

# 천연가스 구성 성분들에 대한 물성 및 열역학적 모델식 소개

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GERG-2008 모델식과 다른 모델식 사이의 비교

# 1

## 천연가스 구성 성분들의 고정 물성

# 천연가스(Natural Gas)란?

- 주성분은 메탄( $\text{CH}_4$ )이고, 에탄( $\text{C}_2\text{H}_6$ ) 함량이 많고 적음에 따라서 rich gas와 lean gas로 구분한다.
- 천연가스 처리공정의 3개의 키워드:
  - Purification(전처리 공정)
    - 천연가스 중의 불순물: 이산화탄소, 황화수소, 수분, 수은 등
    - 불순물 제거 공정: AGRU, Dehydration Process 등
  - Volume Reduction(액화공정: Liquefaction Process)
    - 천연가스를 액화시키는 이유
    - 부피가 600분의 1로 줄어들기 때문에 저장 및 수송이 용이하다.
    - 동일한 저장 부피에 600배 많은 천연가스를 저장할 수 있다.
    - 이송시에 가스배관보다 액체 배관의 직경이 더 작다.
    - 기체 이송시에 압축기를 사용하는 것 보다 액체 이송 시에 펌프를 사용하면 동력을 줄일 수 있다.
  - Separation(NGL 회수공정)
    - 에탄 이상의 성분을 회수하는 공정

# 천연가스 구성 성분들:

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## ➤ 천연가스 구성 성분들:

- $\text{CO}_2$ : 불순물로 AGRU 공정에 의해서 제거되어야 할 성분
- $\text{H}_2\text{O}$ : 불순물로 Dehydration 공정에 의해서 제거되어야 할 성분
- $\text{N}_2$ : 천연가스 구성성분 중의 하나이지만 열량은 없음
- $\text{CH}_4$ : 대부분을 차지하는 성분임
- $\text{C}_2\text{H}_6$ : 에탄 함량의 많고 적음에 따라서 Rich와 Lean으로 나뉘어짐
- $\text{C}_3\text{H}_8$ : 소량 존재
- Iso- $\text{C}_4\text{H}_{10}$ : 미량 존재
- N- $\text{C}_4\text{H}_{10}$ : 미량 존재

# 3가지 기본적인 물성들:

## ➤ 3 Most Fundamental Fixed Properties:

- Molecular Weight
- Standard Liquid Density
- Normal Boiling Point

Component	MW (kg/k-mol)	Density (kg/m <sup>3</sup> )	NBP (°C)
N <sub>2</sub>	28.0135	807.96	-195.81
CO <sub>2</sub>	44.0098	816.43	-78.48
CH <sub>4</sub>	16.0428	299.70	-161.49
C <sub>2</sub> H <sub>6</sub>	30.0696	355.04	-88.60
C <sub>3</sub> H <sub>8</sub>	44.0965	505.79	-42.04
Iso-C <sub>4</sub> H <sub>10</sub>	58.1234	563.84	-11.72
N-C <sub>4</sub> H <sub>10</sub>	58.1234	584.33	-0.50

# 2

## Aspen HYSYS 내의 Peng-Robinson 모델식의 BIP's Regression

# 천연가스 구성 성분들의 물성:

## ➤ Critical Properties:

Simulator	Properties	Unit	N <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	iC <sub>4</sub> H <sub>10</sub>	nC <sub>4</sub> H <sub>10</sub>
<b>Critical Temperature</b>	HYSYS	<b>K</b>	126.19	304.10	190.69	305.42	369.89	408.09	425.19
	PRO/II		126.20	304.21	190.56	305.32	369.83	408.14	425.12
	Aspen Plus		126.20	304.21	190.56	305.32	369.83	407.80	425.12
<b>Critical Pressure</b>	HYSYS	<b>kPa</b>	3,394.37	7,370.00	4,640.68	4,883.85	4,256.66	3,647.62	3,796.62
	PRO/II		3,400.00	7,383.00	4,599.00	4,872.00	4,248.00	3,648.00	3,796.00
	Aspen Plus		3,400.00	7,383.00	4,599.00	4,872.00	4,248.00	3,640.00	3,796.00
<b>Acentric Factor</b>	HYSYS	<b>-</b>	0.03998	0.23894	0.01155	0.09860	0.15240	0.18479	0.20100
	PRO/II		0.03772	0.22362	0.01155	0.09949	0.15229	0.18077	0.20016
	Aspen Plus		0.03772	0.22362	0.01154	0.09949	0.15229	0.18352	0.20016



# 각각의 이성분계 쌍에 대한 BIP's:

➤ BIP's Built-in P2, A+, HYSYS and DECHEMA:

	N2	CO2	CH4	C2H6	C3H8	iC4H10	nC4H10	
N2			-0.0170	0.0350	0.0500	0.0800	0.0900	P2
			-0.0170	0.0311	0.0515	0.0852	0.1033	A+
			-0.0200	0.0360	0.0500	0.0800	0.0950	HYSYS
			-0.0200	0.0300	0.0440	0.0780	0.1000	DECHEMA
CO2			0.0919	0.1322	0.1241	0.1200	0.1333	
			0.0919	0.1322	0.1241	0.1200	0.1333	
			0.1000	0.1298	0.1350	0.1298	0.1298	
			0.0900	0.1300	0.1200	0.1300	0.1350	
CH4				-0.0026	0.0140	0.0256	0.0133	
				-0.0026	0.0140	0.0256	0.0133	
				-0.00224	0.00683	0.01311	0.01230	
				-0.0030	0.0160	0.0260	0.0190	
C2H6					0.0011	-0.0067	0.0096	
					0.0011	-0.0067	0.0096	
					0.00126	0.00457	0.00410	
					0.0010	-0.0070	0.0100	
C3H8						-0.0078	0.0033	
						-0.0078	0.0033	
						0.00104	0.00082	
						-0.0070	0.0030	
iC4H10							-0.0004	
							-0.0004	
							0.00001	
							0.0000	

# 물성 연구에 사용된 천연가스 구성 성분들:

➤ Number of Systems for Each Binary Pairs: **21 Binary Pairs !!!**

	$N_2$	$CO_2$	$CH_4$	$C_2H_6$	$C_3H_8$	$iC_4H_{10}$	$nC_4H_{10}$
$N_2$		Set No. <b>1</b>	Set No. <b>2</b>	Set No. <b>3</b>	Set No. <b>4</b>	Set No. <b>5</b>	Set No. <b>6</b>
$CO_2$			Set No. <b>7</b>	Set No. <b>8</b>	Set No. <b>9</b>	Set No. <b>10</b>	Set No. <b>11</b>
$CH_4$				Set No. <b>12</b>	Set No. <b>13</b>	Set No. <b>14</b>	Set No. <b>15</b>
$C_2H_6$					Set No. <b>16</b>	Set No. <b>17</b>	Set No. <b>18</b>
$C_3H_8$						Set No. <b>19</b>	Set No. <b>20</b>
$iC_4H_{10}$							Set No. <b>21</b>
$nC_4H_{10}$							

# Peng-Robinson Equation of State:

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The PR equation is represented by:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)-b(v-b)} \quad \text{Peng-Robinson Equation of State}$$

where:

$$a = a_c \alpha$$
$$a_c = 0.45724 \frac{R^2 T_c^2}{P_c} \quad b = 0.07780 \frac{RT_c}{P_c}$$

The alpha function to estimate pure component vapor pressure is shown:

$$\alpha = \left[ 1 + \kappa \left( 1 - \sqrt{T_r} \right) \right]^2 \quad \kappa = 0.37464 + 1.5422\omega - 0.26992\omega^2$$

# Peng-Robinson Equation of State:

The mixing rules available for the PR EOS state are shown below,

$$a_{mix} = \sum_{i=1}^N \sum_{j=1}^N x_i x_j a_{ij} \quad b_{mix} = \sum_{i=1}^N b_i x_i$$

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij})$$

← Regressed binary interaction parameter

- Mixing Rule 1:  $k_{ij} = a_{ij}$
- Mixing Rule 2:  $k_{ij} = 1 - a_{ij} + \frac{b_{ij}}{T}$
- Mixing Rule 3:  $k_{ij} = 1 - a_{ij} + b_{ij}T$

# Searching for Experimental VLE Data:

- Isothermal vapor-liquid equilibrium data in DECHEMA DB for each binary pairs containing  $N_2$ ,  $CO_2$ ,  $CH_4$ ,  $C_2H_6$ ,  $C_3H_8$ ,  $iC_4H_{10}$ ,  $nC_4H_{10}$

	$N_2$	$CO_2$	$C_1$	$C_2$	$C_3$	$IC_4$	$NC_4$
$N_2$		54	145	102	45	16	31
$CO_2$			96	69	41	15	67
$C_1$				106	86	12	106
$C_2$					70	20	33
$C_3$						45	27
$IC_4$							36
$NC_4$							

**Total: 1,222 Binary Experimental Isothermal Binary Data !!!**

# Binary Experimental VLE Data:

Dortmund Data Bank (DDB) Finder

[ Components ]

Number of Component to Search : 2

Component 1 : 1051 Find METHANE

Component 2 : 1054 Find ETHANE

Search DDB

Isothermal P,T,X,Y of METHANE + ETHANE at 180.00 K ( 2) - 11 pts

Isothermal P,T,X,Y of METHANE + ETHANE at 260.00 K ( 2) - 14 pts

Isothermal P,T,X,Y of METHANE + ETHANE at 270.00 K ( 2) - 11 pts

Isothermal P,T,X,Y of METHANE + ETHANE at 280.00 K ( 2) - 16 pts

Isothermal P,T,X,Y of METHANE + ETHANE at 233.00 K ( 2) - 2 pts

Isothermal P,T,X,Y of METHANE + ETHANE at 250.00 K ( 2) - 2 pts

Isothermal P,T,X,Y of METHANE + ETHANE at 172.04 K ( 2) - 2 pts

Isothermal P,T,X,Y of METHANE + ETHANE at 199.82 K ( 2) - 4 pts

Isothermal P,T,X,Y of METHANE + ETHANE at 227.59 K ( 2) - 5 pts

Show Data

Total Number of Systems : 106

Sort Option : References + T or P Condition

Data Sets : Binary Only

Over 100 binary pairs are available in DECHEMA DB for C1-C3 pair.

Dortmund Data Bank (DDB) Finder

[ Components ]

Number of Component to Search : 2

Component 1 : 1051 Find METHANE

Component 2 : 237 Find PROPANE

Search DDB

Isothermal P,T,X of METHANE + PROPANE at 91.70 K ( 2)

Isothermal P,T,X of METHANE + PROPANE at 112.60 K ( 2)

Isothermal P,T,X of METHANE + PROPANE at 128.40 K ( 2)

Isothermal P,T,X,Y of METHANE + PROPANE at 172.04 K ( 2)

Isothermal P,T,X,Y of METHANE + PROPANE at 199.82 K ( 2)

Isothermal P,T,X,Y of METHANE + PROPANE at 227.59 K ( 2)

Isothermal P,T,X,Y of METHANE + PROPANE at 255.37 K ( 2)

Isothermal P,T,X,Y of METHANE + PROPANE at 283.15 K ( 2)

Isothermal P,T,X,Y of METHANE + PROPANE at 277.59 K ( 2)

Show Data

Total Number of Systems : 86

Sort Option : References + T or P Condition

Data Sets : Binary Only

Dortmund Data Bank (DDB) Finder

[ Components ]

Number of Component to Search : 2

Component 1 : 1051 Find METHANE

Component 2 : 41 Find BUTANE

Search DDB

Isothermal P,T,X,Y of METHANE + BUTANE at 177.59 K ( 2) - 9 pts

Isothermal P,T,X,Y of METHANE + BUTANE at 210.93 K ( 2) - 14 pts

Isothermal P,T,X,Y of METHANE + BUTANE at 244.26 K ( 2) - 25 pts

Isothermal P,T,X,Y of METHANE + BUTANE at 277.59 K ( 2) - 30 pts

Isothermal P,T,X,Y of METHANE + BUTANE at 377.59 K ( 2) - 5 pts

Isothermal P,T,X,Y of METHANE + BUTANE at 410.93 K ( 2) - 7 pts

Isothermal P,T,X,Y of METHANE + BUTANE at 294.26 K ( 2) - 24 pts

Isothermal P,T,X,Y of METHANE + BUTANE at 310.93 K ( 2) - 23 pts

Isothermal P,T,X,Y of METHANE + BUTANE at 327.59 K ( 2) - 20 pts

Show Data

Total Number of Systems : 106

Sort Option : References + T or P Condition

Data Sets : Binary Only

Exit

T(K)	P(kPa)	X	Y
280	2796.6	0.0000	0.0000
280	2887.8	0.0081	0.0279
280	3075.2	0.0231	0.0744
280	3203.9	0.0335	0.1036
280	3655.8	0.0693	0.1864
280	4037.8	0.0996	0.2404
280	4415.7	0.1292	0.2818
280	4711.6	0.1528	0.3091
280	5040.9	0.1798	0.3336
280	5329.7	0.2044	0.3512
280	5645.8	0.2333	0.3654
280	5984.3	0.2668	0.3719
280	6086.6	0.2774	0.3711
280	6191.0	0.2913	0.3675
280	6265.9	0.3046	0.3609
280	6292.3	0.3109	0.3557

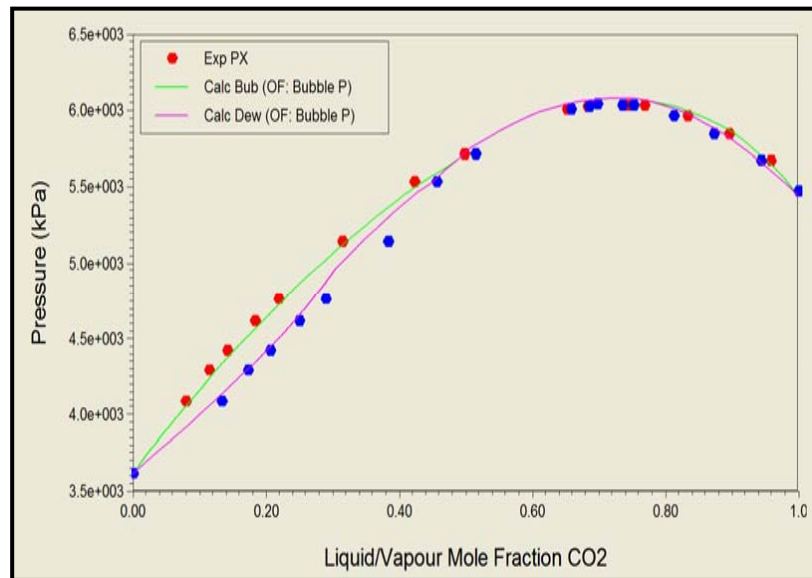
ISOTHERMAL P,T,X,Y OF METHANE + ETHANE AT 280.00 K ( 2) - 16 PTS

Reference: GUPTA M.K., GARDNER G.C., HEGARTY M.J., KIDNAY A.J., J.CHEM.ENG.DATA, 25,313(1980)

# VLE Data Regression: Objective Functions

## Bubble Pressure

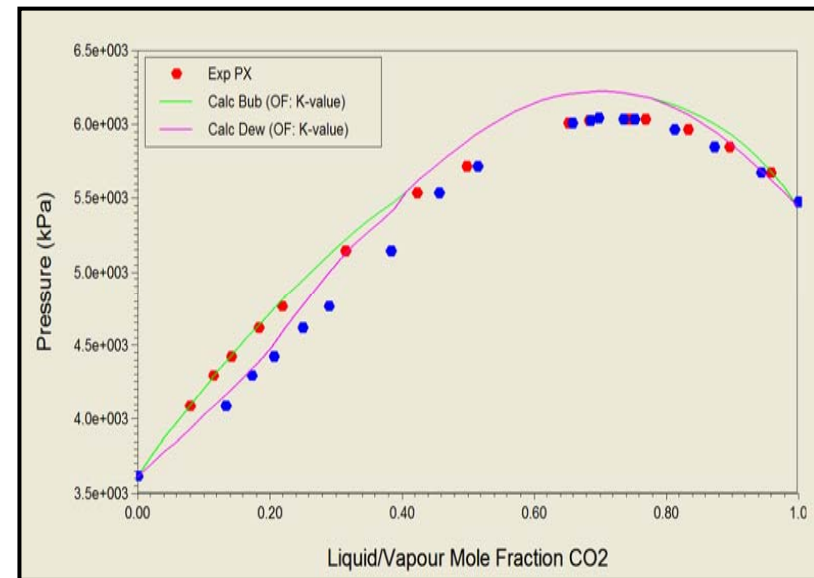
$$Obj. = \sum_{j=1}^N \left( \frac{P_j^{\text{exp}} - P_j^{\text{cal}}}{P_j^{\text{exp}}} \right)^2$$



## K-Value

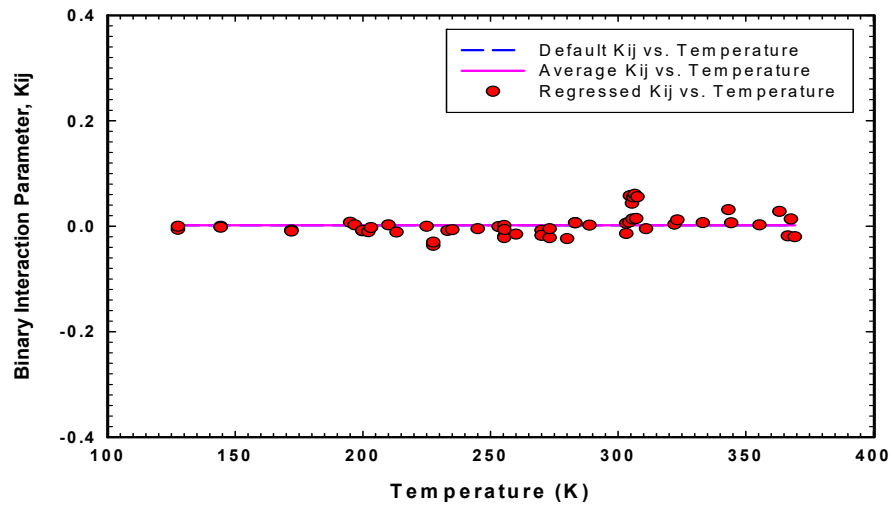
$$Obj. = \sum_{j=1}^N \left( \frac{K_j^{\text{exp}} - K_j^{\text{cal}}}{K_j^{\text{exp}}} \right)^2$$

이 경우에는 **Bubble Pressure** 추산을 다소 희생시켜야 함

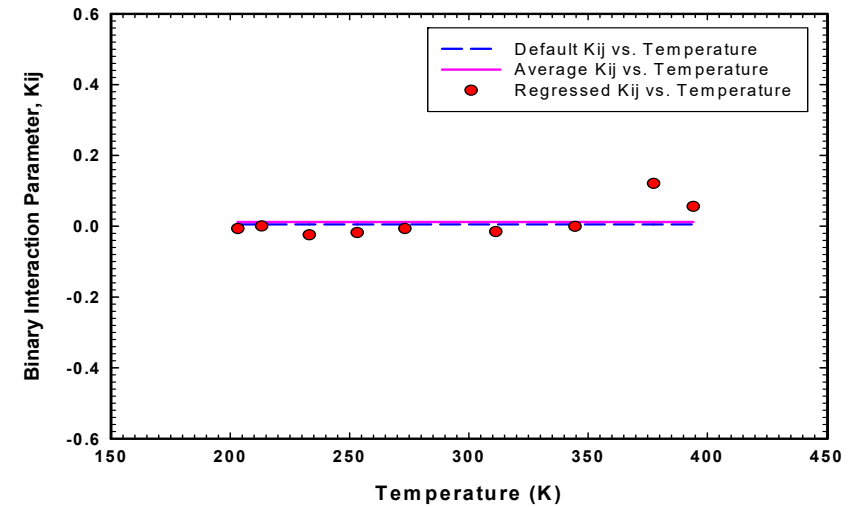


# Result: Regressed BIP's vs. Temperature

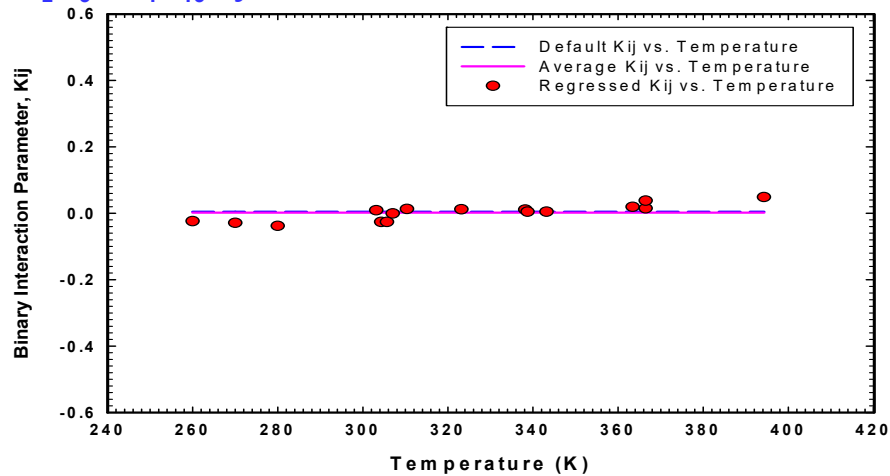
## ➤ $C_2H_6-C_3H_8$ System



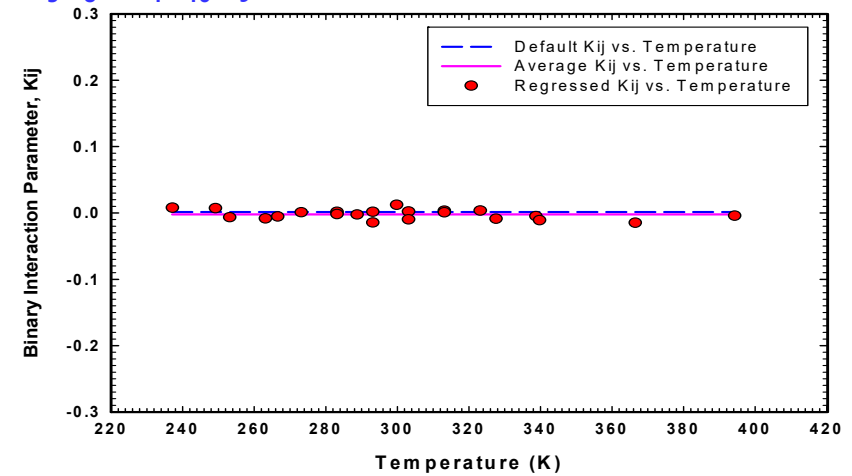
## ➤ $C_2H_6-iC_4H_{10}$ System



## ➤ $C_2H_6-nC_4H_{10}$ System



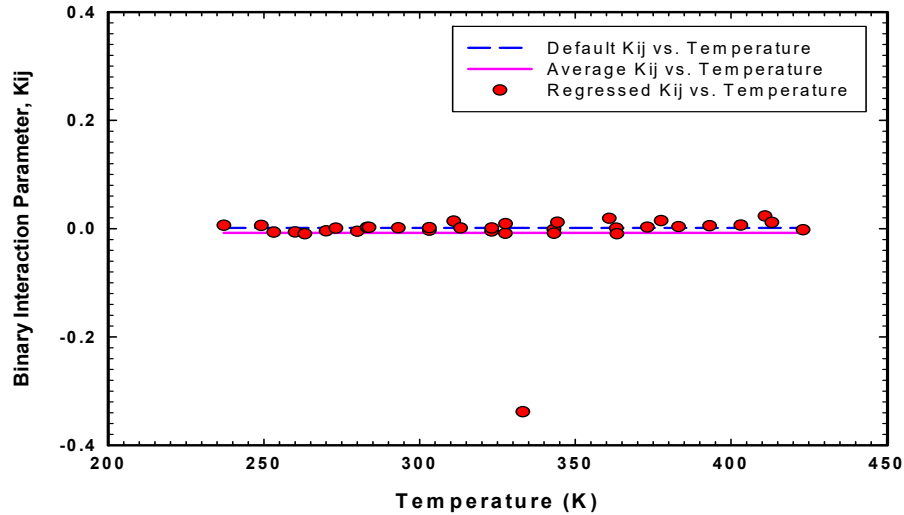
## ➤ $C_3H_8-nC_4H_{10}$ System



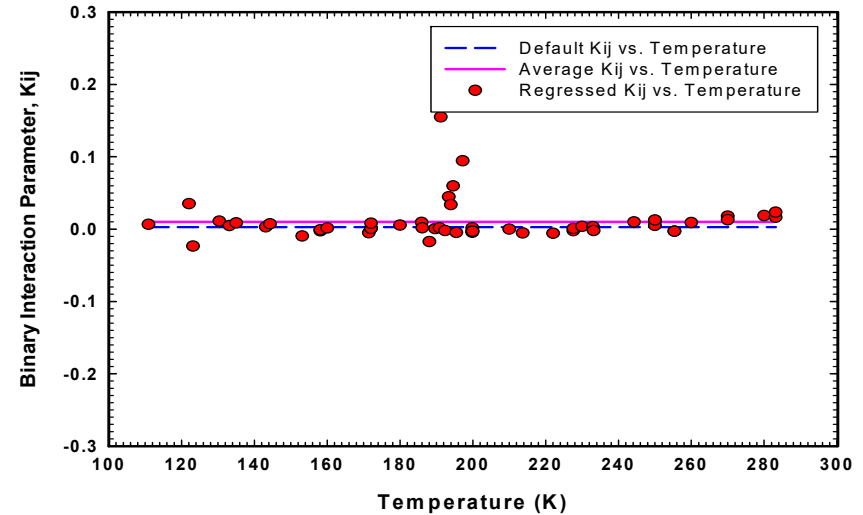


# Result: Regressed BIP's vs. Temperature

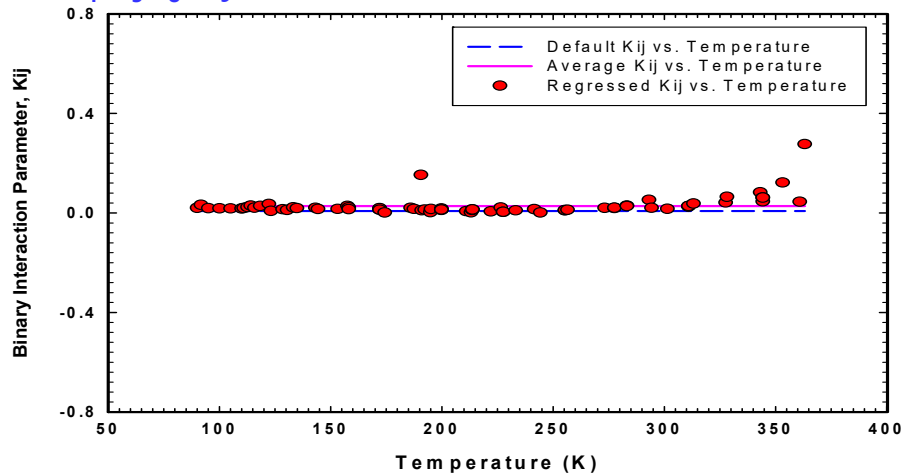
## ➤ C<sub>3</sub>H<sub>8</sub>-nCH<sub>4</sub> System



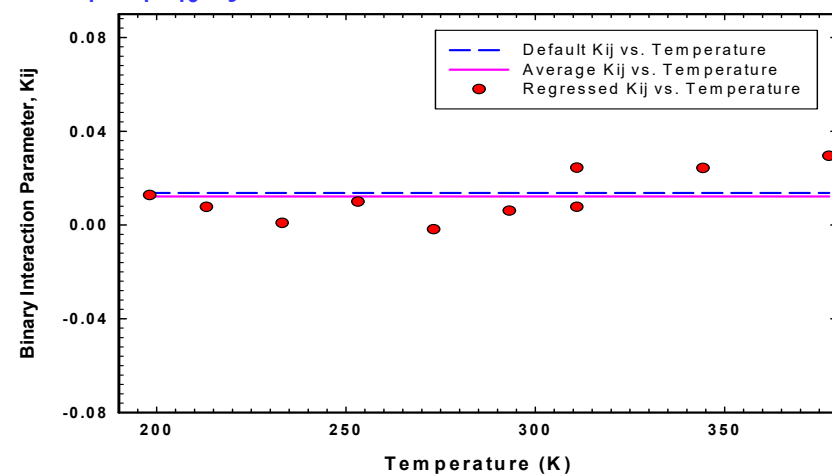
## ➤ CH<sub>4</sub>-C<sub>2</sub>H<sub>6</sub> System



## ➤ CH<sub>4</sub>-C<sub>3</sub>H<sub>8</sub> System

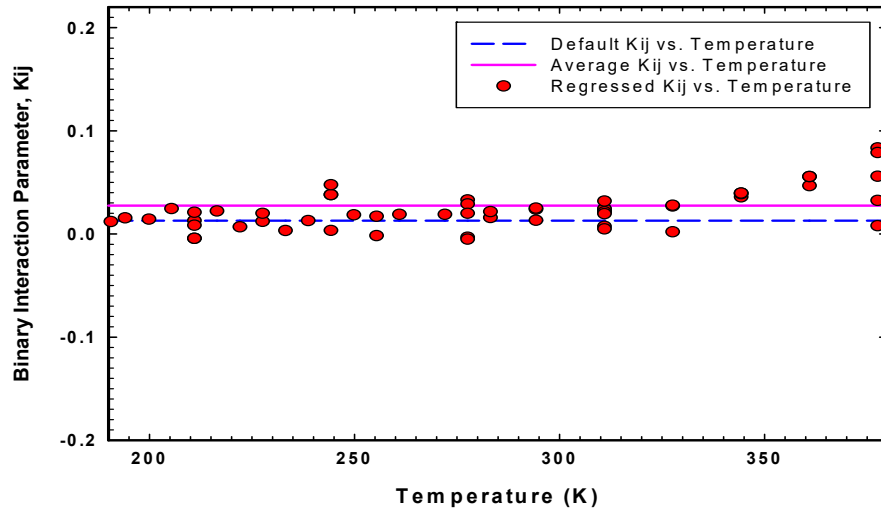


## ➤ CH<sub>4</sub>-iC<sub>4</sub>H<sub>10</sub> System

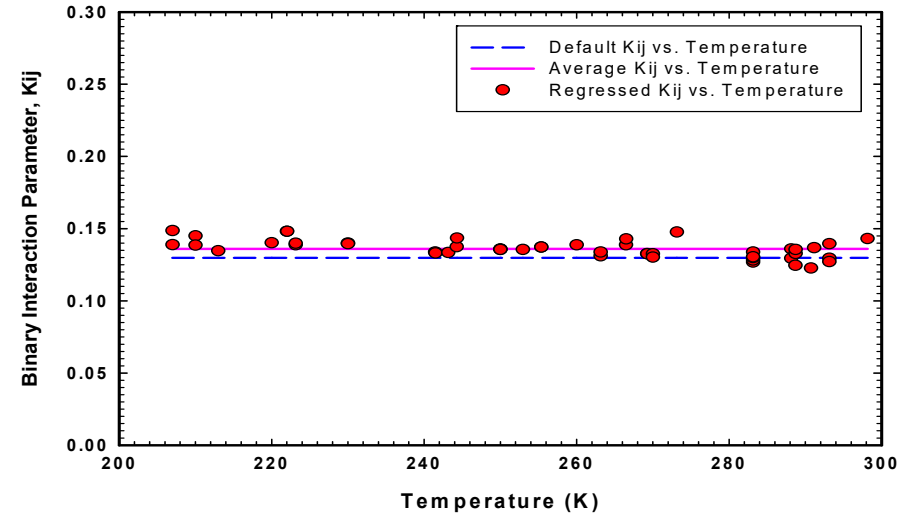


# Result: Regressed BIP's vs. Temperature

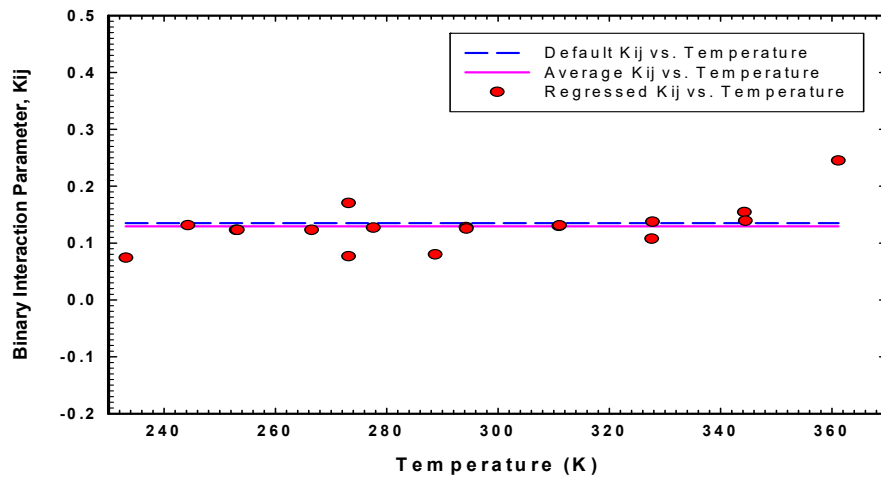
## CH<sub>4</sub>-nC<sub>4</sub>H<sub>10</sub> System



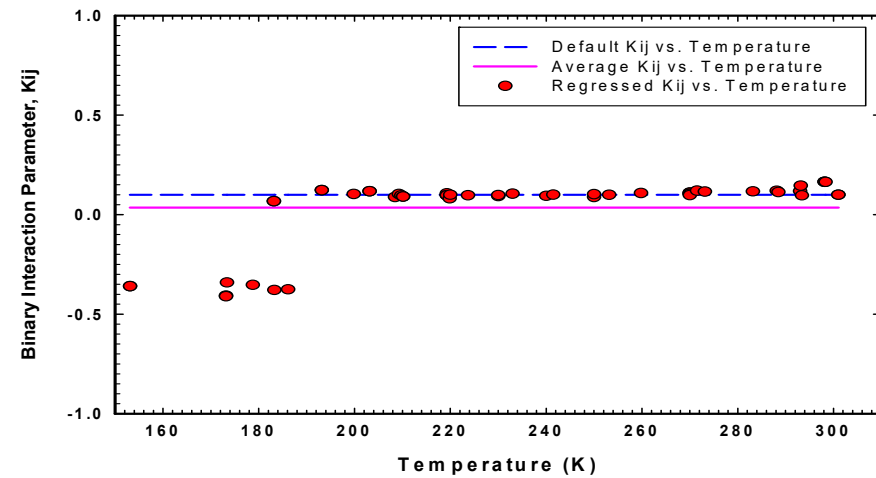
## CO<sub>2</sub>-C<sub>2</sub>H<sub>6</sub> System



## CO<sub>2</sub>-C<sub>3</sub>H<sub>8</sub> System

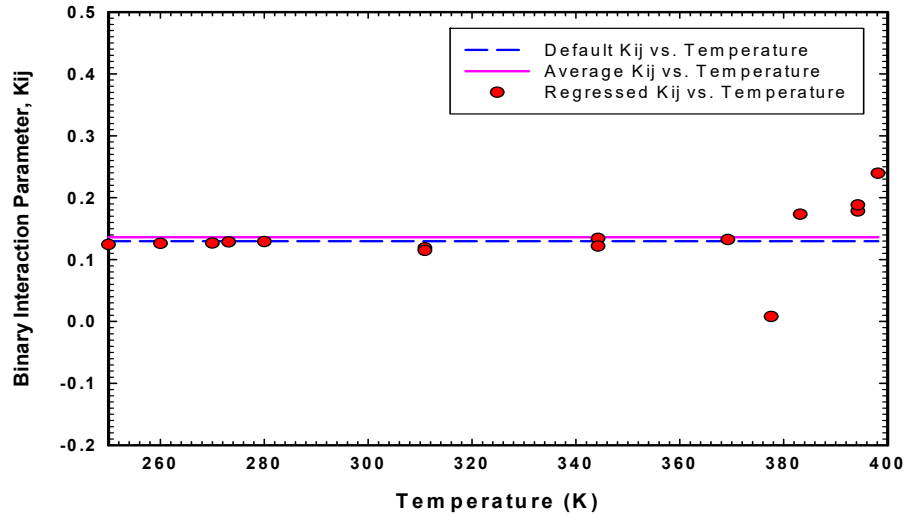


## CO<sub>2</sub>-CH<sub>4</sub> System

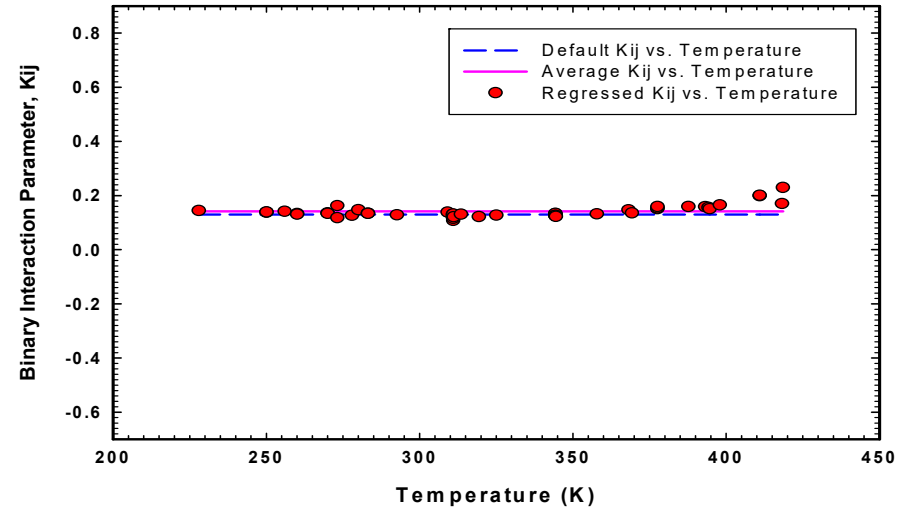


# Result: Regressed BIP's vs. Temperature

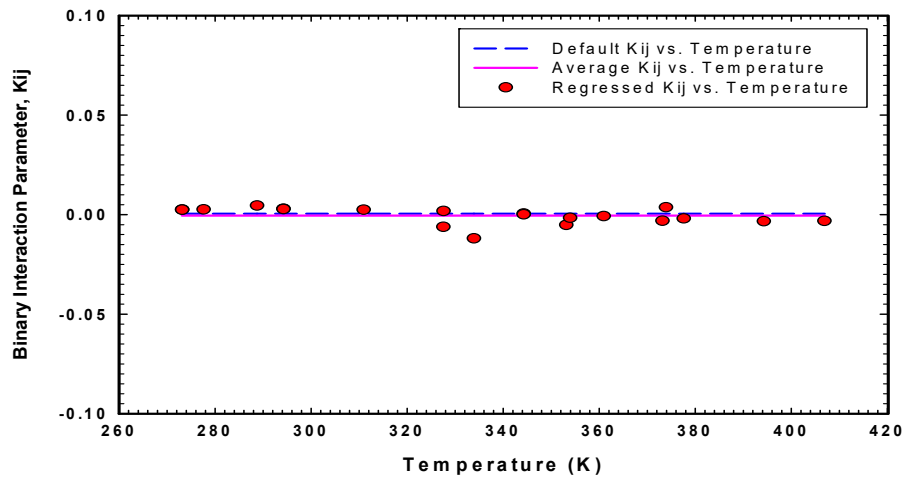
➤  $\text{CO}_2\text{-iC}_4\text{H}_{10}$  System



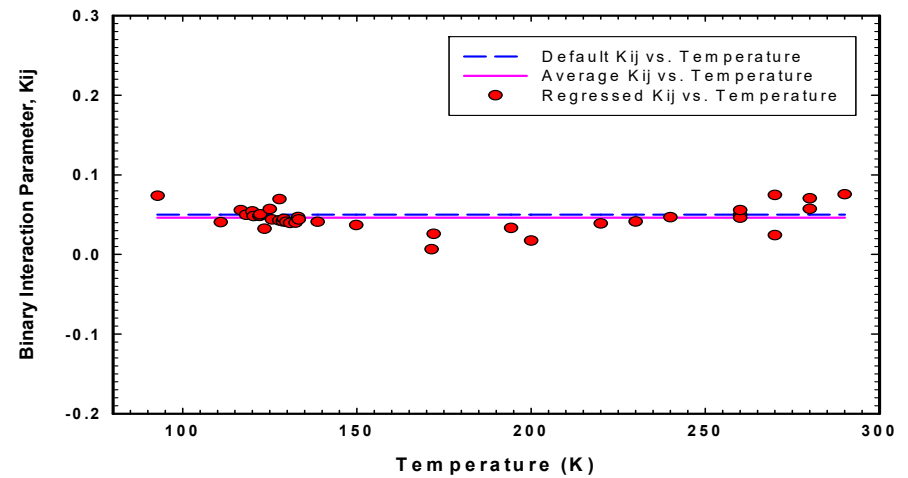
➤  $\text{CO}_2\text{-nC}_4\text{H}_{10}$  System



➤  $\text{iC}_4\text{H}_{10}\text{-nC}_4\text{H}_{10}$  System

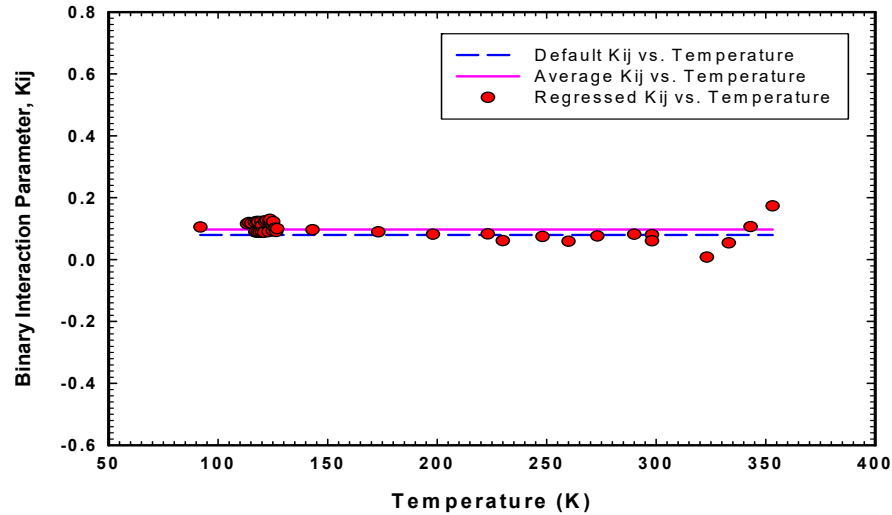


➤  $\text{N}_2\text{-C}_2\text{H}_6$  System

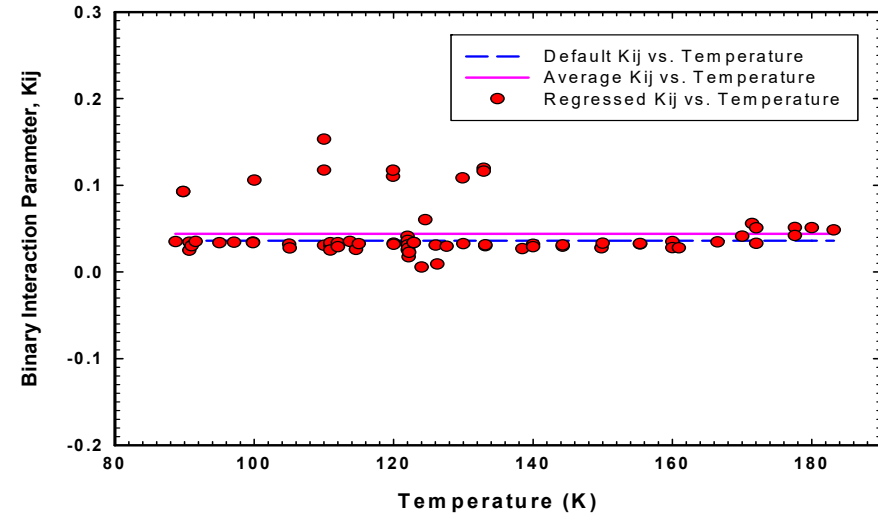


# Result: Regressed BIP's vs. Temperature

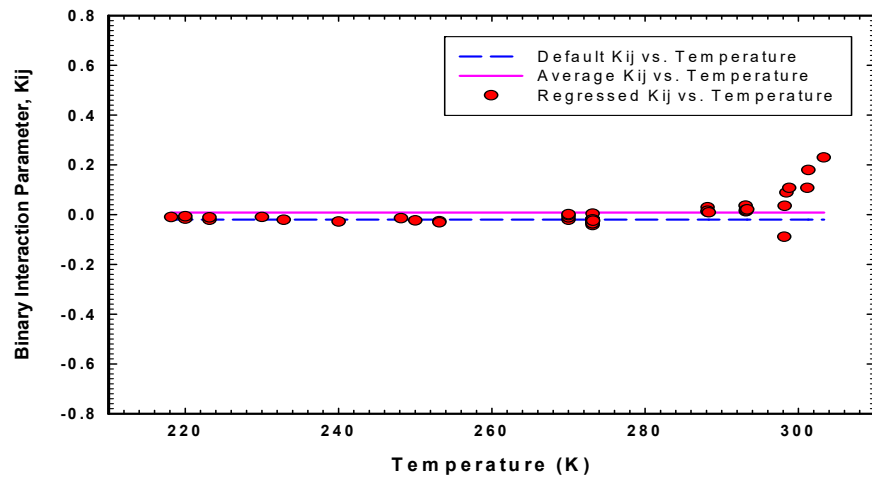
## ➤ N<sub>2</sub>-C<sub>3</sub>H<sub>8</sub> System



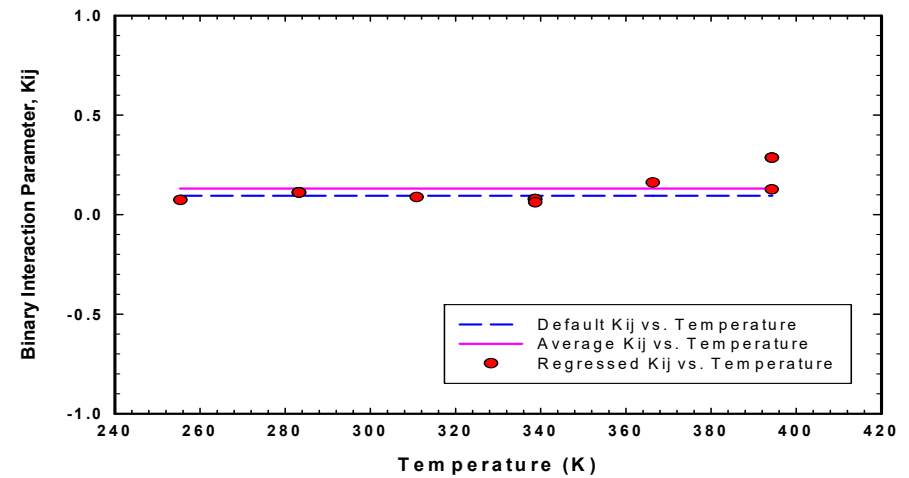
## ➤ N<sub>2</sub>-CH<sub>4</sub> System



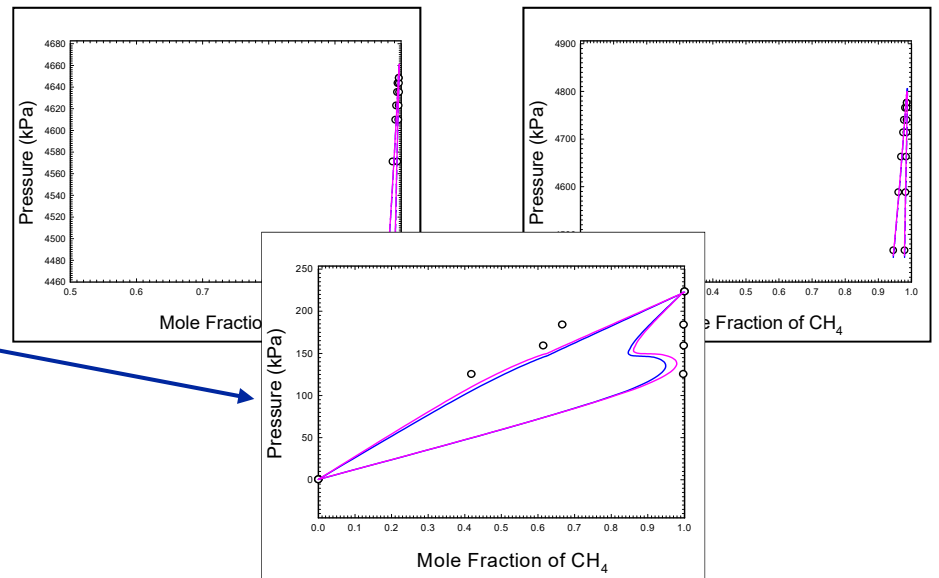
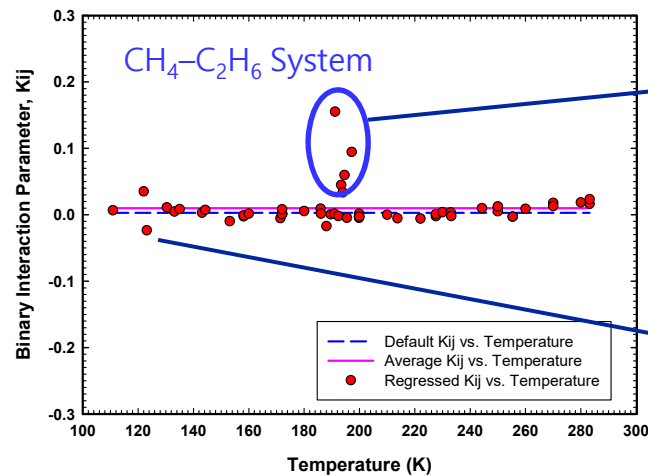
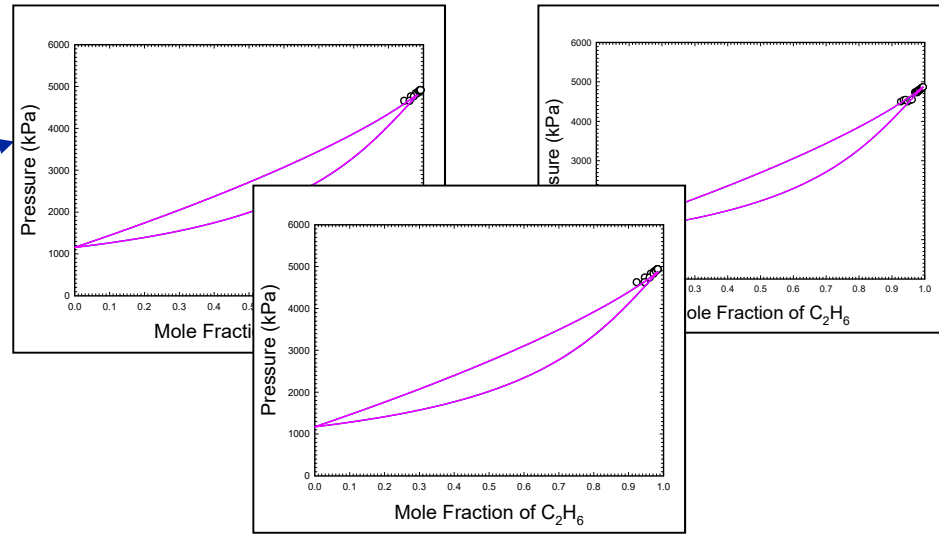
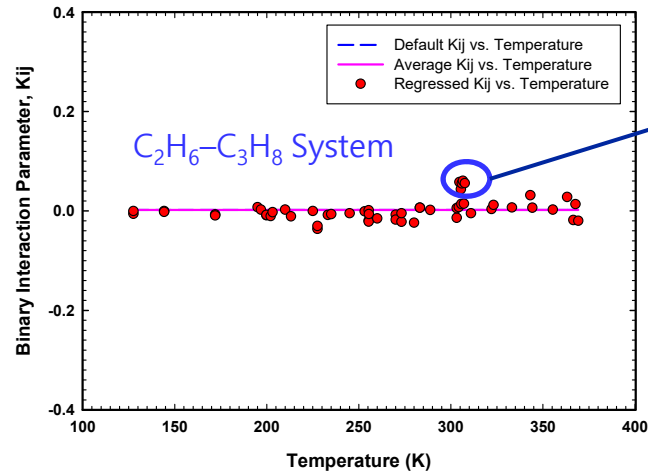
## ➤ N<sub>2</sub>-CO<sub>2</sub> System



## ➤ N<sub>2</sub>-iC<sub>4</sub>H<sub>10</sub> System

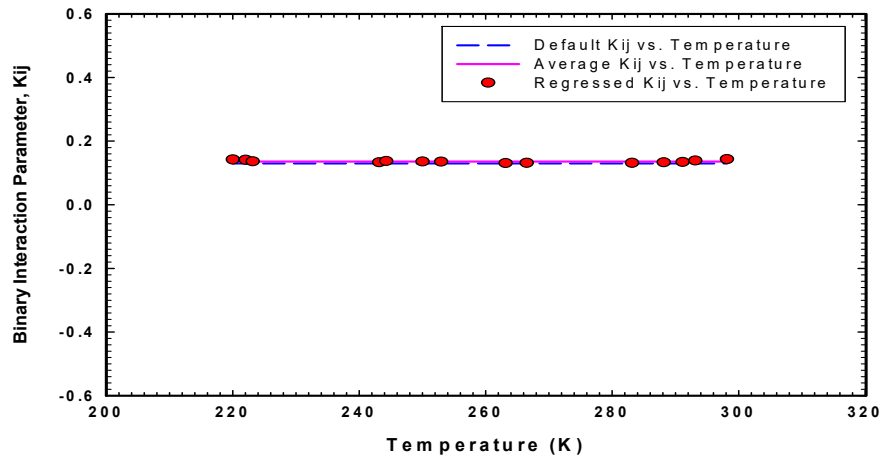


# 부정확한 실험 데이터 제외:

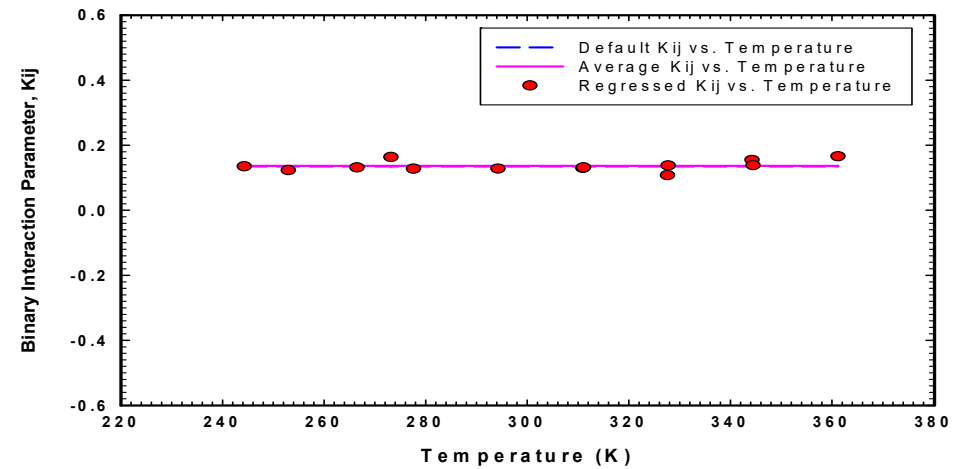


# Result: Regressed BIP's vs. Temperature (개선 후)

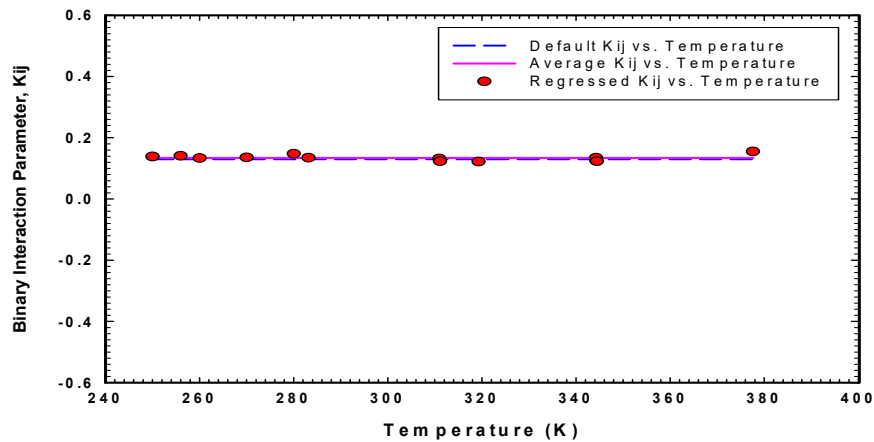
## ➤ CO<sub>2</sub>-C<sub>2</sub>H<sub>6</sub> System



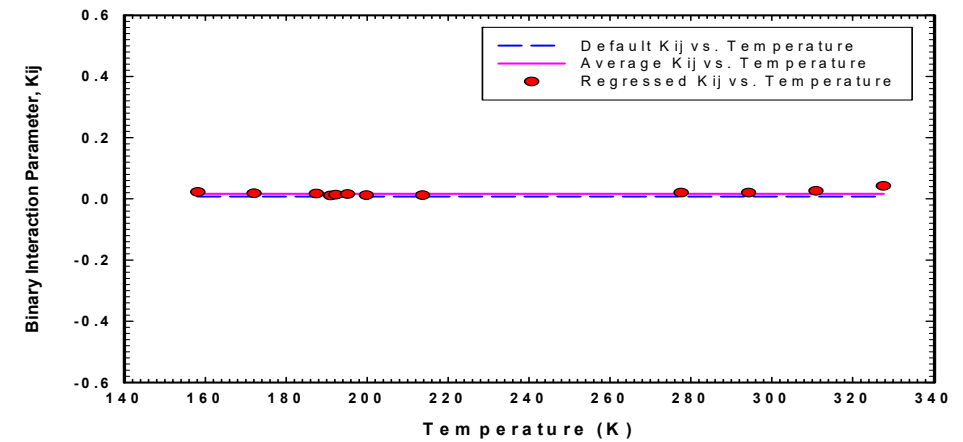
## ➤ CO<sub>2</sub>-C<sub>3</sub>H<sub>8</sub> System



## ➤ CO<sub>2</sub>-nC<sub>4</sub>H<sub>10</sub> System

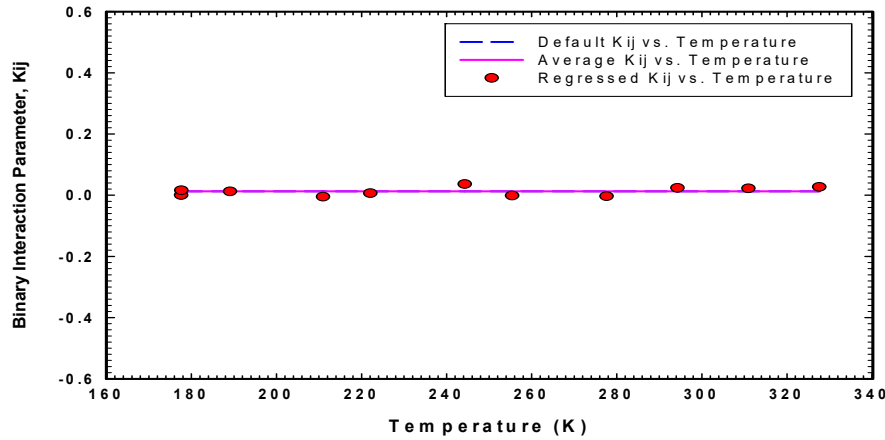


## ➤ CH<sub>4</sub>-C<sub>3</sub>H<sub>8</sub> System

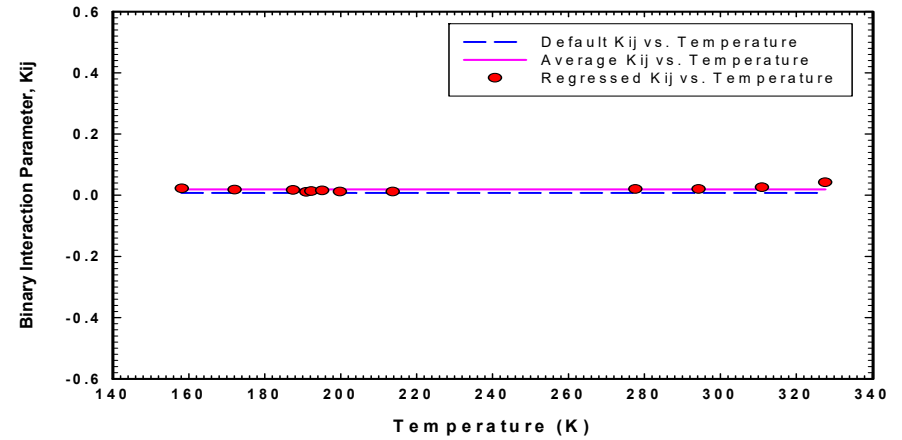


# Result: Regressed BIP's vs. Temperature (개선 후)

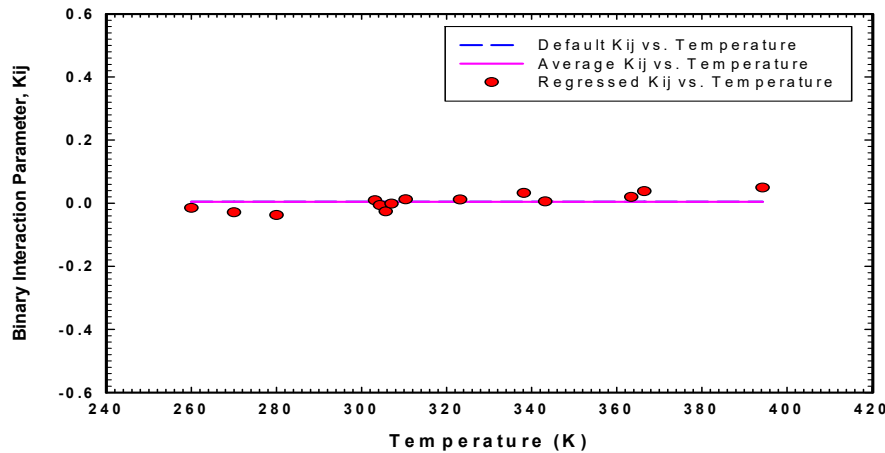
## ➤ CH<sub>4</sub>-nC<sub>4</sub>H<sub>10</sub> System



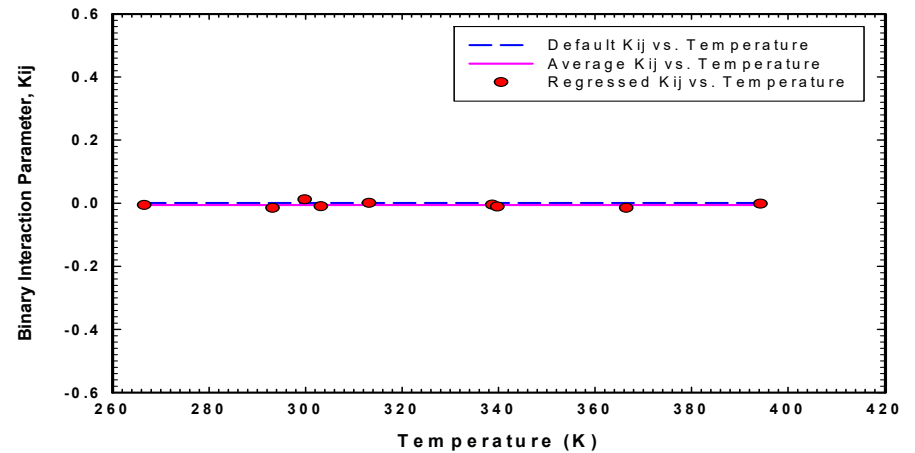
## ➤ C<sub>2</sub>H<sub>6</sub>-C<sub>3</sub>H<sub>8</sub> System



## ➤ C<sub>2</sub>H<sub>6</sub>-nC<sub>4</sub>H<sub>10</sub> System



## ➤ C<sub>3</sub>H<sub>8</sub>-iC<sub>4</sub>H<sub>10</sub> System



# Result: kij Built-in HYSYS & Bew Regressed kij:

	N <sub>2</sub>	CO <sub>2</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	IC <sub>4</sub>	NC <sub>4</sub>
N <sub>2</sub>		-0.0200	0.0360	0.0500	0.0800	0.0950	0.0900
		0.0080	0.0440	0.0461	0.0973	0.1311	0.0962
CO <sub>2</sub>			0.1000	0.1298	0.1350	0.1298	0.1298
			0.0358	0.1360	0.1290	0.1363	0.1418
C <sub>1</sub>				-0.00224	0.00683	0.01311	0.0123
				0.0100	0.0282	0.0120	0.0273
C <sub>2</sub>					0.00126	0.00457	0.0041
					0.1290	0.1360	0.0022
C <sub>3</sub>						0.00104	0.00082
						-0.00227	-0.0077
IC <sub>4</sub>							0.00001
							0.0004725
NC <sub>4</sub>							

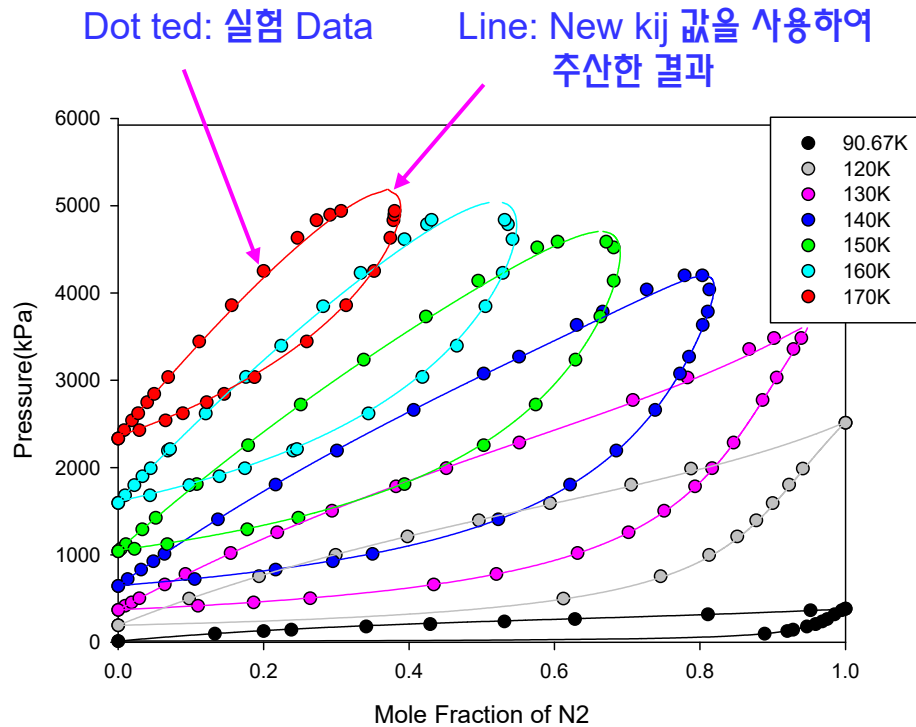
kij Built-in HYSYS  
New kij



# Result: Comparison of AAD(%) vetween kij built-in HYSYS and New kij

AAD(absolute average deviation) (%)

$$AAD(\%) = \sum_{j=1}^N \left| \frac{P_j^{\text{exp}} - P_j^{\text{cal}}}{P_j^{\text{exp}}} \right| \times 100$$

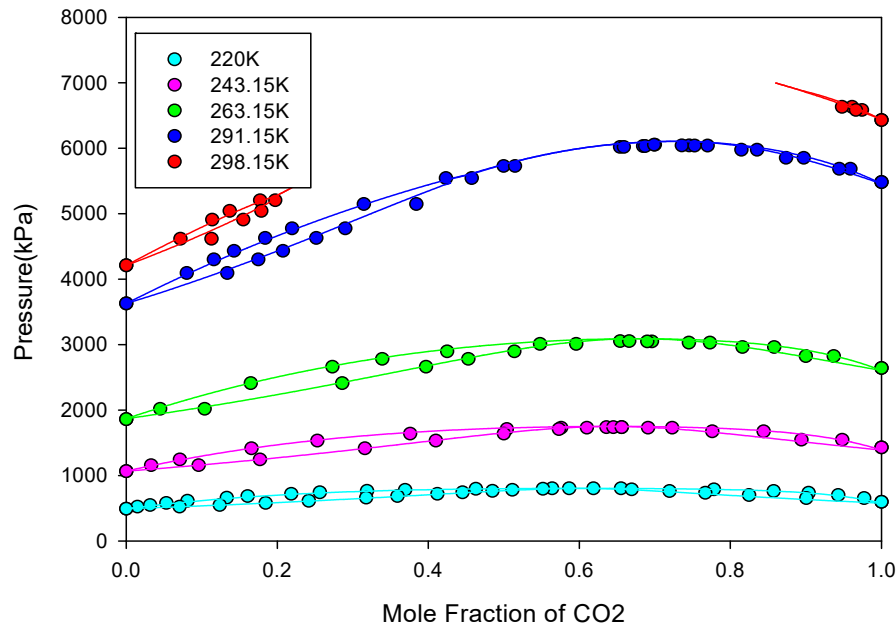


Temperature (K)	<b>N<sub>2</sub>-CH<sub>4</sub> AAD(%)</b>	
	k <sub>ij</sub> built-in HYSYS	new k <sub>ij</sub>
90.67	4.449%	2.787%
100.00	0.989%	0.686%
115.00	0.836%	0.417%
120.00	1.142%	0.570%
127.59	0.885%	0.652%
130.00	1.006%	0.710%
133.15	1.597%	0.990%
138.46	1.525%	0.824%
140.00	1.124%	0.705%
144.26	1.457%	0.682%
149.82	1.306%	0.882%
150.00	0.920%	0.731%
153.37	0.681%	0.288%
160.00	0.865%	0.779%
160.93	1.275%	1.111%
166.48	0.476%	0.562%
170.00	1.172%	0.892%
<b>Average</b>	<b>1.277%</b>	<b>0.839%</b>

# Result: Comparison of AAD(%) vetween kij built-in HYSYS and New kij

AAD(absolute average deviation) (%)

$$AAD(\%) = \sum_j^N \left| \frac{P_j^{\text{exp}} - P_j^{\text{cal}}}{P_j^{\text{exp}}} \right| \times 100$$

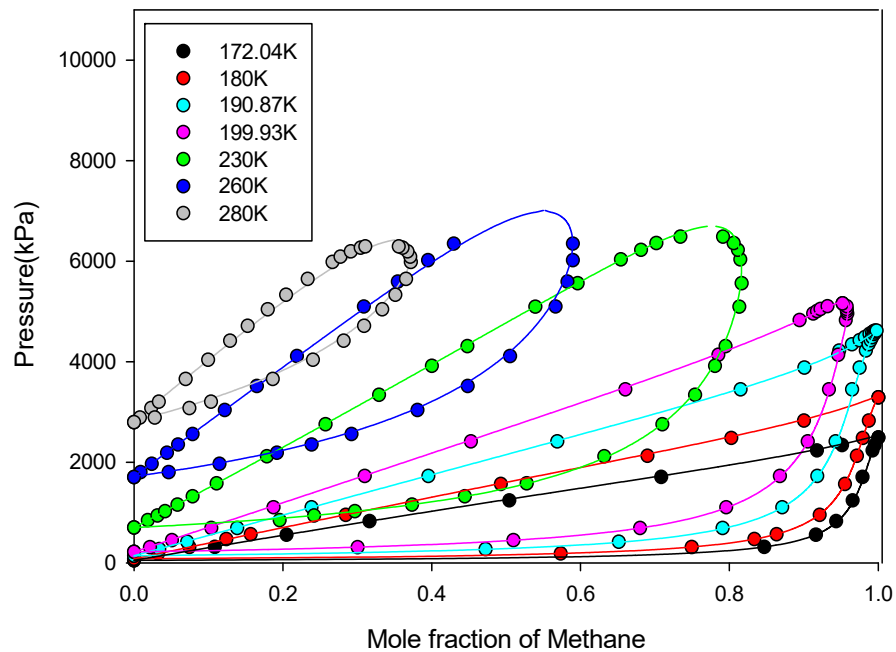


Temperature (K)	<b>CO<sub>2</sub>-C<sub>2</sub>H<sub>6</sub> AAD(%)</b>	
	k <sub>ij</sub> built-in HYSYS	new k <sub>ij</sub>
220.00	2.457%	1.279%
222.04	2.861%	1.294%
223.15	1.643%	0.624%
243.15	0.891%	0.792%
244.26	1.568%	0.776%
250.00	1.193%	0.580%
252.95	1.298%	1.241%
263.15	0.435%	0.853%
266.48	0.824%	0.924%
283.15	0.752%	0.867%
288.15	0.695%	0.656%
291.15	0.664%	0.626%
293.15	0.966%	0.671%
298.15	0.521%	0.375%
<b>Average</b>	<b>1.198%</b>	<b>0.826%</b>

# Result: Comparison of AAD(%) vetween kij built-in HYSYS and New kij

AAD(absolute average deviation) (%)

$$AAD(\%) = \sum_j^N \left| \frac{P_j^{\text{exp}} - P_j^{\text{cal}}}{P_j^{\text{exp}}} \right| \times 100$$

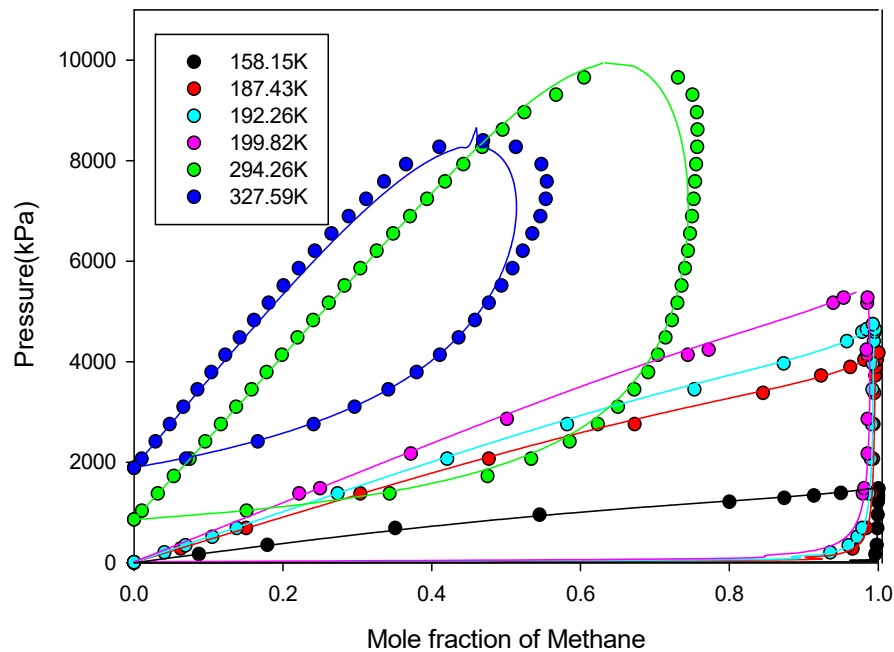


Temperature (K)	<b>CH<sub>4</sub>-C<sub>2</sub>H<sub>6</sub> AAD(%)</b>	
	k <sub>ij</sub> built-in HYSYS	new k <sub>ij</sub>
172.04	1.118%	1.231%
180.00	1.325%	0.880%
190.87	0.636%	0.832%
199.93	1.064%	1.447%
230.00	0.369%	0.345%
260.00	0.844%	0.694%
280.00	1.430%	1.248%
<b>Average</b>	<b>0.969%</b>	<b>0.954%</b>

# Result: Comparison of AAD(%) vetween kij built-in HYSYS and New kij

AAD(absolute average deviation) (%)

$$AAD(\%) = \sum_j^N \left| \frac{P_j^{\text{exp}} - P_j^{\text{cal}}}{P_j^{\text{exp}}} \right| \times 100$$

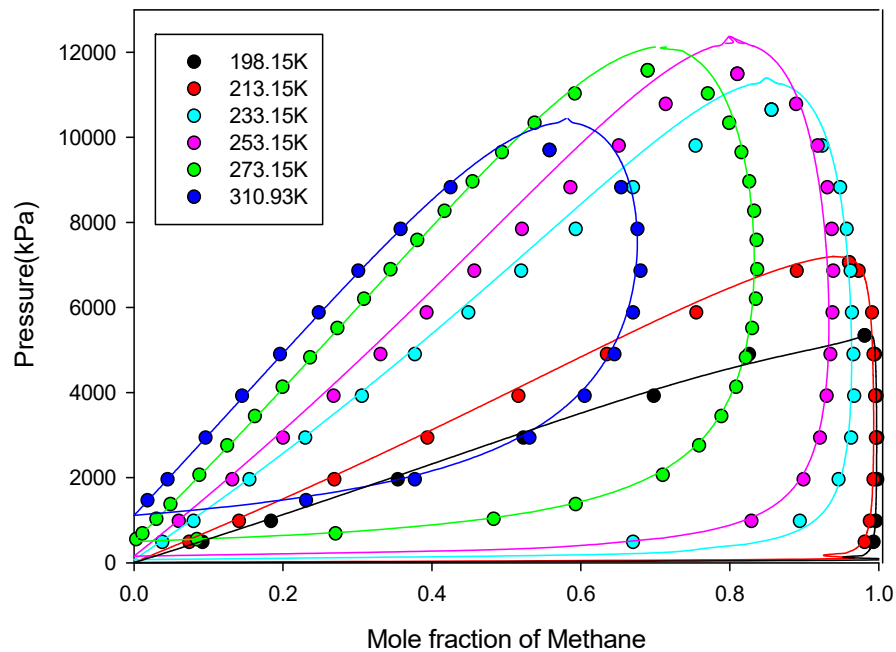


Temperature (K)	<b>CH<sub>4</sub>-C<sub>3</sub>H<sub>8</sub> AAD(%)</b>	
	k <sub>ij</sub> built-in HYSYS	new k <sub>ij</sub>
158.15	6.051%	3.300%
172.04	4.105%	1.984%
187.43	2.588%	1.406%
190.93	1.144%	1.575%
192.26	2.300%	2.202%
195.15	2.706%	1.717%
199.82	2.936%	1.986%
213.71	2.379%	3.281%
277.59	2.620%	1.199%
294.26	2.128%	0.713%
310.93	2.277%	0.951%
<b>Average</b>	<b>2.840%</b>	<b>1.847%</b>

# Result: Comparison of AAD(%) vetween kij built-in HYSYS and New kij

AAD(absolute average deviation) (%)

$$AAD(\%) = \sum_j^N \left| \frac{P_j^{\text{exp}} - P_j^{\text{cal}}}{P_j^{\text{exp}}} \right| \times 100$$



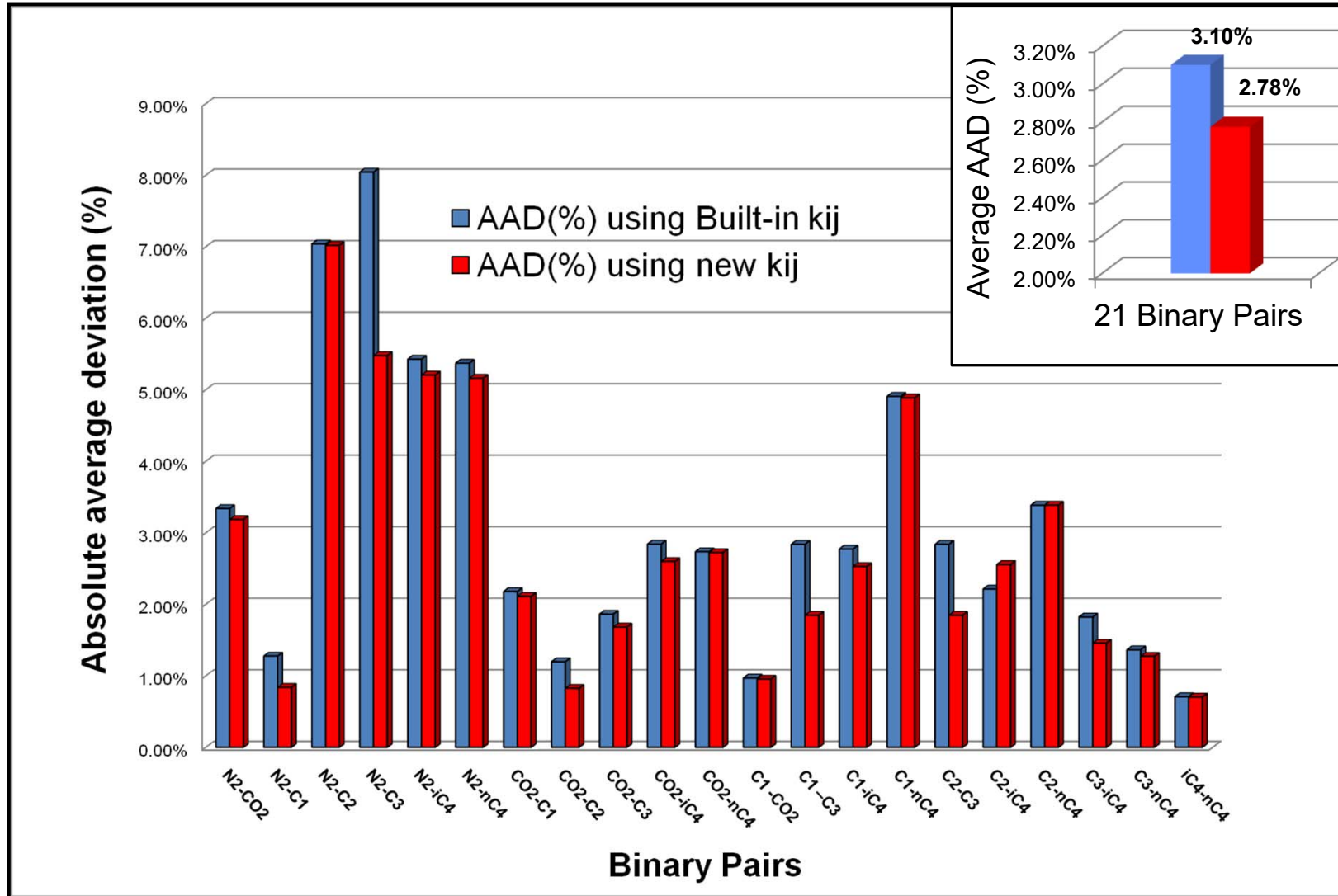
Temperature (K)	<b>CH<sub>4</sub>-iC<sub>4</sub>H<sub>10</sub> AAD(%)</b>	
	k <sub>ij</sub> built-in HYSYS	new k <sub>ij</sub>
198.15	1.306%	1.287%
213.15	2.256%	1.545%
233.15	4.602%	4.207%
253.15	2.731%	2.556%
273.15	5.030%	3.943%
293.15	2.655%	2.247%
310.93	2.321%	2.805%
310.95	2.495%	2.275%
344.25	1.555%	1.895%
<b>Average</b>	<b>2.772%</b>	<b>2.529%</b>

# Result: Comparison of AAD(%) vetween kij built-in HYSYS and New kij

	N <sub>2</sub>	CO <sub>2</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	IC <sub>4</sub>	NC <sub>4</sub>
N <sub>2</sub>		3.340%	1.277%	7.040%	8.044%	5.428%	5.372%
		3.187%	0.839%	7.020%	5.478%	5.206%	5.161%
CO <sub>2</sub>			2.179%	1.198%	1.862%	2.842%	2.735%
			2.112%	0.826%	1.683%	2.599%	2.723%
C <sub>1</sub>				0.969%	2.840%	2.772%	4.909%
				0.954%	1.847%	2.529%	4.887%
C <sub>2</sub>					2.840%	2.214%	3.387%
					1.847%	2.556%	3.387%
C <sub>3</sub>						1.823%	1.364%
						1.457%	1.274%
IC <sub>4</sub>							0.708%
							0.703%
NC <sub>4</sub>							

kij Built-in HYSYS  
**New kij**

# Result: Comparison of AAD(%) vetween kij built-in HYSYS and New kij



# 3

## Fortran을 이용한 다양한 목적함수 Regression



# CO<sub>2</sub>-C<sub>2</sub>H<sub>6</sub> System에 대해서 우선 적용:

## PRO/II

case	Object Function	BIP Mixing Rule	a <sub>ij</sub>	b <sub>ij</sub>	P AAD (%)	y AAD (%)
1_1	Bubble P	k <sub>ij</sub> = a <sub>ij</sub>	0.1341		0.9083	2.6029
1_2	Bubble P	k <sub>ij</sub> = a <sub>ij</sub> + b <sub>ij</sub> /T	0.1123	5.2223	0.8602	2.6051
2_1	Bubble P + y	k <sub>ij</sub> = a <sub>ij</sub>	0.1331		0.8735	2.6085
2_2	Bubble P + y	k <sub>ij</sub> = a <sub>ij</sub> + b <sub>ij</sub> /T	0.0981	8.2761	0.8427	2.6148

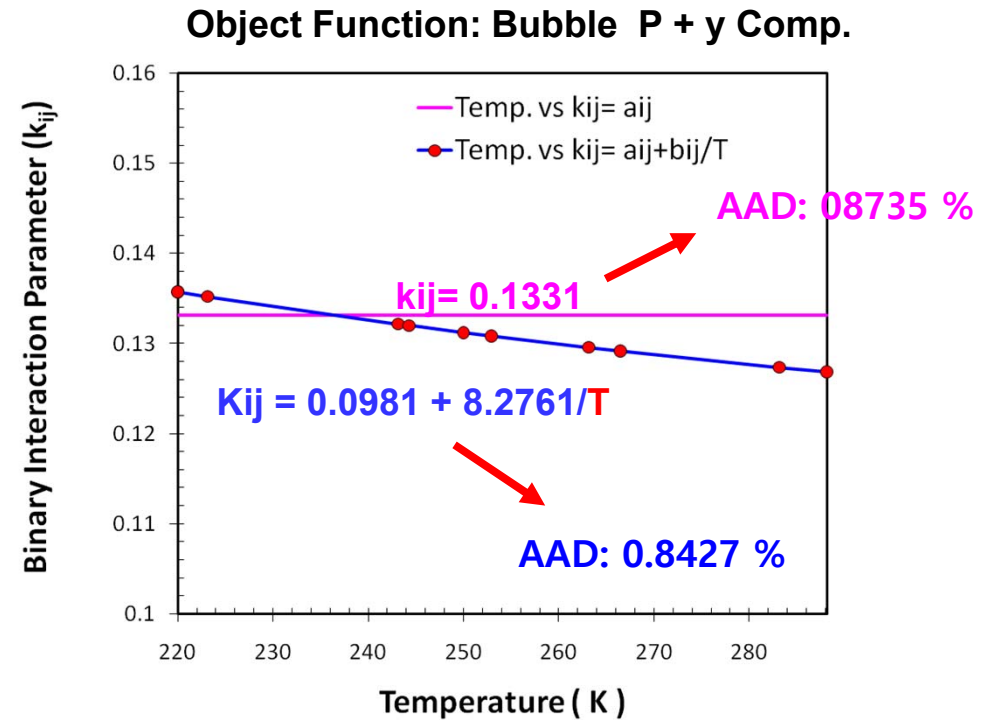
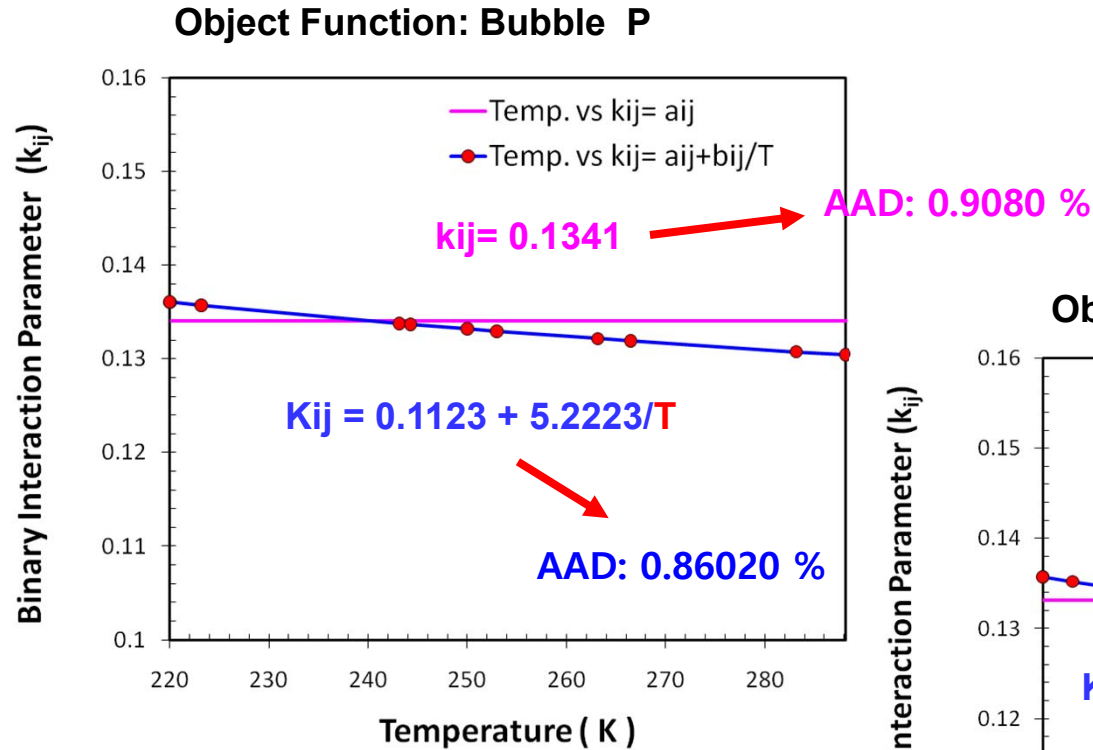
AspenPlus (T<sub>c</sub>, P<sub>c</sub>, w 값이 PRO/II와 동일하여 값이 같음)

case	Object Function	BIP Mixing Rule	a <sub>ij</sub>	b <sub>ij</sub>	P AAD (%)	y AAD (%)
1_1	Bubble P	k <sub>ij</sub> = a <sub>ij</sub>	0.1341		0.9083	2.6029
1_2	Bubble P	k <sub>ij</sub> = a <sub>ij</sub> + b <sub>ij</sub> /T	0.1123	5.2223	0.8602	2.6051
2_1	Bubble P + y	k <sub>ij</sub> = a <sub>ij</sub>	0.1331		0.8735	2.6085
2_2	Bubble P + y	k <sub>ij</sub> = a <sub>ij</sub> + b <sub>ij</sub> /T	0.0981	8.2761	0.8427	2.6148

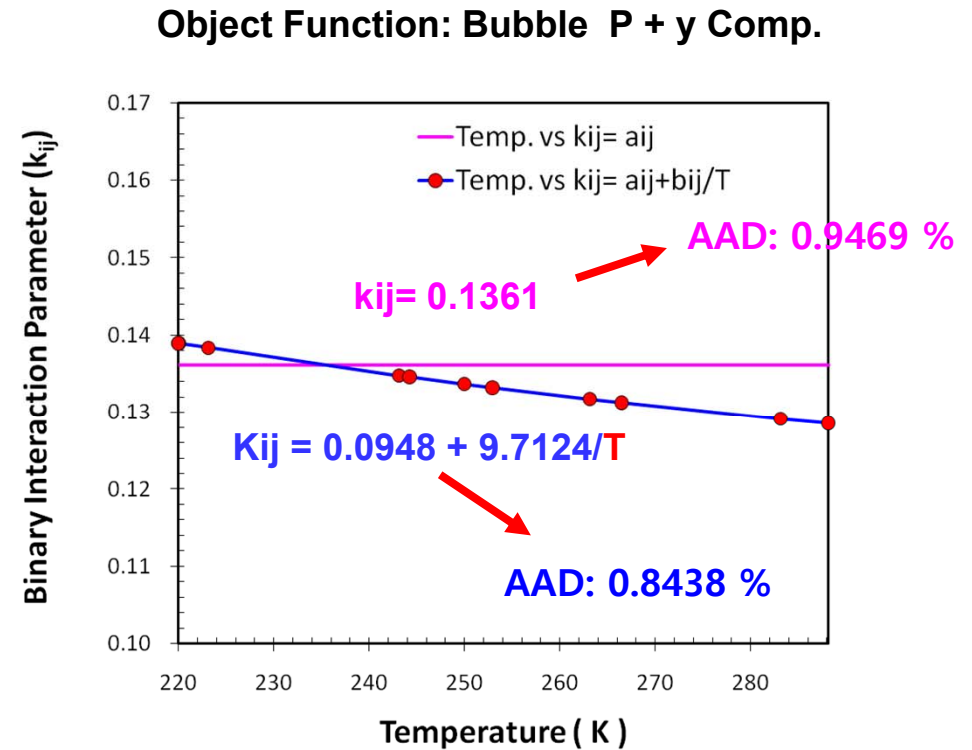
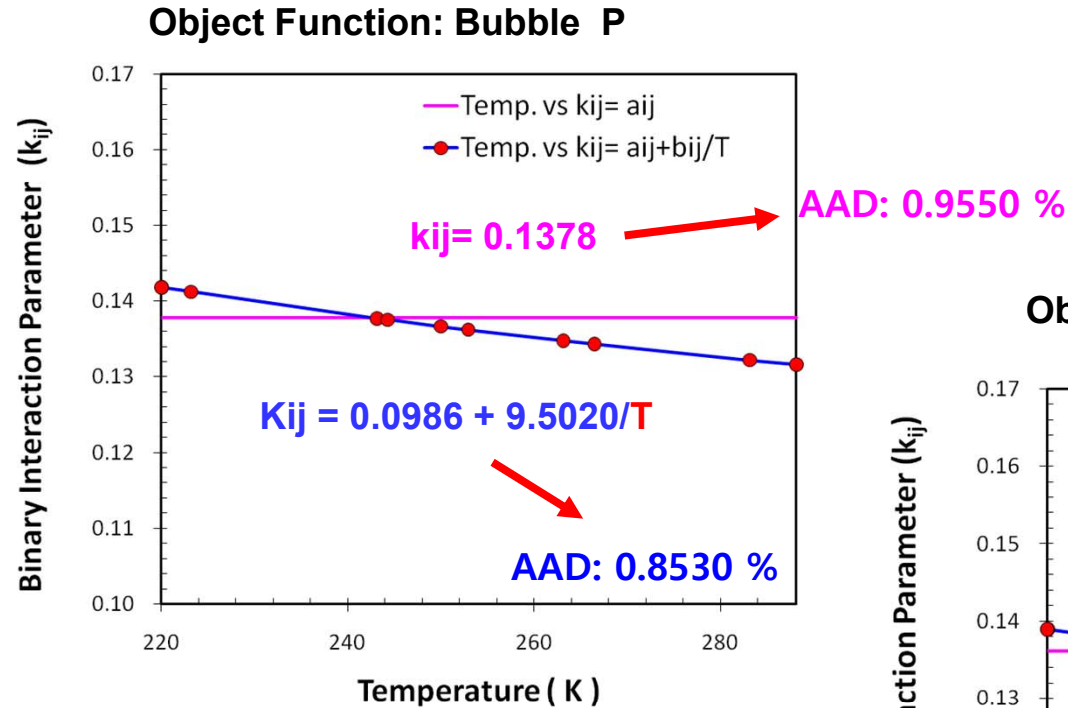
## HYSYS

case	Object Function	BIP Mixing Rule	a <sub>ij</sub>	b <sub>ij</sub>	P AAD (%)	y AAD (%)
1_1	Bubble P	k <sub>ij</sub> = a <sub>ij</sub>	0.1378		0.9550	2.6618
1_2	Bubble P	k <sub>ij</sub> = a <sub>ij</sub> + b <sub>ij</sub> /T	0.0986	9.5020	0.8530	2.6642
2_1	Bubble P + y	k <sub>ij</sub> = a <sub>ij</sub>	0.1361		0.9469	2.6688
2_2	Bubble P + y	k <sub>ij</sub> = a <sub>ij</sub> + b <sub>ij</sub> /T	0.0948	9.7124	0.8438	2.6590

# Using $T_c$ , $P_c$ , $\omega$ in Aspen Plus or PRO/II:



# Using $T_c$ , $P_c$ , $\omega$ in Aspen HYSYS:



# 4

## GERG-2008 모델식과 다른 모델식 사이의 비교

# GERG-2008 Model:

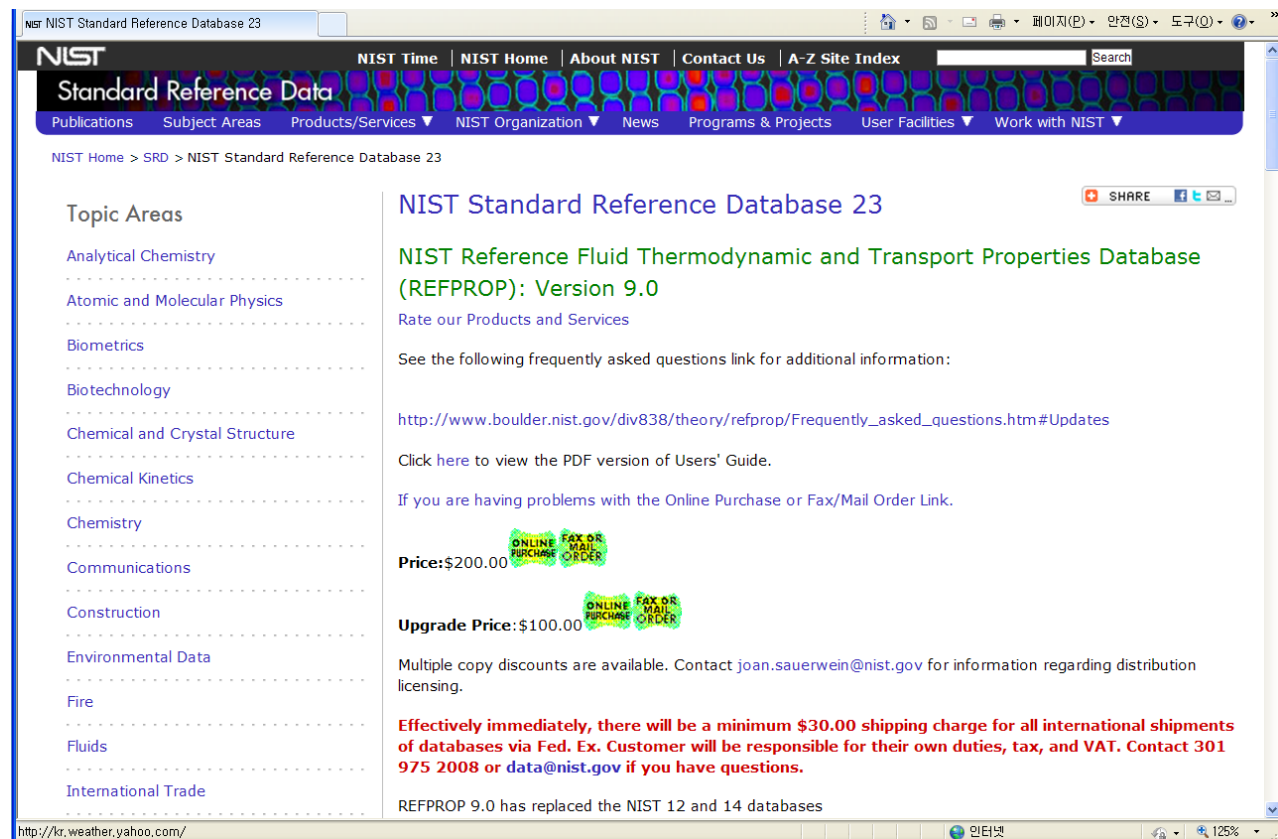
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- **GERG-2008 Equation of State**
  - The European Gas Research Group
  - Founded in 1961
  - Developed based on Wagner's EOS
  - Ruhr University, Bochum, Germany

# REFPROP: Physical Property DB in NIST

## ➤ REFPROP

- Widely used in the Refrigeration Industry
- Available from Web Site



The screenshot displays the NIST Standard Reference Database 23 website. The page title is "NIST Standard Reference Database 23". The main heading is "NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP): Version 9.0". The page includes a navigation menu with options like "Publications", "Subject Areas", "Products/Services", "NIST Organization", "News", "Programs & Projects", "User Facilities", and "Work with NIST". A sidebar on the left lists "Topic Areas" such as Analytical Chemistry, Atomic and Molecular Physics, Biometrics, Biotechnology, Chemical and Crystal Structure, Chemical Kinetics, Chemistry, Communications, Construction, Environmental Data, Fire, Fluids, and International Trade. The main content area provides information about the database, including a price of \$200.00 and an upgrade price of \$100.00. It also includes a frequently asked questions link and contact information for licensing.

NIST Standard Reference Database 23

Standard Reference Data

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NIST Home > SRD > NIST Standard Reference Database 23

Topic Areas

- Analytical Chemistry
- Atomic and Molecular Physics
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- Biotechnology
- Chemical and Crystal Structure
- Chemical Kinetics
- Chemistry
- Communications
- Construction
- Environmental Data
- Fire
- Fluids
- International Trade

NIST Standard Reference Database 23

NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP): Version 9.0

Rate our Products and Services

See the following frequently asked questions link for additional information:

[http://www.boulder.nist.gov/div838/theory/refprop/Frequently\\_asked\\_questions.htm#Updates](http://www.boulder.nist.gov/div838/theory/refprop/Frequently_asked_questions.htm#Updates)

Click [here](#) to view the PDF version of Users' Guide.

If you are having problems with the Online Purchase or Fax/Mail Order Link.

Price: \$200.00

Upgrade Price: \$100.00

Multiple copy discounts are available. Contact [joan.sauerwein@nist.gov](mailto:joan.sauerwein@nist.gov) for information regarding distribution licensing.

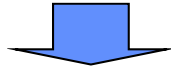
**Effectively immediately, there will be a minimum \$30.00 shipping charge for all international shipments of databases via Fed. Ex. Customer will be responsible for their own duties, tax, and VAT. Contact 301 975 2008 or [data@nist.gov](mailto:data@nist.gov) if you have questions.**

REFPROP 9.0 has replaced the NIST 12 and 14 databases

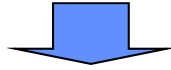
# GERG-2008:

## ➤ History of EOS in terms of Residual Helmholtz Free Energy ( $a^r$ )

Ideal gas:  $a^r = 0$



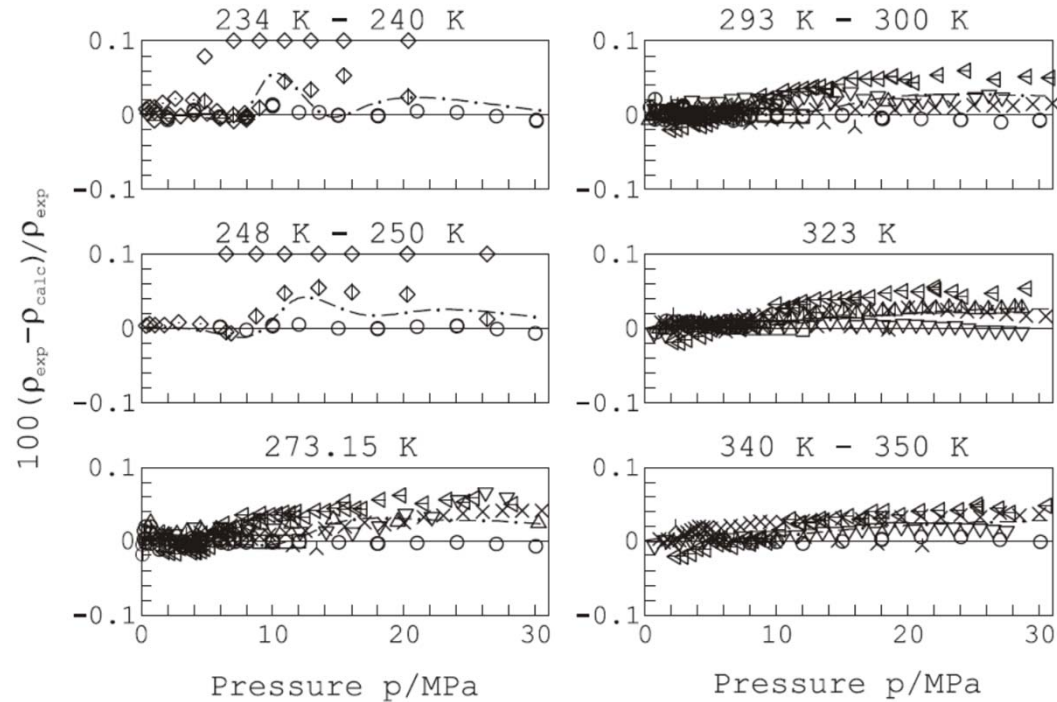
Peng-Robinson:  $\frac{a^r}{RT} = \alpha^r(\rho, T, \bar{x}) = \ln\left(\frac{1}{1-b\rho}\right) - \frac{a}{2\sqrt{2}RT} \ln\left(\frac{1+(\sqrt{2}+1)b\rho}{1-(\sqrt{2}-1)b\rho}\right)$



Improved virial  
Type EOS  
GERG 2004:

$$\begin{aligned} \alpha^r = & \sum_{k=1}^4 \sum_{l=0}^{16} n_{kl} \delta^k \tau^{l/8} \\ & + \exp(-\delta) \sum_{k=1}^6 \sum_{l=0}^{22} n_{kl} \delta^k \tau^{l/8} + \exp(-\delta^2) \sum_{k=1}^4 \sum_{l=0}^{20} n_{kl} \delta^k \tau^{l/4} \\ & + \exp(-\delta^3) \sum_{k=1}^5 \sum_{l=4}^{36} n_{kl} \delta^k \tau^{l/2} + \exp(-\delta^4) \sum_{k=4}^5 \sum_{l=0}^{16} n_{kl} \delta^k \tau^l \\ & + \exp(-\delta^5) \sum_{k=1}^2 \sum_{l=2}^{10} n_{kl} \delta^{2k-1} \tau^{2l} + \exp(-\delta^6) \sum_{k=4}^8 \sum_{l=8}^{18} n_{kl} \delta^k \tau^{2l}. \end{aligned}$$

# Accuracy of GERG-2008 EOS for Liquid Density:

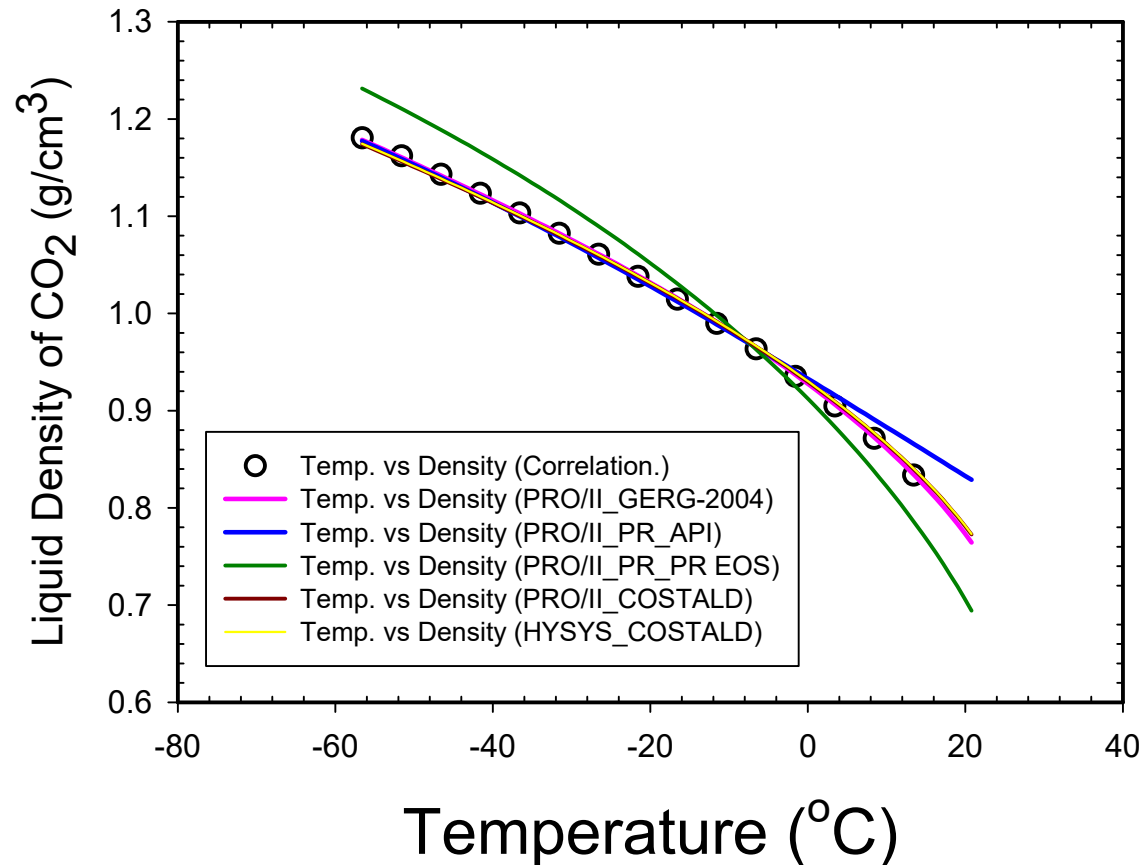


- ◇ Roe (1972)
- ◇ Händel et al. (1992)
- ◇ Goodwin (1974), corrected
- △ Jaeschke & Hinze (1991), Bu
- ▽ Jaeschke & Hinze (1991), Op
- ◁ Trappeniers et al. (1979)
- △ Achtermann et al. (1986)
- Setzmann & Wagner (1991)
- Klimeck et al. (2001)
- ◇ Goodwin (1974), original
- Kleinrahm et al. (1988)
- × Achtermann et al. (1992)
- ∧ Schamp et al. (1958)
- Nowak et al. (1995)

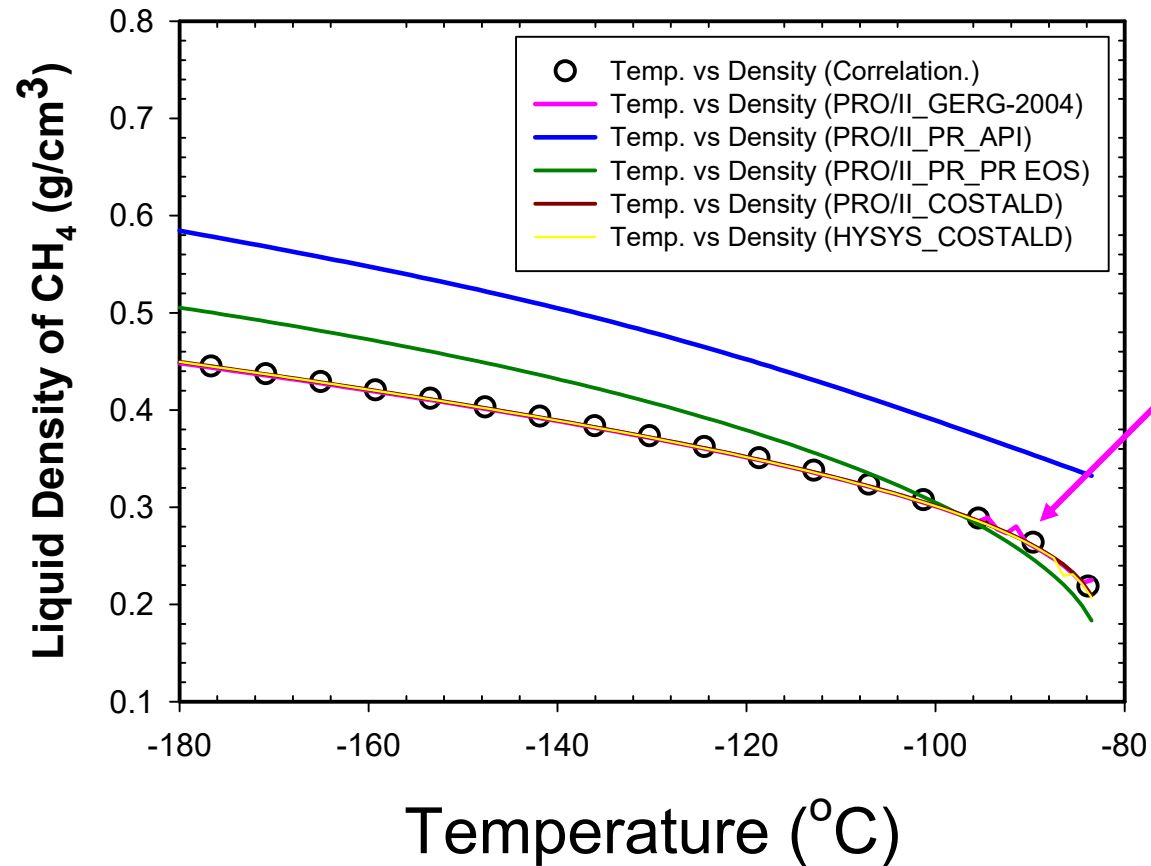
Kunz, O., R. Klimeck, W. Wagner, M. Jaeschke; „The GERG-2004 Wide-Range Equation of State for Natural Gases and Other Mixtures”,  
[http://www.gerg.info/publications/tm/tm15\\_04.pdf](http://www.gerg.info/publications/tm/tm15_04.pdf)



# Liquid Density for Carbon Dioxide:

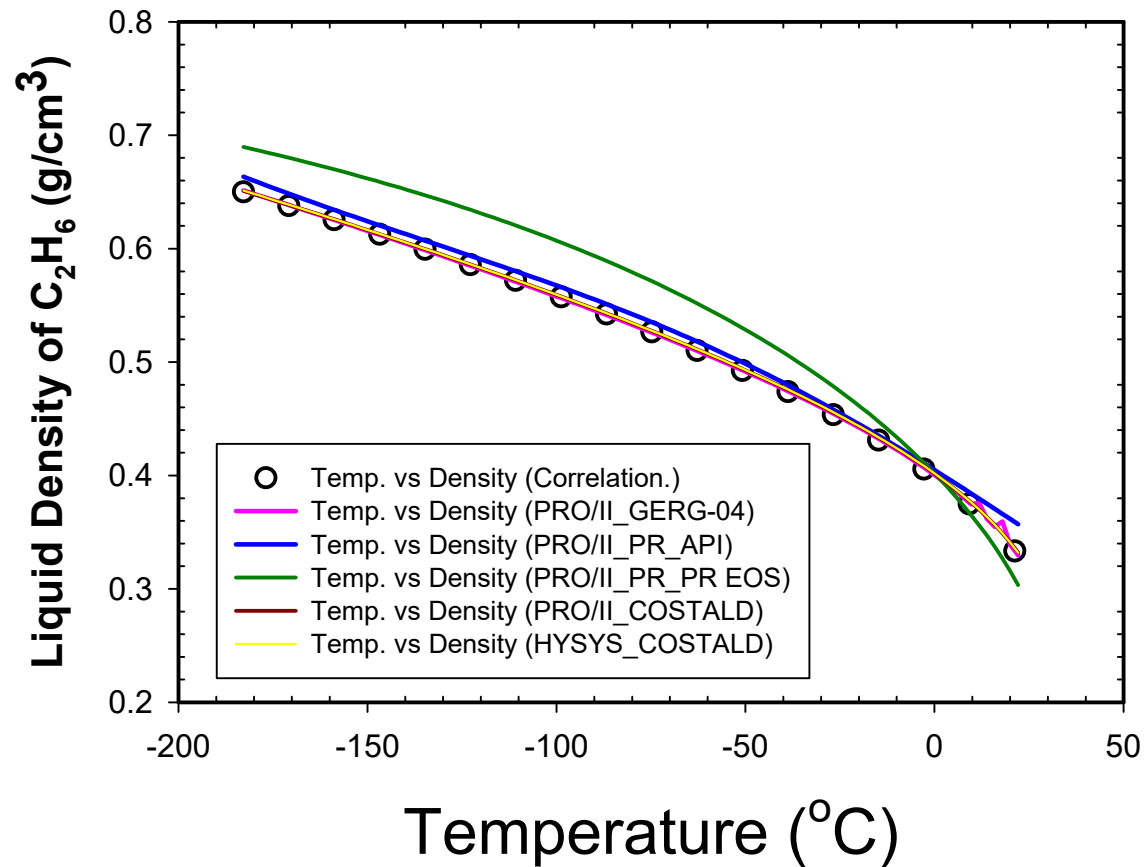


# Liquid Density for Methane:

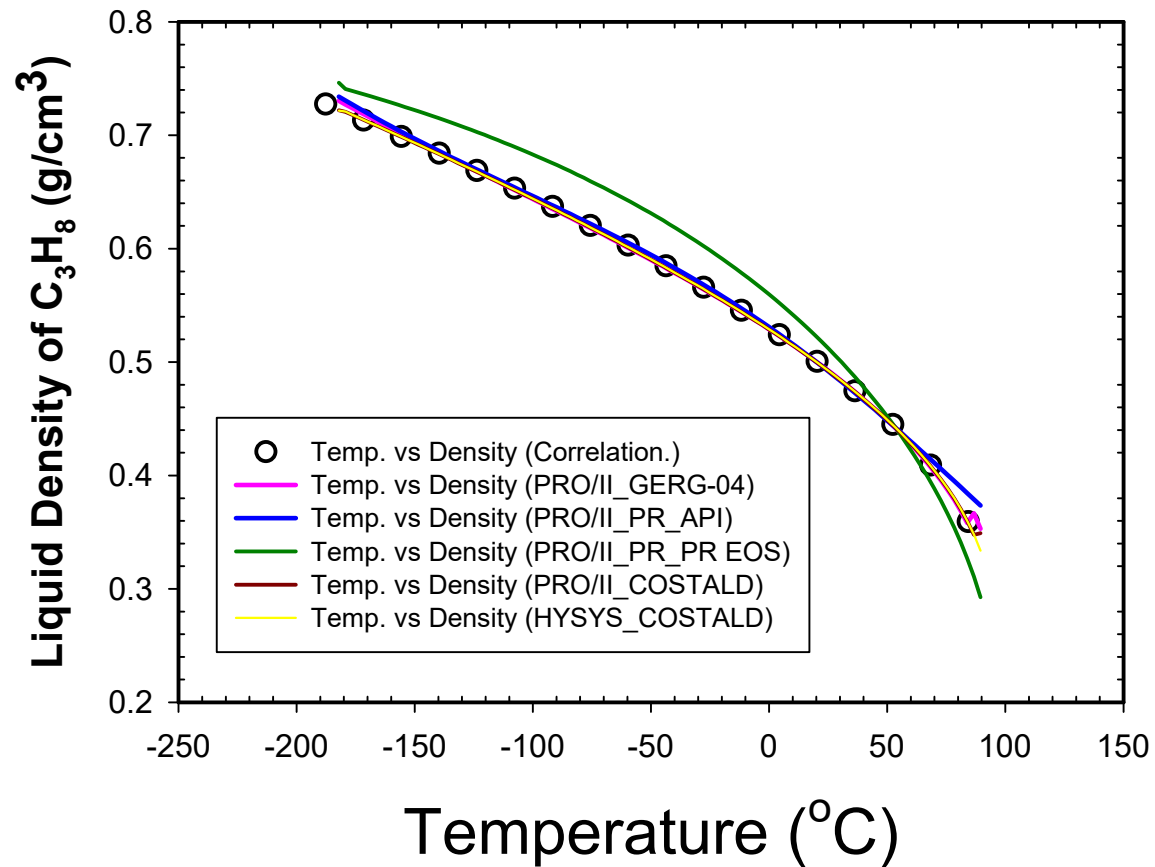


GERG의 경우  
약간 Fluctuation

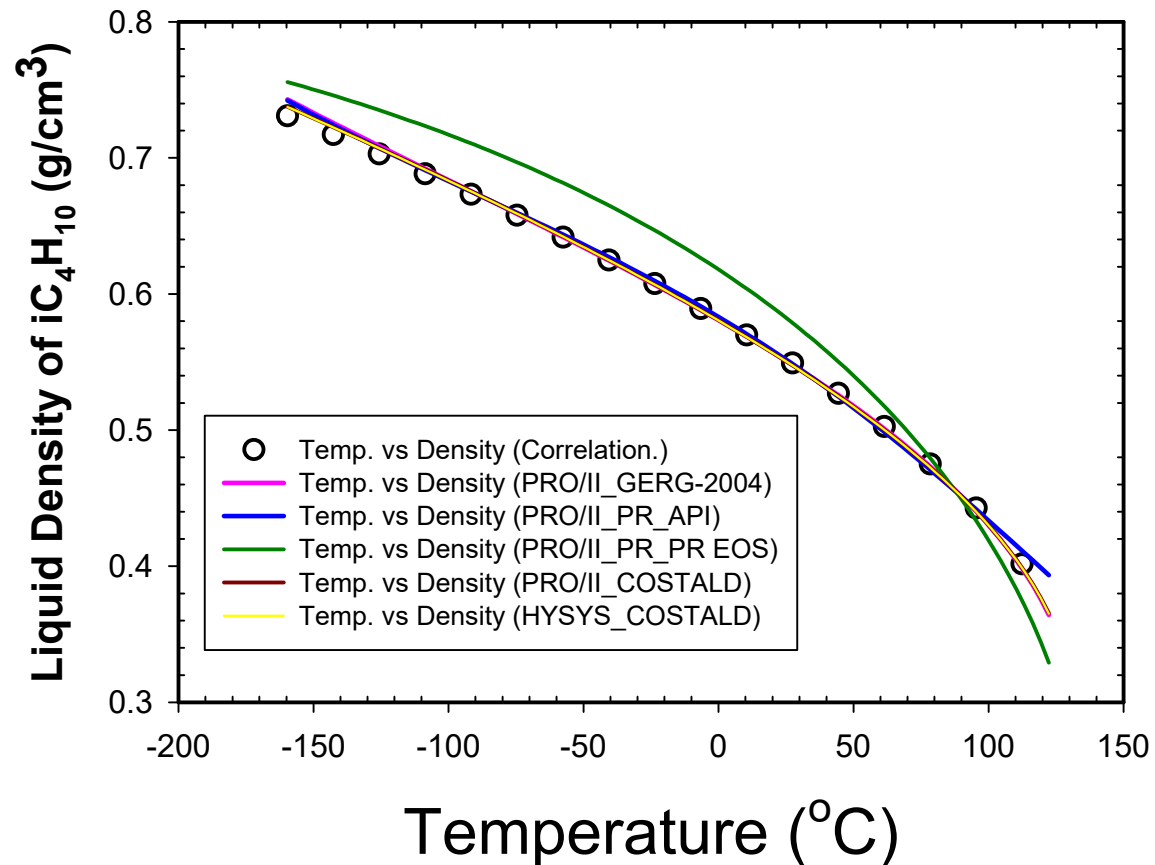
# Liquid Density for Ethane:



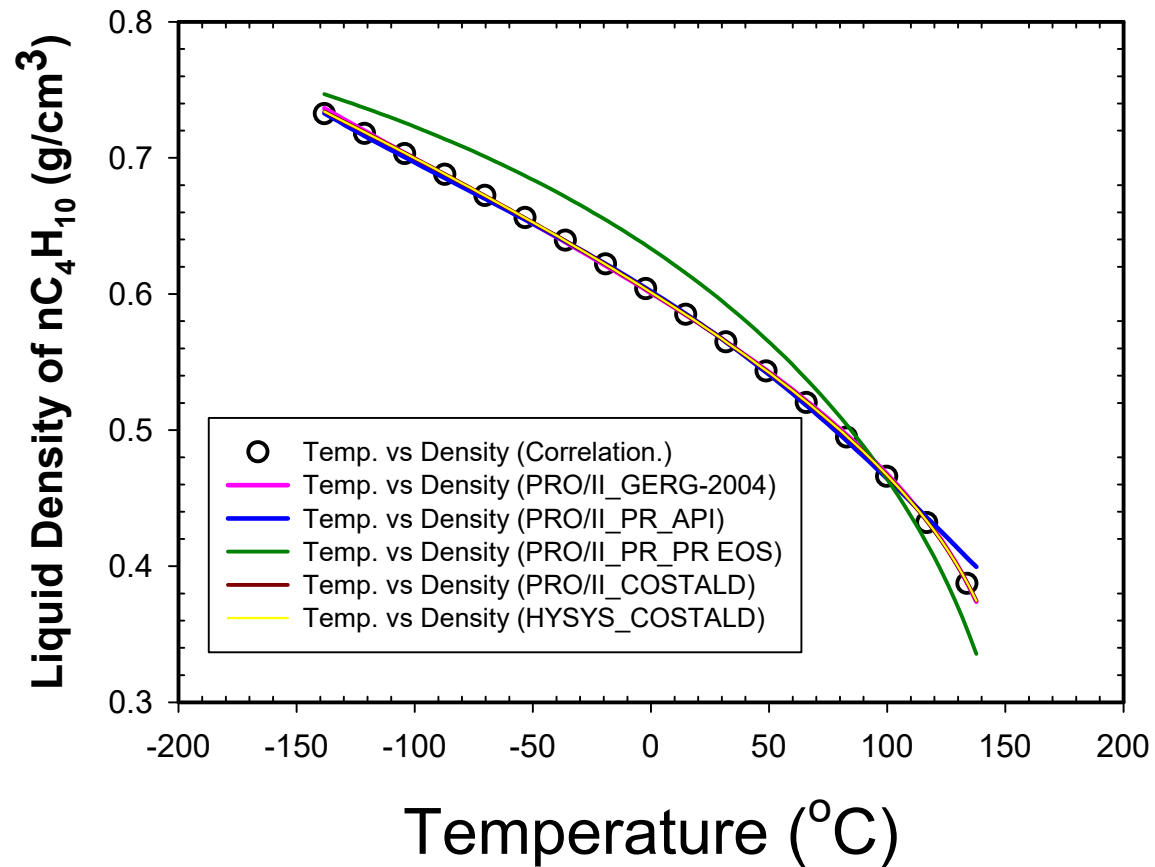
# Liquid Density for Propane:



# Liquid Density for Isobutane:



# Liquid Density for Normal Butane:



# Costald Model for LNG Liquid Density Estimation:

The corresponding-states liquid density model is suitable for prediction the liquid densities of “LNG-like” fluids. This accurate and reliable method is over 99.8% accurate in predicting the densities of light hydrocarbon mixtures.

$$V_S / V^* = V_Y^{(0)} \left[ 1 - \omega_{SPK} V_Y^{(\delta)} \right]$$

$$V_Y^{(0)} = 1 + \sum_1^4 A_k (1 - T_Y)^{k/3}, \quad 0.25 < T_Y < 0.95$$

$$V_Y^{(\delta)} = \left[ \sum_0^3 B_k T_Y^k \right] / (T_Y - 1.00001) \quad 0.25 < T_Y < 1.0$$

# GERG-2008 EOS:

## ➤ Available Components

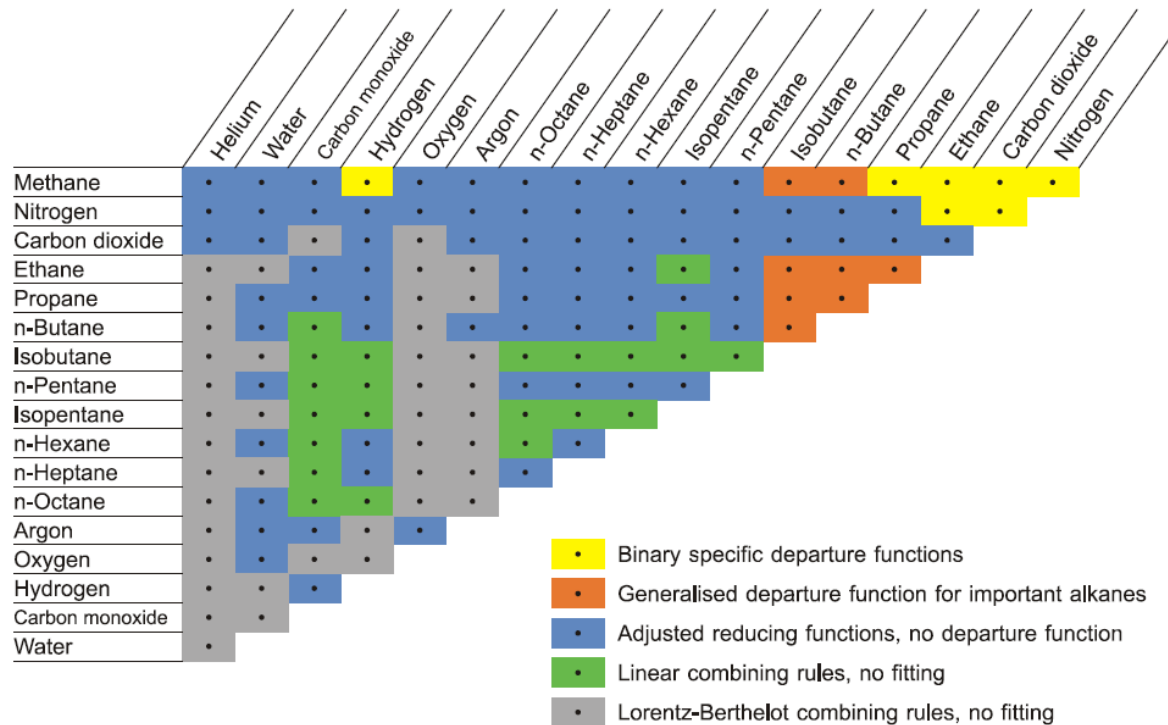
Methane	n-Butane	Hydrogen
Nitrogen	Isobutane	Oxygen
Carbon dioxide	n-Pentane	Carbon monoxide
Ethane	Isopentane	Water
Propane	n-Hexane	Helium
	n-Heptane	Argon
	n-Octane	



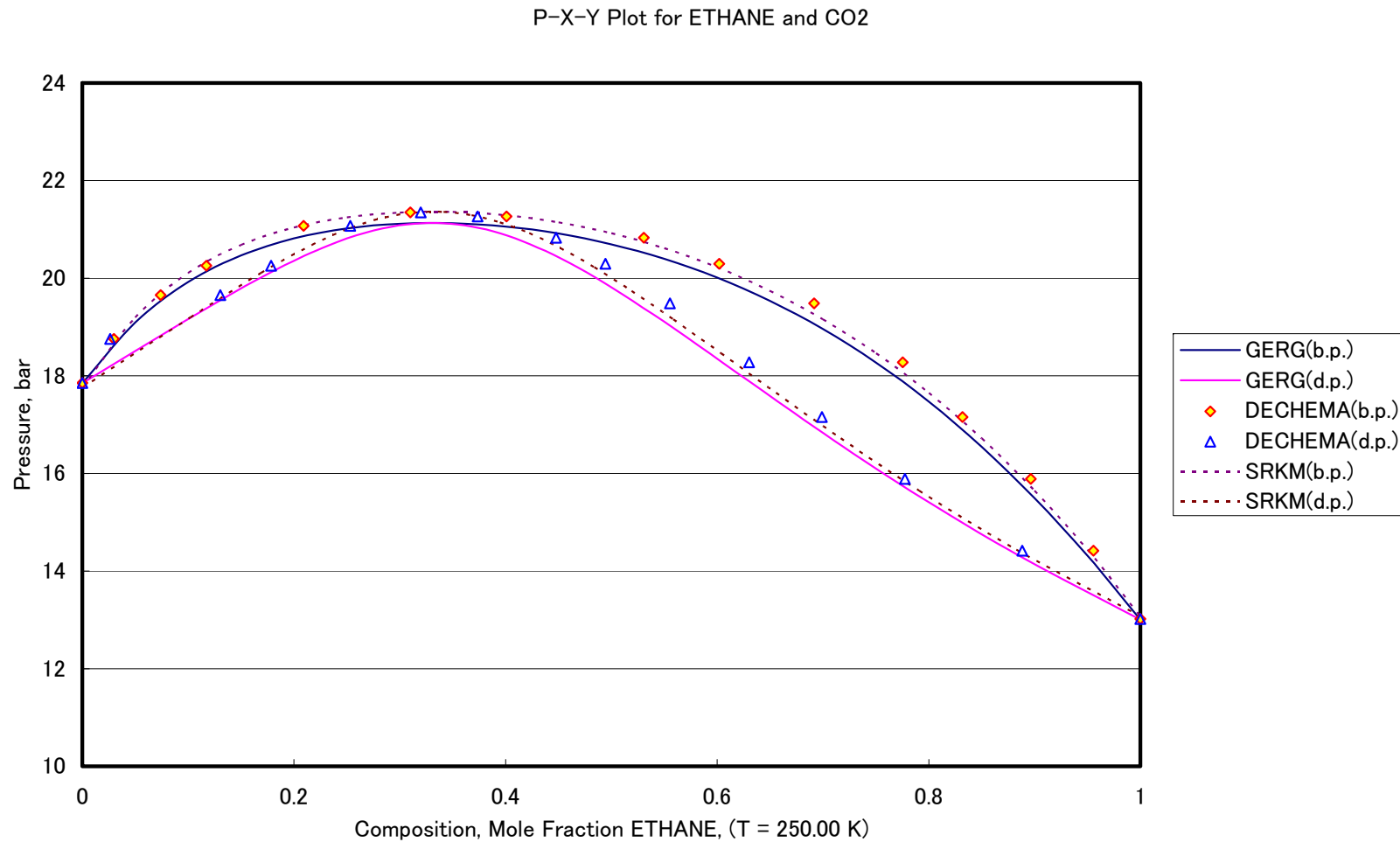
# GERG-2008 EOS: Binary Interaction Parameters

## ➤ Binary Interaction Parameters:

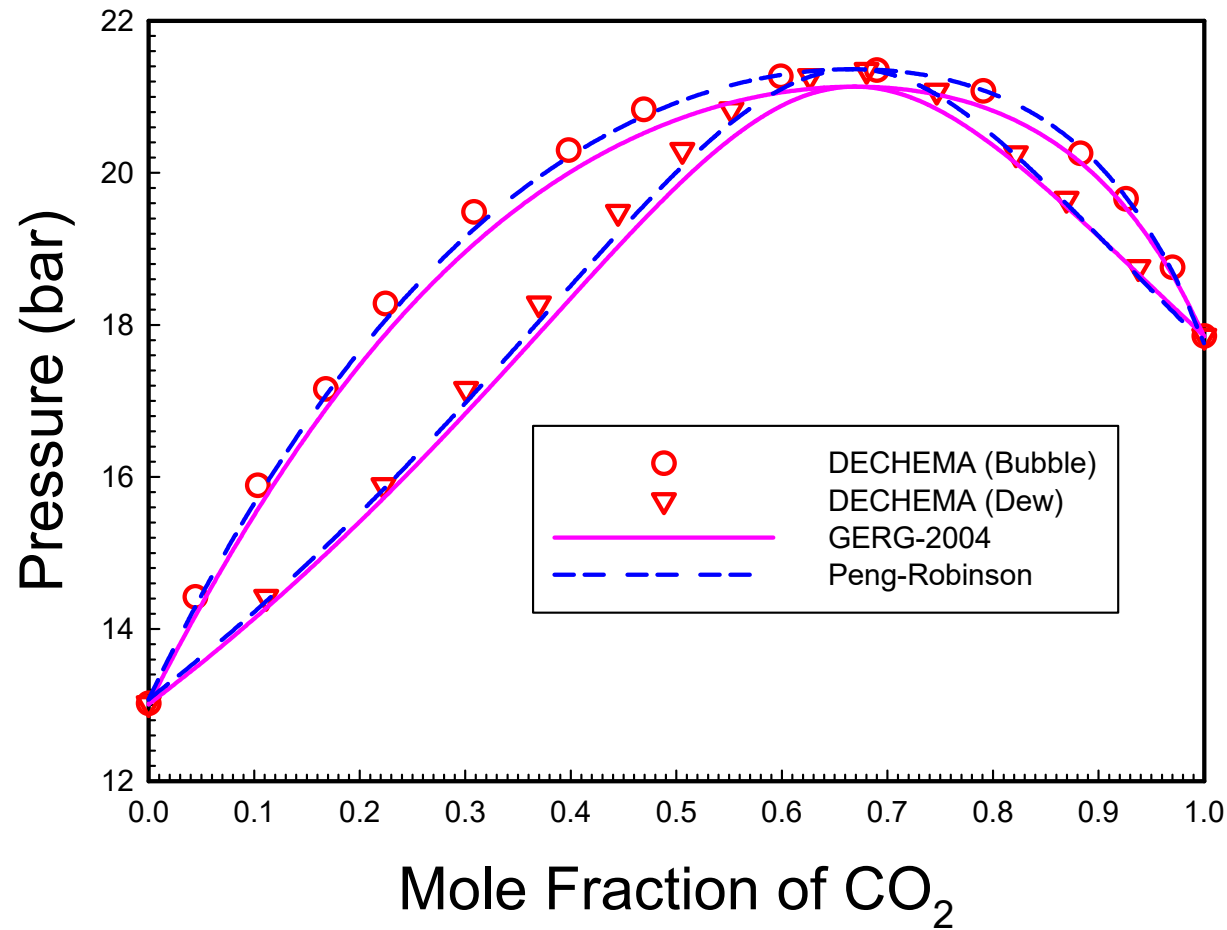
$$\alpha^r(\delta, \tau, \bar{x}) = \sum_{i=1}^N x_i \alpha_{oi}^r(\delta, \tau) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N x_i x_j F_{ij} \alpha_{ij}^r(\delta, \tau),$$



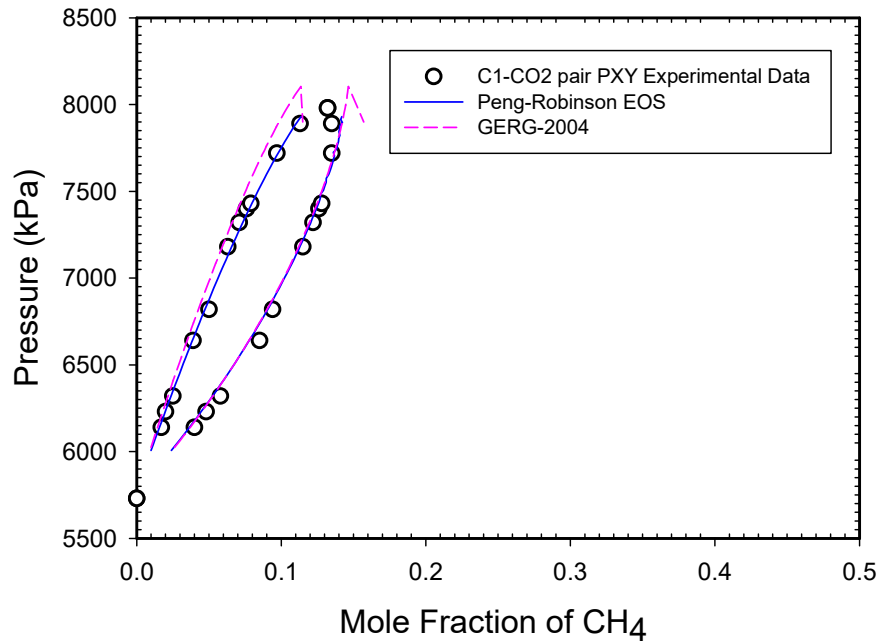
# GERG is not superior to SRK in Predicting VLE:



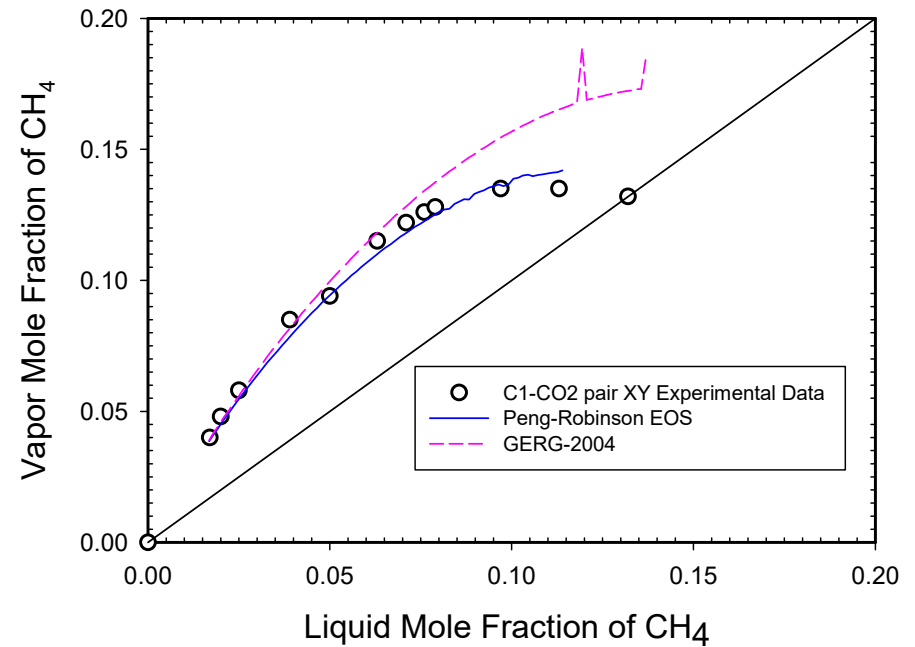
# GERG is not superior to SRK in Predicting VLE:



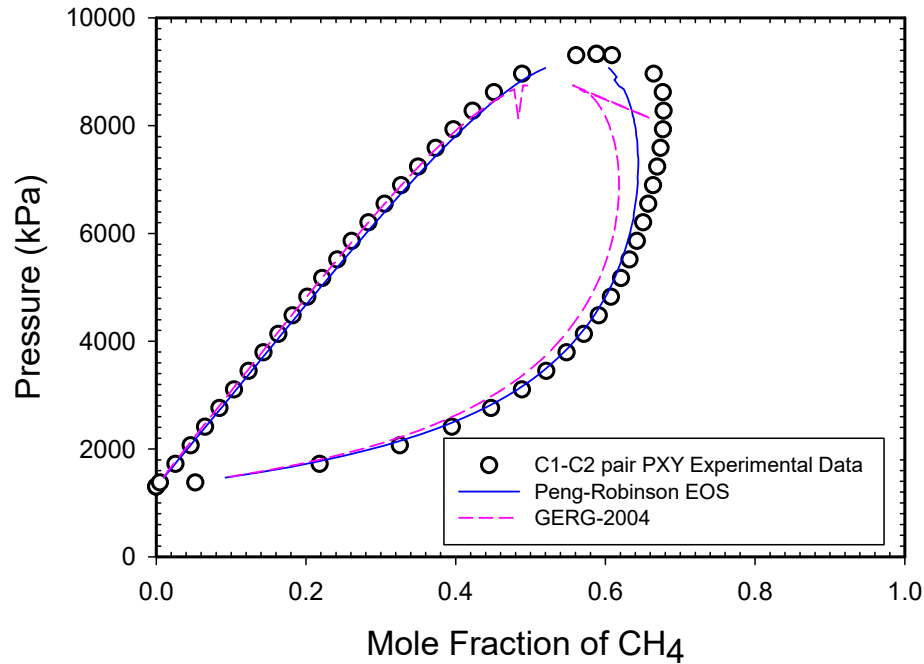
# Isothermal Pxy & XY of CH<sub>4</sub> + CO<sub>2</sub> at 293.40K:



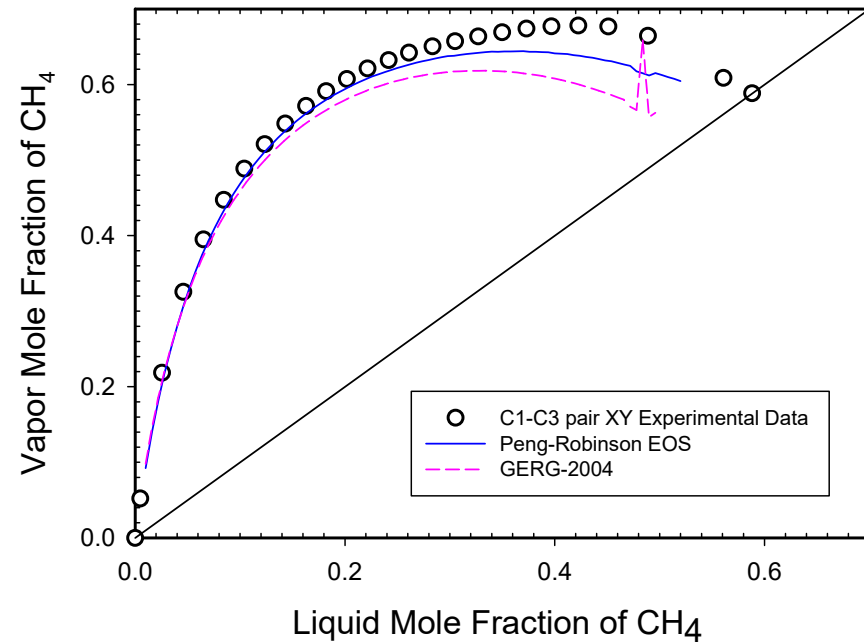
Reference: XU N., DONG J., WANG Y., SHI J., FLUID PHASE EQUILIB., 81, 175 (1992)



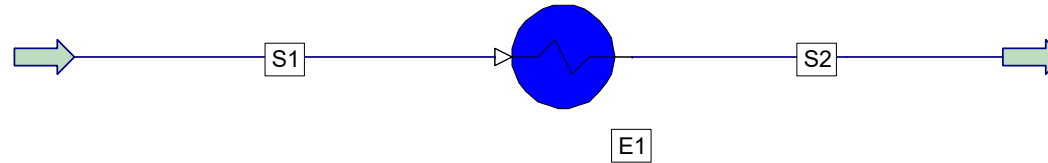
# Isothermal Pxy & XY of CH<sub>4</sub> + C<sub>3</sub>H<sub>8</sub> at 310.93K:



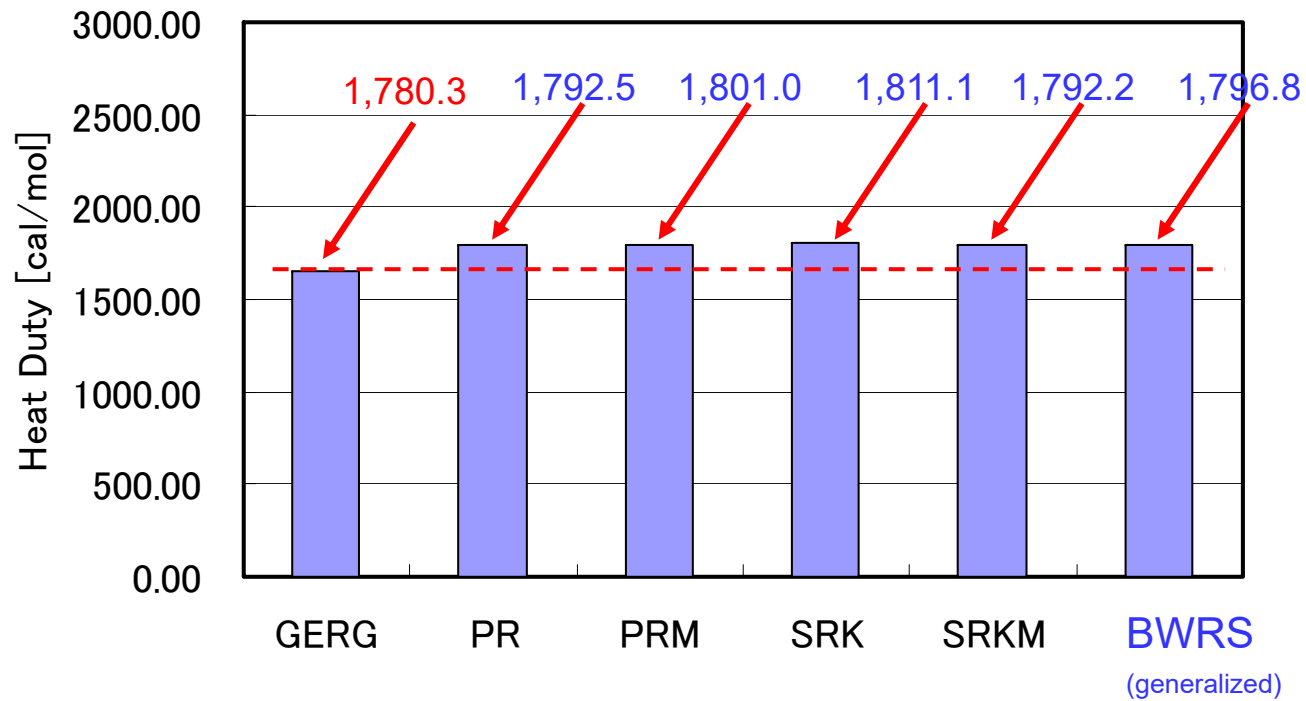
Reference: SAGE B.H., LACEY W.N., API PROJECT, 37, THERMODYN. PROP. LIGHT. PAR./N2 (1950)



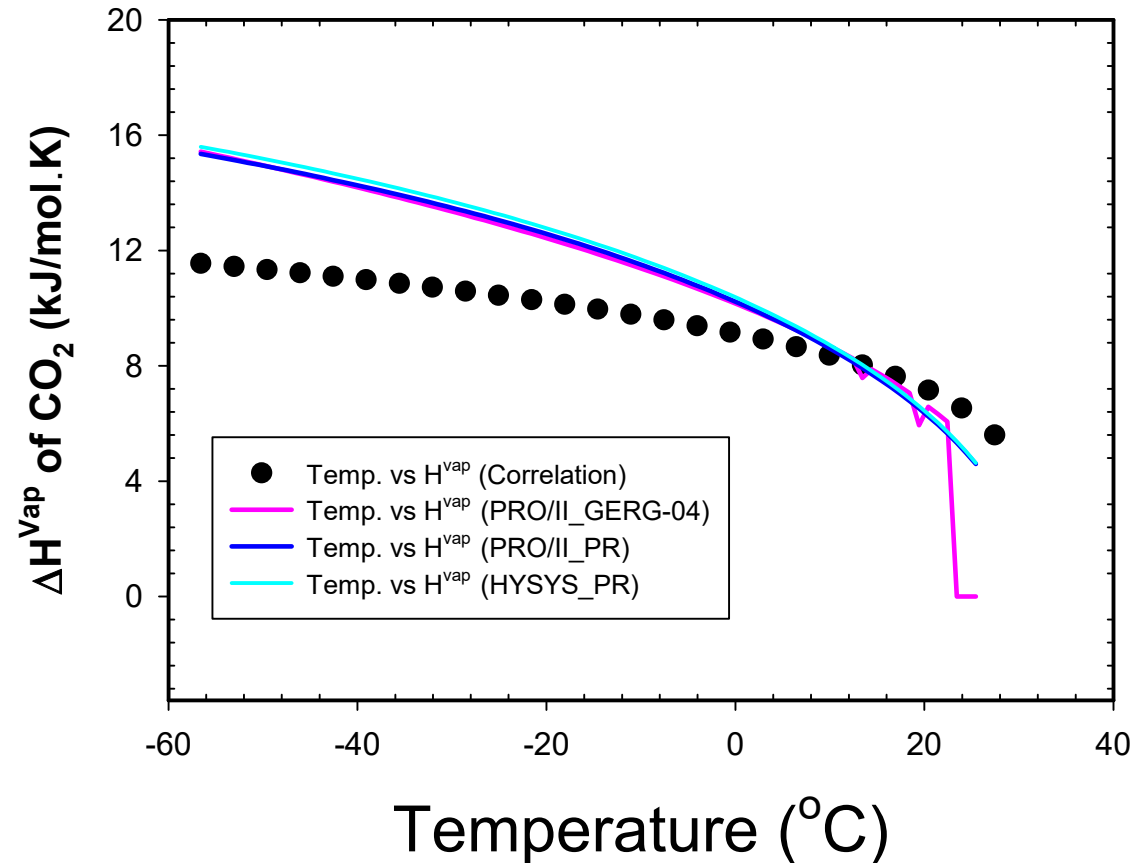
# Enthalpy Prediction Example:



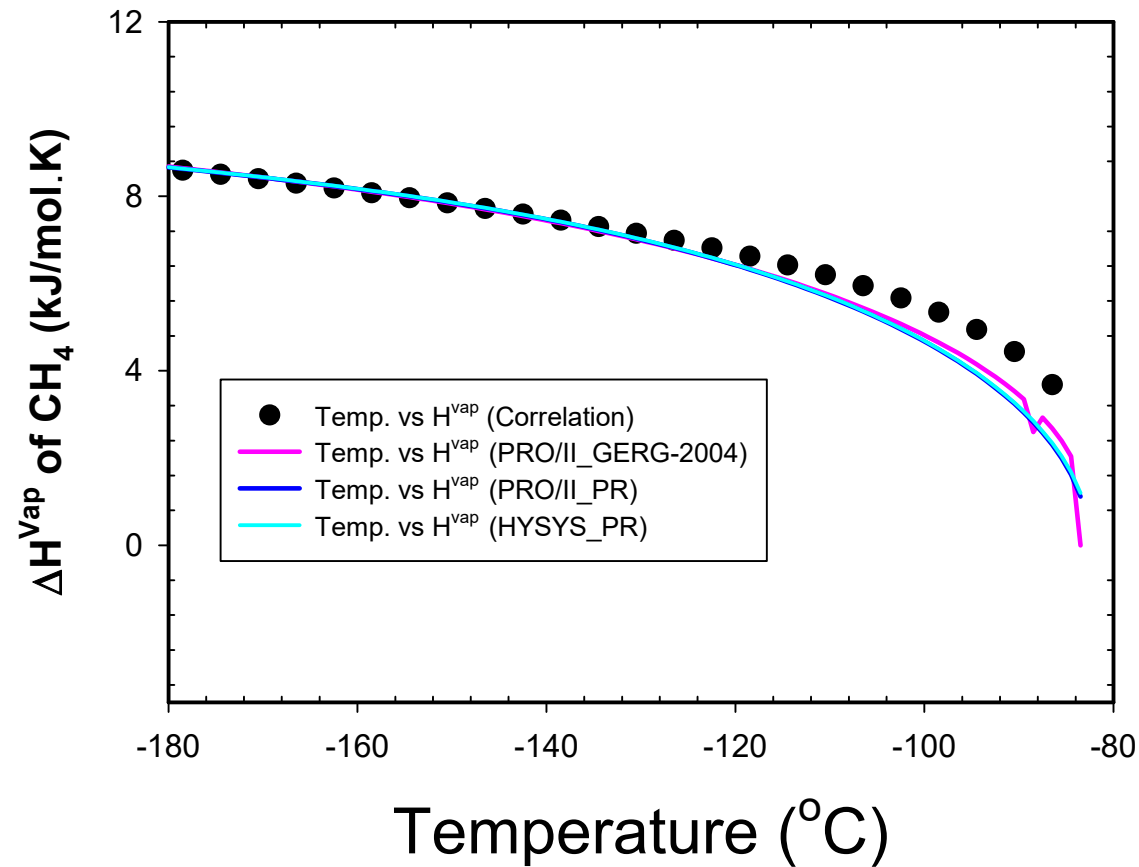
Stream Name	S1	S2
Temperature K	253.150	313.150
Pressure MPA	10.101	10.101
Flowrate KG-MOL/HR	1.000	1.000



# Heat of Vaporization for Carbon Dioxide:

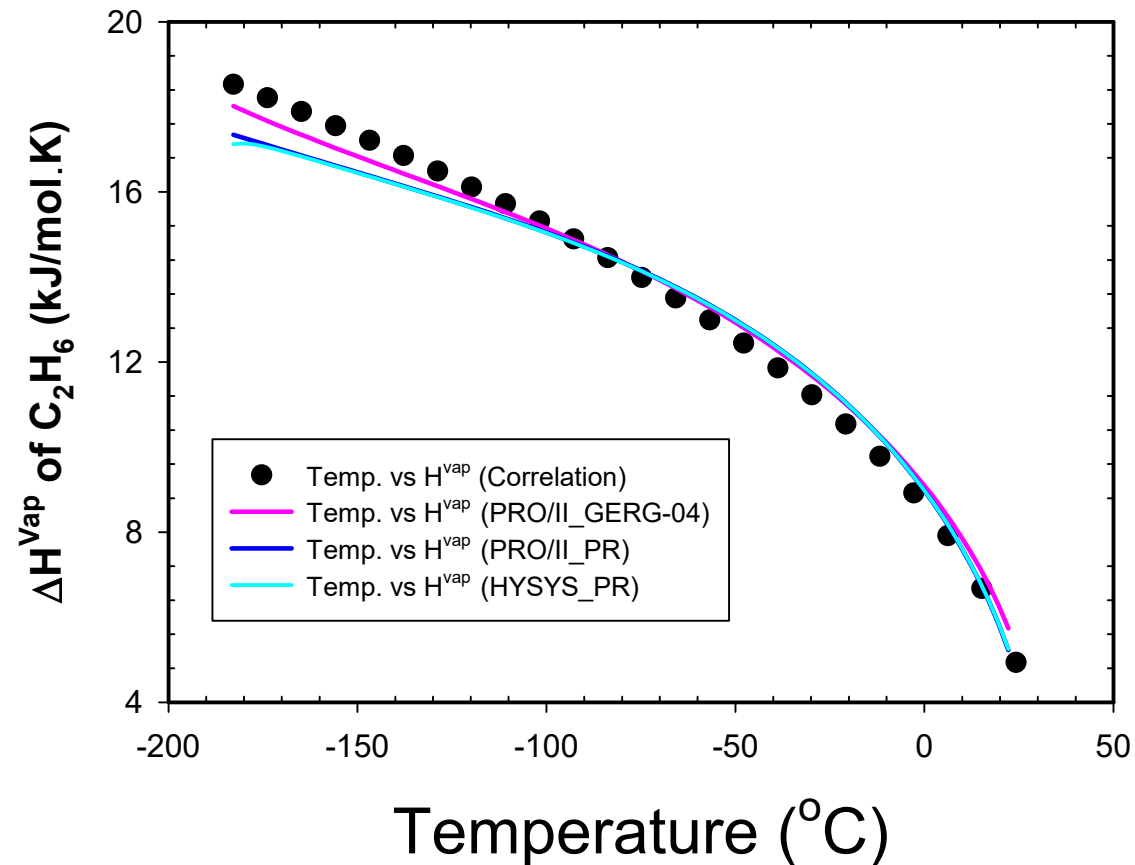


# Heat of Vaporization for Methane:

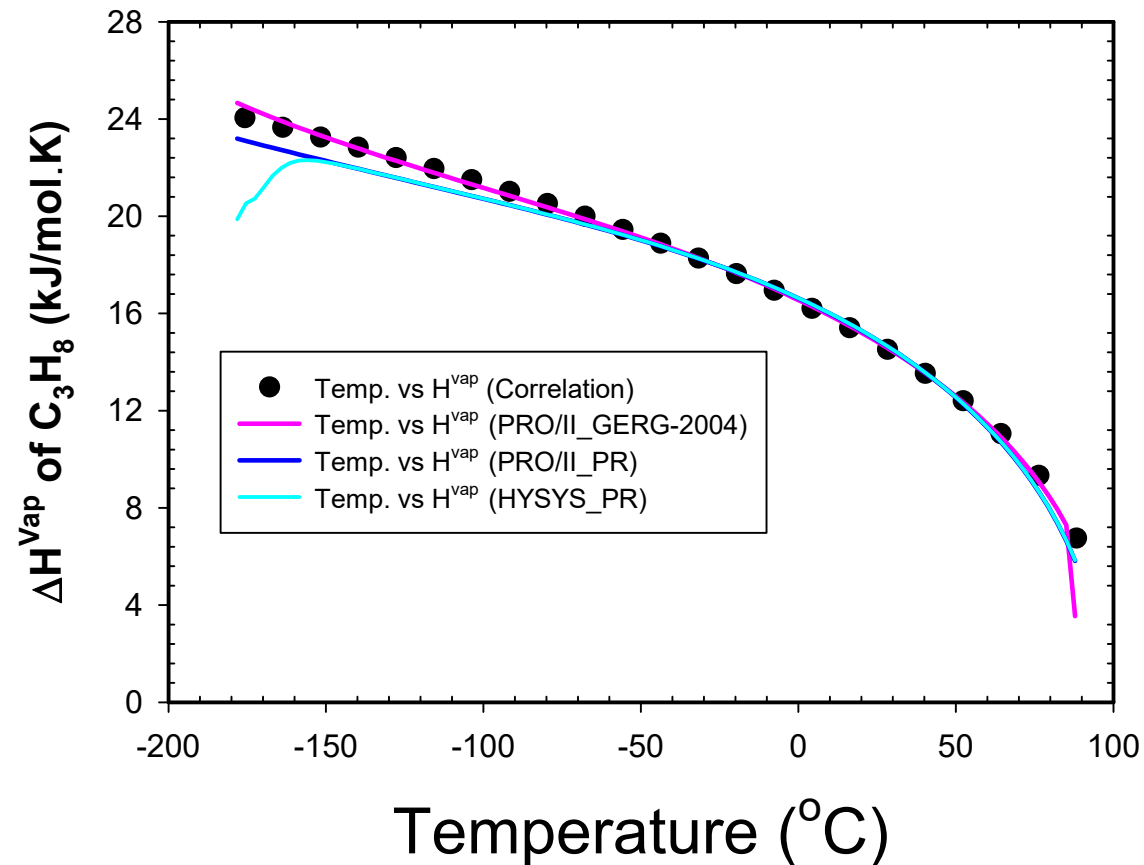




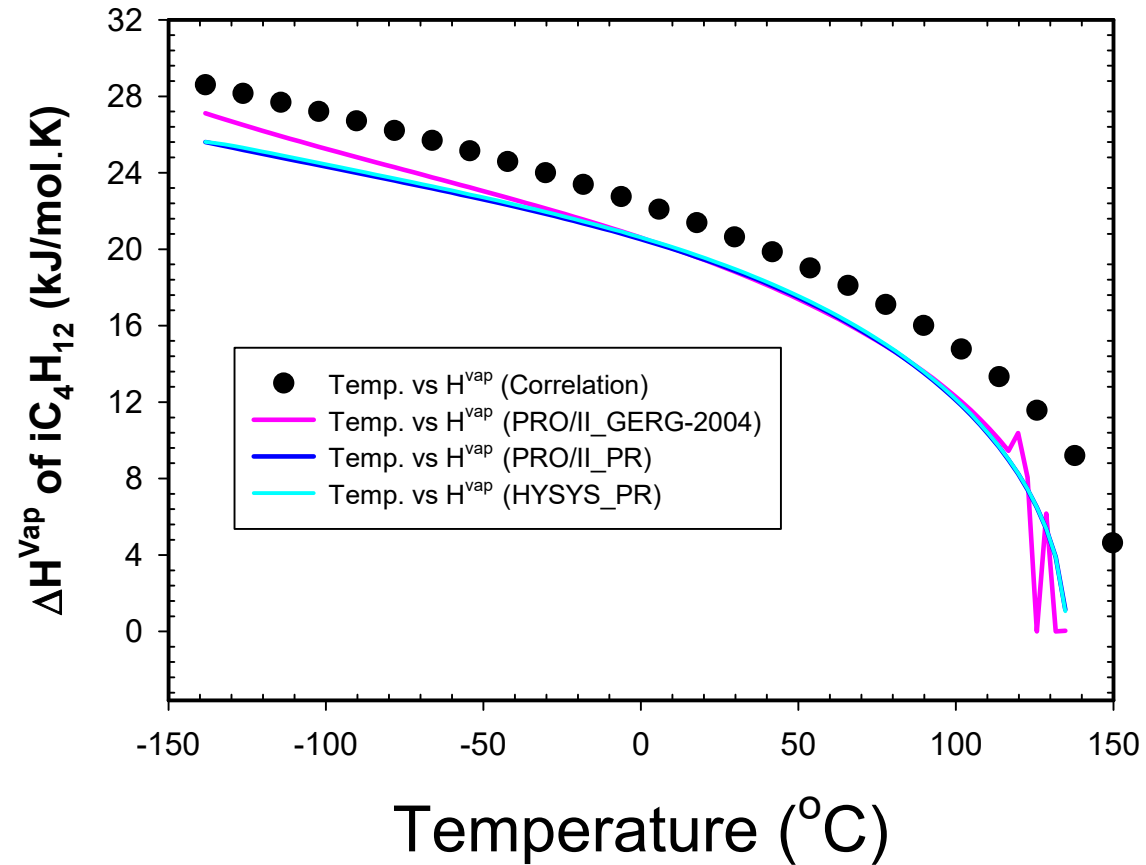
# Heat of Vaporization for Carbon Ethane:



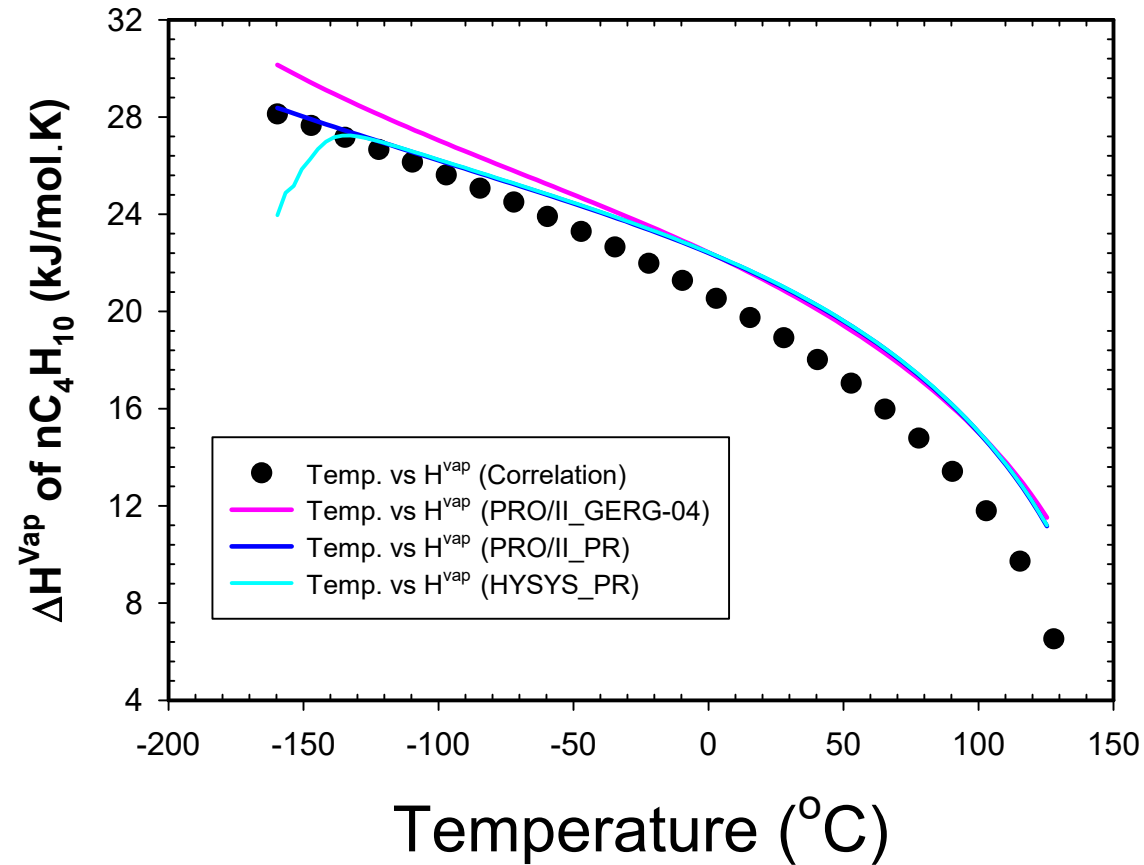
# Heat of Vaporization for Propane:



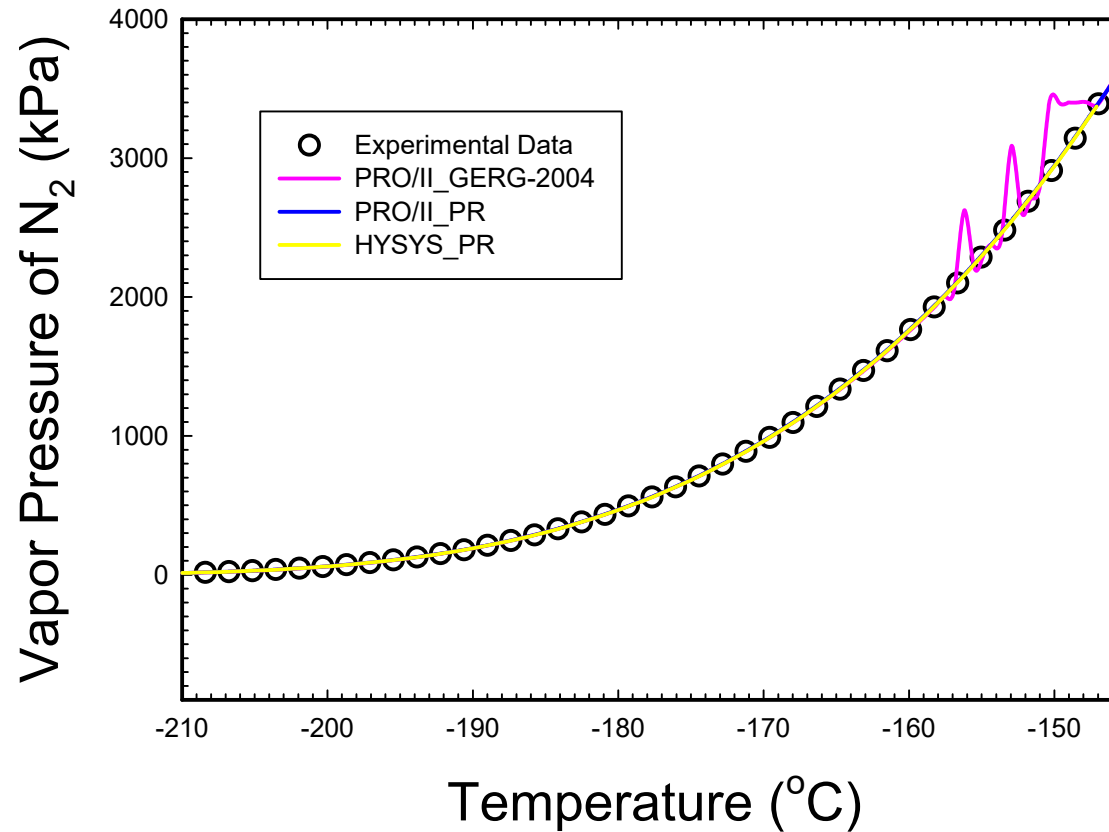
# Heat of Vaporization for Isobutane:



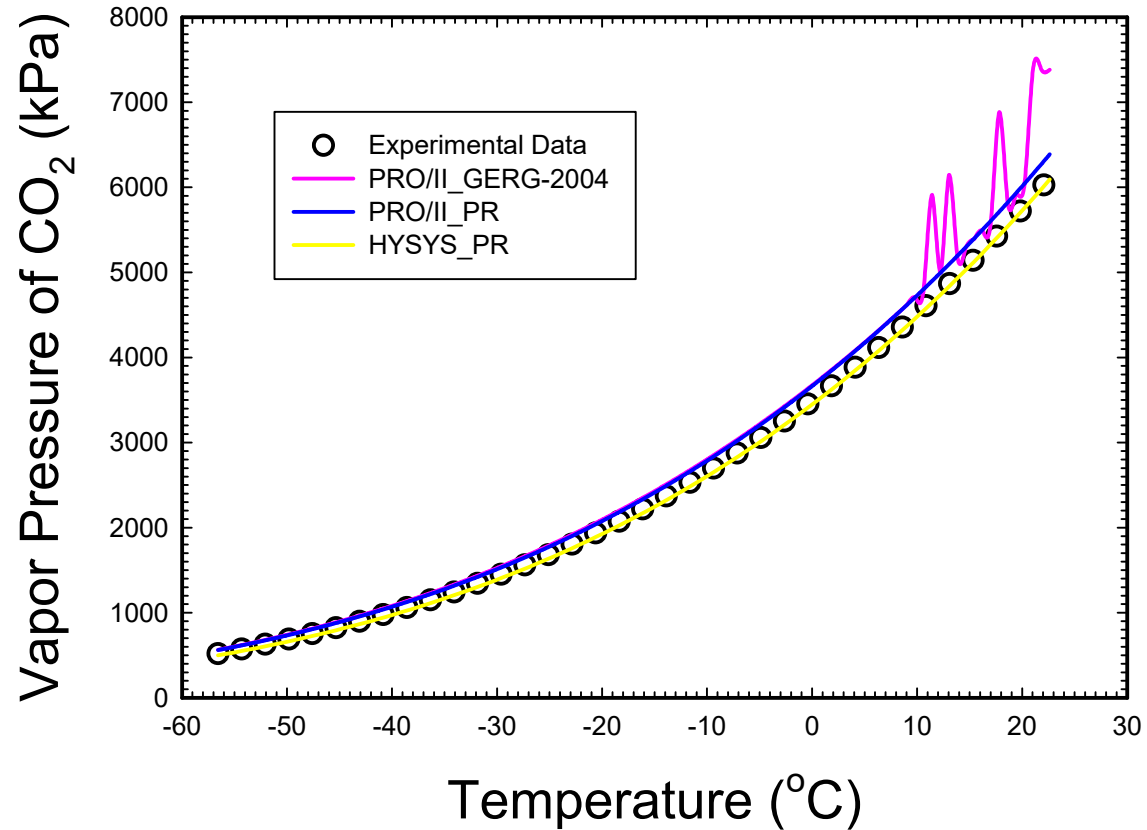
# Heat of Vaporization for Normal Butane:



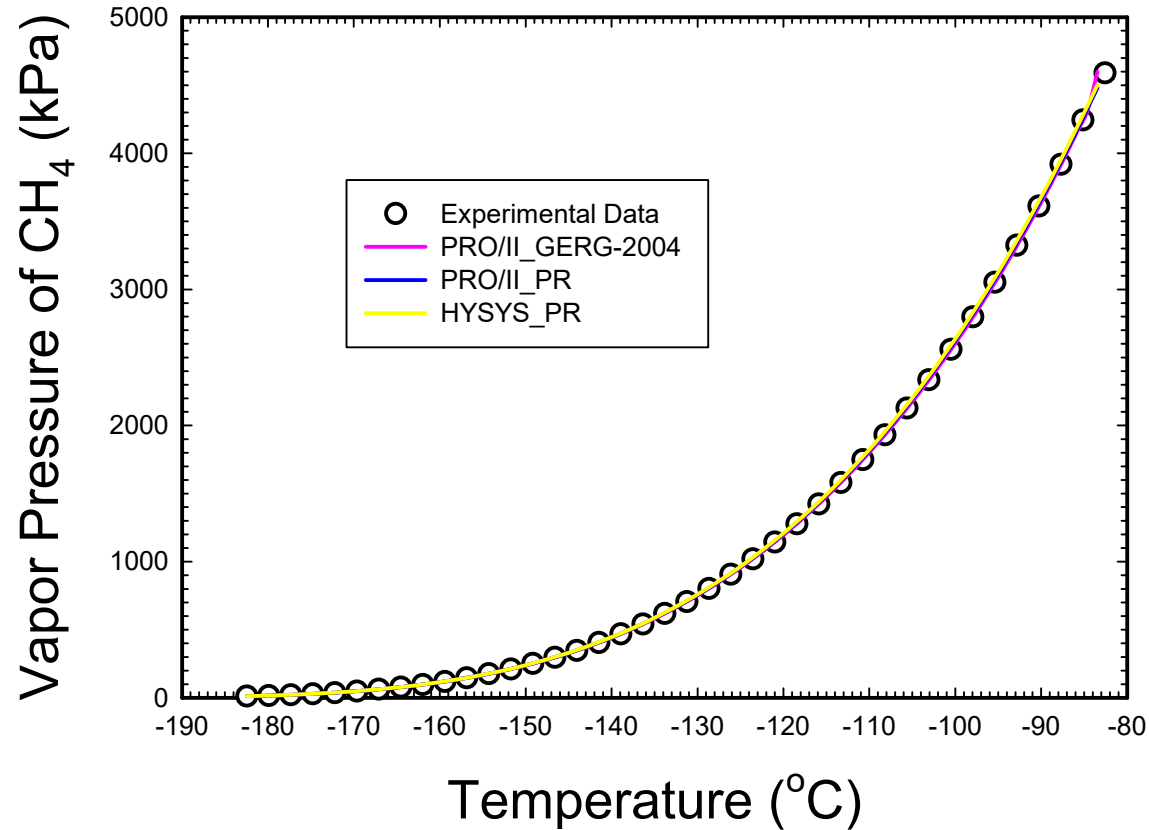
# Vapor Pressure for Nitrogen:



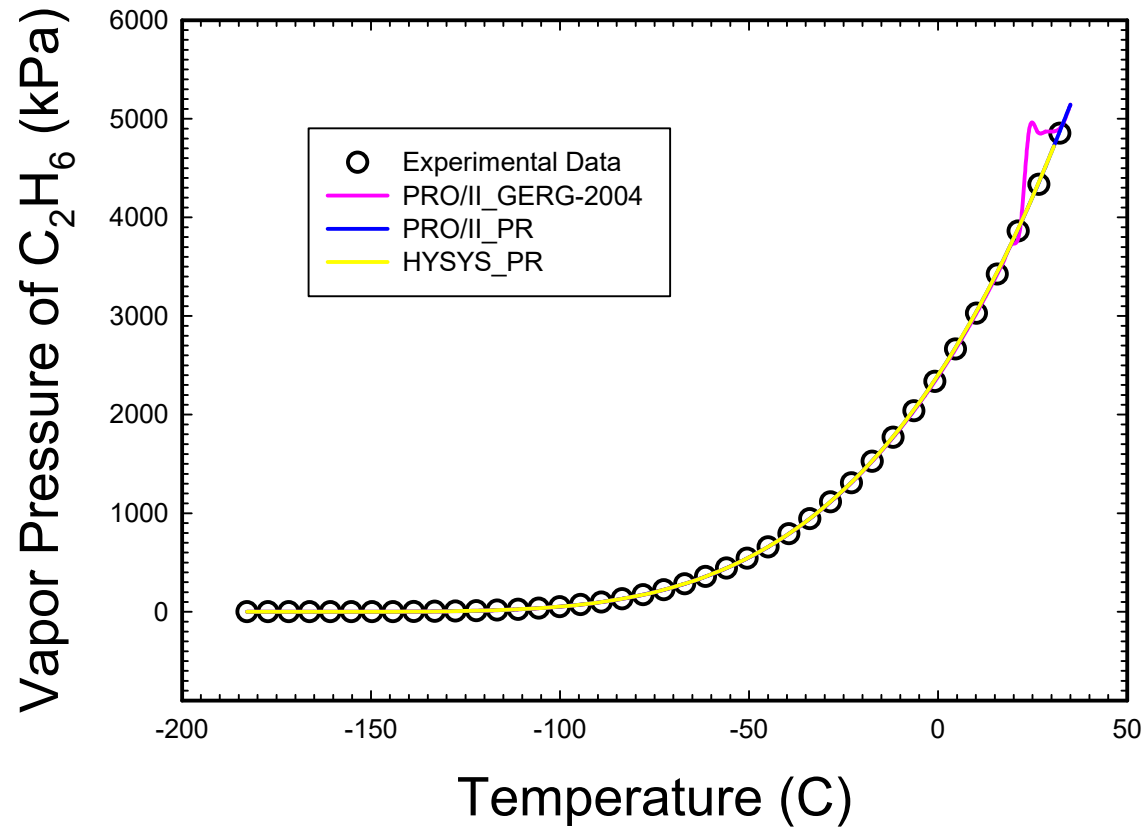
# Vapor Pressure for Carbon Dioxide:



# Vapor Pressure for Methane:

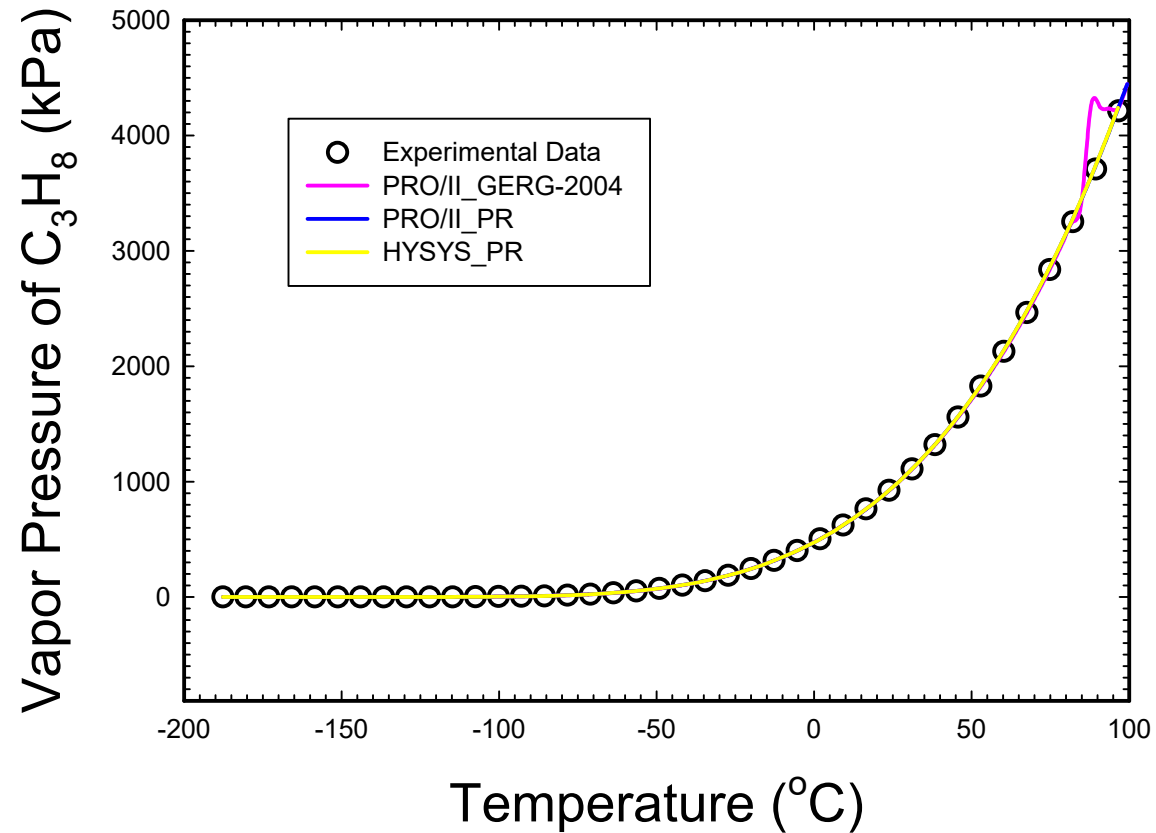


# Vapor Pressure for Ethane:

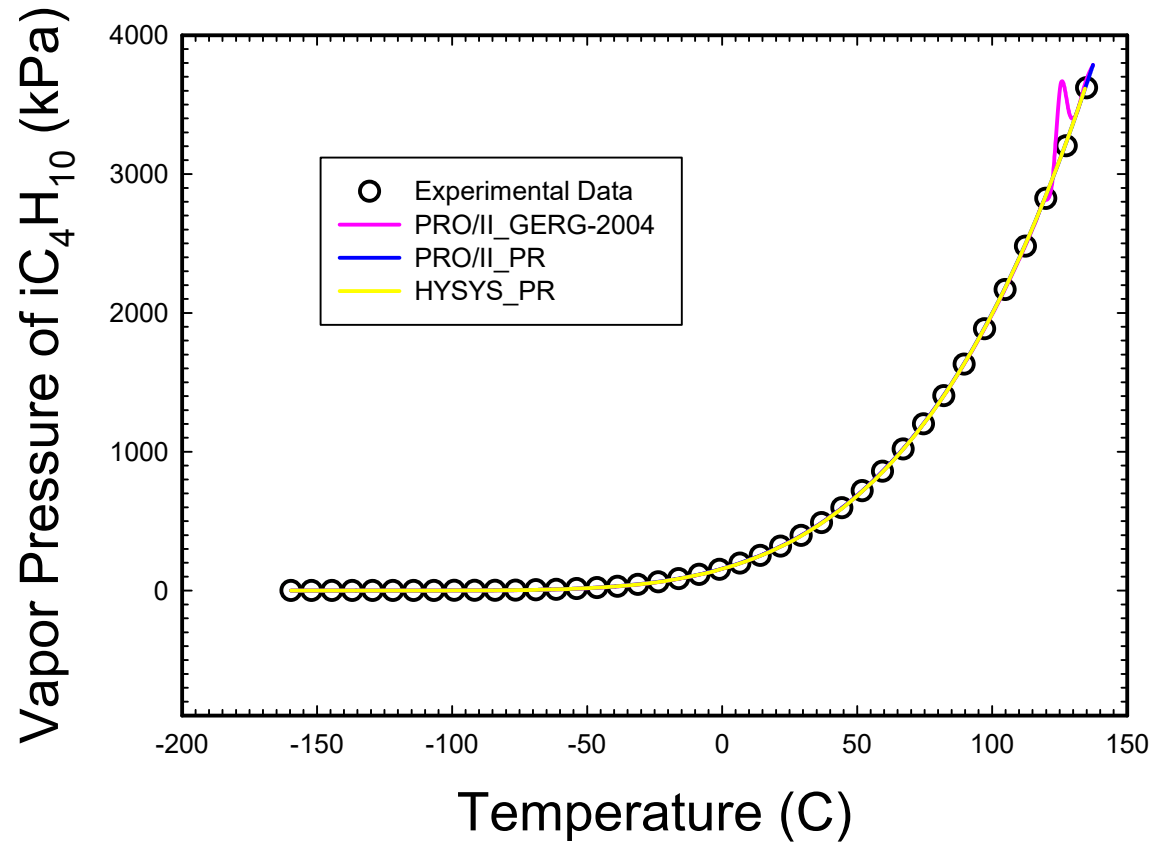




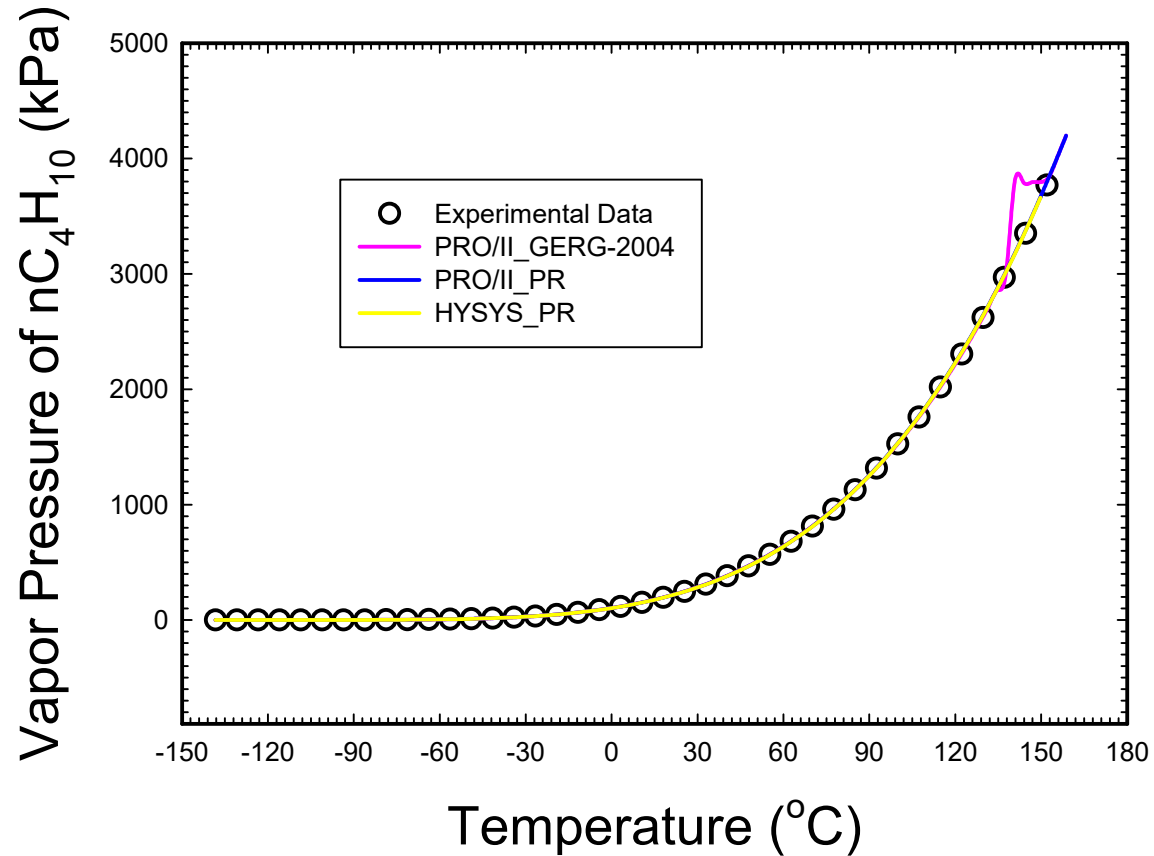
# Vapor Pressure for Propane:



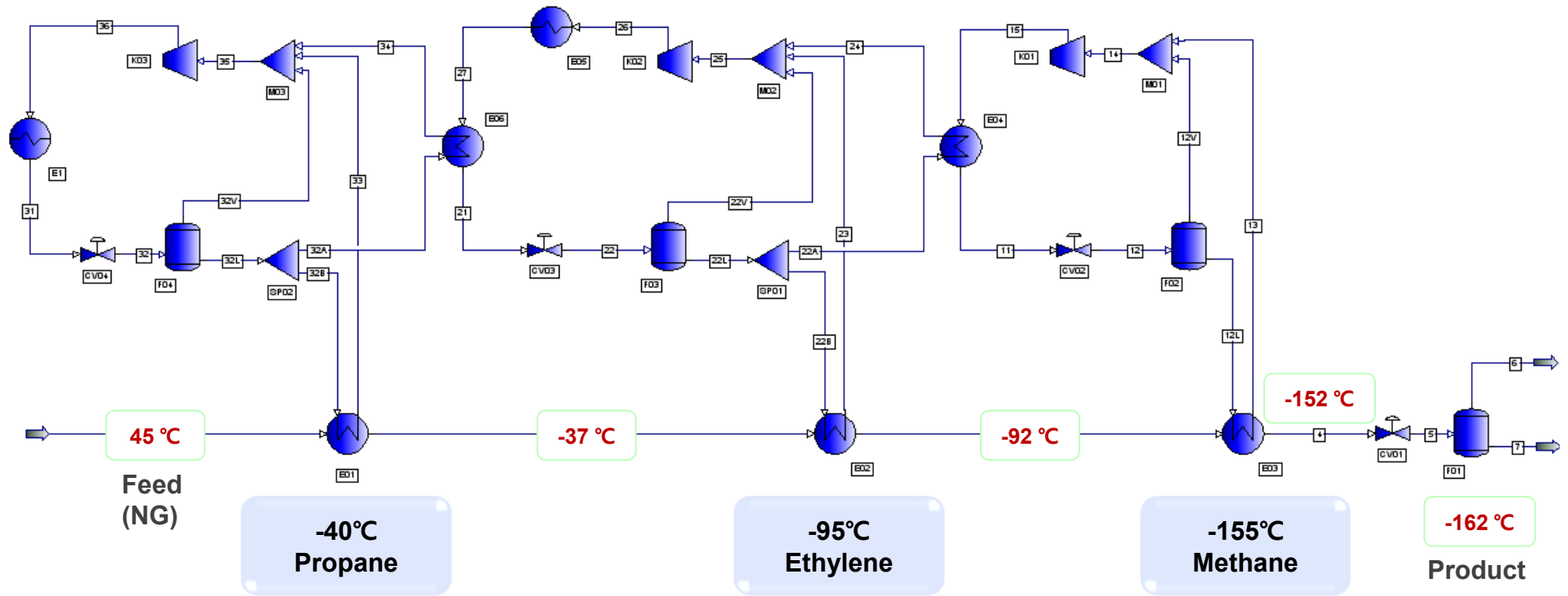
# Vapor Pressure for Isobutane:



# Vapor Pressure for Normal Butane:



# Propane-Ethylene-Methane 냉동 사이클:





**THANK YOU**

