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A Novel Scheme for Predicting the Behaviors of Liquid and Vapor Phases of Water Using the Ideal Gas Theory

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Abstract

The ideal gas equation of state is the simplest equation of state for estimating the values of temperature, pressure and volume. This equation of state has a simple structure based on its simple theory. Hence, it has an explicit relation between these variables. In addition, calculating other thermodynamic properties (such as, internal energy, enthalpy and specific heats) is very simple for ideal gases. In this study, the ideal gas theory has been applied to the liquid and vapor phases of water. To this aim, the temperature and molar volume have been modified as power functions of the fluid molecular compressibility by fitting with empirical values using an optimization algorithm. In the presented method, effects of the temperature and volume on the non-ideality of the behaviors are considered, separately. These modifications let us to investigate the thermodynamic properties of these phases as ideal gases. Comparing the predicted values with the real data shows at least R-squared value equal to 0.98. Attending to the obtained equations, it is resulted that, the kinetic energy of liquid particles is independent of the compressibility factor and is a power function of temperature. The molecular volume has an important effect on the pressure of the liquid phase. In the vapor phase, both of the molecular size and intermolecular forces have significant effects on the pressure, as functions of the molecular compression.

Keywords: *Water; ideal gas theory; equation of state; modified temperature and volume*.

1. Introduction

Heretofore, various theories have been presented for investigating *PvT* behaviors of various substances in the liquid or vapor phases [1-6]. Their common characteristic is affecting intermolecular forces on the investigated variables. A comprehensive review of these theories indicates that, fundamental assumptions of most of them (such as, Virial [7], Van der waals [8] or Peng-Robinson [1] equation) were based on the existed differences between the behaviors of real states and ideal gas. These theories modified the ideal gas equation of state and affected ignored factors in this theory using a set of utilized assumptions. Therefore, their modified equations of state have the ability to predict the behaviors real state of pure substances or mixtures, accurately. Usually, such studies only obtained the existed relation among the pressure (P), molar volume (v) and temperature (T), and had no investigation for obtaining other thermodynamic parameters, such as, internal energy (u), enthalpy (h) and specific heats (i.e. C_P or C_v). In addition, their equations of states are usually too complex to calculate each of *PvT* variables (for example v) using two other variables (for example P and T).

In this study, a new scheme is proposed for predicting the behaviors of liquid and vapor phases of water as ideal gases using modified values of temperature and molar volume. The earliest achievements of this scheme are the simplicity of relations and the coverage of all the characteristics, which can be obtained using the ideal gas theory. Attending to the simple form of the presented equation of state (based on the kinetic theory of gases [9]), it is possible to calculate each of the triple variables using two other variables. In this equation, effects of molecular size and exchange of forces resulting from molecular collisions on the non-ideal behavior of liquid and vapor phases of water are specified, separately. Modifications of temperature and molar volume in the ideal gas equation of state independent these effects. Then, other thermodynamic parameters, i.e. C_P, C_v, h and u, are obtained based on the assumptions of the ideal gas theory. Finally, the presented theory and also equations are validated using experimental data of different states of water (i.e. subcooled liquid, saturated liquid, saturated vapor and super-heated vapor).

2. Theory

Based on the kinetic theory of gases [9], the pressure of a gas is the entered forces by molecular (or atomic) collisions in a certain area of the walls. When a particle impacts the wall in a certain direction (for example x direction), and then returns with a same velocity in the reverse direction (as an elastic collision [10]), its momentum changes in the x direction (i.e. $\Delta(mu_x)$) would be:

$$(m\upsilon_x)_{in} - (m\upsilon_x)_{out} = 2m\upsilon_x \tag{1}$$

where m is the mass of particle and υ_x is its velocity in the x direction. Without interfering with other particles, the average time interval of a molecule (or atom) between its collisions with two parallel walls (perpendicular to x-axis)

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of a cubic reservoir (with edge length equal to L) is $\Delta t = \frac{2L}{v_x}$. Therefore, the total force exerted on the wall by this collision (i.e. $F = \frac{\Delta(mv_x)}{\Delta t}$) is $F = \sum_{j=1}^{N} F_j = \sum_{j=1}^{N} \frac{m_j v_{jx}^2}{L} = \frac{Nm\overline{v_x^2}}{L}$. Where $\overline{v_x}$ is the mean velocity of N particles in the x direction. Attending to the random motion of molecules (or atoms) of a gas with no bias in any direction (so, $\overline{v_x} = \overline{v_y} = \overline{v_z}$ and $\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = 3\overline{v_x^2}$ based on the Pythagorean theory [11], which shows the homogeneity of the kinetic energy), we have $F = \frac{Nm\overline{u^2}}{3L}$. According to the definition of pressure (i.e. $P = \frac{F}{A}$), this force is exerted on an area L^2 of a wall. Therefore, the pressure of the gas is:

$$P = \frac{Nm\overline{u^2}}{3V} \tag{2}$$

Hence, attending to the definition of kinetic energy of gas (i.e. $k = \frac{1}{2}m\overline{u^2}$), we have $Pv = \frac{2}{3}k$. Where v is the molar volume of the gas. The kinetic energy of gas is a function of temperature (i.e. $k=f(T)$), which is a liner function for an ideal gas as below [12]:

$$Pv = RT \tag{3}$$

Where R is the universal gases constant. On the other hand, attending to the absence of intermolecular forces in an ideal gas, its internal energy changes only with changing the kinetic energy of its particles. Since the kinetic energy of these particles is a liner function of temperature, the internal energy and also enthalpy of this gas are liner functions of temperature [12] as following equations:

$$u = C_v T + u_1 \tag{4}$$

$$h = C_P T + h_1 \tag{5}$$

Where u_1 and h_1 are internal energy and enthalpy of the reference point. C_v and C_p are the molar heat capacity of this gas at constant v and P, respectively. These capacities are assumed constant and their difference is equal to R (i.e. $C_P - C_v = R$) [12].

This theory is not applicable for non-ideal phases (such as real gases or liquids) for the following reasons:

- Attending the molecular (or atomic) compression and also comparable volume of molecules (or atoms) with the container volume (V), of real gases or liquids, these particles create spatial constraints, which limits the collisions of particles with the container walls. Therefore, modification of the effective volume is necessary in this theory.
- The molecular (or atomic) compression and also intermolecular forces in a non-ideal condition lead to a more complex dependency of the temperature to the kinetic energy. Therefore, using a liner function for $f(t)$ is not applicable in this condition.

Therefore, T and v should be modified for using this theory for non-ideal states. Attending the importance of the molecular (or atomic) compression in the both of the presented reasons for variation from the ideal condition, these modifications should include this factor. Therefore, T and v were modified using power equations of compressibility factor (Z) as follows:

$$T_{\text{ideal}} = [T + T_0(Z)]^{\alpha}$$
(6)

$$v_{\text{ideal}} = [v + v_0(Z)]^{\beta}$$
(7)

These power equations let us to calculate each of T_{ideal}, v_{ideal} and P variables using other two variables [3]. Therefore, the modified equation of state has been defined as below:

$$Pv_{ideal} = R_{cor} T_{ideal}$$
(8)

where R_{cor} is a constant in this equation. Now, the kinetic energy (and also the internal energy and enthalpy, subsequently) can be obtained using a liner function of the modified temperature, if the effects of temperature and molar volume on the non-ideal behavior of fluid have become properly independent. Therefore, the following equations calculate the internal energy and enthalpy of vapor and liquid phases of water:

$$u = C_{v_{ideal}} T_{ideal} + u_0 \tag{9}$$

$$h = C_{P_{ideal}} T_{ideal} + h_0 \tag{10}$$

Where $C_{v_{ideal}}$ and $C_{P_{ideal}}$ are the modified molar heat capacity of these phases at constant v and P, respectively. Similar to the ideal gas, these capacities are assumed constant and their difference is equal to R_{cor} (i.e. $C_{P_{ideal}} - C_{v_{ideal}} = R_{cor}$).

3. Validation

Eqs. (6-10) were fitted with the empirical values of P, v, T, u and h of vapor and liquid phases of water [12], in order to obtain the values of R_{cor}, $T_0(Z)$, $v_0(Z)$, α, β, $C_{v_{ideal}}$, u_0 and h_0. The “fminsearch” optimization algorithm [13] was used for this purpose. It minimized the value of $1 - R_{mean}^2$, where R_{mean}^2 is the mean of values of R_P^2, R_v^2, R_T^2, R_u^2 and R_h^2. These values were calculated using the empirical and predicted values of each of these parameters (M) as follow:

$$R_M^2 = 1 - \frac{\sum\left(M_{\text{Predicted}} - M_{\text{Emperical}}\right)^2}{\sum\left(M_{\text{Predicted}} - \overline{M_{\text{Predicted}}}\right)^2} \tag{11}$$

For a better global searching, the “fminsearch” optimization algorithm of the MATLAB software functions with maximum numbers of iterations and function evaluations equal to 2000, and also x and function tolerances equal to 10^{-6}, has been used in a loop of a homemade code for testing different start points. Figures 1 and 2 show the convergences of this algorithm for optimizing the constants of Eqs. (6-10) for the liquid and vapor phases of water, respectively. As seen in these Figures, admitted values of R_2 (i.e. R_{mean}^2~1) were achieved after enough iterations. It clears the high accuracy of the fitted equations and approves the suitability of the presented forms of Eqs. (6-10) for predicting the values of P, v, T, u and h for the liquid and vapor phases of water. Table 1 presents the fitted values of the defined constants.

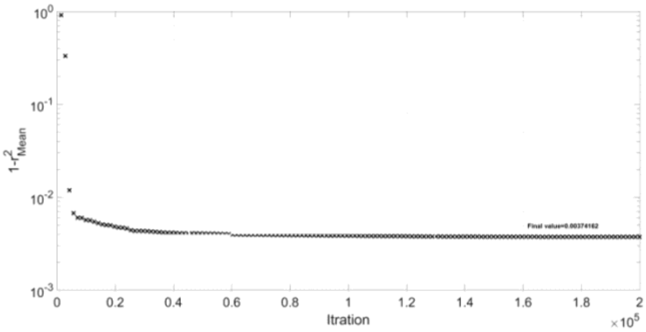

Figure 1. Convergences of "fminsearch" algorithm for optimizing the constants of Eqs. (6-10) for the liquid phase of water.

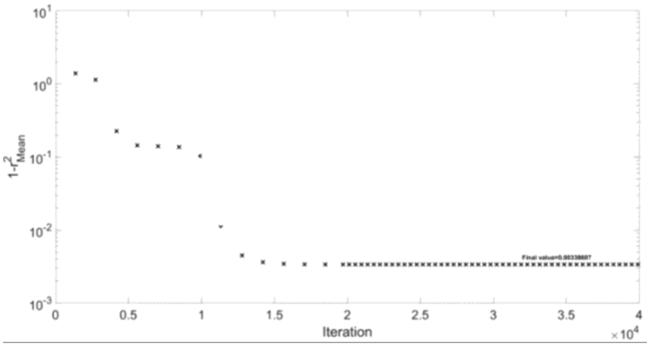

Figure 2. Convergences of "fminsearch" algorithm for optimizing the constants of Eqs. (6-10) for the vapor phase of water.

Table 1. Fitted values of the defined constants in Eqs. (6-10).

	Vapor	Liquid
R_{cor}	126.202	0.548
$T_0(Z)$	$381.639Z^{1.746}$	501.274
α	1.534	2.051
$v_0(Z)$	$0.016Z^{-0.588}$	$0.8405Z^{-0.02754}$
β	-1.013	-36.997
$C_{v_{ideal}}$	443.768	29.492
u_0	339.906×10^5	-245.254×10^5
h_0	337.348×10^5	-249.881×10^5

4. Results and Discussions

Figure 3 compares the predicted values of P, v and T with Eqs. (6-8) with the real data for different states of the water. It is clear that, the curves of the saturated liquid and saturated vapor are common border of two other states (i.e. subcooled liquid and superheated vapor). The presented values of R^2 in this Figure are more than 0.984. It approves the accuracy of this model for predicting each desired parameter of P, v or T using two other parameters. This important ability is rarely observed in other presented equations of states. This scheme approves that, the modified values of temperature and molar volume (i.e. T_{ideal} and v_{ideal}, respectively) made the ideal gas equation of state usable for the liquid and vapor phases of water. It means that, the effects of molecular volume and also intermolecular forces on the non-ideal behavior of these phases have been obtained as separate functions of the molecular compression (i.e. the compressibility factor, Z). Figures 4 and 5 compare the predicted values of u and h with Eqs. (9-10) with the real values of these quantities for different states of the water, respectively. The minimum values of the presented R^2 in these Figures are 0.983 and 0.985, respectively, which approve the ability of this model for predicting these parameters. As previously mentioned, suitable modifications of the temperature and volume cause the internal energy (or enthalpy) of the fluid, which represent the kinetic energy of fluid particles, to be a liner equation of T_{ideal} (see Eqs. (9-10)). The presented curves in these Figures show this liner dependency between the internal energy (or enthalpy) and the modified temperature. The slopes of these curves are almost constant, which are $C_{v_{ideal}}$ and $C_{P_{ideal}}$, respectively. As presented in Table 1, the difference between these two constant values is equal to R_{cor}, for each of the liquid and vapor phases of water.

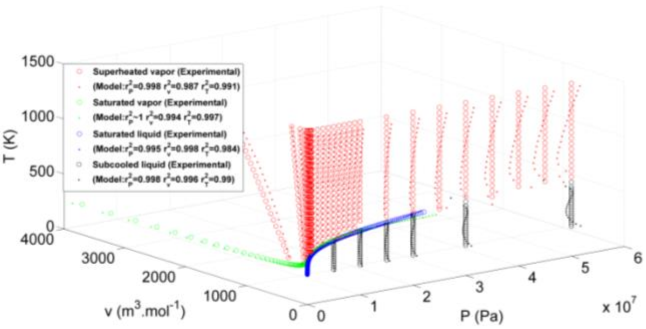

Figure 3. Comparing the predictions of each parameter of P, v or T using two other parameters using Eqs. (6-8) with the real values.

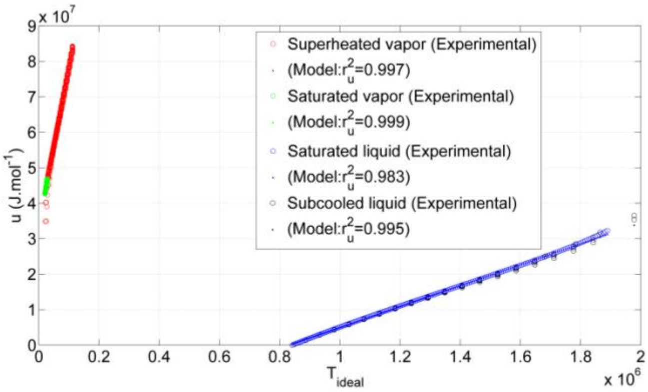

Figure 4. Obtained dependency between the internal energy and the modified temperature.

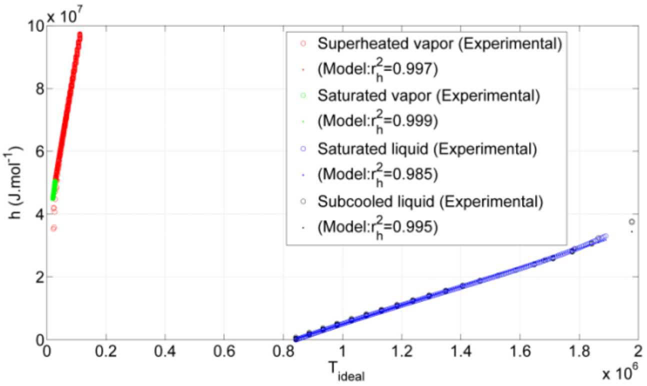

Figure 5. Obtained dependency between the enthalpy and the modified temperature.

Figure 6 shows the calculated values of Z_{ideal} (i.e. $\frac{Pv_{ideal}}{R_{cor}T_{ideal}}$) versus Z (i.e. $\frac{Pv}{RT}$). It is clear that, behaviors of the liquid phase of the water, and also wide ranges of its vapor phase (with Z<<1), are too far from the real gas (with Z = 1). But, as shown in this Figure, the calculated values of Z_{ideal} are close to 1 for various conditions of both of these phases. It approves the ideal behavior of the modified fluid (i.e. water with the modified temperature and molar volume). As expected, it is observed that, the molecular compression in different thermodynamic conditions (i.e. Z) has no important effect on the modified fluid behavior (i.e. Z_{ideal}).

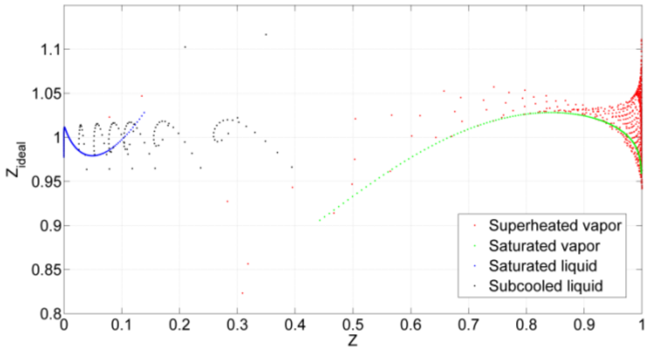

Figure 6. Calculated values of Z_{ideal} versus real values of Z.

Now, we have water as a modified fluid (with the presented values in Table 1) with the ideal gas behaviors (i.e. Eqs.(6-10)). Considering the obtained effects of molar volume and temperature on the non-ideal behavior of water, independently, investigating the obtained parameters for this modification clears the types and reasons of non-ideal behaviors of this fluid. The presented $T_0(Z)$ in Table 1 is a power function of Z for the vapor phase and is a constant value for the liquid phase. It clears that, the kinetic energy of liquid particles is independent of the compressibility factor and is only a power function of temperature, unlike the vapor phase. The reason of this phenomenon is the high molecular compression in the liquid water. But, the presented $v_0(Z)$ in Table 1 for both of the liquid and vapor phases of water are power functions of Z. Therefore, effects of the molecular compression on the modified molar volume of both of these phases are significant. Attending to the obtained great value of β for the liquid phase, the molar volume is heavily dependent on the molecular compressibility in the liquid phase. Therefore, the extent of the impacts entered by the liquid particles on the walls of the reservoir is not a function of intermolecular forces, and is depended to its molecular volume. Attending to the presented values of α, β, $T_0(Z)$ and $v_0(Z)$ in Table 1, in the vapor phase, both of the molecular size and intermolecular forces, as functions of the molecular compression, have significant effects on its pressure. A low molecular compression in the vapor phase causes a strong effect of the compressibility factor on the molecular size and intermolecular forces.

5. Conclusions

In this study, temperature and molar volume of the fluid water have been modified for estimating the thermodynamic properties of the liquid and vapor phases of water using the ideal gas theory. It approves that, it is possible to investigate the effects of molecular size and intermolecular forces on the non-ideal behavior of these phases, independently. The molecular compression may have important effect on these two factors. Nevertheless, attending to the high molecular compression in the liquid water, the kinetic energy of fluid particles is independent of the compressibility factor and is a power function of temperature. In contrast, effect of the molecular compression on the modified molar volume is heavily dependent on this parameter in the liquid phase. It means that, the extent of the impacts entered by the fluid particles on the walls is not a function of intermolecular forces in this phase; On the other hand, the molecular volume has an important effect on the entered forces by these impacts on the walls. In the other phase, both of the molecular size and intermolecular forces have significant effects on the pressure, as functions of the molecular compression. A low molecular compression in the vapor phase causes a strong effect of this parameter (i.e. the compressibility factor) on these two factors (i.e. the molecular size and intermolecular forces).

Nomenclature

A	Area of a wall of the cubic reservoir, m^2
C_P, C_v	Heat capacity, $J.mol^{-1}.K^{-1}$
$C_{P_{ideal}}$, $C_{v_{ideal}}$	Modified heat capacity, $J.mol^{-1}.K^{-\alpha}$
F	Total force exerted on the wall by particles collision, N
h	Enthalpy, $J.mol^{-1}$
h_0	Enthalpy of modified reference point, $J.mol^{-1}$
h_1	Enthalpy of reference point, $J.mol^{-1}$
k	Kinetic energy of gas, J
N	Number of particles
m	Mass of particle, kg
L	Edge length of the cubic reservoir, m
P	Pressure, pa
R	The universal gases constant, $pa.m^3.mol^{-1}.K^{-1}$
R^2	Coefficient of determination
R_{cor}	A constant in Eq. (8), $pa.\ (m^3.mol^{-1})^{\beta}.\ K^{-\alpha}$
T	Temperature, K
$T_0(Z)$	A set point for the modified temperature Eq. (6), K
T_{ideal}	Modified temperature, K^{α}
t	Time, sec
u	internal energy , $J.mol^{-1}$
u_0	Internal energy of modified reference point, $J.mol^{-1}$
u_1	Internal energy of reference point, $J.mol^{-1}$
V	Volume of the cubic reservoir, m^3
v	Molar volume, $m^3.mol^{-1}$
$v_0(Z)$	A set point for the modified molar volume Eq. (7), $m^3.mol^{-1}$
v_{ideal}	Modified molar volume, $(m^3.mol^{-1})^{\beta}$
Z	Compressibility factor
Z_{ideal}	Modified Compressibility factor
α	Power of the modified temperature Eq. (6)
β	Power of the modified molar volume Eq. (7)
υ_x	Velocity of particle in the x direction, $m.sec^{-1}$
$\overline{\upsilon_x}$	Mean velocity of particles in the x direction, $m.sec^{-1}$

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