The Modification of the Martin-Hou Equation of State and its application in Liquid-phase State

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Abstract

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ABSTRACT: In order to further improve the accuracy in liquid-phase state and get a simpler algorithm, the Martin-Hou Equation of State is modified after rigorous data analyses in different cases. A new revision factor h , a function of critical compression factor, is introduced into the novel M-H EOS. According to the derivation of the new EOS, only a few number of physical properties are needed to characterize a given substance, which greatly reduced the difficulty of the solution about the EOS. The novel M-H EOS is applied to argon, methane, nitrogen, propane, benzene and water to verify the applicability and the accuracy in liquid-phase state. The overall average deviation for the six substance is 1.29% by the novel M-H EOS; as a comparison, the overall average deviation is 2.51% by Hou's M-H EOS, the novel M-H EOS obviously reduces the deviation and can universally be applied to most kinds of substances.

Keywords: the M-H EOS, liquid-phase, deviation, derivation, characteristic constant.

INTRODUCTION

The research of equation of state (EOS) has always been an important field in chemical engineering thermodynamics. In general, EOS can be divided into the specific EOS for a given substance and the general

EOS for many kinds of substances[1-3]. Differently, the latter always has a wider range of applications while the precision is less than the former. Fortunately, some multi-parameter EOSs both possess a high calculation precision and a wide range of applications[4,5], although their solutions with unknown multiple-parameters are always very difficult and time-consuming. Among the large number of multi-parameter EOSs, the Benedict-Webb-Rubin[6-8] EOS (B-W-R EOS) and the Martin-Hou EOS (M-H EOS)[9-12] are very representative and excellent in terms of the accuracy. On the one hand, the calculation accuracy of the two equation in gas-phase state is approximately equivalent and high enough for the practical application while the B-W-R EOS is more accurate in liquid-phase state; On the other hand, the M-H EOS has a much broader scope of applications for most kinds of substances, even the strong polar substances such as H_2O and NH_3 and so on, while the B-W-R EOS is mainly used to calculate the properties of hydrocarbons. Moreover, the initial value conditions for the derivation of the M-H EOS are more accessible and easy to use.

Although the M-H EOS was originally put forward in the form of an empirical equation, its theoretical formula had been strictly proved[13,14] by the theory of Hard-particle Perturbation theory[15-18]. Nowadays, the main investigation of the M-H EOS has changed from the theory's exploration to the applications in different cases. First and foremost, the M-H EOS is widely applied as a specific EOS for a given substance, such as NH_3[19], H_2O[20,21], CO_2[22], natural gas[23], substances in refrigeration industry[24-26] and so on. Second, the M-H EOS is extended to achieve diversified applications[27-32], e.g., the crossover multi-parameter EOS[31,32]. Last but not least, the combination of the M-H EOS with other theories is further developed, which has solved many thorny problems in the past[33-37].

Although many satisfying researches have been achieved, the improvement of the M-H EOS itself is essentially stagnant for the application in liquid-phase state after the modified M-H EOS put forward by Hou[12]. In fact, the original M-H EOS is not very proper to the calculation in liquid-phase state[9], Hou's M-H EOS is also not as satisfactory as desired in term of the calculation precision. In general, most average deviation by Hou's M-H EOS is about 5% in liquid-phase state, while partial maximum deviations are up to 15%~20%[12]. It is still of great potential to improve the calculation accuracy of the M-H EOS in liquid-phase state.

In this work, we mainly focus on improving the accuracy of the M-H EOS in liquid-phase state. First, based on rigorous derivation and a large number of literature data analyses, the M-H EOS is further modified and the novel M-H EOS will be put forward by introducing an appropriate revision factor h , which is a function ofZ_c. Then, the novel M-H EOS will be applied to six representative substances: argon, methane, nitrogen, propane, benzene and water to verify the applicability of the novel EOS and the improvement of calculation accuracy in liquid-phase state, all the data calculated by different EOSs are listed in **the supplementary material** . At last, the conclusion about the novel M-H EOS is drawn. In the appendixes, the unknown characteristic constants in the novel M-H EOS are derived in details.

THE ESTABLISHMENT OF THE NOVEL M-H EOS

The bases of arithmetic solution of the novel M-H EOS

The M-H EOS was originally proposed as an empirical equation by Martin and Hou in 1955 on the bases of a large number of P-V-T data analyses about many kinds of substances. The initial formula can be expressed as follows[9]:

$$\mathrm{P} = \sum_{i=1}^{5} \frac{\mathrm{f_i(T)}}{(\mathrm{V-b})^{\mathrm{i}}} \quad (1)$$

with$$\mathrm{f_i\,(T) = A_i + B_i T + C_i e^{-k\frac{T}{T_c}}} \quad (2)$$

where $k = 5.475$, A_i, B_i, C_i , and b are the characteristic constants for a given substance.

Based on the universal physical properties of substances, there are 10 initial value conditions for the EOS, however, the unknown characteristic constants are up to 16[9]. Fortunately, not every characteristic constant is of equal importance or necessary, that means those less important characteristic constants can be omitted. Ref. [9] gives the detailed reasons for the simplification of the related unknown characteristic constants and the theory foundations of the initial value conditions. In this work, we just exhibit the results of the simplified $f_i\ (T\ )$ and the initial value conditions of the M-H EOS.

The simplified $f_i\ (T\ )$ are expressed as follows[9]:

$f_1\ (T) = B_1 T$ (3)

$f_2\ (T) = A_2 + B_2 T + C_2 e^{-5.475\frac{T}{T_c}}$ (4)

$f_3\ (T) = A_3 + B_3 T + C_3 e^{-5.475\frac{T}{T_c}}$ (5)

$f_4\ (T) = A_4$ (6)

$f_5\ (T) = B_5 T$ (7)

The number of the unknown characteristic constants is 10: A_1, A_2, B_2, C_2, A_3, B_3, C_3, A_4, B_5, b .

The initial value conditions of the M-H EOS are expressed as follows[9]:

$P_c = P\ (T_c, V_c)$ (8)

$PV = RT$ as $P \to 0$ (9)

$(dP/dV)_{T_c} = 0$ (10)

$\left(\frac{d^2P}{dV^2}\right)_{T_c} = 0$ (11)

$\left(\frac{d^3P}{dV^3}\right)_{T_c} = 0$ (12)

$\left(\frac{d^4P}{dV^4}\right)_{T_c} = 0$ (13)

$\left[\left(\frac{dZ}{dP_r}\right)_{T_r}\right]_{P_r=0} = -(1-Z_c) \quad \text{at} \quad T' \cong 0.8T_c$ (14)

$\left[\left(\frac{dZ}{dP_r}\right)_{T_r}\right]_{P_r=0} = 0 \quad \text{at} \quad \text{Boyle} - \text{Point Temperature } T_B$ (15)

$(dP/dT)_V = m = -M\frac{P_c}{T_c} \quad \text{at} \quad V = V_c$ (16)

$\left(\frac{d^2P}{dT^2}\right)_V = 0 \quad \text{at} \quad V = V_c$ (17)

Here, the number of the initial value conditions of the M-H EOS is also 10.

Although the arithmetic solutions of the unknown characteristic constants can be obtained by using the initial value conditions above, there still is a major defect that the accuracy calculated by the M-H EOS in liquid-phase state is too low in practical applications[9,12]. In fact, the original EOS was mostly suitable for the calculation in gas-phase state.

After the original M-H EOS was put forward, Martin[10,11] and Hou[12] independently revised the original M-H EOS in order to extend application range to liquid-phase state. Among them, the new formula modified by Hou is more prominent[12]. According to the constraint condition of gas-liquid equilibrium, Hou introduced a new initial value condition and a new characteristic constant B_4 into the original M-H EOS, which expands the range of applications to liquid-phase state[12].

The formula of Hou's M-H EOS is similar to the original M-H EOS except that $f_4(T)$ has a change which adds a new characteristic constant B_4. The new $f_4\ (T)$ is expressed as follows[12]:

$f_4\ (T) = A_4 + B_4 T$ (18)

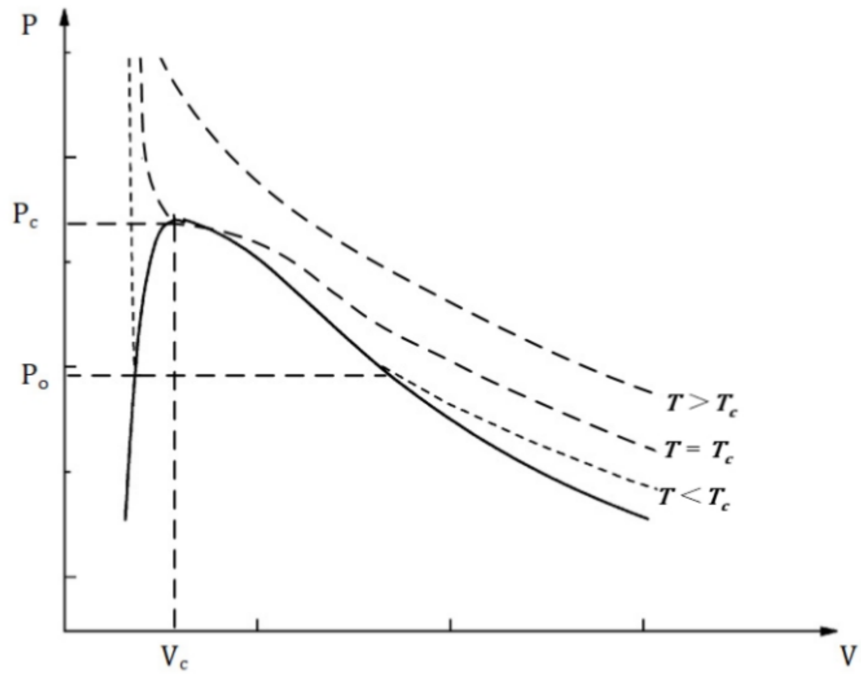

Figure 1 Pressure-Volume diagram

Due to the introduction of B_4, a new initial value condition should be introduced. Based on the thermodynamic equilibrium that the Gibbs molar free enthalpy of pure substances is equal at vapor-liquid equilibrium under a given temperature and pressure condition, the new initial value condition finally can be deduced as[12]:

$$\int_{V_l}^{V_v} PdV = P_o (V_v - V_l) \quad (19)$$

The establishment of the novel M-H EOS

After rigorous experimental calculations and a large number of data analyses about substances in liquid-phase state and on the consideration of improving the calculation accuracy and simplifying the derivation, the novel M-H EOS is put forward as follows:

$$P = \sum_{i=1}^{5} \frac{f_i(T)}{[(V-b)h]^i} \quad (20)$$

$$\text{where } h = \left[\frac{\ln(1+Z_c)}{Z_c}\right]^{Z_c} \quad (21)$$

The revision factor h , which is a function of Z_c, is mainly proposed to correct the molar volume in liquid-phase state. The structure of h is mainly established on the consideration that h is a characteristic constant for a given substance, which can minimize the interference of h in the solving of the novel M-H EOS; Meanwhile, h should balance its influence between the unknown characteristic constants and improve the calculation accuracy of the novel M-H EOS at the same time.

After analyzing Hou' M-H EOS and the novel M-H EOS, we achieve the conclusion that the initial value conditions and the unknown characteristic constants of Hou's M-H EOS are the same as the novel M-H EOS and can be used to solve the new EOS. However, h changes the relationships between the unknown characteristic constants, a new solving method should be proposed. After a large number of analyses about the novel M-H EOS and draw lessons from the derivation of Hou's M-H EOS, we achieve the solving method of the novel M-H EOS. Refer to the appendixes for the details.

DISCUSSION ABOUT THE VERIFICATION AND APPLICATION OF THE NOVEL M-H EOS

The analyses of the derivations about the unknown c haracteristic constants

The solving details of the unknown characteristic constants in the novel M-H EOS are presented in the Appendix I and Appendix II. The new revision factor h is a constant for a given substance, it avoids the difficulty of discussion about variables. However, after analyzing the derivation process of the novel M-H EOS, we found a defect that over-revision maybe exists when the state is beyond liquid-phase state because the space between molecules will be obviously affected by temperature and pressure, the influence may be amplified by $h$because the solutions of all the characteristic constants are affected by$h$ in some degree, although the design of h has been considered to balance the influence of h between the unknown characteristic constants.

In the novel M-H EOS, only a minimum amount of information is necessary to characterize a given substance. In this work, the novel M-H EOS has been applied to six representative substances: argon, methane, nitrogen, propane, benzene and water to verify its applicability and calculation deviation in liquid-phase state. The physical constants of these substances are listed in **Table 1** [38, 39] except $\frac{\text{R= } 82.055(\text{atm.cm}^3)}{(\text{K.mol})}$ and its calculated characteristic constants are listed in **Table2** .

Table 1 The physical constants of given substances

Constant	ω	b	Z_c	V_c	P_c	T_c	T_B	T'	h
Unit	/	**cm^3/mol**	/	**cm^3/mol**	**atm**	**K**	**K**	**K**	/
A_r	-0.002	16.432	0.291	74.48	48.34	150.86	382.18	116.16	0.96276
CH_4	0.011	20.811	0.286	98.83	45.80	190.55	470.54	147.30	0.96394
N_2	0.037	19.958	0.289	92.14	33.52	126.25	326.49	99.74	0.96323
C_3H_8	0.152	38.084	0.276	200.00	41.92	369.83	847.44	296.08	0.96626
C_6H_6	0.210	44.651	0.268	256.00	48.31	562.05	1211.05	453.00	0.96807
H_2O	0.344	5.396	0.229	55.950	217.75	647.14	1358.62	538.62	0.97627

Table 2 The calculated characteristic constants of given substances

Constant	A_2	B_2	C_2
A_r	-1792898.66	3441.51	872181.85
CH_4	-3084719.67	4968.95	211562.88
N_2	-1701726.30	3692.77	-10298588.83
C_3H_8	-13129207.68	12574.69	-78043586.37
C_6H_6	-27992807.70	19682.00	-173091564.06
H_2O	-8067873.54	5517.51	-164164167.15
Constant	A_3	B_3	C_3
A_r	81961752.04	-108838.45	-48738662.73
CH_4	195188464.79	-255914.35	-15910815.83
N_2	94850730.88	-150115.81	716037146.24
C_3H_8	1785767971.59	-1501172.10	12209442501.92
C_6H_6	5086922374.24	-3281019.89	35414754826.18
H_2O	429538013.90	-324584.19	8102254816.01
Constant	A_4	B_4	B_5
A_r	-1451145885.12	-1568975.71	116294369.50
CH_4	-4521170115.59	-2675888.63	365167238.20
N_2	-2636587322.41	1568766.87	239858253.73

Constant	A_2	B_2	C_2
C_3H_8	-108027874348.69	38740752.52	7451592484.28
C_6H_6	-395623942694.11	121873139.75	22580920915.78
H_2O	-10866343662.24	7209626.01	93881687.29

By substituting these parameters in **Table 2** into the novel M-H EOS, the novel M-H EOS of a given substance will be achieved. The detailed calculation results and their corresponding deviations about the six substances have been listed **in the supplementary material** [40- 42].

The comparison between the novel M-H EOS and other EOSs.

The result of volume can be calculated when temperature and pressure are given. In order to avoid imaginary root, the corresponding volumes are calculated by dichotomy using Matlab. In this work, we mainly focus on the volume calculated in liquid-phase state because the precision of volume calculated in gas-phase state is high enough by the previous M-H EOS[9,12].

Besides Hou's M-H EOS, we select the Soave-Redlich-Kwong EOS (S-R-K EOS) and the Peng-Robinson EOS (P-R EOS) as comparisons, which are very typical in general EOSs[43,44].

The S-R-K EOS is expressed as follows:

$P = \frac{\mathrm{RT}}{\mathrm{V}-\delta} - \frac{\mathrm{a(T)}}{\mathrm{V(V}+\delta)}$ (22)

where $\mathrm{a(T)} = 0.42748\frac{\mathrm{R^2T_c^2}}{\mathrm{P_c}}\left[1 + (0.48 + 1.534\omega - 0.176\omega^2)(1-\mathrm{T_r^{0.5}})\right]^2$ (23)

$\delta = 0.08664\frac{\mathrm{RT_c}}{\mathrm{P_c}}$ (24)

The P-R EOS is expressed as follows:

$\mathrm{P} = \frac{\mathrm{RT}}{\mathrm{V}-\delta} - \frac{\mathrm{a(T)}}{\mathrm{V(V}+\delta)+\delta(V-\delta)}$ (25)

where $\mathrm{a(T)} = 0.45724\frac{\mathrm{R^2T_c^2}}{\mathrm{P_c}}\left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1-\mathrm{T_r^{0.5}})\right]^2$ (26)

$\delta = 0.07780\frac{\mathrm{RT_c}}{\mathrm{P_c}}$ (27)

The deviation of volume between the calculated data (V_{Cal}) and the experiment data in literatures (V_{Exp}) is defined as:

$\mathrm{Dev.} = \left|\frac{\mathrm{V_{Exp}} - \mathrm{V_{cal}}}{\mathrm{V_{Exp}}}\right| \times 100\%$ (29)

Table 3 The average deviation by EOSs in liquid-phase region

Deviation (%)	**EOS**	A_r	CH_4	N_2	C_3H_8	C_6H_6	H_2O	**Average value**
The average deviation	**The S-R-K EOS**	2.05	2.83	3.06	8.64	12.03	41.82	*11.74
	The P-R EOS	12.17	8.74	5.80	3.68	2.04	25.62	*9.68
	Hou's M-H EOS	2.89	3.49	3.62	1.58	1.31	2.18	2.51
	The Novel EOS	1.83	1.47	1.17	0.95	0.81	1.50	1.29

*The average values are non-serviceable because the data of water by the S-R-K EOS and the P-R EOS are no practical significance.

As **Table 3** shows, the novel M-H EOS is more prominent on the deviation compared with Hou's M-H EOS. The overall average deviation by the novel M-H EOS for A_r, CH_4, N_2, C_3H_8, C_6H_6 and H_2O is 1.29%; As a comparison, the overall average deviation by Hou's M-H EOS is 2.51%, twice than those by the novel M-H

EOS. At the same time, the deviation by the novel M-H EOS is much better than those from the general EOSs: the overall average deviations for the selected five substances except water are 5.72% and 6.49% by the S-R-K EOS and the P-R EOS respectively, much higher than 1.25% by the novel M-H EOS. Meanwhile. both the S-R-K EOS and the P-R EOS are not suitable for strong polar substance water with respect to the large average deviations of 41.82% and 25.62%, respectively. The average deviation of water by our formula is just 1.50%. Therefore, the good performance on the calculation about the six representative substances exhibits the good applicability of the novel M-H EOS

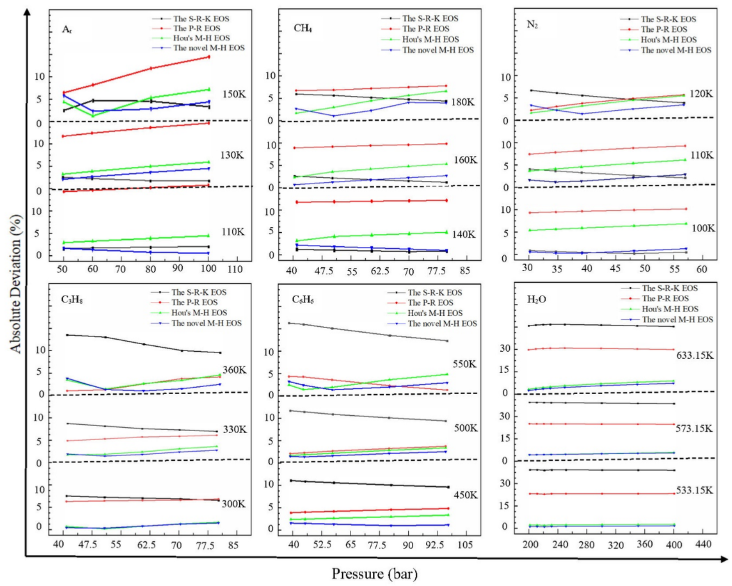

Figure 2 Diagram of deviation versus pressure and temperature

Figure 2 is drawn to illustrate the regulations of deviations versus pressure and temperature in liquid-phase region for the six substances. For each substance, the change tendencies of the deviations at three representative temperatures are drawn against the pressures. The deviations by the novel M-H EOS and Hou's M-H EOS always show a monotonic increase trend with the increase of temperature and pressure, while the deviations by the novel M-H EOS are smaller than those by Hou's M-H EOS, agreeing well with the data in **Figure 2** and**the supplementary material** . The deviations by the S-R-K EOS always show a gradually increase trend with the rising temperature and a decrease trend with the rising pressure while the deviations by the P-R EOS show an opposite trend, and the variation range of the deviation by the two EOSs is much broader than those by the novel M-H EOS Therefore, the novel M-H EOS is more prominent than the other EOSs.

There is another significant phenomenon about the change trend of deviations associated with the eccentric factor (ω), which has the order of$\omega_{A_r}<\omega_{CH_4}<\omega_{N_2} < \omega_{C_3H_8}< \omega_{C_6H_6}< \omega_{H_2O}$. The deviations calculated by the S-R-K EOS monotonically increase while the deviations by the P-R EOS monotonically decrease with the increase ofωexcept water. The phenomenon is obviously implicated in **Figure 2** and **Table 3** , the average deviations of A_r, CH_4, N_2, C_3H_8, C_6H_6 are 2.05%, 2.83%, 3.06%, 8.64%, 12.03% by the S-R-K EOS, and they are 12.17%, 8.74%, 5.80%, 3.68%, 2.04% by the P-R EOS. The deviations of the five substances by the novel M-H EOS are 1.83%, 1.47%, 1.17%, 0.95%, 0.81%, and the effect of ω for the novel M-H EOS is not obvious.

CONCLUSION

Because of the application defects of the original and Hou's M-H EOS in the liquid phase state, the novel M-H EOS is put forward. A new revision factor h is introduced into Hou's EOS to reduce the deviations of calculation in liquid-phase state. According to the new detailed derivation of the novel M-H EOS in the appendixes, only a few number of physical properties are needed to characterize a given substance. The novel M-H EOS has been applied to six representative substances to verify its calculation precision in liquid-phase state. According to the analyses of the data by the above EOSs, the overall average deviation for the selected six representative substances reduces from 2.51% by Hou's M-H EOS to 1.29% by the novel M-H EOS, the deviation of Hou's M-H EOS is almost twice than the deviation by the novel M-H EOS. The deviation of the novel M-H EOS is much better than those by the general EOS's: the overall average deviations for A_r, CH_4, N_2, C_3H_8, C_6H_6 are 5.72% and 6.49% by the S-R-K EOS and the P-R EOS compared with 1.25% by the novel M-H EOS. Meanwhile, both the S-R-K EOS and the P-R EOS are not suitable for the strong polar substance water with respect to the average deviations by the two EOSs, which are 41.82% and 25.62% respectively, as a comparison, the average deviation by the novel M-H EOS is 1.50%, it shows an excellent performance on the computation about water by the novel M-H EOS. Therefore, the conclusion can be drawn that the precision is obviously improved in liquid-phase by applying the novel M-H EOS.

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Supplementary material

The supplemented data of the solution by the novel M-H EOS, Hou's modified M-H EOS, the S-R-K EOS and the P-R EOS.

Notes

$$\text{Ai, Bi, Ci,}-\text{Characteristic constants}$$

G−Gibbs molar free enthalpy

$$\text{A}-\text{Helmholtz molar free energy}$$

$$\text{P}-\text{Pressure, atm}$$

$$\frac{\text{R}-\text{Gas constant, } 82.055\left(\text{atm.cm}^3\right)}{(\text{K.mol})}$$

$$\text{T}-\text{Absolute temperature, K}$$

$$\text{T}_\text{B}-\text{ Boyle temperature, K}$$

$$\text{V}-\text{Molar volume,}\frac{\text{cm}^3}{\text{mol}}$$

$$\text{Z}-\text{Compressibility factor,PV/RT}$$

$$\text{b}-\text{Characteristic constants,}\frac{\text{cm}^3}{\text{mol}}$$

$$\omega-\text{Characteristic constants, Acentric factor}$$

h−Characteristic constants, revision factor

m−The slope of critical molar volume line in P ∼ T chart, at $V = V_c$

Subscript:

c−Critical value

l−Saturated liquid phase

v−Saturated gas phase

o−Vapor pressure data point, e.g. T_o,P_o.

r−Reduced property, e.g. $T_r = \frac{T}{T_c, P_r = \frac{P}{P_c}}$.

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APPENDIX I

THE SOLVING PROCESS OF THE NOVEL M-H EOS

The solution of $f_i(T_c)$

Based on the initial value condition of Eq. (9), the solutions of $f_1(T)$ can be deduced as follows:

$\mathrm{f_1(T) = RT}$ (A1)

Based on the initial value conditions of Eqs. (8), (10), (11) and (13), the solutions of other $f_i(T_c)$ can be deduced as follows:

$\mathrm{f_2(T_c) = 9P_c[(V_c-b)h]^2 - 3.8RT_c(V_c-b)h}$ (A2)

$\mathrm{f_3(T_c) = 5.4RT_c[(V_c-b)h]^2 - 17P_c[(V_c-b)h]^3}$ (A3)

$\mathrm{f_4(T_c) = 12P_c[(V_c-b)h]^4 - 3.4RT_c[(V_c-b)h]^3}$ (A4)

$\mathrm{f_5(T_c) = 0.8RT_c[(V_c-b)h]^4 - 3P_c[(V_c-b)h]^5}$ (A5)

The solution of *b*

By substituting the solutions about $f_i(T_c)$: Eqs. (A1) - (A5) into Eq. (20) at the critical point, and based on Eq. (12), *b* can be solved as the following equation:

$\mathrm{b = V_c - \frac{RT_c}{5P_c h}}$ (A6)

It also can be expressed in the form of the critical compression factor:

$\mathrm{b = V_c - \frac{RV_c}{5Z_c h}}$ (A7)

Similar to the treatment in the original M-H EOS, the coefficient β is introduced into Eq. (A7)[9]. In order to verify whether the new coefficient β was valid, a large number of calculations have been carried out rigorously and the final data presented in **the support information** have verified its feasibility. The new formula of *b* is expressed as follows:

$\mathrm{b} = \mathrm{V_c} - \frac{\beta V_c}{15 Z_c h}$ (A8)

β is a constant for a given substance which depends upon Z_c, the value of β is between 3.0 and 4.0[9]. **Figure A1** shows the relationship between β and β/Z_c, it also can be expressed as the following formula:

$$\beta = -31.883\mathrm{Z_c^2} + 20.533\mathrm{Z_c} \text{(A9)}$$

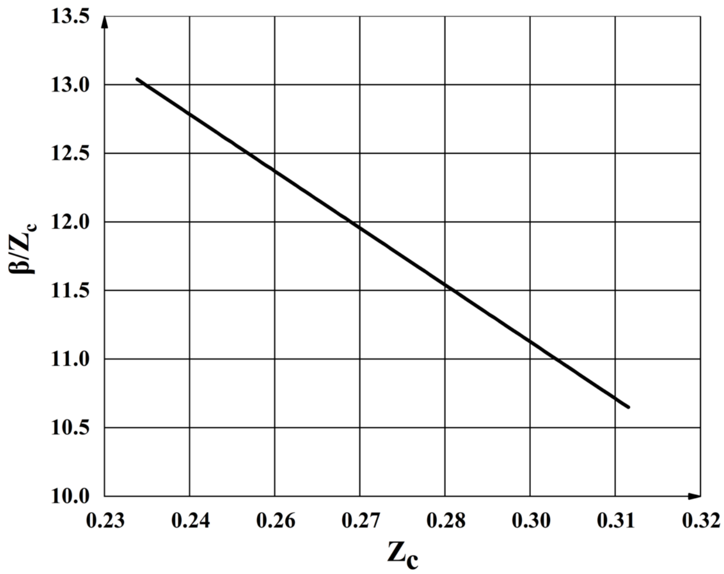


Figure A1 Relation schema between β/$Z_c$and Z_c [12]

The solution of B_5,C_2, B_2, andA_2

In the light of Eqs. (7) and (A5), B $_5$ can be solved as follows:

$$\mathrm{B_5} = \frac{\mathrm{f_5(T_c)}}{\mathrm{T_c} = \frac{\{0.8\mathrm{RT_c}[(\mathrm{V_c}-\mathrm{b})\mathrm{h}]^4 - 3\mathrm{P_c}[(\mathrm{V_c}-\mathrm{b})\mathrm{h}]^5\}}{\mathrm{T_c}}} \text{(A10)}$$

Each term of Eq. (20) is multiplied by (V-b)h and then substitute V=RTZ/Pinto the obtained formula, considering$B$ $_1$=R , the following equation can be derived:

$$(\mathrm{ZRT}-\mathrm{Pb})\,\mathrm{h} = \mathrm{RT} + \sum_{\mathrm{i}=2}^{5} \frac{\mathrm{f_i(T)}}{\left[\left(\frac{\mathrm{ZRT}}{\mathrm{P}}-\mathrm{b}\right)\mathrm{h}\right]^{\mathrm{i}-1}} \text{(A11)}$$

Then Z differentiates partially to P at a given temperature and it finally obtains Eq. (A12):

$$\left(\frac{\mathrm{dZ}}{\mathrm{dP}}\right)_{\mathrm{T}} = \frac{\mathrm{bh} + \frac{\mathrm{f_2(T)RTZ}}{\mathrm{hP^2}\left(\mathrm{b}-\frac{\mathrm{RTZ}}{\mathrm{P}}\right)^2} - \frac{\mathrm{2f_3(T)RTZ}}{\mathrm{h^2P^2}\left(\mathrm{b}-\frac{\mathrm{RTZ}}{\mathrm{P}}\right)^3} + \frac{\mathrm{3f_4(T)RTZ}}{\mathrm{h^3P^2}\left(\mathrm{b}-\frac{\mathrm{RTZ}}{\mathrm{P}}\right)^4} - \frac{\mathrm{4f_5(T)RTZ}}{\mathrm{h^4P^2}\left(\mathrm{b}-\frac{\mathrm{RTZ}}{\mathrm{P}}\right)^5}}{\mathrm{hRT} + \frac{\mathrm{f_2(T)RTZ}}{\mathrm{hP}\left(\mathrm{b}-\frac{\mathrm{RTZ}}{\mathrm{P}}\right)^2} - \frac{\mathrm{2f_3(T)RTZ}}{\mathrm{h^2P}\left(\mathrm{b}-\frac{\mathrm{RTZ}}{\mathrm{P}}\right)^3} + \frac{\mathrm{3f_4(T)RTZ}}{\mathrm{h^3P}\left(\mathrm{b}-\frac{\mathrm{RTZ}}{\mathrm{P}}\right)^4} - \frac{\mathrm{4f_5(T)RTZ}}{\mathrm{h^4P}\left(\mathrm{b}-\frac{\mathrm{RTZ}}{\mathrm{P}}\right)^5}} \text{(A12)}$$

When P=P_r= 0, Z= 1, Eq. (A12) is simplified to the following form:

$$\mathrm{f_2\,(T)} = \left\{\left[\left(\frac{\mathrm{dZ}}{\mathrm{dP_r}}\right)_{\mathrm{P_r}=0}\right]\frac{(\mathrm{RTh})^2}{\mathrm{P_c}}\right\} - \mathrm{bRTh^2} \text{(A13)}$$

According to Eqs. (14) and (A13) at the point of$T$= T$'$, the following formula can be derived:

$$\mathrm{f_2}\left(\mathrm{T'}\right) = \mathrm{A_2} + \mathrm{B_2T'} + \mathrm{C_2}\mathrm{e}^{-5.475\frac{\mathrm{T'}}{\mathrm{T_c}}} = \left\{[\mathrm{Z_c}-1]\,\frac{\left(\mathrm{RT'}\right)^2}{\mathrm{P_c}} - \mathrm{bRT'}\right\}\mathrm{h^2} \text{(A14)}$$

According to Eqs. (15) and (A13) at the point of$T$=T_B , the following formula can be derived:

$f_2(T_B) = A_2 + B_2T_B + C_2e^{-5.475\frac{T_B}{T_c}} = -bRT_Bh^2$(A15)

Meanwhile,

$f_2(T_c) = A_2 + B_2T_c + C_2e^{-5.475} = 9P_c\left[(V_c-b)h\right]^2 - 3.8RT_c(V_c-b)h$(A16)

Combine Eqs. (A14), (A15) and (A16), the arithmetic solutions of C_2, B_2 , and A_2 are finally deduced as follows:

$$C_2 = \frac{\left[f_2(T_c)+bRT'h^2\frac{(1-Z_c)}{P_c}\right](T_B-T_c)+\left[f_2(T_c)+bRT_Bh^2\right]\left(T_c-T'\right)}{\left(e^{-5.475}-e^{\frac{-5.475T'}{T_c}}\right)(T_B-T_c)-\left(e^{\frac{-5.475T_B}{T_c}}-e^{-5.475}\right)\left(T_c-T'\right)} \text{(A17)}$$

$$B_2 = \frac{\left[-f_2(T_c)-bRT_Bh^2-C_2\left(e^{\frac{-5.475T_B}{T_c}}-e^{-5.475}\right)\right]}{T_B\ -T_c} \text{(A18)}$$

$A_2 = f_2(T_c) - B_2T_c - C_2e^{-5.475}$(A19)

The solution of B_3, A_3, C_3, A_4 and B_4

By substituting Eqs. (3), (4), (5), (7) and (18) into the novel M-H EOS (20), then the first-order and second-order differential equations about P with respect to T at a given volume can be achieved as follows:

$$\left(\frac{dP}{dT}\right)_V = \frac{R}{(V-b)h} + \sum_{i=2}^{5}\frac{B_i}{[(V-b)h]^i} + \left(-\frac{5.475}{T_c}\right)\left[\frac{C_2}{[(V-b)h]^2}+\frac{C_3}{[(V-b)h]^3}\right]e^{\frac{-5.475T}{T_c}} \text{(A20)}$$

$$\left(\frac{d^2P}{dT^2}\right)_V = \left(-\frac{5.475}{T_c}\right)^2\left[\frac{C_2}{[(V-b)h]^2}+\frac{C_3}{[(V-b)h]^3}\right]e^{\frac{-5.475T}{T_c}} \text{(A21)}$$

According to the equations about Eqs. (16), (17), (18), (A20) and (A21), the following formulas can be achieved:

$C_3 = -C_2(V_c-b)h$(A22)

$B_3 = B_3^0 - \frac{B_4}{(V_c-b)h}$(A23)

$B_3^0 = m\left[(V_c-b)h\right]^3 - R\left[(V_c-b)h\right]^2 - B_2(V_c-b)h - \frac{B_5}{[(V_c-b)h]^2}$(A24)

$A_3 = A_3^0 - \frac{B_4T_c}{(V_c-b)h}$(A25)

$A_3^0 = f_3(T_c) - B_3^0T_c - C_3e^{-5.475}$(A26)

$A_4 = f_4(T_c) - B_4T_c$(A27)

By substituting A_2, B_2, C_2; A_3, B_3, C_3; A_4, B_4 and B_5 into the novel M-H EOS (20), the following equation can be derived:

$$P = \frac{RT}{(V-b)h} + \frac{A_2+B_2T+C_2e^{-5.475\frac{T}{T_c}}}{[(V-b)h]^2} + \frac{A_3^0+B_3^0T+C_3e^{-5.475\frac{T}{T_c}}}{[(V-b)h]^3} + \frac{f_4(T_c)}{[(V-b)h]^4} + \frac{B_5T}{[(V-b)h]^5} + \frac{B_4(V-V_c)(T_c-T)}{(V_c-b)[(V-b)h]^4} \text{(A28)}$$

By introducing Eq. (A28) into Eq. (19), the definite integral about V can be derived at a given vapor pressure and temperature (P_o, T_o):

$P_o(V_v-V_l) =$

$$\left\{\begin{array}{c}\frac{RT_o}{h}\ln(V-b) - \frac{A_2+B_2T_o+C_2e^{-5.475\frac{T_o}{T_c}}}{(V-b)h^2} - \frac{A_3^0+B_3^0T+C_3e^{-5.475\frac{T_o}{T_c}}}{2(V-b)^2h^3} - \frac{f_4(T_c)}{3(V-b)^3h^4} \\ -\frac{B_5T_o}{4(V-b)^4h^5} - \frac{B_4}{h^4}\left[\frac{1}{2(V_c-b)(V-b)^2}-\frac{1}{3(V-b)^3}\right](T_c-T_o)\end{array}\right\}_{V_v}^{V_l} \text{(A29)}$$

Set $\Phi(V, B_4)$ is the function of volume and B_4, as follows:

$\Phi\ (V,B_4) = P_oV -$

$$\left\{\begin{array}{c}\frac{RT_o}{h}\ln(V-b)-\frac{A_2+B_2T_o+C_2e^{-5.475\frac{T_o}{T_c}}}{(V-b)h^2}-\frac{A_3^0+B_3^0T+C_3e^{-5.475\frac{T_o}{T_c}}}{2(V-b)^2h^3}-\frac{f_4(T_c)}{3(V-b)^3h^4}\\-\frac{B_5T_o}{4(V-b)^4h^5}-\frac{B_4}{h^4}\left[\frac{1}{2(V_c-b)(V-b)^2}-\frac{1}{3(V-b)^3}\right](T_c-T_o)\end{array}\right\} \quad (A30)$$

Set $f_{1i}(V_i)$ and $f_{2i}(V_i)$ as follows:

$$f_{1i}(V_i)=P_oV_i-\frac{RT_o}{h}\ln(V_i-b)+\frac{A_2+B_2T_o+C_2e^{-5.475\frac{T_o}{T_c}}}{(V_i-b)h^2}+\frac{A_3^0+B_3^0T+C_3e^{-5.475\frac{T_o}{T_c}}}{2(V_i-b)^2h^3}+\frac{f_4(T_c)}{3(V_i-b)^3h^4}+\frac{B_5T_o}{4(V_i-b)^4h^5} \quad (A31)$$

$$f_{2i}(V_i)=\frac{(T_c-T_o)}{h^4}\left[\frac{1}{2(V_c-b)(V-b)^2}-\frac{1}{3(V-b)^3}\right] \quad (A32)$$

Due to $\Phi(V_v,B_4)=\Phi(V_l,B_4)$, B_4 can be solved as the following formula:

$$B_4=\frac{f_{1v}(V_v)-f_{1l}(V_l)}{f_{2v}(V_v)-f_{2l}(V_l)} \quad (A33)$$

The remaining unsolved parameters: A_3, B_3 and A_4 can be solved through the application of B_4 achieved from Eq. (A33).

$$A_3=f_3(T_c)-\left\{m[(V_c-b)h]^3-R[(V_c-b)h]^2-B_2(V_c-b)h-\frac{B_5}{[(V_c-b)h]^2}\right\}T_c-C_3e^{-5.475}+\frac{B_4T_c}{(V_c-b)h} \quad (A34)$$

$$B_3=m[(V_c-b)h]^3-R[(V_c-b)h]^2-B_2(V_c-b)h-\frac{B_5}{[(V_c-b)h]^2}-\frac{B_4}{(V_c-b)h} \quad (A35)$$

$$A_4=f_4(T_c)-B_4T_c \quad (A36)$$

APPENDIX II

THE DEFINITION AND SOLUTION OF PARAMETERS APPEARING IN THE DERIVATION OF THE NOVEL M-H EOS

The definition of *m* and its solution

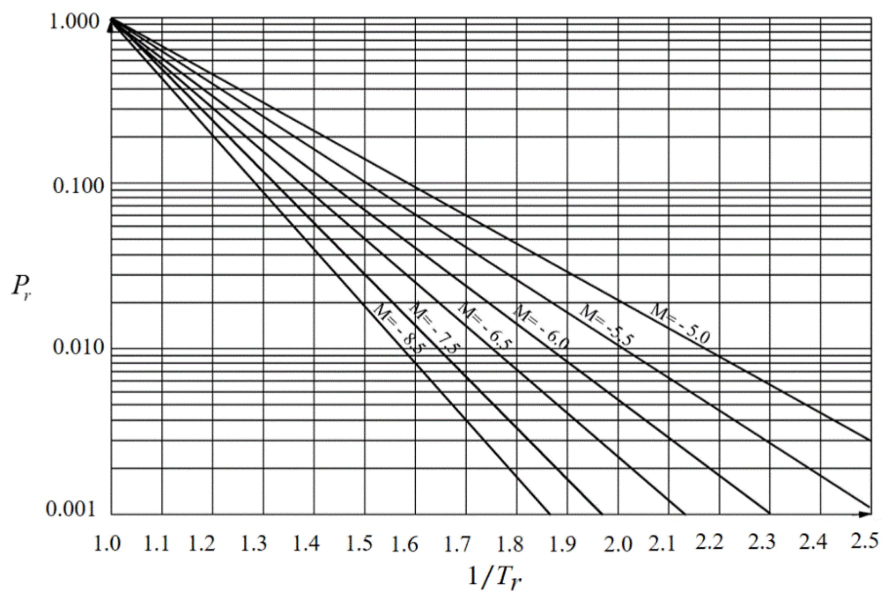


Figure A2 Reduced vapor-pressure plot[12]

The definition of m can be found in Eq. (16). The solution of m involves the solution of M and the critical property of a given substance [9,12].

M is defined as:

$\left(\frac{\mathrm{dP_r}}{\mathrm{dT_r}}\right)_{\mathrm{T}\to\mathrm{T_c}} = -\mathrm{M}$ (A37)

The value of M can be achieved by checking **Figure A2** and then m can be calculated by Eq. (16). The value of m also could be achieved by the following equation while the precision is not as good as the former method[9, 12].

$\mathrm{m} = (5.82 + 4.92\omega)\,\frac{\mathrm{P_c}}{\mathrm{T_c}}$ (A38)

ω is the eccentric factor for a given substance.

The definition of T' and its solution

T' is a constant for a given substance, which approximates to $0.8T_c$. T' can be achieved from **Figure A3** . Eq.(A39) shows the relationship between T'/T_c and Z_c [9,12]:

$\mathrm{T'/T_c}=0.9869 - 0.6751\mathrm{Z_c}$(A39)

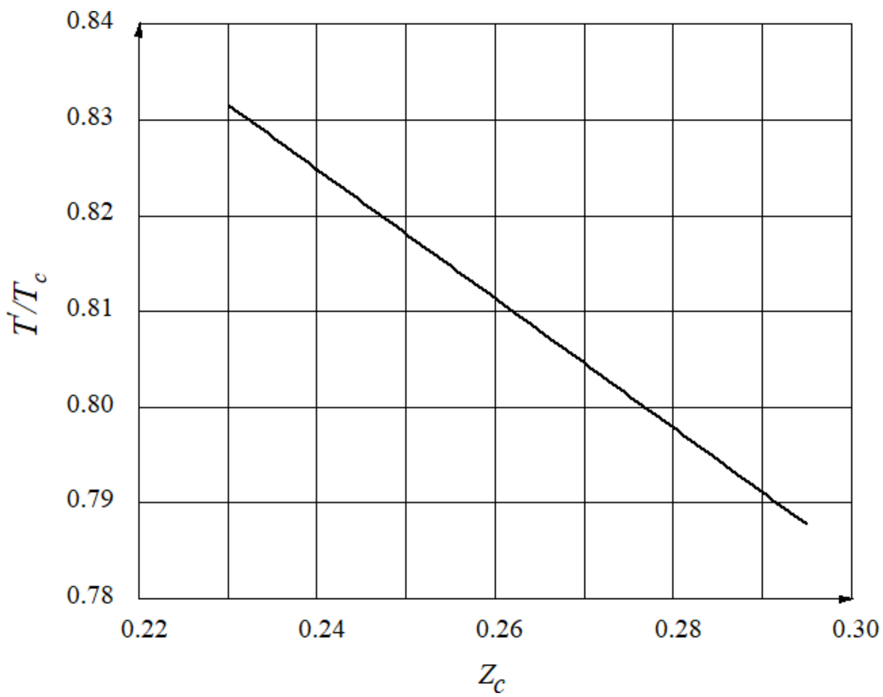


Figure A3 Relation schema between T'/T_c and Z_c [12]

The definition of T_B and the its solution

T_B is Boyle-Point Temperature and can be achieved by checking **Figure A4** . At the same time, it can be calculated by the following equation[9,12]:

$\mathrm{T_B}= 30 + 2.42\mathrm{T_c} - 5.67\times10^{-4}\mathrm{T_c^2}$(A40)

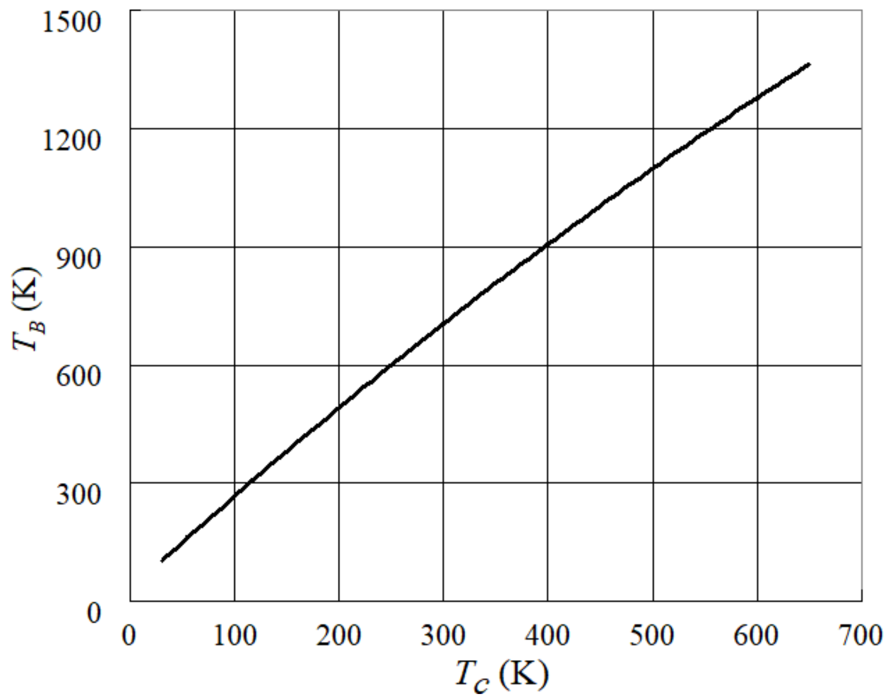
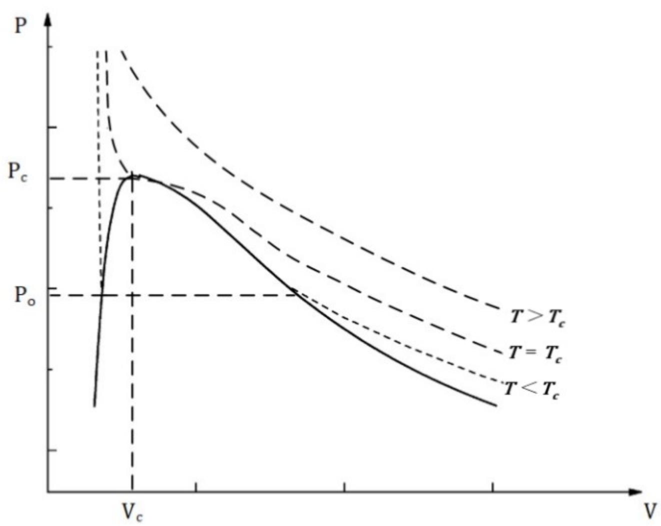
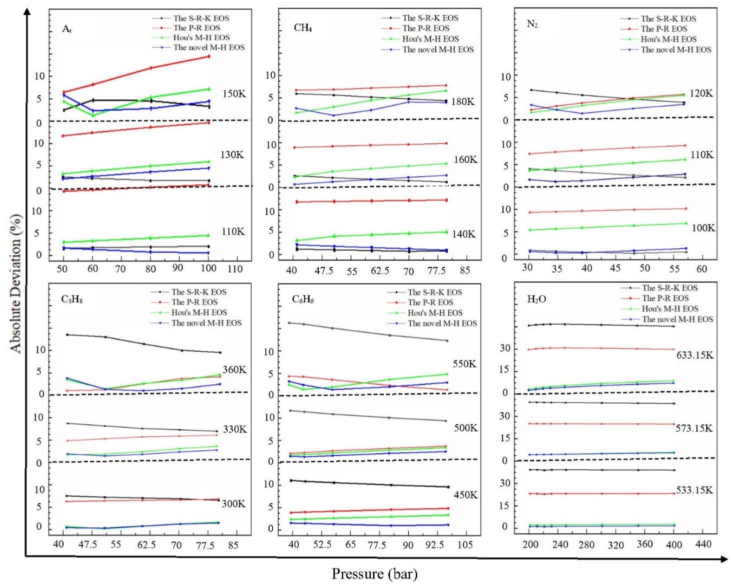


Figure A4 Relation schema between T_B and T_c [12]

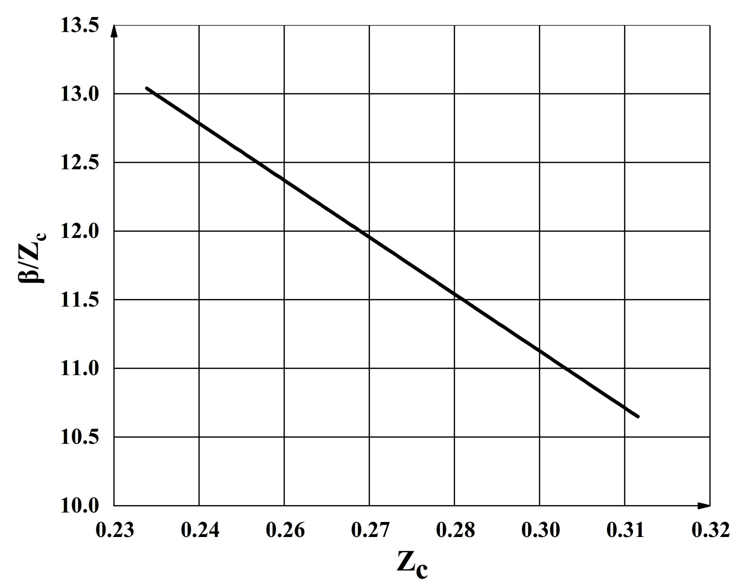
The definition of Boyle-Point Temperature is expressed as the following equation:

$\left(\frac{\partial Z}{\partial P}\right)_{T_B, P \to 0} = 0$(A41)

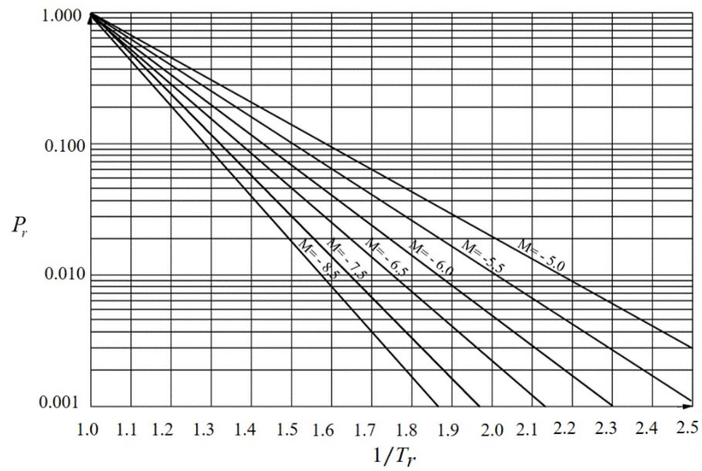


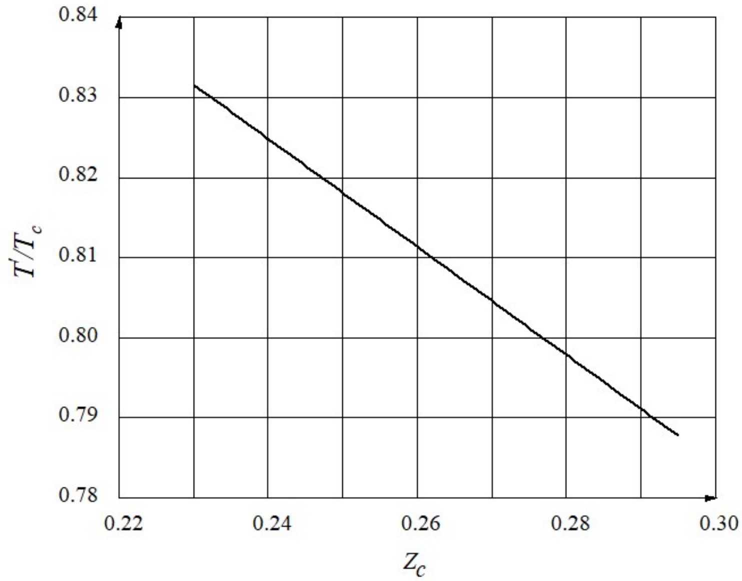


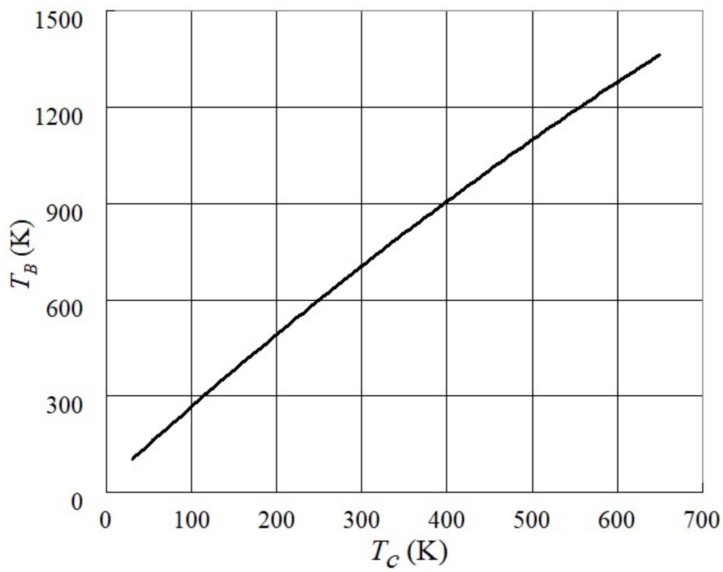
Absolute Deviation (%)
Pressure (bar)
The S-R-K EOS
The P-R EOS
Hou's M-H EOS
The novel M-H EOS
Ar
150K
130K
110K
CH4
180K
160K
140K
N2
120K
110K
100K
C3H8
360K
330K
300K
C6H6
550K
500K
450K
H2O
633.15K
573.15K
533.15K



β/Zc
Zc
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
0.23
0.24
0.26
0.27
0.28
0.30
0.31
0.32


1.000
0.100
0.010
0.001
P_r
M= - 8.5
M= - 7.5
M= - 6.5
M= - 6.0
M= -5.5
M= - 5.0
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.5
$1/T_r$


0.84
0.83
0.82
0.81
0.80
0.79
0.78
T'/T_c
0.22
0.24
0.26
0.28
0.30
Z_c


1500
1200
900
600
300
0
T_B (K)
0
100
200
300
400
500
600
700
T_c (K)