A Predictive Equation of State for Selected Saturated Gases

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Abstract

An accurate correlation for calculating the saturated specific volume of gases is obtained by nonlinear regression based on experimental data collected after a thorough survey of literatures. This equation can be used to calculate saturated specific volume of gases independently, it is also to be of great significance in building the equation of state for hydrocarbons in gas region. The average deviation between the results obtained by this equation and experimental data is about 6% for 201 data points. For a better understanding of the equation, the saturated specific volume curves of observed and predicted are compared.

Keywords: saturated specific volume equation; saturated vapor; gases

الخلاصة

تم ايجاد علاقة رياضية دقيقة لحساب الحجم النوعي للغازات المشبعة بالاعتماد على الاساس اللا خطـي الرياضـي للنتـائج العملية المـاخوذة مـن المصـادر المختلفـة . يمكـن استخـدام هذه المعادلـة لحسـاب الحجـم النـوعي للغـازات بشكل مستقل، فضلا على كون هذه العلاقة مهمة لبناء المعادلة العامـة للهايدروكربونات فـي الطور الغـازي . اظهرت النتـائج بـان معدل نسبه الخطا مقارنـة بالنتـائج العمليـة هـي ٦% لـ ٢٠١ نقطـة عمليـة . ولغرض فهم المعادلـة بشكل افضل ، تـم مقارنـة منحنيات النتائج النظرية (المحسوبة بالاعتماد على المعادلة المقترحة) مع منحنيات البيانات العملية.

Introduction

In physics and thermodynamics, the equation of state is a relation between state variables [1]. More specifically, an equation of state is a thermodynamic equation describing the state of matter under a given set of physical conditions. It is a constitutive equation which provides a mathematical relationship between two or more state functions associated with the matter, such as its temperature, pressure, volume, or internal energy. Equations of state are useful in describing the properties of fluids, mixtures of fluids [2]. The most prominent use of an equation of state is to predict the state of gases and liquids. One of the simplest equations of state for this purpose is the ideal gas law, which is roughly accurate for gases at low pressures and high temperatures. However, this equation becomes increasingly inaccurate at higher pressures and lower temperatures, and fails to predict condensation from a gas to a liquid.

Therefore, a number of much more accurate equations of state have been developed for gases and liquids. At present, there is no single equation of state that accurately predicts the properties of all substances under all conditions. In addition to predicting the behavior of gases and liquids, there are also equations of state for predicting the volume of solids, including the transition of solids from one crystalline state to another. There are equations that model the interior of stars, including neutron stars. A related concept is the perfect fluid equation of state used in cosmology. Boyle's Law was perhaps the first expression of an equation of state. In 1662, the noted Irish physicist and chemist Robert Boyle performed a series of experiments employing a J-shaped glass tube, which was sealed on one end. Mercury was added to the tube, trapping a fixed quantity of air in the short, sealed end of the tube. Then the volume of gas was carefully measured as additional mercury was added to the tube. The pressure of the gas could be determined by the difference between the mercury level in the short end of the tube and that in the long, open end. Through these experiments, Boyle noted that the gas volume varied inversely with the pressure. In 1787 the French physicist Jacques Charles found that oxygen, nitrogen, hydrogen, carbon dioxide, and air expand to the same extent over the same 80 kelvin interval. Later, in 1802, Joseph Louis Gay-Lussac published results of similar experiments, indicating a linear relationship between volume and temperature. In 1834 Émile Clapeyron combined Boyle's Law and Charles' law into the first statement of the ideal gas law. Initially the law was formulated as $pV_m=R(T_C+267)$ (with temperature expressed in degrees Celsius). However, later work revealed that the number should actually be closer to 273.2, and then the Celsius scale was defined with 0 °C = 273.15 K, giving. In 1873, J. D. van der Waals introduced the first equation of state derived by the assumption of a finite volume occupied by the constituent molecules. His new formula revolutionized the study of equations of state, and was most famously continued via the Redlich-Kwong equation of state and the Soave modification of Redlich-Kwong.

Major Equations of State

For a given amount of substance contained in a system, the temperature, volume, and pressure are not independent quantities; they are connected by a relationship of the general form:

$$f\left(P,V,T\right) = 0 \qquad\qquad\qquad\text{..... (1)}$$

In the following equations the variables are defined as follows. Any consistent set of units may be used, although SI units are preferred. Absolute temperature refers to use of the Kelvin (K) or Rankine (°R) temperature scales, with zero being absolute zero.
The classical ideal gas law may be written as:

$$PV = nRT \qquad\qquad\qquad\text{..… (2)}$$

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The Van der Waals equation of state which was proposed in 1873 may be written as:

$$\left(P + aV^2\right)\!/\!\left(V_m - b\right) = RT \qquad\qquad \text{.... (3)}$$

Note that V_m is molar volume, a and b are constants that depend on the specific material. They can be calculated from the critical properties P_c, T_c and V_c .The van der Waals equation of state was one of the first to perform markedly better than the ideal gas law. In this landmark equation a is called the attraction parameter and b the repulsion parameter or the effective molecular volume. While the equation is definitely superior to the ideal gas law and does predict the formation of a liquid phase, the agreement with experimental data is limited for conditions where the liquid forms. While the van der Waals equation is commonly referenced in text-books and papers for historical reasons, it is now obsolete. Other modern equations are slightly complex but are much more accurate.

In 1949 the Redlich-Kwong equation of state had a considerable improvement over other equations of that time. It is still of interest primarily due to its relatively simple form, but it is performs poorly with respect to the liquid phase and thus cannot be used for accurately calculating vapor-liquid equilibrium.

The Redlich-Kwong equation is adequate for calculation of gas phase properties when the ratio of the pressure to the critical pressure (reduced pressure) is less than about one-half of the ratio of the temperature to the critical temperature (reduced temperature):

The Peng-Robinson equation was developed in 1976 in order to satisfy the following goals **[4]**:

Peng-Robinson equation exhibits performance similar to the Soave equation, although it is generally superior in predicting the liquid densities of many materials, especially nonpolar ones. The departure functions of the Peng-Robinson equation are given on a separate article. Values of the various parameters for 15 substances can be found in, K.E. Starling **[5]**.

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The Elliott, Suresh, and Donohue (ESD) equation of state was proposed in 1990 **[6]**. The equation seeks to correct a shortcoming in the Peng-Robinson EOS (Equation of state) in that there was an inaccuracy in the van der Waals repulsive term. The EOS accounts for the effect of the shape of a non-polar molecule and can be extended to polymers with the addition of an extra term. The EOS itself was developed through modeling computer simulations and should capture the essential physics of the size, shape, and hydrogen bonding. Perhaps, it is

noteworthy to refer for Bruce E. Poling, et al. work **[7]** . They present a comprehensive study, analysis and discussion, for different EoS and its role in estimation of properties of substance that exist in different phases.

Herein, after what has been mentioned, it is difficult to find a unique equation of state that capable to cover the properties calculations at all different phases for any substance, and usually more than one equation is required even in one phase if the accuracy of the equation is to match that of the experimental results **[8]**.

Suggested Formula

An accuracy satisfying equation of saturated specific volume of gases is obtained by nonlinear regression based on experimental data collected after a thorough survey of Marks' literatures **[9]**. The collected data include the saturated specific volumes of gases; Hg, NH_3, CO_2, C_2H_5Cl, C_3H_8, CCL_2F, CCL_2F_2, $CHCL_2F$ within a wide temperatures range (i.e. a wide corresponding saturated pressures range). The suggested formula is:

$$V_C = \left[A_1 T_R^{A_1} P_R^{A_2} \left(T_R + \frac{A_4}{P_R} + A_5 \right) + B_1 T_R + B_2 T_R^2 + B_3 T_R^3 + B_4 P_R + B_5 P_R^2 \right] \left[C_1 T_R^{C_2} P_R^{C_3} \right] ..(4)$$

Constants of Eq.4 are available in Table ١.

Where V_C is the predicted specific saturated volume in ft^3/Ibm and T_R, P_R are reduced temperature and pressure respectively.

The objective of this integration is to ensure that the engineer who works with systems containing saturated hydrocarbons gases is not constrained by a lack of data on properties and that he has predictive methods to estimate them. Thus, he can save time while preserving full reliability of the calculations.

Results and Discussion

The observed data of these gases are summarized in Fig.1. The average deviation between the results by the proposed formula (Eq.4) and experimental data, Marks **[9]**, is about 6% for 201 data points. For a better understanding of the equation, the saturated specific volumes curves of observed and predicted are compared, as shown in Fig.2**.**

Conclusion

The present work made a collection of specific volume of saturated gases, and obtained an accuracy satisfying formula and this noticed from the average relative deviation of calculated values from experimental values (6%). This equation is not only used to calculate saturated

density of gases independently, but also is to be of great significance in building the equation of state for hydrocarbons in gas regions.

Table 10 Constants of Eq.4

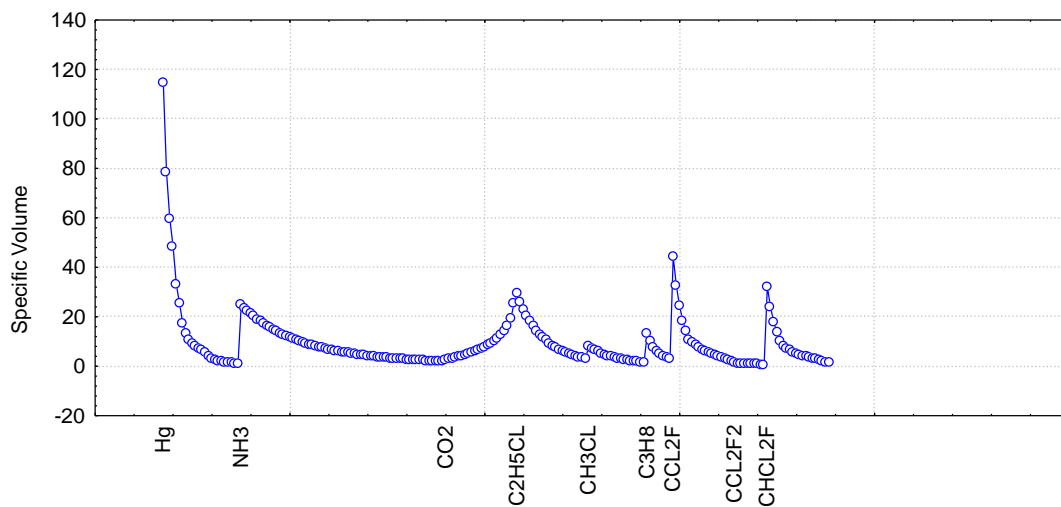| A_1	A_2	A_3	A_4	A_5
19.61573	-27.1140	3.232606	2572.686	11806.66
B_1	B_2	B_3	B_4	B_5
-13615.8	14837.56	-674.998	-40310.6	217.946
C_1	C_2	C_3		
0.000263	0.429625	-1.02324		

Fig.1: Experimental Saturated Specific Volume of Gases
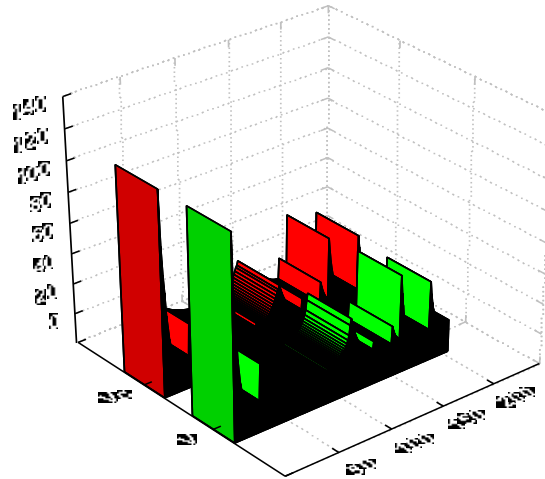
Fig.2: Comparisons of Measured and Predicted Saturated Specific Volumes

Nomenclature

Symbol	Quantity	Unit
n	number of moles of a substance	-------
P	pressure (absolute)	KPa, atm
P_c	pressure at the critical point	KPa, atm
P_R	reduced pressure, P/P_C	
R	ideal gas constant, (8.314472 J/(mol·K))	J/(mol·K)
T	absolute temperature	K, R
T_c	absolute temperature at the critical point	K, R
T_R	reduced temperature, T/T_c	
V	volume	m^3
V	experimental saturated specific volume of gases (Eq.4)	ft^3/Ibm
V_C	molar volume at the critical point	m^3/kg
V_C	predicted saturated specific volume of gases (Eq.4)	ft^3/Ibm

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