

Computation Thermodynamic Properties of Superheated Water* Far from Critical Region

Tawfeeq Kadheem Faleh Al-Hamdi
Al-Mustansiriya University
College of Engineering
Assistant Lecturer
Bab Al-Moudham, P.O.Box 14150

Abstract

A general equation has been presented in the present work to calculate specific volume, internal energy, enthalpy and entropy of superheated steam. The developed equation appeared in one context in order to confer upon it the status of generalizing form and away it from complexity that accompanies many equations and great number of mathematical terms that appear in those equations, where the number of terms in the equation presented in present work were eleven terms.

Present equations showed a good accuracy for 523 experimental data points to evaluate a selected thermodynamic property of superheated steam. The average absolute percentage of error for those properties not exceed 1%, where the average absolute percentage of error 0.687% for specific volume, 0.767% for the internal energy, 0.867% for enthalpy and 0.654% for entropy.

Keywords: specific volume, internal energy, enthalpy, entropy, Superheated Water.

*In our daily life, water means liquid water whilst steam means water vapor. According to the principles of thermodynamics both water and steam usually asserts only one thing: H_2O [1]

الخلاصة

لحساب الحجم النوعي، الطاقة الداخلية، المحتوى الحراري والعشوائية للبخار المحمص تم استحداث معادلة لهذا الغرض. المعادلة المستحدثة ظهرت بسياق واحد مما اضفى عليها صفة الشمولية وبعدها عن التعقيد الذي يرافق العديد من المعادلات الاخرى وكثرة الحدود الرياضية التي تظهر في تلك المعادلات حيث بلغ عدد الحدود في المعادلة المقدمة في البحث الحالي احد عشر حداً رياضياً.

اظهرت هذه المعادلات دقة جيدة عند استخدامها مع 523 قراءة عملية لحساب اي خاصية من خصائص البخار المحمص. لم يتجاوز المعدل المطلق للنسبة المنوية للخطأ لتلك الخصائص عن 1%، حيث كان المعدل المطلق للنسبة المنوية للخطأ 0.687% للحجم النوعي و 0.767% للطاقة الداخلية و 0.867% للمحتوى الحراري و 0.654% للعشوائية.

Nomenclature

Symbol	Quantity	Unit
a, b	Constant in Equation (4)	-----
B	Second Virial Coefficient in Equations (6) and (7)	cm ³ /mol
C	Third Virial Coefficient in Equations (6) and (7)	cm ⁶ /mol ²
C ₁ ,C ₂ ,...C ₁₁	Constants in Equations (8-11)	-----
<i>h</i>	Enthalpy	kJ/kg
<i>m</i>	Mass of a substance	kg
P	Saturated Pressure	MPa
P _{cr}	Critical Pressure	MPa
P _R	Reduced Pressure	-----
R	Gas Constant	kJ/kg·K or kPa·m ³ /kg·K
R _u	Universal Gas Constant (R _u =8.314 is the same for all substances)	kJ/kmol·K or kPa·m ³ /kmol·K
<i>S</i>	Entropy	kJ/kg·°C
T	Saturated Temperature	°C
T _{cr}	Critical Temperature	°C
T _R	Reduced Temperature	-----
<i>u</i>	Internal Energy	kJ/kg
<i>v</i>	Specific Volume	m ³ /kg
V	Molar Volume	m ³ /kmol
Z	Compressibility Factor	-----

Introduction

One of the most significant series of events shaping (Forming, creating, changing, diversiform) today's world is the industrial revolution that began in the late seventeenth century. One of the most prominent pillars of the industrial revolution is the use of generating steam to do useful work. The idea of generating steam was born in 200 B.C. by a Greek man named Hero who labeled the device "*aeolipile*", meaning rotary steam engine [2].

Although water is not only one of the most common substances and indispensable to life, its steam one of the most important and common working fluid in engineering applications, such as for the design and operating of equipment in steam power plants. Indeed, in about 40% of the power cycle points the steam is superheated [3]. Steam importance results from many of its desirable characteristics, such as low cost, availability and high enthalpy of vaporization [1]. That is why a good deal of work has been spent on the investigation and measurement over the years to present clear concepts about steam, governing equations that explained its behavior, properties of water for each phase.

Obviously, when one talk about steam properties, it is important to highlight upon the equation of state that is consider one of famous techniques in specifying the properties of steam. In the next two sections, a brief explanation from the literature for equation of state and thermodynamics properties evaluation will present. Then, the general concepts that must be taken into consideration when calculating the properties of superheated steam will be attached at the end of third section as a prelude to direct review of the equations have been reached in the present work to calculate the properties of superheated steam. Last section will be devoted for discussion and conclusions of the results of the present work.

Equation of State

Several definitions have been presented to explain the concept of "Equation of State (EoS)". Any equation that relates the pressure, temperature, and specific volume of a substance is called an equation of state. Property relations that involve other properties of a substance at equilibrium states are also referred to as equations of state [1]. **Sears and Salinger** [4] believe that the equation of state of a substance is a relationship between any four thermodynamic properties of the substance. An example, as they presented, of the equation of state involves pressure P , volume V , temperature T and mass of system, which can be expressed in general as:

$$f(P, V, T, m) = 0 \quad (1)$$

The equation of state, as clarified by **Pierre Perrot**[5], is a relation between state variables. EoS is an algebraic relation between P , V , and T or it is a mathematical representation of graphical information, according to **Poling, et al** [6].

Although there are many definitions for the EoS, but it is possible to say that all these definitions are shared, with each other, in the establishment of comprehensive concept for the meaning of EoS and refer to its importance in describing the properties of fluid (in its different phases), mixtures of fluids, solid.

The equation of state can also be written in a form, which depends only on the nature of the system and not on how much of the substance is present; hence, all extensive properties are replaced by their corresponding specific values [1, 4].

In 1662, Robert Boyle, noticed during his experiments with a vacuum chamber that the pressure of gases is inversely proportional to their volume. In 1802, J. Charles and J. Gay-Lussac, experimentally determined that at low pressures the volume of a gas is proportional to its temperature, this observation led to what so called ideal-gas equation of state and a gas that obeys this relation closely at low pressures and high temperatures is called an ideal gas.

$$Pv = RT \quad (2)$$

In order to reduce the gases deviation from ideal gas behavior especially near the saturation zone and the critical point, compressibility factor Z , has been introduced into ideal-gas equation of state.

$$Z = Pv/RT \quad (3)$$

Gases behave differently at a given temperature and pressure, but they behave very much the same at temperatures and pressures normalized with respect to their critical temperatures and pressures. The normalization, which is called the principle of corresponding states, is done is called the reduced pressure P_R and T_R the reduced temperature as

$$P_R = P/P_{cr} \quad \text{and} \quad T_R = T/T_{cr} \quad (4)$$

Even with these improvements, gases still suffer from great deviation in their behavior as ideal gases at the vicinity of the critical point. Therefore, in 1873, Van der Waals presented a new equation of state to improve ideal-gas one. This is done by added the effect of intermolecular attraction forces and volume occupied by the molecules themselves.

$$\left(P + \frac{a}{v} \right) (v - b) = RT \quad (5)$$

Despite of its inadequate accuracy, Van der Waals EoS represents the first attempt to demonstrate the behavior of real gases [1]. Poling, et al. [6] present a comprehensive study, analysis and discussion, for different EoS of substance that exist in different phases. Herein we will refer to EoS discussed by Bruce E. Poling, et al. [6] that related to our research scope. These equations approved their reliability and accuracy, to somewhat, in use.

They believed that the following and any similar equations that called virial equation of state, which is a polynomial series in pressure or in inverse volume whose coefficients are functions only of T for a pure fluid. The consistent forms for the initial terms are:

$$Z = 1 + B \left(\frac{P}{R_u T} \right) + (C - B^2) \left(\frac{P}{R_u T} \right)^2 + \dots \quad (6)$$

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \dots \quad (7)$$

Where V is molar volume (m^3/kmol) (equal to the product of multiplying molar mass by specific volume), R is universal gas constant, P is the pressure, T the absolute temperature, while B , C and so on, are called second, third,..... virial coefficients. These coefficients can be determined experimentally or theoretically from statistical mechanics [1, 6]. The virial equation is usually truncated at the second or third term and applied only to the vapor phase [6] and should not be used for liquids or liquid–vapor mixtures [1].

Thermodynamic Properties Calculations of Water

From a thermodynamic point of view, it is well-known that the relationship between saturation pressure, saturation temperature and other thermodynamic properties for water properties available into two forms; either in tabular or in graphical form. Steam tables and Moiller chart are good examples for the two forms and these can be found in most standard thermodynamic textbooks. Commercially programs, nowadays, are available through some websites in the form of computer diskettes in order to compute the desired property. Originally, and for all cases mentioned above, the accuracy of the properties derived (or some of them) based on comparison with that observed through experiments made with real substances [7]. Certain steam property can be determined or extracted from steam tables or from formulae, for each property expressed as a function (or in terms) of the independent parameters P and T [8, 9]. Thermodynamically, temperature and pressure are independent properties for single-phase systems, but are dependent properties for multiphase systems and it is well-known that the superheated region is a single-phase region (vapor phase only) [1].

Based on the significance of the equation of state in the calculation of thermodynamic properties, a truncated virial equation of state at the third coefficient, that dubbed a cubic equation of state by **J. L. M. Fernandes** [3], used for calculating thermodynamic properties of superheated steam through limited range for temperatures from 1°C to 800°C and pressures from 2 kPa up to 20 MPa. The equation presented by **Fernandes** [3] should not be used outside the range it is designed for because extrapolation at high pressures can be highly inaccurate, also, the region close to the critical point is out of the scope of **Fernandes** work [3]. **V. I. Lachkov, et al.** [10] presented a set of expressions, each of them in terms of temperature and pressure, to calculate the density, dynamic viscosity, the adiabatic exponent and enthalpy of superheated steam.

The expressions hold for the temperature range (100-600) °C and absolute pressure (0.05-30) MPa. These expressions give a relative error not exceeded 0.09% when compared the output data computed via expressions with tabulated ones.

Perhaps, it is noteworthy to refer for Wagner and Kretzschmar [11]. They have highlighted one of the distinguished work in the field of steam properties calculations that published by IAPWS⁽¹⁾. In 1997, IAPWS adopted the “IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam” for industrial use, called IAPWS-IF97 for short. The most recent equations for the transport properties like dynamic viscosity and thermal conductivity in addition to the thermodynamic properties based on IAPWS-IF97 of water and steam have been presented in their work. Moreover, equations for the surface tension, static dielectric constant, and refractive index also have been introduced.

Concerning the accuracy of properties and their deviation from the experimental data, the computed properties show different uncertainty for each property depending on the region. These deviations, for instant, range from 0.1 to 0.3 percent for specific enthalpy and may be reaching 1percent for another property as in the case of specific heat at constant pressure C_p .

(1) IAPWS (The International Association for the Properties of Water and Steam) is an international non-profit association of national organizations concerned with the properties of water and steam, particularly thermophysical properties and other aspects of high-temperature steam, water and aqueous mixtures that are relevant to thermal power cycles and other industrial applications. IAPWS has organized as an association of member countries (currently over 15 countries). Current Members are Britain and Ireland, Canada, the Czech Republic, Germany, Greece, Japan, Russia, Scandinavia (Denmark, Finland, Norway, Sweden), and the United States, plus Associate Members Argentina & Brazil, France, Italy, and Switzerland. One of IAPWS mainly objectives is to provide internationally accepted formulations for the properties of light and heavy steam, water and selected aqueous solutions for scientific and industrial applications.

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 [12].

Suggested Formula

Equations for producing tables of water properties cover a wide range of conditions, are consistent from the thermodynamic point of view and accurate for experimental data [9]. These equations are based on a fundamental equation, the Helmholtz free energy function from which all other properties can be determined.

This approach has been introduced by Keenan, et al. [7]. However, such equations are, in most instances, orientated towards the production of tables rather than to meet the needs of engineering computations. Formulations by Saul and Wagner [13] seem adequate from the accuracy point of view and they considerably extend to cover a wide range of applicability. The faster of their formulations, however, still has more than 38-coefficient expansion [13].

For most substances, the relationships among thermodynamic properties are too complex to be expressed by simple equations. Therefore, properties are frequently presented in the form of tables. Some thermodynamic properties can be measured easily, but others cannot and are calculated by using the relations between them and measurable properties [1]. Taking into consideration the fact, stated by Cengel & Turner [1], that temperature and pressure are independent properties for single-phase systems, and applying nonlinear regression based on experimental data of superheated water adopted by Cengel & Turner [1]. This resulting to the following equations give specific volume, enthalpy, internal energy and entropy as a function, for each of them, of their corresponding saturated temperature T (45.81 to 1300 °C) and saturated pressure P (0.01 to 60 MPa) of superheated water:

$$v = C_1 + C_2T + C_3P + C_4(TP) + \frac{C_5}{TP^2} + \frac{C_6}{P} + \frac{C_7}{T^{C_8}} + \frac{C_9}{P^{C_{10}}} + C_{11} \frac{T}{P} \quad (8)$$

$$u = C_1 + C_2T + C_3P + C_4(TP) + \frac{C_5}{TP^2} + \frac{C_6}{P} + \frac{C_7}{T^{C_8}} + \frac{C_9}{P^{C_{10}}} + C_{11} \frac{T}{P} \quad (9)$$

$$h = C_1 + C_2T + C_3P + C_4(TP) + \frac{C_5}{TP^2} + \frac{C_6}{P} + \frac{C_7}{T^{C_8}} + \frac{C_9}{P^{C_{10}}} + C_{11} \frac{T}{P} \quad (10)$$

$$s = C_1 + C_2T + C_3P + C_4(TP) + \frac{C_5}{TP^2} + \frac{C_6}{P} + \frac{C_7}{T^{C_8}} + \frac{C_9}{P^{C_{10}}} + C_{11} \frac{T}{P} \quad (11)$$

Where C_1, C_2, \dots, C_{11} are constants of equations (8-11) and their values are listed in Table1.

Results and Discussion

Equations (8-11) are valid for pressures from 0.01 MPa up to 60 MPa and temperatures from 45.81 to 1300°C. The temperature range (354.75-425 °C), that is near-critical temperature point, is out of the scope of present work and this range is close to that has been specified by Keenan, et al. [7].

This exception due to the fact that, near the critical point, many transport and thermodynamic properties show anomalous or singular behavior [14, 15]. This fact has been ascertained in the present work when applying these equations with the experimental data laid near-critical temperature region and the error in some cases exceeded 100% at the critical temperature and at 400 °C decreased to less than 35%.

Using eqs. 8-11, to estimate thermodynamic properties of superheated steam, show a closed fitness between calculated and measured thermodynamic properties and very low average absolute percentage error has been recorded when compared the calculated properties from the proposed correlations with the experimental data tabulated by Cengel & Turner[1]. These errors were 0.687%, 0.767%, 0.867% and 0.654% for specific volume, internal energy, enthalpy and entropy respectively. Thus, the thermodynamic properties of superheated steam obtained from that single and short-terms equations in the present work competitive, in their accuracy, when compared them with that obtained from other equations. Figures (1-4) give the graphical results have been obtained by applying equations (8-11) and a comparison between them with measured data. In Figures (1-4), thermodynamic properties obtained by applying equations (8-11) have been labeled with "d, e and f" while experimental data of superheated water adopted by Cengel & Turner [1] have been labeled with "a, b and c".

Conclusions

1. The equations, introduced in the present paper, represent an attempt to present equations combined between single and short-terms form (9 terms with 11 constants) with considerable accuracy to predict thermodynamic properties of superheated water over wide ranges of saturated pressures and their corresponding saturated temperatures. Those equations, on the other hand, may be capable of competitive with multi and long-terms equations.
2. The equations should not be used to calculate thermodynamic properties for the critical point and near-critical region of superheated steam, specifically within the temperature range (354.75-425) °C.

Table 1: Constants of Equations (8-11)

Constants	Specific Volume ν	Internal Energy u	Enthalpy h	Entropy s
C_1	0.015461	1179.828	2457.562	-1915.82
C_2	-0.000005	2.037999	-41.1175	0.948128
C_3	3.136615	1849.285	2667.668	-0.011926
C_4	0.000000	0.004144	0.006607	0.000015
C_5	0.000278	-130.142	-154.704	-0.072414
C_6	0.126073	0.019978	0.557417	0.000030
C_7	-0.629711	1836.409	42.03696	-0.933309
C_8	0.595804	0.106097	-1.00447	-1.00175
C_9	-3.13669	-1876.57	-2703.19	1921.263
C_{10}	-0.999999	-0.996372	-0.996866	0.000256
C_{11}	0.000461	-0.000405	-0.001119	-0.000002

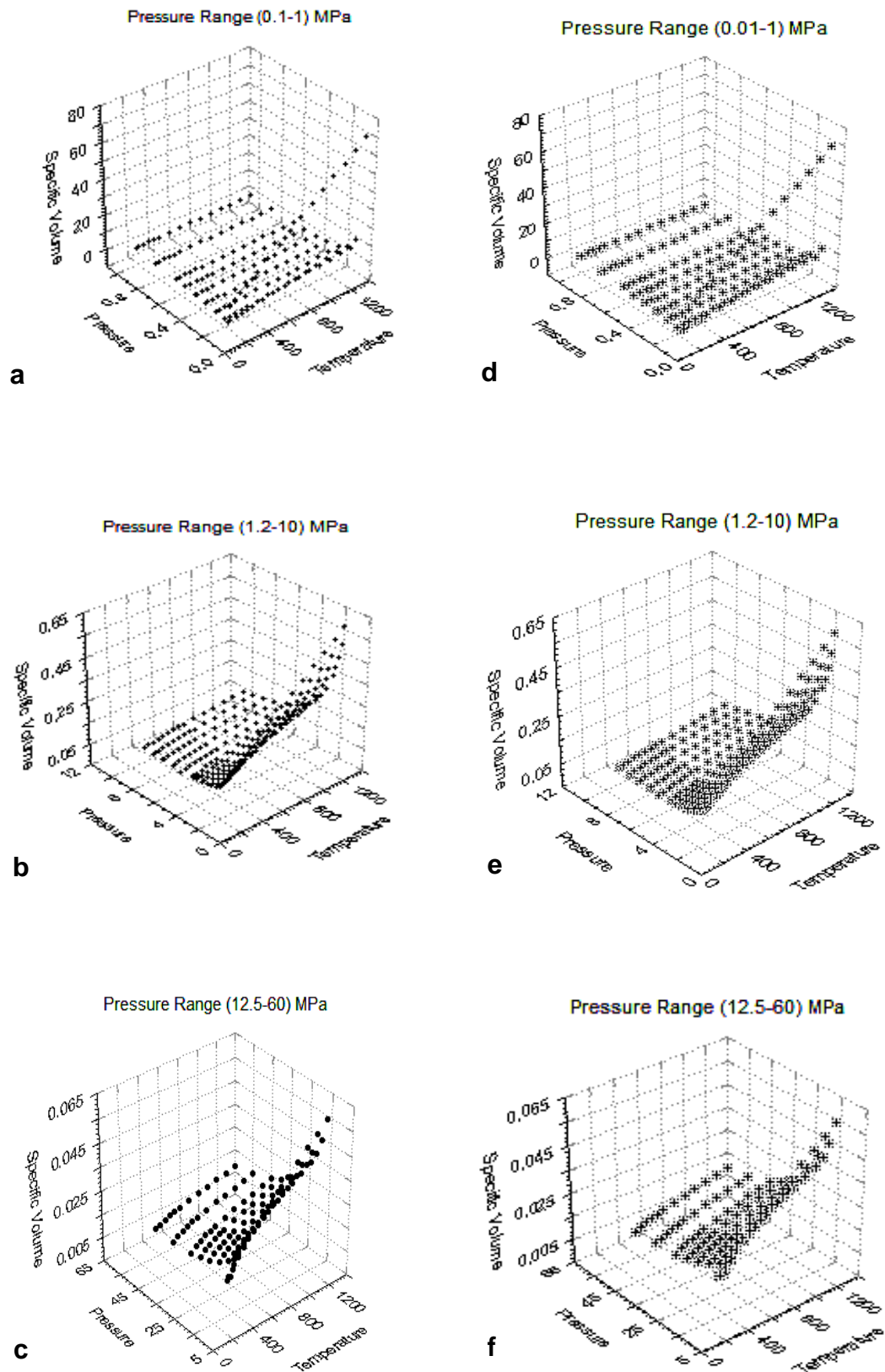


Figure 1: Comparison between Measured and Calculated Specific Volume

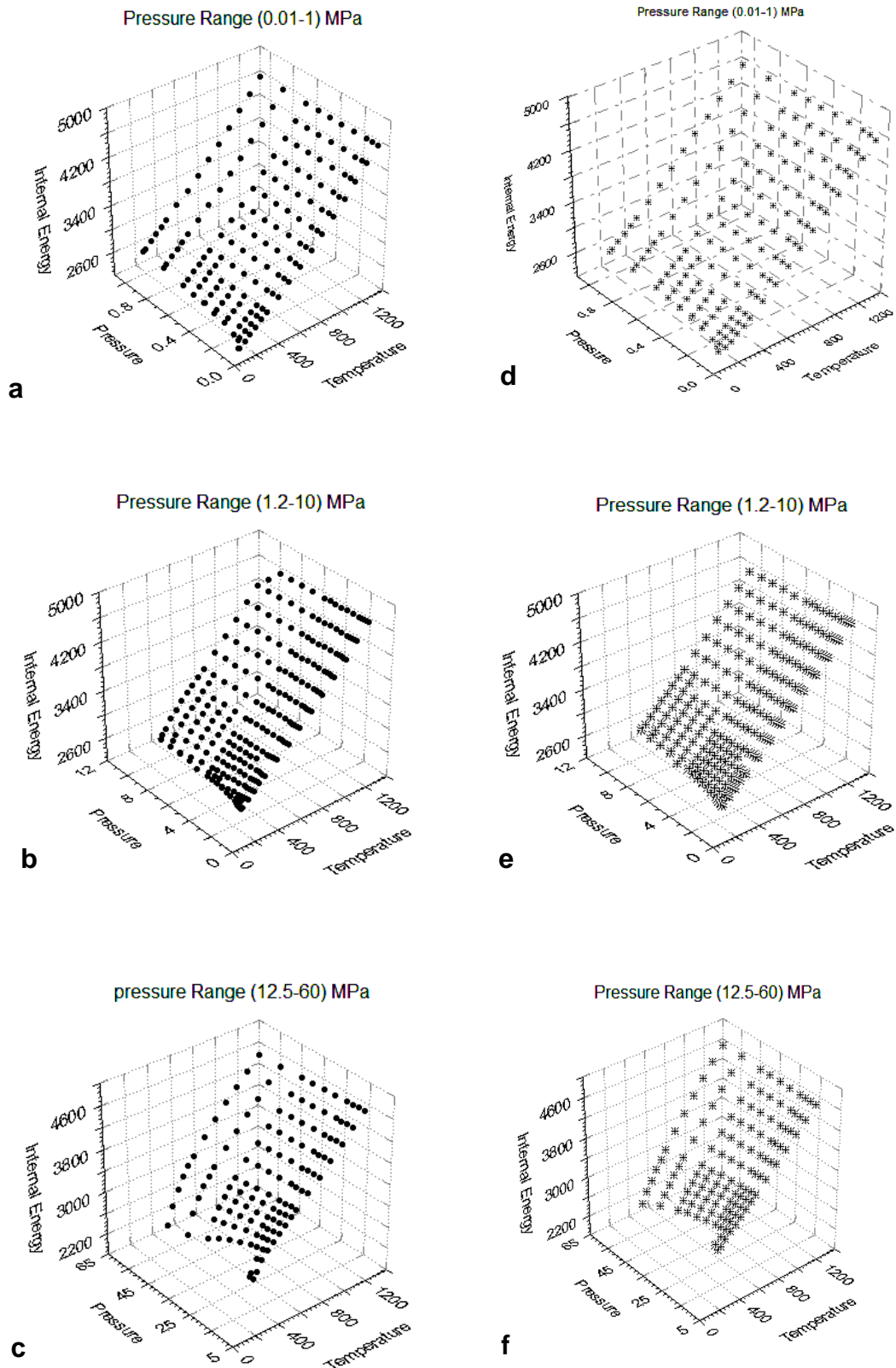


Figure 2: Comparison between Measured and Calculated Internal Energy

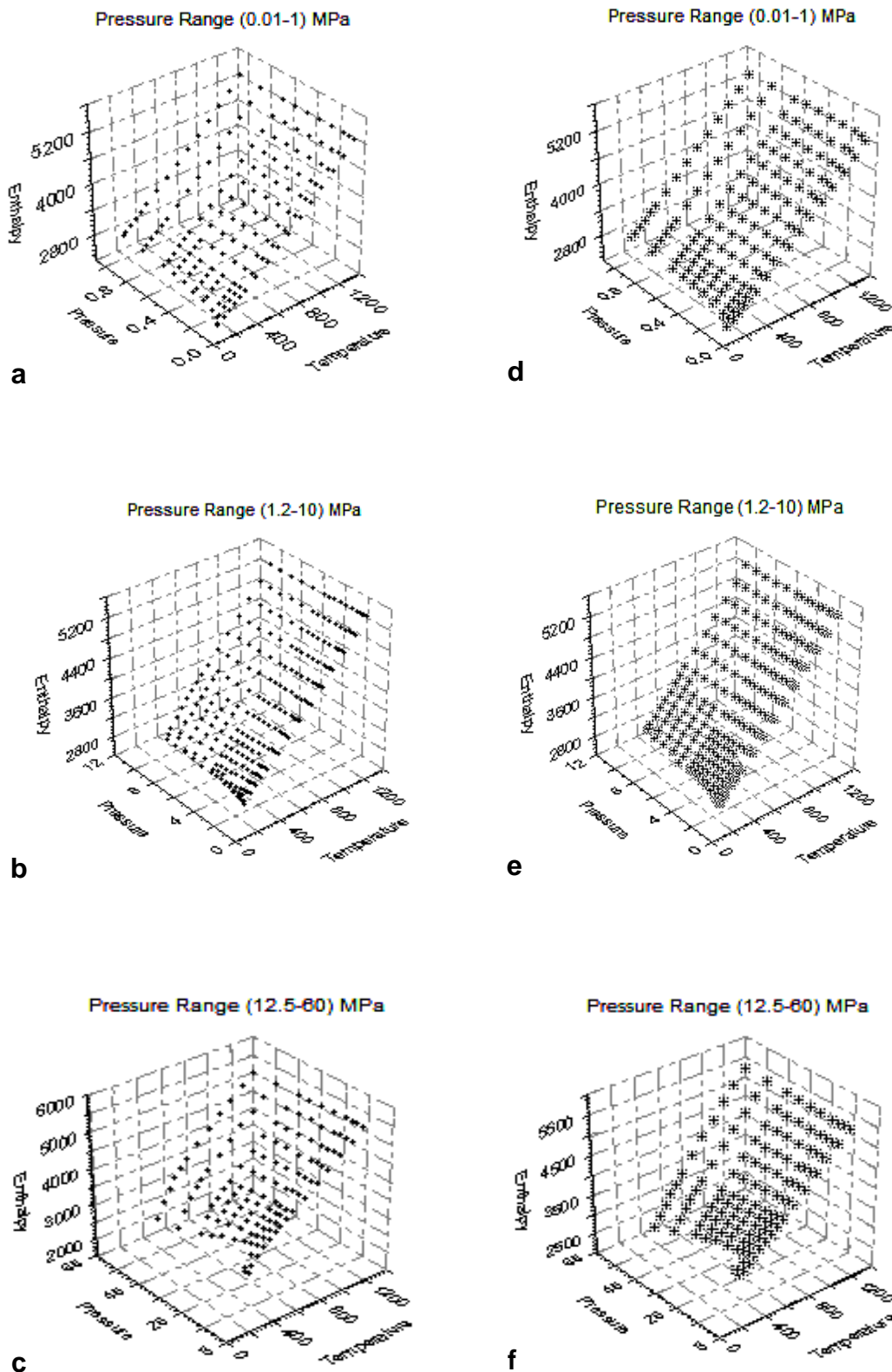


Figure 3: Comparison between Measured and Calculated Enthalpy

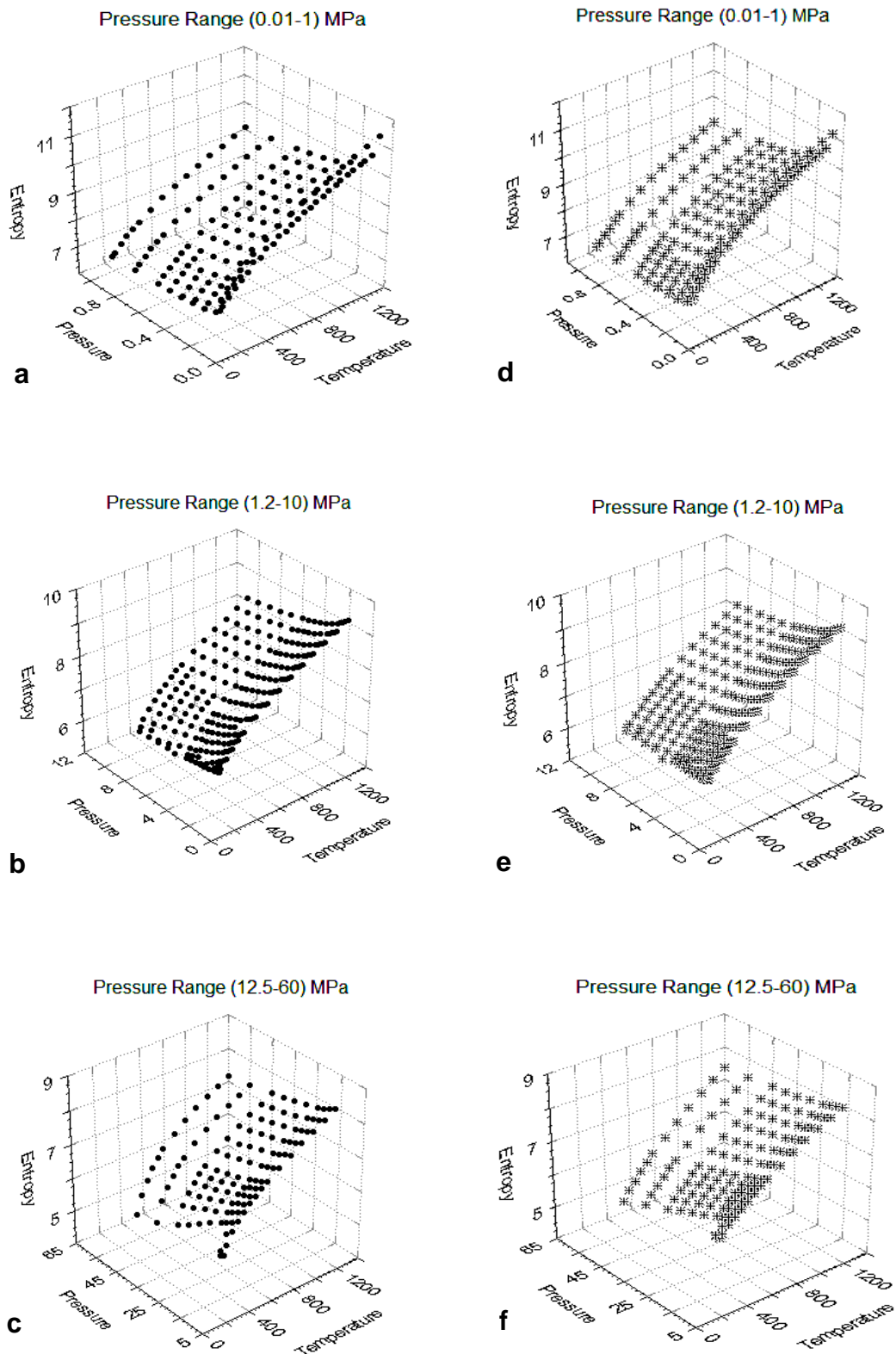


Figure 4: Comparison between Measured and Calculated Entropy

References

- [1] Yunus A. Cengel & Robert H. Turner, "**Fundamentals of Thermal-Fluid Science**", The McGraw-Hill Companies, Inc., 2nd Edition, 2005.
- [2] John B. Kitto and Steven C. Stultz, "**Steam, Its Generation and Use**", 41st edition, Babcock & Wilcox Company, 2005.
- [3] J. L. M. Fernandes, "*Fast Evaluation of Thermodynamic Properties of Superheated Steam: A Cubic Equation of State*", Applied Thermal Engineering Vol. 16, No. 1, pp. 71-79, 1996.
- [4] F.W. Sears and G.L. Salinger, "**Thermodynamics, Kinetic Theory, and Statistical Thermodynamics**", Addison-Wesley Publishing Company, Third Edition, 1975.
- [5] Pierre Perrot, "**A to Z of Thermodynamics**", Oxford University Press, 1998.
- [6] Bruce E. Poling, John M. Prausnitz and John P. O'Connell, "**Properties of Gases and Liquids**", The McGraw-Hill Companies, Inc., Fifth Edition, 2001.
- [7] Joseph H. Keenan, Frederick G. Keyes, Philip G. Hill and Joan G. Moore, "**Steam Tables: Thermodynamic Properties Of Water Including Vapor, Liquid and Solid Phases (S.I. UNITS)**", John Wiley & Sons, 1978.
- [8] Meyer, C.A. et al., "*Thermodynamic and Transport Properties of Steam*", ASME, New York, 1967.
- [9] L. Haar, J.S. Gallagher, and G.S. Knell, "**NBS&NRC STEAM TABLES: Thermodynamic and Transport Properties and Computer Programs for Vapor and Liquid States of Water in SI Units**", Hemisphere Publishing Corporation, 1984.
- [10] V. I. Lachkov, A. I. Lysenkov and Yu. V. Mamonov, "*Expressions for Thermophysical Properties of Superheated Steam*", Measurement Techniques, Vol. 42, No.1. pp. 58-60, 1999.
- [11] Wolfgang Wagner & Hans-Joachim Kretzschmar, "**International Steam Tables Properties of Water and Steam Based on the Industrial Formulation IAPWS-IF97**", Springer-Verlag Berlin Heidelberg, Second edition, 2008.
- [12] R.K. Rajput, "**Engineering Thermodynamics**", Laxmi Publications (P) Ltd, 3rd Edition, 2007.
- [13] A. Saul and W. Wagner, "A fundamental equation for water covering the range from melting ice to 1273 K at pressures up to 25,000 MPa", J. Phys. Chem. Ref. Data 18 (4), (1989).
- [14] Eldred H. Chimowitz "**Introduction to Critical Phenomena in Fluids**", Oxford University Press, 2005
- [15] J. V. Sengers, R. A. Perkins, M. L. Huber and D. G. Friend, "*Viscosity of H₂O in the Critical Region*", [International Journal of Thermophysics, Volume 30, Number 2](#), 374-384, 2009