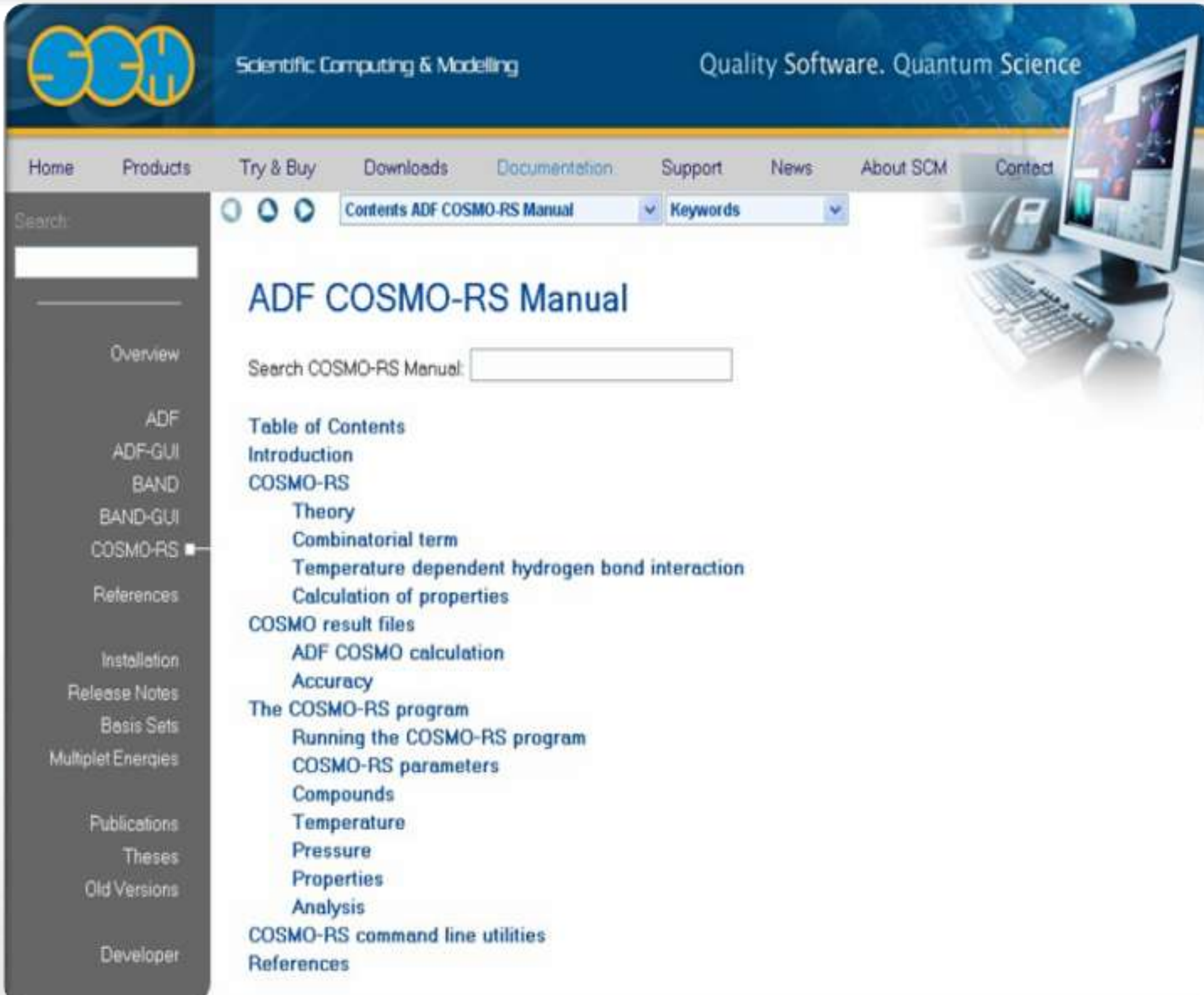
COSMO-RS



http://www.scm.com/Doc/Doc2008.01/CRS/CRS/page1.html

Antoine Eq. & Reidel Eq.