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1 **Modeling solubility of nitrogen in clean fire extinguishing agent by Peng-Robinson**  
2 **equation of state and a correlation of Henry's law constants**

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10  
11 **Abstract:** Nitrogen is usually used to increase the total pressure of the fluid in aircraft fire  
12 suppression bottle. The amount of nitrogen required in the bottle is a significant factor to assure  
13 complete and effective discharge into the protected area and it depends on the solubility of the  
14 nitrogen in the fire extinguishing agent. In this article, the Peng-Robinson equation of state (PR  
15 EOS) including both the classical van der Waals mixing rule and the Wong-Sandler mixing rule  
16 is utilized to correlate the Gas-Liquid Equilibrium (GLE) data from available open published  
17 literature and to analyze the solubility of nitrogen in halon alternatives such as HFC227ea  
18 (C<sub>3</sub>HF<sub>7</sub>), CF<sub>3</sub>I, FC218 (C<sub>3</sub>F<sub>8</sub>), and HFC125 (C<sub>2</sub>HF<sub>5</sub>) with Halon1301 (CF<sub>3</sub>Br) as a reference. A  
19 new method is proposed to compute the adjustable interaction parameters in the van der Waals  
20 mixing rule and in the Wong-Sandler mixing rule based on the measurements of nitrogen  
21 required to pressurize the fire suppression bottle to a specified equilibrium pressure at room  
22 temperature. Results show that the PR EOS reproduces the GLE data very well with both van  
23 der Waals mixing rule and the Wong-Sandler mixing rule and it is then utilized to predict the  
24 temperature dependence of the Henry's law constants of nitrogen dissolved in the fire  
25 extinguishing agents. The PR EOS with van der Waals mixing rule is much more appropriate for  
26 determining the Henry's constants than that with the Wong-Sandler mixing rule and the results  
27 calculated by the current model are used to establish a new correlation for the Henry's law  
28 constants. This correlation will be very helpful for fire extinguishing bottle designers to acquire  
29 the pressure-temperature relationships for the mixture of nitrogen and agents.

30 **Keywords:** PR EOS, mixing rule, nitrogen, fire extinguishing agent, solubility, Henry's law  
31 constants

32 **Nomenclature**

33	$a$	Cohesive energy parameter in the PR equation of state, Pa m <sup>6</sup> mol <sup>-2</sup>
34	$b$	Volumetric parameter in the PR equation of state, m <sup>3</sup> mol <sup>-1</sup>
35	$k$	Binary interaction parameter
36	$p$	Pressure, Pa
37	$R$	Molar gas constant, 8.31447 J mol <sup>-1</sup> K <sup>-1</sup>
38	$T$	Absolute temperature, K
39	$M$	Mole weight, g mol <sup>-1</sup>
40	$v$	Molar volume, m <sup>3</sup> /mol
41	$x$	Mole fraction in liquid phase
42	$y$	Mole fraction in vapor phase
43	$z$	Compressibility factor
44	$Z$	Total mole fraction of nirtrogen in bottle
45	$m$	Mass, kg
46	$A_{\infty}^E$	Excess Helmholtz free energy at infinite pressure
47	$G_0^E$	Excess Gibbs free energy at low pressure
48	$g$	Local composition factor in the NRTL model
49	$N$	Number of data points
50	$k_H$	Henry's law constant, MPa
51	$f$	Fugacity, Pa
52	$C$	Constants in Krause and Benson's correlation
53	<b><i>Greek letters</i></b>	
54	$\alpha$	Function of temperature in the PR equation of state
55	$\alpha_{ij}$	Binary parameter in the NRTL model
56	$\tau$	Binary interaction parameter in the NRTL model
57	$k_0$	Function of the acentric factor
58	$\varphi$	Fugacity coefficient
59	$\omega$	Acentric factor
60	<b><i>Subscripts</i></b>	
61	$c$	Critical point

62	i, j	Component i, j
63	m	Mixture
64	cal	Calculated
65	exp	Experimental
66	max	Maximum
67	min	Minimum
68	V	Vapor

69 **Abbreviations**

70	PR EOS	PR Equation of State
71	vdW	Van der Waals mixing rule
72	WS	Wong-Sandler mixing rule
73	NRTL	Non-Random Two-Liquid model
74	GLE	Gas-Liquid Equilibrium
75	PC-SAFT	Perturbed-Chain Statistical Associating Fluid Theory
76	ECS	Extended Corresponding State
77	OBJ	Objective Function

78

79 **1. Introduction**

80 As effective and nontoxic fire extinguishing agent, CF<sub>3</sub>Br (Halon1301) has been widely used  
81 in aircraft fire protection over the past six decades. However, Halon1301 has been banned from  
82 production and utilization under Montreal Protocol with global environmental concerns and high  
83 ozone depletion potentials [1]. Many researchers [2-8] have presented alternatives, such as  
84 HFC227ea, CF<sub>3</sub>I, FC218, and HFC125, to replace halon1301 in flight fire protection applications.  
85 Due to the low vapor pressure of the alternative agents, nitrogen is usually used for the purpose  
86 of shortening the discharging time. For a binary mixture of nitrogen and fire extinguishing agent,  
87 the GLE data is very important since the amount of nitrogen in the vessel plays a significant role  
88 in determining the final pressure of the vessel. However, very few GLE data for nitrogen and  
89 alternative agents are available in the open published literatures.

90 Yang et al. [2] presented a combined experimental and numerical study to determine the  
91 solubility of nitrogen and Freon-23 in alternative halon replacement agents. They applied mass

92 balance on the agent and nitrogen to obtain the total amount of nitrogen in the bottle. But the  
93 effect of dissolved nitrogen on the density of the liquid phase was neglected. Later on, Yang et  
94 al. [3, 5] also developed an extended corresponding state (ECS) model to predict the  
95 thermodynamic properties of the selected halon alternative and nitrogen mixtures using van der  
96 Waals one fluid mixing rule. Compared with the measured amount of nitrogen, a good prediction  
97 was achieved by the ECS model except for the mixture of  $N_2+CF_3I$ . Using Yang's model [2],  
98 Grosshandler et al. [7] and Gann [8] calculated the amount of nitrogen and  $CF_3H$  that needed to  
99 super-pressurize the fire suppression agents in the vessel.

100 Lim and Kim [4] conducted GLE experiments in the pressure range from 3.0 MPa to 10.0  
101 MPa and temperature range from 293.2 K to 313.2 K for the binary systems of  $N_2+Halon1301$ ,  
102  $N_2+Halon1211$ ,  $N_2+HFC227ea$ , and  $N_2+CF_3I$ . However, the values of  $k_{ij}$ ,  $A_{ij}$ ,  $A_{ji}$  in the literature  
103 [4] gave a poor prediction for the amount of nitrogen required to pressurize the alternative agent  
104 to a typical pressure of 4.2 MPa when compared with the experimental data of Yang et al. [5].

105 Kao et al. [6] used a semi-automated vapor-liquid-equilibrium static cell to measure the  
106 solubility of the nitrogen in three halon replacements. Based on PR EOS, the Henry's law  
107 constant, the weight of the nitrogen needed for super-pressurization of HFC227ea, HFC236fa,  
108 and HFC125, and pertinent isometric diagrams were calculated, respectively. However, only the  
109 bubble pressures and phase compositions for the mixture of  $N_2+HFC227ea$  were given in detail.  
110 Kim et al. [9] selected HFC22, HFC125 and HFC134a as solvent and measured the bubble  
111 pressures with temperature ranging from 283.15 K to 303.15 K to obtain the solubility of the  
112 nitrogen. Compared with their experimental data, the calculated values from Peng-Robinson-  
113 Stryjek-Vera equation of state showed good agreement except for the mixture of  $N_2+HFC125$ .

114 Many refrigerants such as saturated fluorocarbon have similar properties with halons, i.e. FC-  
115 218 is a popular refrigerant and a replacement of Halon1301. Vrabec et al. [10] reviewed binary  
116 interaction parameters of 267 binary mixtures using PR EOS, including 16 mixtures with  
117 nitrogen, of which only one binary mixture was nitrogen and Halon1301. They suggested a value  
118 of 0.076 for the interaction parameter  $k_{ij}$  at 313.2 K. Vinš and Hrubý [11, 12] used both Perturbed-  
119 Chain Statistical Associating Fluid Theory (PC-SAFT) and PR EOS to determine the solubility  
120 of the nitrogen in all fifteen one-component refrigerants including HFC125 and FC218. Their  
121 results indicated that it was difficult to confirm which equation of state showed superiority over

122 the others. The Henry's law constants for all thirteen mixtures were also correlated as a function  
123 of the reduced temperature. However, the GLE data for the mixture of N<sub>2</sub>+HFC125 and  
124 N<sub>2</sub>+FC218 were not provided. Consequently, the binary interaction parameter  $k_{ij}$  for nitrogen  
125 dissolved in HFC125 and FC218 was set to zero. Using PR EOS and the Wong-Sandler mixing  
126 rule, Claudio et al. [13] represented the similar results compared with one from other researchers,  
127 i.e. Yakoumis et al. [14], Al-Saifi et al. [15], Soo et al. [16], and Courtial et al. [17]. They  
128 concluded that by only analyzing the average deviations, complex models showed no superiority  
129 over the model of PR EOS.

130 To the best knowledge of the authors, few experimental data were available on the solubility  
131 of nitrogen in fire extinguishing agents, which were restricted to limited temperature ranges and  
132 some were suspected inaccurate. The present research focused on the solubility of nitrogen in  
133 HFC227ea, CF<sub>3</sub>I, FC218, and HFC125, with Halon1301 as a reference. Of the many equations  
134 of state available, the cubic equations such as PR EOS offered a compromise between generality  
135 and simplicity that was suitable for many purposes. They were valuable tools for correlating  
136 experimental data and were often used in technical applications. Therefore, the PR EOS was  
137 utilized to predict the solubility of the nitrogen in halon alternatives in the present paper. The  
138 available GLE data about nitrogen and fire extinguishing agents were summarized and  
139 reproduced though the PR EOS associating with van der Waals mixing rule and the Wong-  
140 Sandler mixing rule. In the current work, a new method is proposed to compute the adjustable  
141 interaction coefficient of van der Waals mixing rule and the three adjustable parameters of Wong-  
142 Sandler mixing rule for those binary mixtures of which the GLE data were not found in the  
143 literature. For the proposed new method, the measurements for the amount of nitrogen required  
144 to pressurize the fire suppression bottle to a specified equilibrium pressure at room temperature  
145 were used, which attracted more attention for the fire extinguishing system designers. Based on  
146 the interactive parameters obtained by the GLE data and the new method, a theoretical approach  
147 using PR EOS with two mixing rules was conducted to estimate the temperature dependency of  
148 the Henry's law constants. Moreover, a new simple temperature correlation for the Henry's law  
149 constants of nitrogen dissolved in CF<sub>3</sub>I and FC218 at a relatively high gas partial pressure was  
150 established.

151

152 **2. Model development**

153 Due to the limited experimental data on the solubility of nitrogen in clean fire extinguishing  
 154 agents, a theoretical model is proposed to correlate the collected GLE data. The PR EOS [18] is  
 155 one of the simplest methods for accurately calculating the GLE. So it is used in this paper and  
 156 can be written as:

$$157 \quad p = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \quad (1)$$

158 where  $p$  is the system total pressure,  $R$  is the gas constant,  $T$  is the absolute temperature and  $v$  is  
 159 the molar volume.

160 Both  $a$  and  $b$  are the characteristic parameters specific for each substance, and

$$161 \quad a = \frac{0.45724R^2T_c^2\alpha(T)}{p_c} \quad (2)$$

$$162 \quad b = \frac{0.07780RT_c}{p_c} \quad (3)$$

163 where  $p_c$  is the critical pressure,  $T_c$  is the critical temperature.

164  $\alpha(T)$  in Eq. (2) is a temperature function in the PR equation of state defined as:

$$165 \quad \alpha(T) = [1 + k_0(1 - T_r^{0.5})]^2 \quad (4)$$

166 where  $T_r = T/T_c$  is the reduced temperature.  $k_0$  can be represented by the following formulation:

$$167 \quad k_0 = 0.3746 + 1.54226\omega - 0.26992\omega^2 \quad (5)$$

168 where  $\omega$  is the acentric factor.

169 For mixtures the parameters  $a$  and  $b$  of Eq. (1) are substituted by  $a_m$  and  $b_m$ :

$$170 \quad p = \frac{RT}{v-b_m} - \frac{a_m}{v(v+b_m)+b_m(v-b_m)} \quad (6)$$

171 According to the PR EOS, two different mixing rules are applied. They are the one-parameter  
 172 van der Waals one-fluid mixing rule [19] and the Wong-Sandler mixing rule [20], respectively.

173 The one-parameter vdW mixing rule can be summarized as follows:

$$174 \quad a_m = \sum \sum x_i x_j \sqrt{a_i a_j} (1 - k_{ij}) \quad (7)$$

$$175 \quad b_m = \sum x_i b_i \quad (8)$$

176 where  $k_{ij}$  is the binary interaction coefficient that satisfies  $k_{ij}=k_{ji}$  and  $k_{ii}=k_{jj}=0$ .

177 The Wong-Sandler mixing rule for a cubic equation of state such as the PR EOS can be  
178 expressed as :

$$179 \quad b_m = \frac{\sum \sum x_i x_j (b - \frac{a}{RT})_{ij}}{1 - \sum x_i \frac{a_i}{b_i RT} - \frac{A_\infty^E}{CRT}} \quad (9)$$

$$180 \quad (b - \frac{a}{RT})_{ij} = \frac{1}{2} [(b - \frac{a}{RT})_i + (b - \frac{a}{RT})_j] (1 - k_{ij}) \quad (10)$$

$$181 \quad \frac{a_m}{b_m} = \sum x_i \frac{a_i}{b_i} + \frac{A_\infty^E}{C} \quad (11)$$

182 In Eq. (9),  $C$  is a constant (-0.62323) for the PR EOS,  $k_{ij}$  is an interaction parameter,  $x_i$  and  
183  $x_j$  represent the mole fraction of component  $i$  and  $j$  in the liquid phase or in the vapor phase.  $A_\infty^E$   
184 is an excess Helmholtz free energy model at infinite pressure, which can be calculated assuming  
185 that  $A_\infty^E = G_\infty^E$ , where  $G_\infty^E$  is the excess Gibbs free energy. Several models [13, 17, 19] were  
186 reported to determine  $G_\infty^E$ , whereas in the current study, the NRTL model [21] is employed:

$$187 \quad \frac{A_\infty^E}{RT} = \sum x_i \left[ \frac{\sum x_j G_{ji} \tau_{ji}}{\sum x_k G_{ki}} \right] \quad (12)$$

$$188 \quad G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \quad (13)$$

$$189 \quad \tau_{ji} = A_{ji} / RT \quad (14)$$

$$190 \quad A_{ji} = g_{ji} - g_{ii} \quad (15)$$

191 where  $G_{ji}$  is the local composition factor for the NRTL model,  $\tau_{ji}$  is the binary interaction  
192 parameter for the NRTL model,  $g_{ii}$ ,  $g_{jj}$ ,  $g_{ij}$ , and  $g_{ji}$  are related to the interaction energy between  
193 molecules  $i$  and  $j$ ,  $\alpha_{ji}$  is a non-randomness parameter which is equal to 0.3 for all the binary  
194 mixtures studied in the present work.

195 For a binary mixture, the van der Waals mixing rule includes one adjustable binary interaction  
196 coefficient ( $k_{ij}$ ) for  $a_m$ . On the other hand, the Wong-Sandler mixing rule consists of one variable  
197 binary interaction parameter ( $k_{ij}$ ) for  $b_{ij} - (a_{ij}/RT)$  and two parameters,  $A_{ij}$  and  $A_{ji}$ , included in the  
198  $G_\infty^E$  model. In summary, the proposed model combined the PR EOS, the van der Waals mixing



199 rule and the Wong-Sandler mixing rule, which is designated as PR/vdW and PR/WS in the rest  
 200 of the paper.

### 201 3. Sample data

202 In the current study, five different binary mixtures are considered, namely,  
 203  $N_2(1)+HFC227ea(2)$ ,  $N_2(1)+CF_3I(2)$ ,  $N_2(1)+FC218(2)$ ,  $N_2(1)+HFC125(2)$ , and  
 204  $N_2(1)+Halon1301(2)$ . Here, 1 refers to the component of nitrogen and 2 refers to the other  
 205 component. Pure component properties that used to calculate the parameters of the PR EOS are  
 206 listed in Table 1. And the collected GLE data for nitrogen and agent mixtures are listed in Table  
 207 2.

208 Both PR/vdW model and PR/WS model are applied to perform bubble pressure calculations  
 209 for binary mixtures. The Levenberg-Marquardt algorithm implemented in the MATLAB [26]  
 210 software is used to determine the adjustable parameter  $k_{12}$  of PR/vdW model and the parameters  
 211  $(k_{12}, A_{12}, A_{21})$  of PR/WS model. Two objective functions are defined and given by Eq. (16) and  
 212 Eq. (17):

$$213 \quad OBJ-1 = \sqrt{\frac{1}{N} \sum_{i=1}^N \left( \frac{P_{i,exp} - P_{i,cal}}{P_{i,exp}} \right)^2} \quad (16)$$

$$214 \quad OBJ-2 = \sqrt{\frac{1}{2N} \sum_{i=1}^N \left[ \left( \frac{P_{i,exp} - P_{i,cal}}{P_{i,exp}} \right)^2 + \left( \frac{y_{i,exp} - y_{i,cal}}{y_{i,exp}} \right)^2 \right]} \quad (17)$$

215 where  $N$  is the number of points in the experimental data,  $p$  is the bubble pressure, and ‘exp’ and  
 216 ‘cal’ represent experimental values and calculated values, respectively.

217 For the measured amount of nitrogen required to pressurize the binary mixture to a given  
 218 pressure [3, 5], another objective function is defined as follows:

$$219 \quad OBJ-3 = \sqrt{\frac{1}{N} \sum_{i=1}^N \left( \frac{m_{i,exp} - m_{i,cal}}{m_{i,exp}} \right)^2} \quad (18)$$

220 In Eq. (18),  $m_{exp}$  is the amount of nitrogen,  $m_{cal}$  refers to the calculated amount of nitrogen.

221 To accurately estimate the amount of nitrogen required in the fire suppression bottle, a new  
 222 method is proposed and it is determined by four control parameters such as (1) the total mass of  
 223 agent in the bottle, (2) bottle volume ( $V_{bot}$ ), (3) initial equilibrium temperature ( $T$ ) and (4) initial  
 224 equilibrium pressure ( $P$ ). Fig. 1 depicts the overall flowchart of the method in the current study.  
 225 The computational procedure mainly includes three-level iterative loops and they are (1) Z-loop

226 ( $Z$  refers to the total molar ratio of nitrogen in the binary mixture), (2)  $e$ -loop ( $e$  refers to the  
 227 evaporation rate), and (3)  $K$ -loop ( $K$  refers to the final phase equilibrium constant). Firstly, the  
 228 binary interaction coefficient  $k_{12}=0.01$  and  $Z_1=0.10$  are assumed. Then the calculations of bubble  
 229 point and dew point are carried out to ensure that the binary mixtures are in the two-phase region.  
 230 Afterwards, a flash calculation is conducted to determine the values of  $Z$ ,  $e$ ,  $K$  as well as  $m_{cal}$ .  
 231 Finally, Eq. (18) is optimized using the Levenberg-Marquardt algorithm to determine the optimal  
 232 value of  $k_{12}$ . For the adjustable parameters ( $k_{12}$ ,  $A_{12}$ ,  $A_{21}$ ) of PR/WS model, a similar calculation  
 233 is performed for the binary mixtures of  $N_2$ +HFC227ea,  $N_2$ +FC218 and  $N_2$ +HFC125.

## 234 4. Results and discussion

### 235 4.1 Binary interaction parameter

236 The optimized binary interaction parameter ( $k_{12}$ ) in the vdW mixing rule are shown in Table  
 237 3. This can be achieved by minimizing Eq. (16) and Eq. (17). The mean absolute deviation for  
 238 the pressure and mean relative deviation for the mole fraction of nitrogen in gas volume are  
 239 calculated according to the following expression:

$$240 \quad |\% \Delta p| = \frac{100}{N} \sum_{i=1}^N \left| \frac{P_{i,exp} - P_{i,cal}}{P_{i,exp}} \right| \quad (19)$$

$$241 \quad \% \Delta y_1 = \frac{100}{N} \sum_{i=1}^N \left[ \frac{y_{1,cal} - y_{1,exp}}{y_{1,exp}} \right]_i \quad (20)$$

242 Based on the PR/vdW model with the value of  $k_{12}$  determined from Eq. (16) and Eq. (17), it  
 243 is observed that the mean absolute deviations of the bubble pressure for the binary mixtures  
 244 ( $N_2$ +HFC227ea,  $N_2$ +CF<sub>3</sub>I, and  $N_2$ +halon1301) is less than 1.4% at all temperatures, as illustrated  
 245 in Table 3. For the mixture of  $N_2$ +HFC227ea, the pressure is reproduced with a maximum  
 246 deviation of 1.85% and the vapor mole fraction of nitrogen is correlated with a mean-relative  
 247 deviation less than 1.75%. For the other two mixtures of  $N_2$ +CF<sub>3</sub>I and  $N_2$ +Halon1301, the  
 248 average deviations for the pressure and the mole fraction of nitrogen were less than those in the  
 249 case of  $N_2$ +HFC227ea. However, for the binary mixture of  $N_2$ +HFC125, the PR/vdW model  
 250 correlates the experimental data with a relatively larger error. The absolute deviation of the  
 251 pressure varies from 2.5% to 6.7% and the deviation of the mole fractions of nitrogen in gas  
 252 volume ranging from 6.8% to 8.0%. The relatively large deviations for the mole fraction of  
 253 nitrogen indicates that the GLE data [9] are not suitable for estimating the binary interaction

254 coefficient ( $k_{12}$ ) of vdW mixing rule.

255 Fig. 2 shows the temperature dependence of  $k_{12}$  in vdW mixing rule for nitrogen dissolved in  
256 the fire extinguishing agents. The  $k_{12}$  value is determined by optimizing Eq. (16) and Eq. (17)  
257 except for the mixture of  $N_2+FC218$  which is optimized by minimizing Eq. (18). As shown in  
258 Fig. 2,  $k_{12}$  presents a strong linear variation for the  $N_2+HFC125$  mixture based on the  
259 experimental data of Kim et al. [9]. However,  $k_{12}$  remains almost constant for the other mixtures.  
260 The average value of  $k_{12}$  is found to be -0.00752 for  $N_2+HFC227ea$ , 0.01948 for  $N_2+CF_3I$ ,  
261 0.17789 for  $N_2+HFC125$  and 0.05715 for  $N_2+Halon1301$ , respectively. This fact infers that a  
262 general constant value of  $k_{12}$  can be performed to calculate the Henry's law constant of nitrogen  
263 in a relatively large temperature range.

264 Tables 4 and 5 have shown the results of the optimized parameters ( $k_{12}$ ,  $A_{12}$ ,  $A_{21}$ ) in the WS  
265 mixing rule based on Eq. (16) and Eq. (17), respectively. The bubble pressures for the mixtures  
266 of  $N_2+HFC227ea$ ,  $N_2+CF_3I$ ,  $N_2+HFC125$  and  $N_2+Halon1301$  are reproduced with a mean  
267 absolute deviation less than 0.7% illustrated in Table 4, and with a mean absolute deviation less  
268 than 1.0% shown in Table 5. Of the four studied mixtures, the PR/WS model reproduces the mole  
269 fractions of nitrogen in gas volume lower than the experimental values in both Tables 4 and 5.  
270 For the mole fraction of nitrogen, the average relative deviation is less than 1.5% for  
271  $N_2+HFC227ea$  whereas -0.80% , -17.5% and -6.1% for  $N_2+CF_3I$ ,  $N_2+HFC125$  and  
272  $N_2+Halon1301$ , respectively, as presented in Table 4.

273 Similarly, Table 5 demonstrates the bubble pressure calculated agrees well with the  
274 experimental data, with an average-absolute deviation less than 1.0% for all the binary mixtures.  
275 Moreover, the average relative deviation for mole fraction of nitrogen decreases from -17.5% in  
276 Table 4 to -1.1% in Table 5 for  $N_2+HFC125$ . Generally, the PR/WS model with the parameter  
277 values obtained by both Eq. (16) and Eq. (17) can reproduce the bubble pressures with close  
278 agreement to the experimental data. When correlating GLE data from the references, Eq. (17)  
279 could be a better optimization objective function since both the deviations of pressure and vapor  
280 mole fraction of nitrogen are included.

281 In reference [11], the binary interaction coefficient  $k_{12}$  was set to zero since there is no GLE  
282 data for the mixture of  $N_2+HFC25$  and  $N_2+FC218$ . As a matter of fact, Kim et al. [9] has already  
283 provided GLE data for  $N_2+HFC25$  at three different temperatures of 283 K, 293 K and 303 K.

284 On the other hand, Yang et al. [5] measured the amount of nitrogen that needed to pressurize  
285  $\text{CF}_3\text{I}$ , HFC125 and FC218 to a given pressure at 296 K. DuPont [27-28] reported the mass of  
286 nitrogen required to pressurize HFC227ea and HFC125 to 2.50 MPa and 4.20 MPa, respectively.  
287 In the present study, these experimental data [5, 27, 28] have been employed to determine the  
288 binary interaction parameter ( $k_{12}$ ) in vdW mixing rule and the parameters ( $k_{12}$ ,  $A_{12}$ ,  $A_{21}$ ) in WS  
289 mixing rule. The computational procedure is shown in Fig. 1 and results are listed in Table 6.

290 Table 6 shows the results of the adjustable parameters of the vdW mixing rule and WS mixing  
291 rule for the  $\text{N}_2+\text{HFC227ea}$ ,  $\text{N}_2+\text{CF}_3\text{I}$ ,  $\text{N}_2+\text{HFC125}$  and  $\text{N}_2+\text{FC218}$ , respectively. Considering the  
292 large errors when correlating the GLE data [9] of  $\text{N}_2+\text{HFC125}$  through PR/vdW model and  
293 PR/WS model, the adjustable parameters obtained by Eq. (18) will be used to estimate the  
294 Henry's law constants.

#### 295 4.1.1. $\text{N}_2+\text{HFC227ea}$

296 Lim and Kim [4] reported the GLE data for  $\text{N}_2+\text{HFC227ea}$  at three different temperatures of  
297 293.2 K, 303.2 K and 313.2 K and pressures from 30 to 100 bar. Kao et al. [6] also measured the  
298 nitrogen solubility in super-pressurized HFC227ea at 294 K but the data of the mole fraction for  
299 nitrogen in gas volume were not included. In addition, Yang et al. [2-3, 5] provided the amount  
300 of nitrogen required to pressurize HFC227ea to a given pressure at 296 K. In general, the data  
301 given by Lim and Kim [4] could be convenient for the analysis of the parameter  $k_{12}$  in the vdW  
302 mixing rule and the parameters ( $k_{12}$ ,  $A_{12}$ ,  $A_{21}$ ) in the WS mixing rule.

303 Fig. 3 compares the solubility of  $\text{N}_2$  in HFC227ea predicted by PR/vdW model and PR/WS  
304 model. The values for the interaction parameters in Tables 3 and 5 determined by Eq. (17) are  
305 used. It is obvious that the PR/WS model reproduces a better result than that of the PR/vdW  
306 model.

#### 307 4.1.2. $\text{N}_2+\text{CF}_3\text{I}$

308 The binary mixture of  $\text{N}_2+\text{CF}_3\text{I}$  is also investigated by Lim and Kim [4] in the pressure range  
309 of 3.0 MPa to 10.0 MPa and temperature range of 293.2 K to 313.2 K. Yang et al. [2, 3, 5]  
310 measured the amount of nitrogen required to pressurize  $\text{CF}_3\text{I}$  to 2.9 MPa and 4.2 MPa at 296 K.  
311 The binary interaction coefficient of  $k_{12}$  is 0.025 at 293 K. Fig. 4 compares the PR/vdW and the  
312 PR/WS predictions with the GLE data by Lim and Kim [4] for the solubility of  $\text{N}_2$  in  $\text{CF}_3\text{I}$ . The  
313  $k_{12}$  value in the vdW mixing rule is from Table 3 and the values of  $k_{12}$ ,  $A_{12}$ ,  $A_{21}$  in WS mixing

314 rule are from Table 5. As can be seen in Fig. 4, PR/vdW model has almost the same accuracy  
315 with PR/WS model compared with the GLE data of  $N_2+CF_3I$ .

#### 316 4.1.3. $N_2+HFC125$

317 In the current work, Kim et al. [9] provided GLE data for  $N_2+HFC25$  at three different  
318 temperatures of 283 K, 293 K and 303 K. Fig. 5 shows the comparison of GLE data with the  
319 prediction by PR/vdW model and PR/WS model, respectively. The  $k_{12}$  value in Table 3 and the  
320 values of  $k_{12}$ ,  $A_{12}$ ,  $A_{21}$  in Table 5 are obtained from Eq. (17). From Fig. 5, it is noted that both the  
321 PR/vdW and PR/WS model reproduce the GLE data by Kim et al. [9] with a large error.  
322 Therefore, it is suggested that these adjustable parameters are not suitable to predict the Henry's  
323 law constant for  $N_2$  dissolved in HFC125. Meanwhile, the values of the adjustable parameters  
324 determined by Eq. (18) and shown in Table 6 will be utilized to calculate the Henry's law constant  
325 for the mixture of  $N_2 + HFC125$ .

#### 326 4.1.4. $N_2+FC218$

327 Similarly, for the case of  $N_2+HFC125$ , no GLE data for nitrogen solubility in FC218 was  
328 found [11]. As a result,  $k_{12}$  for the Berthelot-Lorentz combining rule is suggested as 0.00685,  
329 assuming that  $k_{12}$  changes with the carbon number of n-perfluorocarbons. Here, the interaction  
330 parameter ( $k_{12}$ ) of vdW mixing rule and parameters ( $k_{12}$ ,  $A_{12}$ ,  $A_{21}$ ) of WS mixing rule are obtained  
331 through a new method (as shown in Fig.1) for  $N_2+FC218$ . The results are that  $k_{12}=0.1206$  in the  
332 vdW mixing rule and  $k_{12}=-0.106895$ ,  $A_{12}=3770.15$ , and  $A_{21}=660.39$  in the WS mixing rule. These  
333 values will be utilized to predict the Henry's law constant for  $N_2$  dissolved in FC218.

#### 334 4.1.5. $N_2+Halon1301$

335 Lim and Kim [4] carried out an experimental study for  $N_2+Halon1301$  below 9.2 MPa at 303.3  
336 K and 7.7 MPa at 313.2 K. Their data can be easily used to predict the interaction coefficient for  
337 vdW and WS mixing rules. Fig. 6 shows the comparison of GLE data between the PR/vdW  
338 model and PR/WS model for  $N_2+Halon1301$ . It shows similar behavior as the case of  
339  $N_2+HFC227ea$ . The deviation for the vapor mole fraction of nitrogen increases with the increase  
340 of the total pressure of equilibrium cell.

341 For the fire suppression bottle designers, they are interest of the amount of nitrogen required  
342 in the bottle and the bottle temperature-pressure relationships. A typical initial condition of the  
343 bottle established by the calculation process of Fig. 1 is shown in Fig. 7. As can be seen from

344 Fig. 7, with the increase of temperature, the mole fraction of nitrogen dissolved in liquid agent  
345 raises quicker than that in lower temperatures. To predict the total pressure in the bottle when the  
346 temperature varies, a flash calculation and material balance should be conducted similar to the  
347 computational procedure given in Fig. 1. More discussions about the temperature-pressure  
348 characteristics for different mixtures of nitrogen and agents can be seen in our previous work  
349 [36, 37].

#### 350 4.2 Henry's law constant

351 The Henry's law constant for nitrogen in an agent is defined as the ratio of the nitrogen  
352 fugacity to the mole fraction of nitrogen dissolved in liquid phase at infinite dilution [6]. The  
353 values of the Henry's law constant ( $k_H$ ) is computed by PR/vdW model and PR/WS model, which  
354 is defined as the following equation:

$$355 \quad k_H = \lim_{x_A \rightarrow 0} \left( \frac{f_1^V}{x_1} \right) = \lim_{x_A \rightarrow 0} \left( \frac{\phi_1^V y_1 P}{x_1} \right) \quad (21)$$

356 where  $f_1^V$  is the fugacity of nitrogen;  $\phi_1^V$  is the fugacity coefficient of nitrogen in the vapor  
357 phase.

358 The temperature-dependent Henry's law constants for nitrogen dissolved in HFC227ea,  
359 HFC125 and Halon1301 are derived from references [27-28, 30]. In the current work, both the  
360 PR/vdW model and PR/WS model are utilized to predict the Henry's law constants for all the  
361 mixtures. Fig. 8 shows the comparisons of the prediction via PR/vdW model and WS model with  
362 literatures [6, 27-28]. For the mixture of N<sub>2</sub>+HFC227ea,  $k_{12}=0.03515$  is calculated by using the  
363 experimental data from [27], which presents an average deviation of approximate 4.9% higher  
364 than the experimental values [27] in the considered temperature range from 263 K to 313 K. For  
365 the case of  $k_{12}=0$ , the mean deviation is approximate 2.1% and the calculated Henry's law  
366 constant are lower than the experimental data of DuPont [27]. Using the same GLE data or the  
367 same amount of nitrogen required, PR/vdW model shows a better prediction for the Henry's law  
368 constant than the PR/WS model, especially for the case of  $k_{12}=0.0173$ . Considering the Henry's  
369 law constant of nitrogen dissolved in HFC125, the values calculated by a universal  $k_{12}=0.039$  in  
370 vdW mixing rule agrees well with the test data of DuPont [28]. Though the PR/WS model  
371 reproduced the GLE data for all the binary mixtures quite well (see section 4.1), it still represents

372 larger deviations when compared with PR/vdW model. The reason for the inaccurate predictions  
373 of Henry's law constant by PR/WS model may be that the three parameters ( $k_{12}$ ,  $A_{12}$ ,  $A_{21}$ ) are  
374 more sensitive to temperatures. As such, the PR/vdW model is selected to estimate the Henry's  
375 law constant for nitrogen dissolved in CF<sub>3</sub>I and FC218.

376 Since no experimental values of Henry's law constant for nitrogen dissolved in CF<sub>3</sub>I and  
377 FC218 were found, a uniform value of  $k_{12}$  in vdW mixing rule is suggested to predict the Henry's  
378 law constant. Fig. 9(a) shows the results of Henry's law constants computed by PR/vdW model  
379 with  $k_{12}=0$  and  $k_{12}=0.025$  for N<sub>2</sub>+CF<sub>3</sub>I. Fig. 9(b) gives the results of Henry's law constants for  
380 N<sub>2</sub>+FC218 with  $k_{12}=0$  and  $k_{12}=0.122$ . The values predicted via PC-SAFT EOS [12] and PR  
381 EOS[12] are also shown in Fig. 9(b).

382 Krause and Benson's [12, 29] three-parameter correlation is used to predict Henry's law  
383 constants of nitrogen dissolved in CF<sub>3</sub>I and FC218 with the following expression:

$$384 \quad \ln k_H = C_1 + C_2 \frac{(1-T_r)^{1/3}}{T_r^2} + C_3 \frac{(1-T_r)^{2/3}}{T_r^2} \quad (22)$$

385 where  $C_1$ ,  $C_2$  and  $C_3$  are coefficients listed in Table 7.

386 Due to lack of available experimental values for the Henry's law constant of nitrogen dissolved  
387 in CF<sub>3</sub>I and FC218, it is not possible to obtain which  $k_{12}$  would give a better prediction  
388 compared with the real solubility of nitrogen in CF<sub>3</sub>I and FC218. Therefore, in the current study,  
389 both  $k_{12}$  values are considered to estimate the Henry's law constant.

## 390 5. Conclusions

391 The available GLE data for nitrogen dissolved in HFC227ea, CF<sub>3</sub>I, FC218, HFC125 and  
392 Halon1301 are correlated using the PR EOS associated with vdW mixing rule and WS mixing  
393 rule. Both the binary interaction coefficient  $k_{12}$  in vdW mixing rule and parameters  $k_{12}$ ,  $A_{12}$ ,  $A_{21}$   
394 in WS mixing rule are obtained based on Eq. (16) and Eq. (17).

395 Compared with the GLE experimental data, the PR/WS model shows a better correlation  
396 compared with the PR/vdW model for all the binary mixtures. For the PR/WS model, the average  
397 absolute deviation for the pressure is less than 1.5% while the average relative deviation for the  
398 mole fraction of nitrogen in gas volume is less than 1.2%. Since there are no experimental data  
399 for N<sub>2</sub>+FC218 or the data may be questionable for N<sub>2</sub>+HFC125, a new computational procedure  
400 has been proposed to determine the interaction coefficient ( $k_{12}$ ) and the parameters ( $k_{12}$ ,  $A_{12}$ ,  $A_{21}$ )

401 for N<sub>2</sub>+HFC227ea, N<sub>2</sub>+CF<sub>3</sub>I, N<sub>2</sub>+FC218 and N<sub>2</sub>+HFC125. These coefficients obtained by the  
402 new method are to be used in prediction of the Henry's law constants.

403 For the calculation of the Henry's law constants for all the binary mixtures, PR/WS model  
404 presents to a poor result than PR/vdW model. The reason may be that the parameters ( $k_{12}$ ,  $A_{12}$ ,  
405  $A_{21}$ ) in WS mixing rule are more sensitive to the temperature. Therefore, PR/vdW model is  
406 selected to predict the Henry's law constants for N<sub>2</sub>+CF<sub>3</sub>I and N<sub>2</sub>+FC218. The results of the  
407 Henry's law constant are correlated by the Krause and Benson relation as a function of reduced  
408 temperature of the fire suppression agents. These obtained correlations can be very helpful for  
409 fire suppression bottle designers to acquire the bottle pressure-temperature relationships for the  
410 mixtures of nitrogen and agents.

411

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513 Fig. 1. Flowchart for calculating the amount of nitrogen required.

514 Fig. 2. Binary interaction parameter for nitrogen and agents using PR/vdW model.

515 Fig. 3. Solubility of N<sub>2</sub> in HFC227ea at three different temperatures. Comparisons of PR/vdW  
516 model and PR/WS model with GLE data by Lim and Kim [4]. (a) prediction by PR/WS  
517 model (b) mole fraction of nitrogen in liquid HFC227ea (c) comparisons of PR/vdW model  
518 and PR/WS model.

519 Fig. 4. Solubility of N<sub>2</sub> in CF<sub>3</sub>I at three different temperatures. Comparisons of PR/vdW model  
520 and PR/WS model with GLE data by Lim and Kim [4]. (a) prediction by PR/WS model (b)

521 mole fraction of nitrogen in liquid  $\text{CF}_3\text{I}$  (c) comparisons of PR/vdW model and PR/WS  
522 model.

523 Fig. 5. Solubility of  $\text{N}_2$  in HFC125 at three different temperatures. Comparisons of PR/vdW  
524 model and PR/WS model with GLE data by Kim et al. [9]. (a) prediction by PR/WS model  
525 (b) mole fraction of nitrogen in liquid HFC125 (c) comparisons of PR/vdW model and  
526 PR/WS model.

527 Fig. 6. Solubility of  $\text{N}_2$  in Halon1301 at three different temperatures. Comparisons of PR/vdW  
528 model and PR/WS model with GLE data by Lim and Kim [4]. (a) prediction by PR/WS  
529 model (b) mole fraction of nitrogen in liquid Halon1301 (c) comparisons of PR/vdW model  
530 and PR/WS model.

531 Fig. 7. Solubility of nitrogen in Halon1301 and HFC227ea at different temperatures with a  
532 typical initial condition.

533 Fig. 8. Henry's law constant predicted by PR/vdW model and PR/WS model. (a) Henry's law  
534 constant for  $\text{N}_2+\text{HFC227ea}$  (b) Henry's law constant for  $\text{N}_2+\text{HFC125}$ .

535 Fig. 9. Henry's law constant predicted by PR/vdW model. (a) Henry's law constant for  
536  $\text{N}_2+\text{CF}_3\text{I}$  (b) Henry's law constant for  $\text{N}_2+\text{FC218}$ .

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546 Table 1. Characteristic properties of all the pure component.

547 Table 2. Details on the phase equilibrium for the systems considered here.

548 Table 3. Optimum binary interaction parameter in the vdW mixing rule with Eq. (16) and Eq.  
549 (17), respectively, and average absolute deviations for pressure and mean relative  
550 deviations for mole fraction of nitrogen in gas volume.

551 Table 4. Optimum binary interaction parameter and NRTL constants in the WS mixing rule at  
552 all temperatures studied and average absolute deviations for pressure and average relative  
553 deviation for vapor mole fraction of nitrogen, using PR/WS model with Eq. (16).

554 Table 5. Optimum binary interaction parameter and NRTL constants in the WS mixing rule at  
555 all temperatures studied and average absolute deviations for pressure and average relative  
556 deviation for vapor mole fraction of nitrogen, using PR/WS model with Eq. (17).

557 Table 6. Optimum binary interaction parameters for PR/vdW model and PR/WS model with  
558 Eq. (18).

559 Table 7. Parameters  $C_1$ ,  $C_2$  and  $C_3$  in Krause and Benson's correlation for the Henry's law  
560 constant of nitrogen dissolved in  $CF_3I$  and FC218.