

A new general state equation of real gases

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Abstract

A new general state equation for all real gases is proposed based on the theory that the inelastic collision leads the gas molecules to liquefy on the walls of container, thereby affords the exchange of heat between the gas and the surrounding via boundary. Therefore, the state equation of gas is equivalent to the equation of gas-liquid phase equilibrium. Based on the Boltzmann distribution of energy, a new general state equation is established. Moreover, in the critical region, the gravimetric potential is introduced to the state equation. P-V-T data at saturation and isobars of 79 substances are applied for fitting the equation. The fitting results are applaudable. Furthermore, the state equation is applicable for the gas-solid phase equilibrium. A calculation result indicates that the critical region starts from ca. 30-40% and ends with ca. 60-70% of the molar fraction of liquefied portion, irrespective of the molecular mass and interactions. Hence, the critical temperature and extraordinarily large specific heat capacity as well are resulted from the interruption of heat exchange circuit between gas and the surroundings. Academically, the new state equation lays a base-stone for the derivative equations of gas specific heat capacity, sound velocity in the gas, etc.

Keywords: Gas state equation, Saturated vapor pressure, Heat transfer, Phase equilibrium, Adsorption isotherm, Catalysis, Atmosphere, Climate

Introduction

The correlation of the pressure (P), density (ρ or V_m) and temperature (T) of gas is called the gas state equation. It is one of the most basic equations over the thermodynamics academically, and the root of knowledge in the chemical engineering and energy industry. For more than a century, numerous papers have been published on the equation. However, the equations are generally empirical and engineering, i.e. single variable polynomials obtained by the simulation of experimental data. A common form of equation likes the following.

$$\frac{P}{\rho RT} = 1 + B(T)\rho + C(T)\rho^2 + \dots \quad (1)$$

$B(T)$, $C(T)$, etc. are all polynomials with T as the unique variable parameter. Moreover, for each gas, the polynomials have to be determined by the simulation of experimental

data. Although those equations of gas state have been widely applied in the chemical industry, and of course, gave the high accuracy of calculation, it is obvious that substantially they are empirical equations, lack of connection with the theory of molecular dynamics. Therefore, it is necessary to further study the molecular dynamics.

In 2022, Ni demonstrated a thermodynamic logic chain, on the basis of the molecular collision of gas and solvent, sequentially solvation, to the structure of interface, and ending with interfacial tension and internal pressure of interface. In this paper, along the logic chain, the collision of gas molecules with the container walls, and the consequence of such collision will be addressed. Based on the analysis of this “shouldn’t be” factor, a new, general and simple gas state equation will be induced.

Theory

First of all, 3 premises should be list prior to the discussion:

- 1) The main difference of gas and liquid molecules in energy is that the gas molecules possess the long-distance kinetic energy, $3/2RT$, according to the classical theory of thermodynamics, and the larger entropy, whereas the liquid molecules not. Interaction of molecules is negligible if it is a gas, since it turns into the internal energy of molecules during the evaporation.
- 2) Boundary of gas is essential due to the infinite and spontaneous decrease of entropy. Gas should be confined or shaped by a container before it becomes the object of research. Beyond the boundary, the concepts of volume and pressure are meaningless. Even the gas in a planet, it is shaped by the boundary of zero entropy. In a container, the walls not only isolate the gas from the out surrounding, but also act as a medium for the exchange of entropy between gas and surrounding.
- 3) Gas molecules collide with the walls. Classically, the overwhelming number of molecular collision is considered as the completely elastic collision, thereby the pressure on the wall is created. Inelastic collision may occur in an extremely small probability, which the gas molecules lose their long-distance kinetic energy, and stay on the surface of walls.

In the classical theory, the number of inelastic collision is so small that it is not considered in the thermodynamic research. Moreover, classical theory has never considered the boundary conditions, though, in the research field of catalysis, numerous facts have implied the liquefaction of gas case by case according to the properties of wall.

Therefore, we consider that it is essential to revise the classical theory of thermodynamics. As shown in Fig 1, the inelastic collision is of importance in the heat (entropy) transfer from gas to the surroundings. Elastic collision creates the pressure on the walls due to its continuity. Inelastic collision makes the gas molecules lose the long-distance kinetic energy, thereby liquefy on the walls. Sequentially, the liquefied molecules evaporate after gaining heat from the outside walls. It constitutes a circuit of entropy exchange. Since such a circuit is affected by the outside conditions, it is

not continuous in the scale of time. Therefore, the contribution of inelastic collision to the pressure is negligible. Moreover, according to our theory, the pure gas state does not exist in a container. Only the system of gas-liquid phase equilibrium exists. Accordingly, the state equation of pure gas does not exist. Or in the other words, the state equation of pure gas is equivalent to the equation of gas-liquid phase equilibrium.

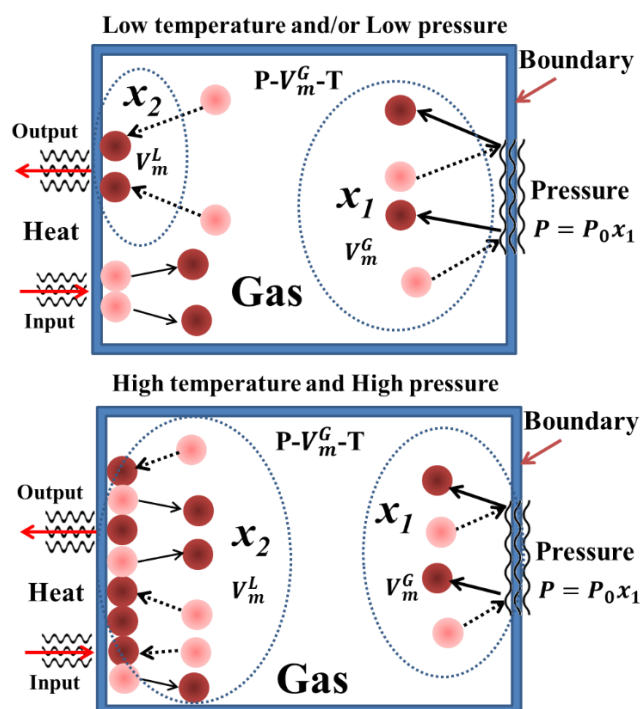


Figure 1, Schematic state of real gas

Furthermore, it is a fact that the temperature of gas will decrease if the input of heat is insufficient. Hence, it is rational to hypothesize that only the most robust gas molecules possessing the high long-distance kinetic energy may inelastically collide with walls, and then liquefy. The lost kinetic energy, and the heat of liquefaction transfer to the wall, in turn exhaust to the surrounding.

Two factors determine the portion of inelastic collisions: gas itself and wall.

For gas, according to the Boltzmann distribution of molecular energy, the molar fraction (x_2) of gas molecules that possess the high energy more than the critical ϵ_c is,

$$x_2 = \frac{\int_{\epsilon_c}^{\infty} e^{-\frac{\epsilon}{RT}} d\epsilon}{\int_0^{\infty} e^{-\frac{\epsilon}{RT}} d\epsilon} = e^{-\frac{\epsilon_c}{RT}} \quad (2)$$

The critical energy included the long-distance energy of gas molecules, and the decrease of entropy in liquefaction.

$$\Delta S = R \ln \frac{V_m^L}{V_m^G} \quad (3)$$

V_m^L and V_m^G are the molar volume of liquid and gas, respectively.

For walls, x_2 is also affected by the properties of wall. If the molecules/ ions/

atoms of wall interact with the gas molecules, the potential energy (E_p) favors the liquefaction of gas, which will move ε_c to the lower range.

Therefore, the critical energy ε_c is,

$$\varepsilon_c = -\frac{3}{2}RT - RT \ln \frac{V_m^L}{V_m^G} + E_p \quad (4)$$

The minus sign shows the lost of energy.

However, E_p is various and pertains to the research object of catalysis. Herein, we just consider the gas, namely $E_p = 0$.

The molar fraction x_1 of gas sustains the pressure, thus,

$$P = P_0 x_1 = P_0 (1 - x_2) \quad (5)$$

$$P = P_0 (1 - e^{-\frac{\varepsilon_c}{RT}}) = \frac{RT}{V_m^G} (1 - e^{-\frac{\varepsilon_c}{RT}}) \quad (6)$$

$$P = \frac{RT}{V_m^G} (1 - \frac{V_m^L}{V_m^G} e^{\frac{3}{2}}) \quad (7)$$

It should be noted that the conventional concept of saturated vapor pressure is solely employed to describe the pressure of a liquid-gas coexisting system. The term of gas pressure is used to describe the single-gas phase. However, as aforementioned, they are one thing in our theory. The unique difference is that in the coexisting system, the liquid phase is visible, and the density of liquid is measurable readily, whereas in the single-phase of gas, the liquid is invisible on the walls.

However, in the above discussion, two factors are not considered. The first is the incompletely inelastic collision, and the second, the interaction of liquid and gas molecules. In the former case, the residue of kinetics energy makes the gas molecules leave off the surface of walls and suspend on the air. In the latter case, the flying gas molecules may collide the liquid molecules. It likely occurs, as shown in Fig 1, at the high temperature and high pressure that the amount of liquid accumulated on the walls is accountable. When a gas molecule collides with a liquid molecule, it will transfer a portion of kinetic energy to the collided liquid molecule prior to the liquefaction, meanwhile the collided liquid molecule bounce to transfer the energy into the gravimetric potential. As a result, the liquid expands in volume. It is considered as the big deviation from the ideal gas near to the critical temperature.

However, concerning the calculation of gravimetric potential, a reference height is needed. Intuitively, the frequency is proportional to the density of gas, the section area of molecule, and the speed of motion. Accordingly, we assume the effective height of molecule (h_0) at 1 mol/m³ (ρ_0) is 1 m, and the correlation of effective height (h) at different density (ρ) is,

$$\frac{h}{\rho} = \pi^\alpha \frac{h_0}{\rho_0} = \pi^\alpha \quad (8)$$

Then, the total gravimetric potential is,

$$E_p^g = mgh = \frac{\pi^\alpha mg}{V_m^G} \quad (9)$$

m is the molar mass of molecule (g/mol); g is the gravity constant (9.8 m/s²); V_m^G is the molar volume of gas (dm³/mol); $\pi = 3.14$, representing the section area; α is a coefficient power of potential energy corresponding to a substance.

Hence, Eq 7 is transformed into,

$$P = \frac{RT}{V_m^G} \left(1 - \frac{V_m^L}{V_m^G} \text{Exp}\left(\frac{3}{2} - \frac{\pi^\alpha m g}{V_m^G RT}\right)\right) \quad (10)$$

Anyway, until now, we have tried many ways to express the gravimetric potential of liquid, but not yet found a more rational expression without any artificial parameter relative to Eq 10. It is disputable, but we believe that we can find the answer one day in the future.

Results and Discussion

Applicability of Eq 7 and Eq 10

We have to confess that it is just the first step forward to understand the gas state equation. At first, the wall material of container should be checked when we measure the P-V-T of gas, especially for some chemically active gases. Examples have been given in our previous paper (Ni, 2022), where the solubilities of gases in water and alkanes were discussed. Provided that water is one of container walls, the hydrogen bond of water does impact the solubility. In general, glass tube was employed for the measurements of P-V, which is inert to most of substances. Therefore, the accuracy of measurement was secured.

Molar volume of liquid phase is indispensable in our equations of gas state. It is resulted from our theory that a container must be provided to define the concepts of volume and pressure of gas. Walls of container can intercept the mass exchange, but cannot stop the exchange of heat (entropy) between gas and the surroundings. Therefore, the state equation of gas is substantially an equation of gas-liquid/solid phase equilibrium. Compared to the conventional state equations of single variable T, [2]-[40] our equations are complicated in the applications. However, academically our equations are convenient, for instance, the differentiation and integration of variables. In addition, it provides a model of heat transfer and mass transfer between gas and surroundings. It takes over the concept of adsorption which is an active behavior of catalyst. Instead, the collision-liquefaction of gas is the main cause of gas accumulating on the surface of catalyst. Furthermore, the presence of wall implies that the geometry of walls also affects P and V, especially the geometry of wall surface.

Therefore, even for a visible single-phase gas, the molar volume of liquid on the container wall must be given for Eq 7 and Eq 10. Fortunately, the coexisting (saturated) systems of liquid and gas have been widely investigated. These data provide a chance for the demonstration of Eq 7 and 10, assumed that the liquid is one of the container walls, and its molar volume is equal to those on all of the walls. In addition, the references data were considered to be accurate enough for scaling the deviation of equation.

Fig 2 shows the saturated vapor pressure of water and errors calculated with Eq 7 and Eq 10 by adopting V_m^G and V_m^L data of NIST Chemistry WebBook. For comparison, the results calculated with Buck and Tetens equations (see Wikipedia) are also shown. It should be noted that all data are obtained from NIST Chemistry WebBook if without declaration, and the error is calculated by,

$$\frac{P_{calc} - P_{Ref}}{P_{calc}} \times 100 \quad (11)$$

P_{calc} and P_{Ref} are the calculated pressure and experimental pressure of reference, respectively.

As shown in Fig 2, below the melting point (M.P.) (Wexler, 1977), Eq 7 and Eq 10 fit the data with very small error, whereas the severe deviation occurs for both of Buck equation and Tetens equation. It indicates that Eq 7 and Eq 10 are not only the equation of gas-liquid phase equilibrium, but also the equation of gas-solid phase equilibrium.

$$P = \frac{RT}{V_m^G} \left(1 - \frac{V_m^S}{V_m^G} e^{\frac{3}{2}} \right) \quad (12)$$

V_m^S is the molar volume of solid. Here, the gravitational item is negligible. The gas-solid equilibrium data (below M.P.) of He (Arp, McCarty & Friend, 1998), CFH_3 , and $n-C_5F_{12}$ are found, and the similar fitting results of Eq 12 are obtained.

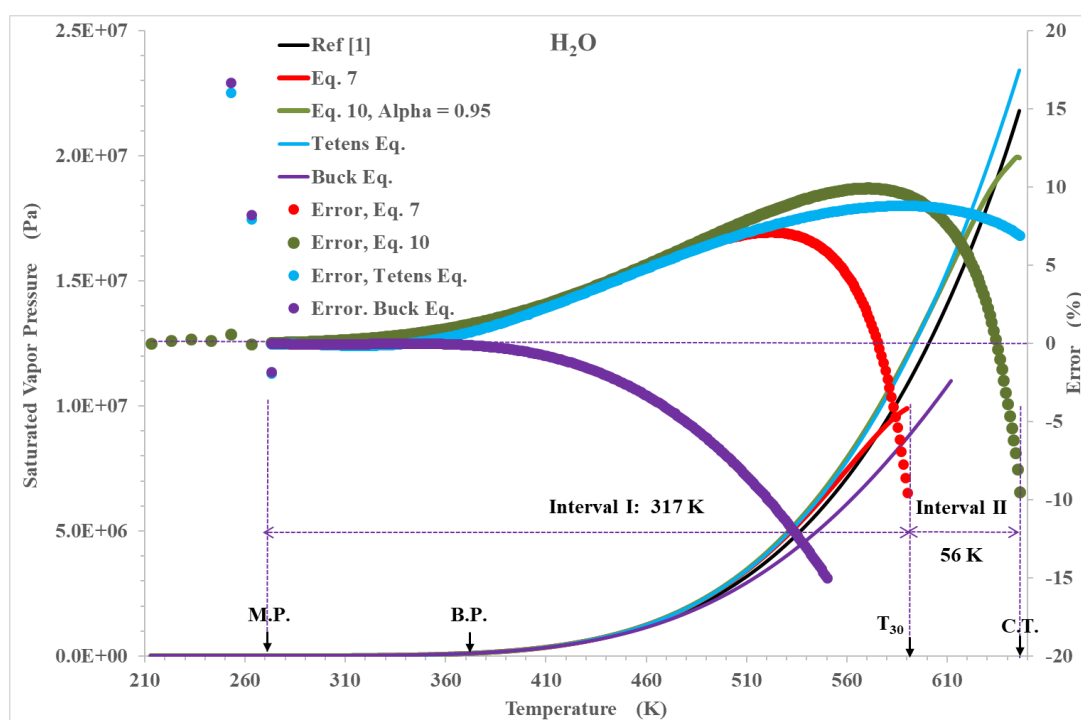


Figure 2, Water saturated vapor pressure and errors calculated with various equations

On the other hand, from M.P. to the critical temperature (C.T.), Tetens equation fits the data well with a maximum error of ca. 10% in the vicinity of 600 K. Taking $\pm 10\%$ error as a criterion, Eq 10 well fits the data by selecting $\alpha=0.95$, whereas Eq 7 falls out at 590 K, and Buck equation falls out at 510 K. It indicates that Eq 10 is the best equation. However, similar to Tetens and Buck equations, Eq 10 has an artificial factor of α which the physical meaning is unclear. Therefore, Eq 7 is the most concise and clear equation. As shown in Fig 2, the temperature range suitable for Eq 7 (Interval I) and the range required the modification of Eq 10 (Interval II) are noted from M.P. to the critical temperature (C.T.) of 647.096 K. 590 K is named after T_{30}

that the subscript 30 denotes the molar fraction of liquefaction which will be discussed in the following section. It is clear that the interval I is 317 K, whereas the interval II is 56 K. Taking the temperature range below M.P. into account, it can be concluded that, Eq 7 is suitable for the major range of temperature, only in a narrow range of temperature near to C.T., the modification is needed.

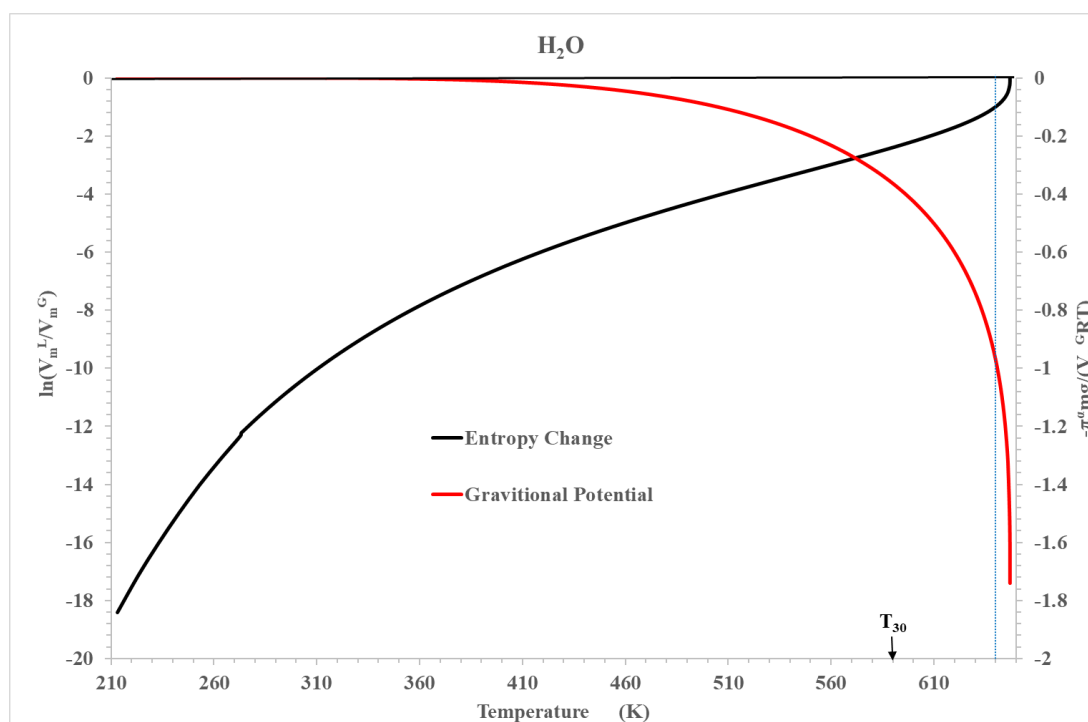


Figure 3, Entropy change and gravimetric potential vs. Temperature

Fig 3 shows the variation of entropy change of liquefaction and gravimetric potential vs. temperature. It is clear that at the lower temperature the entropy change of liquefaction dominates the variation of pressure. At T_{30} , the total energy is $-1.26 RT$. Over T_{30} , the gravimetric energy exponentially increases with the increase of temperature. At 640 K, the entropic change is equal to gravimetric potential. At the critical temperature, 647.096 K, the entropy change of liquefaction is zero since the molar volume of liquid is equal to that of gas. It indicates that the phase transition cannot occur. Meanwhile, the gravimetric potential is $-1.74RT$ and the total energy is $-0.24 RT$, namely that the long-distance kinetic energy of gas molecules is less than the gravimetric potential of system. It implies that above C.T., increasing pressure may just increase the gravimetric potential, regardless to the phase transition.

Table 1 lists the results fitting all the data of gases at saturation that recorded in NIST Chemistry WebBook. It should be noted that x_2 at M.P. is calculated by Eq 7, namely without the gravimetric item, whilst x_2 at C.T. is calculated by Eq 10 with alpha that comprehensively gives the minimum errors of pressure (see Table 2).

Table 1. Suitable temperature ranges for Eq 7 and Eq 10, and x_2 at the characteristic temperatures

Simple molecules

	Eq. 7			Eq. 10		
	T ₃₀ (K)	X ₂ at T ₃₀ (%)	Interval I (K)	C.T. (K)	X ₂ at C.T. (%)	Interval II (K)
He	3.5	27.1	2.6	5.2	64.1	1.7
Ne	36	27.8	11	44.4	61.6	8.4
Ar	124	29.1	40	151	66.8	27
Kr	173	30.3	62	209	67.6	36
Xe	239	29.6	78	290	65.4	51
H ₂	25	26.7	11	33	57.8	8
D ₂	30	26.7	11	38	60.5	8
N ₂	104	28.7	41	126	60.9	22
O ₂	127	28.8	73	154	61.2	27
F ₂	120	28.7	66	144	62.8	24
CO	110	28.2	42	133	64.7	23
H ₂ O	590	40.8	317	647	78.7	57
D ₂ O	590	42.4	314	644	73.8	54
H ₂ S	314	30.2	126	373	65.4	59
CO ₂	262	31.2	46.5	304	62.4	42
SO ₂	376	33.3	178	430	67.8	54
N ₂ O	265	31.5	83	309	67.6	44
COS	319	30.0	185	378	63.5	59
NH ₃	362	39.0	167	406	71.7	44
NF ₃	199	31.0	114	234	64.7	34
SF ₆	273	30.1	50	319	68.7	46

Alkanes

	Eq. 7			Eq. 10		
	T ₃₀ (K)	X ₂ at T ₃₀ (%)	Interval I (K)	C.T. (K)	X ₂ at C.T. (%)	Interval II (K)
CH ₄	157	28.7	66	191	61.0	34
C ₂ H ₆	267	30.2	167	305	62.4	48
C ₃ H ₈	316	31.0	230	370	65.5	54
Cyclo-C ₃ H ₆	340	31.8	195	398	66.2	58
n-C ₄ H ₁₀	366	31.3	216	425	68.8	59
i-C ₄ H ₁₀	349	30.5	235	408	64.8	59
n-C ₅ H ₁₂	409	32.1	265	470	72.2	61
i-C ₅ H ₁₂	398	31.3	285	460	67.1	62
neo-C ₅ H ₁₂	372	30.5	115	434	66.9	62
n-C ₆ H ₁₄	445	32.5	267	508	68.0	63
2-CH ₃ -C ₅ H ₁₁	435	32.7	315	498	70.0	63
Cyclo-C ₆ H ₁₂	476	30.8	196	553	65.6	77
n-C ₇ H ₁₆	478	33.6	295	540	69.9	62
n-C ₈ H ₁₈	506	34.3	290	569	68.5	63
n-C ₉ H ₂₀	533	34.6	313	595	72.8	62

n-C ₁₀ H ₂₂	557	35.8	313	618	74.1	61
n-C ₁₂ H ₂₆	598	37.2	334	658	77.4	60

Alkenes and alkyne

	Eq. 7			Eq. 10		
	T ₃₀ (K)	X ₂ at T ₃₀ (%)	Interval I (K)	C.T. (K)	X ₂ at C.T. (%)	Interval II (K)
CH ₂ =CH ₂	237	29.8	133	282	65.0	45
CH ₃ CH=CH ₂	310	30.4	222	364	68.0	54
CH ₃ C≡CH	348	32.3	177	402	67.1	54
C ₆ H ₆	486	31.8	207	562	67.3	76
CH ₃ -C ₆ H ₅	519	34.3	241	592	72.1	73

Alcohols

	Eq. 7			Eq. 10		
	T ₃₀ (K)	X ₂ at T ₃₀ (%)	Interval I (K)	C.T. (K)	X ₂ at C.T. (%)	Interval II (K)
CH ₃ OH	475	44.3	299	513	76.3	38
C ₂ H ₅ OH	464	31.4	305	515	65.4	50
C ₃ H ₇ OH	483	36.0	336	537	67.0	53
i-C ₃ H ₇ OH	460	35.5	276	506	62.3	46

Methane, Fluoro-

	Eq. 7			Eq. 10		
	T ₃₀ (K)	X ₂ at T ₃₀ (%)	Interval I (K)	C.T. (K)	X ₂ at C.T. (%)	Interval II (K)
CF ₄	193	29.0	103	228	64.5	35
CF ₃ H	264	35.5	146	299	65.8	33
CF ₂ H ₂	314	38.3	178	351	76.4	37
CFH ₃	282	39.6	154	317	75.9	35
CClF ₃	257	29.7	165	302	65.9	45
CCl ₂ F ₂	329	30.5	213	385	66.8	56
CCl ₃ F	403	30.3	240	471	66.3	68
CCl ₂ FH	389	31.4	251	451	67.5	62
CClF ₂ H	320	32.1	222	369	68.7	49

Ethane, Fluoro-

	Eq. 7			Eq. 10		
	T ₃₀ (K)	X ₂ at T ₃₀ (%)	Interval I (K)	C.T. (K)	X ₂ at C.T. (%)	Interval II (K)
CF ₃ CF ₃	252	29.8	79	293	67.2	41
CF ₃ CF ₂ H	297	32.2	126	339	68.1	43
CF ₃ CFH ₂	331	34.5	161	374	68.9	43
CF ₃ CH ₃	305	35.4	135	346	72.1	41
CF ₂ HCH ₃	343	36.0	187	386	71.1	43
CClF ₂ CH ₃	357	32.6	214	410	65.3	53
CCl ₂ HCFH ₂	412	30.6	242	477	68.8	65
CClFHCFC ₃	345	32.3	225	395	69.3	50

CCl_2HCF_3	398	31.7	232	456	67.7	58
$\text{CCl}_2\text{FCClF}_2$	421	30.4	184	487	69.9	66
$\text{CClF}_2\text{CClF}_2$	362	30.5	183	419	65.9	57
CClF_2CF_3	304	29.6	130	353	65.7	49

Propane, etc. Fluoro-

	Eq. 7			Eq. 10		
	T_{30} (K)	x_2 at T_{30} (%)	Interval I (K)	C.T. (K)	x_2 at C.T. (%)	Interval II (K)
C_3F_8	299	30.3	174	345	67.5	45
$\text{CF}_3\text{CFHCF}_3$	328	31.2	182	375	67.6	47
$\text{CF}_2\text{HCFHCF}_3$	362	31.6	192	412	70.2	50
$\text{CF}_3\text{CH}_2\text{CF}_3$	350	32.3	171	398	70.3	47
$\text{CFH}_2\text{CF}_2\text{CF}_2\text{H}$	393	32.3	201	447	68.0	54
$\text{CF}_2\text{HCH}_2\text{CF}_3$	376	32.2	206	427	69.3	51
Cyclo- C_4F_8	338	29.6	105	388	66.5	50
n- C_4F_{10}	336	28.4	192	386	67.4	50
n- C_5F_{12}	371	31.1	213	420	68.7	49

An obvious feature shown in Tab 1 is that, although the values of T_{30} are various, the x_2 values generally fall in ca.30 -40%, at meanwhile, the x_2 values at C.T. fall in the field of ca. 60 -70%. The effects of molecular mass and molecular interaction seem to be insignificant, though some substances such as H_2O , D_2O , NH_3 and CH_3OH give the high x_2 at both of T_{30} and C.T., and also, in some series like the series of diatomic gases and n-alkanes, x_2 increases with the increase of molecular mass. On the other hand, the interval I is always larger than the interval II. The difference of interval I and interval II are dependent to the types of substances, but seemingly relate to the symmetry of molecule. For the noble gases and diatomic gases, the difference is smallest. However, for other gases, the difference is large, except for some symmetric molecules such as CO_2 , SF_6 , etc. Even though, except for some noble gases and diatomic gases, most of interval II fluctuate in a very narrow range of temperature, i.e. 30-60 K, irrespective of the molecular mass and interaction. It indicates that the behavior of gas molecules is independent to the molecular mass and interaction, as x_2 increases from 30% to 60% under the conditions of high temperature and pressure.

According to our theory, x_2 denotes the molar fraction of gas molecules affording the heat transfer between the gas and surroundings. Hence, the above results indicate that at $x_2 < 30\text{-}40\%$, the behavior of gas is ideal because Eq 7 is substantially an equation of ideal gas, whereas at $x_2 > 30\text{-}40\%$, the ideal gas turns into the real gas because the gravity is not negligible. At the critical temperature, about 60-70% gas molecules have to afford the heat exchange. It implies that the critical temperature is results from the interruption of heat exchange circuit, namely that there are no more molecules to afford the heat exchange. Or in other words, the amount of liquid on the walls of container is large enough to shield the intense collision of gas molecules. That is why the specific heat capacities of gas and liquid are extraordinarily large near to the critical temperature. It is the limit of gas-liquid phase equilibrium.

In order to demonstrate the applicability of equations for the so-called pure gas phase, the isobar data of ammonia gas (Haar & Gallagher, 1978) is employed as an example for the demonstration. Since there is no gas density below B. P., and no liquid density over B. P. in the reference, the liquid density at B. P. is selected as a constant density in the calculation. Fig 4 shows the calculated pressures of gas by using the gas density at the different isobars. As shown in Fig 3 A, at 0.1 MPa isobar (B.P. = 239.55 K, $V_m^L = 0.024929 \text{ dm}^3/\text{mol}$), the errors of calculated pressure decrease from 0.23% to 0.005% as the temperature increases from 239.55 K to 760 K. At 1.0 MPa isobar (B.P. = 298.05 K, $V_m^L = 0.028186 \text{ dm}^3/\text{mol}$), the errors decrease from 7.46% to -1.29% as the temperature increases from 298.05 K to 760 K. Of course, the small errors are ascribed to the small fluctuation of liquid density under the low pressure. However, these results indicate that Eq 7 is accurate enough to describe the gas state at the pressure lower than 1.0 MPa by using a constant liquid density at B.P. Moreover, it proves that our theory is correct that there is no pure gas phase in a container. Eq 10 certainly may abate the error, but the effect is not significant. The significant effect of Eq 10 exhibits at the higher pressure. As shown in Fig 3 B, at 5.0 MPa isobar (B.P. = 362.05 K, $V_m^L = 0.035015 \text{ dm}^3/\text{mol}$), Eq 10 may control the errors within $\pm 10\%$. However, at 10.0 MPa isobar, it fails due to the great decrease of liquid density above B.P.

On the other hand, a noticeable point in Fig 4 is that, as the temperature exceeds 450 K, both the curves of calculated pressure and error trends to be straight lines. The critical temperature of NH_3 is 405.56 K, and the corresponding pressure is ca. 11.3 MPa (Haar & Gallagher, 1978). Therefore, it implies that over the critical temperature, the density of liquid may be a constant, though the pressure continues to increase. Fig 5 shows the calculated results at 1 - 12 MPa isobars, provided $V_m^L = 0.012 \text{ dm}^3/\text{mol}$. Eq 7 perfectly describes the gas state with the maximum errors within $\pm 10\%$ in the range of 450 - 760 K. It indicates that the liquid density inclines to a constant when $T > 450 \text{ K}$ and $P < 12 \text{ MPa}$. For other substances, such a law also exists, but the digits are different. It provides the convenience for the application.

Correspondingly, at 10 MPa isobar, x_2 gradually decreases from 30.6% at 400 K to 8.8% at 760 K, whilst at 12 MPa isobar, x_2 decreases from 60.4% at 410 K to 10.6% at 760 K. That is why Eq 7 is applicable.

This result is consistent to the above conclusion that the critical region is stemmed from the interruption of heat exchange circuit. Striding over the critical region, the circuit of heat exchange recovers. However, the portion of liquid due to the liquefaction of gas is too small to be observed. It is the cause that above C.T., the gas cannot be liquefied by increasing the pressure.

At last, it should be remarked that the above principles are applicable for all gases. Water and ammonia are deliberately selected for the demonstrations because they are polar molecules and there are the strong interactions of hydrogen bond in the liquid state. However, the above results of demonstration clearly indicate that water and ammonia do not exhibit their specialties. Hence, the results of demonstration verify the correctness of our theory.

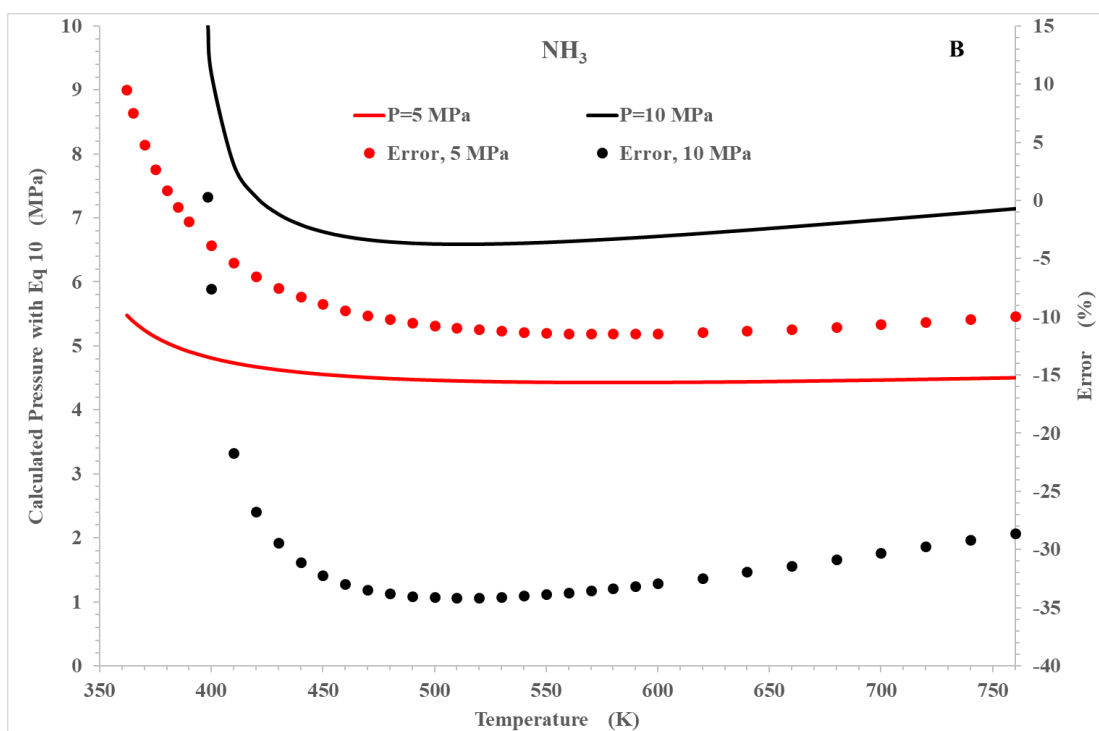
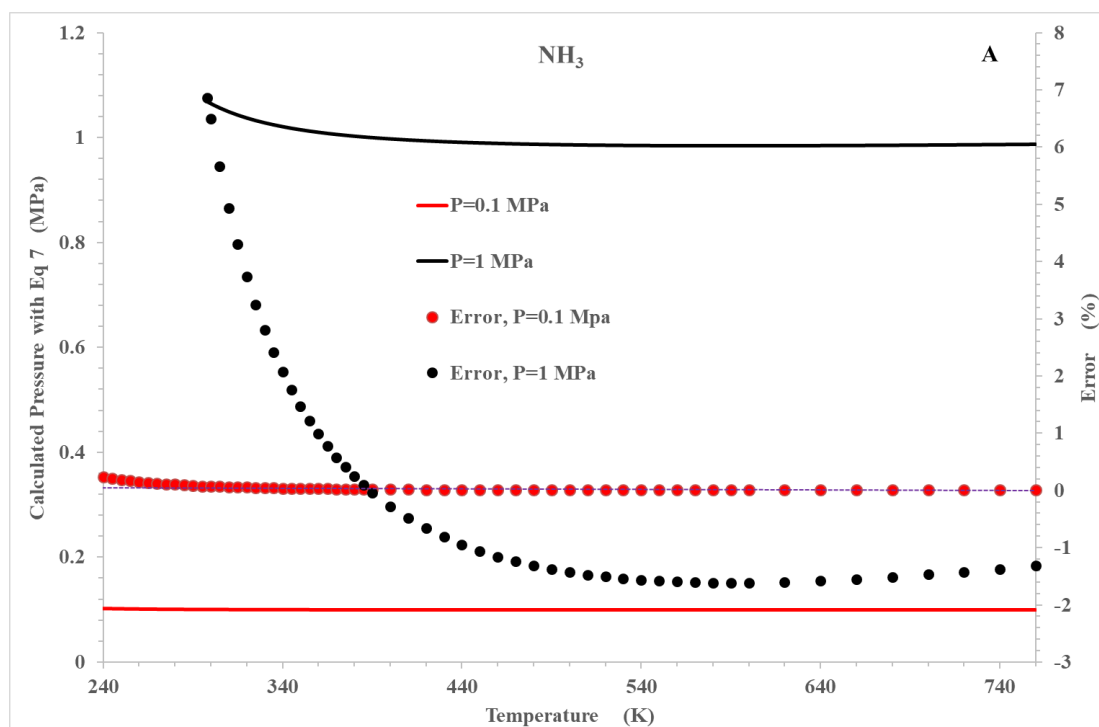


Figure 3, Pressure calculated with the isobar data of ammonia

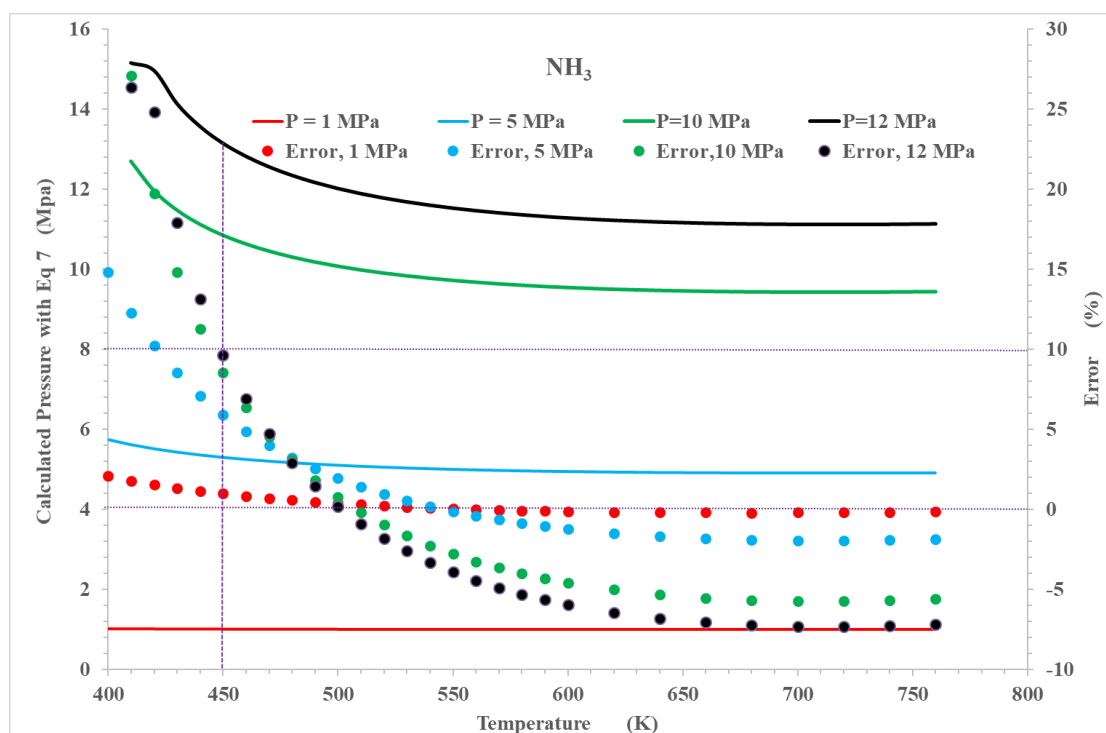


Figure 4, Calculated pressure with $V_m^L = 0.012 \text{ dm}^3/\text{mol}$ at high isobars

Determination of α in Eq 10

α is artificial, thus a shortcoming of Eq 10. Although some figures such as $-2/3$, $-1/3$, 0 , $1/3$, $2/3$ and 1.0 have been naturally appeared in some substances, as shown in Fig 5, the errors are greatly affected by the selection of α , especially near to C.T. For ethane, allowing the max. error of $\pm 10\%$, $\alpha = 0.76$ is the best choice. However, taking account all of the errors near to the critical temperature, $\alpha = 0.82$ is the best, except for one point of -24% at the critical temperature. Therefore, $\alpha = 0.82$ is selected as α with the min. errors. Obviously, the selection of α is based on the comprehensive considerations. As for the generality, $\alpha = 1.0$ is better than $\alpha = 2/3$ because the number of points is smaller that the error is beyond of $\pm 10\%$. It should be noted that the points of errors larger than $\pm 25\%$ are not shown in Fig 5 when $\alpha = 1.0$ and $\alpha = 2/3$.

Anyway, although the difference of $\alpha = 1.0$ and $\alpha = 0.82$ is large, the temperature range is just 14 K, about 4.4% of the total range of temperature (315 K), where the big errors occurs. Moreover, it is a fact that, as α of generality approaches α of mini. error, the temperature range abates. Therefore, the generality of α is meaningful.

Tab 2 lists the value of α in generality and α giving the minimum error of 79 substances that we can collect. By now, we cannot find any relationship among α , molecular mass and interaction. However, except He, Ne and Kr, the α values of the other substances are well sorted along the α values of generality. Generally, the α values of smaller molecules are smaller than 0. Among 79 substances, there are 23 substances that $\alpha = 1.0$; 16 substances that $\alpha = 0$; 14 substances that $\alpha = 1/3$; and 9 substances that $\alpha = -1/3$.

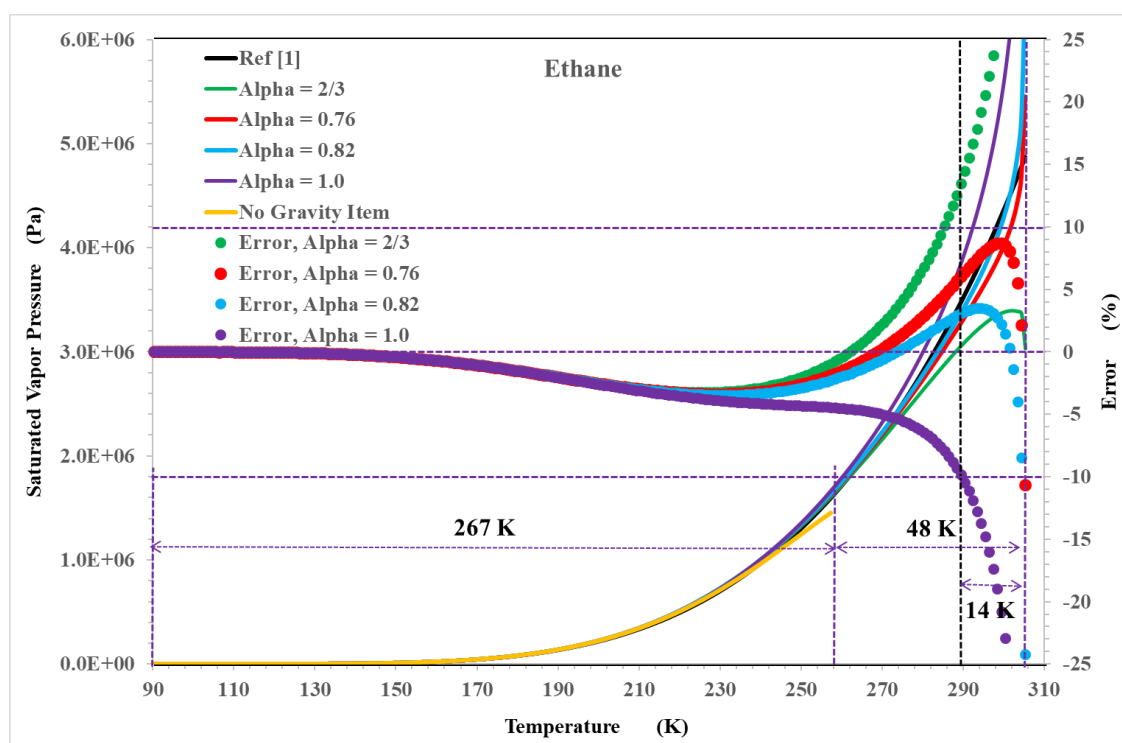


Figure 5, Effects of α on the accuracy of calculation in the critical region

Table 2, α giving the minimum error of 79 gases

He	Ne	Kr							
-1.83	-1.64	-0.87							
$\alpha = -2/3$									
Ar	Xe	F ₂							
-0.69	-0.74	-0.78							
$\alpha = -1/3$									
N ₂	O ₂	CO	N ₂ O	SF ₆	NF ₃	CF ₄	CClF ₃	CF ₃ CF ₃	
-1/3	-0.45	-0.29	-0.19	-1/3	-1/3	-0.45	-0.19	-0.23	
$\alpha = 0$									
D ₂	CO ₂	CFH ₃	CClF ₂ H	CCl ₂ F ₂	CClF ₂ CF ₃				
-0.05	0.07	-0.08	0.1	0.08	-0.06				
CClF ₂ CClF ₂	CF ₃ CFH ₂	CF ₃ CF ₂ H	C ₃ F ₈	Cyclo-C ₄ F ₈	C ₄ F ₁₀				
0.14	0.13	-0.05	-0.11	0.01	-0.01				
C ₅ F ₁₂	R227ea	R-236ea	R-236fa						
0.06	0.01	0.12	0.11						
$\alpha = 1/3$									
SO ₂	COS	CF ₃ H	CF ₂ H ₂	CCl ₃ F	CCl ₂ FH				
0.25	0.30	0.36	0.19	0.28	0.28				
CCl ₂ FCClF ₂	CCl ₂ HCF ₃	CClF ₂ CH ₃	CF ₂ HCH ₃	CF ₃ CH ₃	CCl ₂ HCFH ₂				
0.28	0.25	1/3	0.43	0.19	0.44				
R-245ca	R-245fa								
0.27	0.23								

$\alpha = 2/3$

H₂*	H₂S	CH₄	CH₂=CH₂
0.54	0.49	0.60	0.67

$\alpha = 1.0$

C₂H₆	C₃H₈	Cylco-C₃H₆	n-C₄H₁₀	i-C₄H₁₀	n-C₅H₁₂
0.82	0.88	0.80	0.95	0.96	1.0
i-C₅H₁₂	neo-C₅H₁₂	n-C₆H₁₄	2-CH₃-C₅H₁₁	Cyclo-C₆H₁₂	n-C₇H₁₆
1.0	0.95	1.09	1.05	1.05	1.13
CH₃CH=CH₂	CH₃C≡CH	C₆H₆	CH₃-C₆H₅	H₂O	D₂O
1.05	0.85	0.96	1.0	0.95	0.89
CH₃OH	C₂H₅OH	C₃H₇OH	i- C₃H₇OH	NH₃	
0.93	1.03	1.0	1.0	0.87	

$\alpha = 4/3$

n-C₈H₁₈	n-C₉H₂₀	n-C₁₀H₂₂	n-C₁₂H₂₆	CClFHCFC₃
1.19	1.20	1.22	1.26	1.25

Note: Minimum Error means comprehensively the minimum errors near the critical temperature. * Including normal, para-, ortho-hydrogen. R-218: CF₃-CF₂-CF₃; R227ea: CF₃-CHF-CF₃; R-236ea: CF₃-CHF-CHF₂; R-236fa: CF₃-CH₂-CF₃; R-245ca: CH₂F-CF₂-CF₃; R-245fa: CHF₂-CH₂-CF₃.

Conclusion

Gas must be confined in the space with a physical boundary due to the infinite and spontaneous decrease of entropy. Container is indispensable to define the concepts of gas volume and pressure. However, in the presence of container, the interaction of container walls and gas must be included in the state equation. Accordingly, a new theory is postulated. Collision is the basic interaction of gas molecules and boundary, and can be classified into two types, i.e. inelastic and elastic collision in the extremes. The inelastic collision serves the heat exchange of gas and the surroundings via walls of container by means of liquefaction, whilst the elastic collision creates the pressure due to its continuity. In light of this theory, the state equation of pure gas does not exist. Or in the other words, the state equation of gas is equivalent to the gas-liquid phase equilibrium. In addition, it is hypothesized that only the inelastic collision of gas molecules results in the liquefaction on the walls of boundary. Therefore, based on the Boltzmann distribution of molecular energy, a new and general state equation is built up. In addition, in order to solve the problem of gas-liquid molecular interaction in the critical region, the gravimetric potential is introduced to modify the state equation. P-V-T data at saturation and isobars of 79 substances that can be collected are applied for the fitting of equation. By selecting an appropriate α , the general state equation fits the data well. Moreover, it is found that the state equation is also applicable for the gas-solid phase equilibrium. A result derived from the calculation is that the critical region starts from ca. 30-40% and ends with ca. 60-70% of the molar fraction of liquefying gas, irrespective of the molecular mass and interactions. Hence,

the critical temperature and extraordinarily large specific heat capacity as well are resulted from the interruption of heat exchange circuit between gas and the surroundings. At temperature above the critical temperature, the liquid density inclines to a constant in a range of pressure. It provides the convenience for the application. On the other hand, α of substance is well sorted in the order of $-2/3$, $-1/3$, 0 , $1/3$, $2/3$, 1.0 and $4/3$. Moreover, the theory is also applicable for the liquid by replacing liquefaction with solidification. Furthermore, for both of liquid and gas, the thermodynamic parameters such as the specific heat capacity, compressibility of liquid can be calculated.

Funding

The authors declare that no funds, grants, or other support were received during the preparation of this manuscript.

Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

Author Contributions

Prof. Henmei Ni contributed to the study conception and design. A part of data collection was performed by the master student, Mr. Bing Zhu. The first draft of the manuscript was written by Henmei Ni. All authors read and approved the final manuscript.

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Graphic Abstract

