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Thermodynamics, Equations of State and Experimental Data: A Review

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Abstract: An equation of state (formulation) is an empirical relation to understand the tendency and inter- or extrapolation of experimental thermodynamic data. Two aspects to be considered in creating the empirical formulation are: (a) thermodynamic consistency among the experimental data and (b) retaining the consistency in the formulation for whole range of independent variables. The most recent formulation, IAPWS-95 for the steam tables of pure water was creating by fitting the experimental data in a multi-parameter equation of state. The PVT characteristics of water are consistent with the laws of thermodynamics; however, there are thermodynamic inconsistencies in behavior of U, H, G and S. There are multiple values and crossings in the tendency. The experimental data of heat capacity are used to calculate the values of U, H, G and S. It is found that the experimental values of C_P are inconsistent thermodynamically; consequently, the IAPWS-95 predicts inconsistent values.

Key words: Thermodynamics, state function, steam tables, internal consistency, water

INTRODUCTION

Thermodynamic laws were well established by the end of ninth century and various excellent textbooks were written in the twentieth century to describe the laws from different point of views[1-8]. Therefore, to write something new on thermodynamics is not the subject of this work. The first objective is to present a brief overview on the thermodynamic laws to understand the limitations of ideal gas concept in describing the processes in real systems in nature as well as in the laboratory.

Secondly, the experimental thermodynamic data are fitted in various types of empirical equations of state (formulations). These formulations are used to create the thermodynamic data tables. Recently, these are programmed in computer codes as an ActiveX component[9,10]. Somehow, the internal thermodynamic consistency among different state functions is violated in the formulations. The reasons of such violations are presented.

Water is one of the most important substances on the earth for its geological evolution and existence of life in it. Consequently, water is the most extensively studied component. The recent formulation for its thermodynamic properties is IAPWS-95, approved by the International Association for the Properties of Water and Steam[11]. The IAPWS-95 formulation is analyzed for its internal consistency among its thermodynamic properties.

THERMODYNAMICS: A BRIEF SUMMARY

The basic concepts of thermodynamics are presented in brief with an objective to understand the behavior of experimental data and the limitations in creating empirical formulations to describe their tendencies. The intensive parameters (i.e. molar quality in the case of extensive parameters) are used throughout in this paper to avoid mass factor.

- Temperature (T), Pressure (P), Volume (V), internal energy (U), enthalpy (H), entropy (S), Gibbs free energy (G), Helmholtz energy (A) including conductivity, solubility, equilibrium constant of a reaction, etc. are state functions.
- Any two state functions are sufficient and necessary to define completely a pure homogeneous system. It is in accordance with the Gibbs phase rule.
- The variation of a state function between two points is independent of trajectory (path).
- If Z is a dependent state function of two state variables X and Y, then

$$\left(\frac{\partial^2 Z}{\partial Y \partial X}\right) = \left(\frac{\partial^2 Z}{\partial X \partial Y}\right) \tag{1}$$

$$\left(\frac{\partial Z}{\partial X}\right)_Y \left(\frac{\partial X}{\partial Y}\right)_Z \left(\frac{\partial Y}{\partial Z}\right)_X = -1 \tag{2}$$

If one independent variable (say Y) is constant, then

$$\left(\frac{\partial Z}{\partial X}\right) \left(\frac{\partial X}{\partial Z}\right) = 1 \tag{3}$$

- If the same value of Z exists for two values of X (say X_1 and X_2) at constant Y, there should be at least one minimum or maximum in the behavior of Z between X_1 and X_2 (Fig. 1). At the minimum or maximum, one can write $\triangle X = \pm ve$ and $\triangle Z = 0 \left(\partial Z / \partial X\right) = 0$ and $\left(\partial X / \partial Z\right) = \infty$

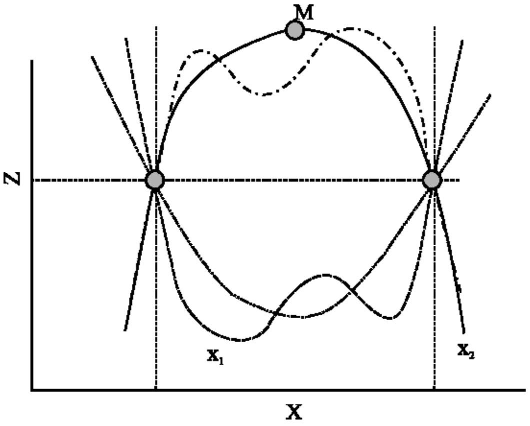

Fig. 1: Possible behaviors of a state function Z, when it has values for two values of independent state variable X. A maximum is shown by a point M

Thus

$$\left(\frac{\partial X}{\partial Y}\right)\left(\frac{\partial Y}{\partial X}\right) = 0 \times \infty \Rightarrow \text{indeterminate, but not} = 1$$

In summary, there cannot be any maximum or minimum in the behavior of a state function with an independent variable in a pure phase when the other independent thermodynamic variable is constant. In other words, a state function (or an exact function) cannot be a multi-valued function unless a phase transition exists. Figure 2 presents the impermissible behavior of a state function X with respect T when P is constant[12].

- Thermodynamics does not impose any restriction on the behavior of a state function (say X) with respect to independent state variables (say T and P). However, if we know the behavior of T with P and behavior of X with T (or P) for a system, we can predict the behavior of X with P (or T). For an ideal gas system of constant V, T increases with increasing P and vice versa. It means if V increases with T, it should decrease with P. On considering T and P as independent variables and V as constant, all the other state functions should be constant (i.e. uniquely defined) under the situation. Thus, the behavior of P and T should be similar for all the other state functions as that for V. There should be similar and systematic behaviors of other state functions.

Let us rewrite the Eq. 2 in term of X, T and P as

$$\left(\frac{\partial X}{\partial P}\right)_T = -\left(\frac{\partial X}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_X \tag{4}$$

If T increases with increasing P at constant X in a system, then $\left(\partial T/\partial P\right)_x = +ve$. If X increases with T, it should decrease with P in order to fulfill the equation 4. Similarly, if T decreases with increasing P at constant X, then $\left(\partial T/\partial P\right)_x = -ve$. If X increases (or decreases) with T, it should also increase (or decrease) with P.

Ideal gas: An ideal gas is a hypothetical gas which does not have intermolecular force and consequently it does not require energy to alter in its intermolecular distance. In this manner the following properties of an ideal gas have been considered:

- The equation of state

$$PV = RT \tag{5}$$

- The internal energy U is independent of P and V and a function of T only.

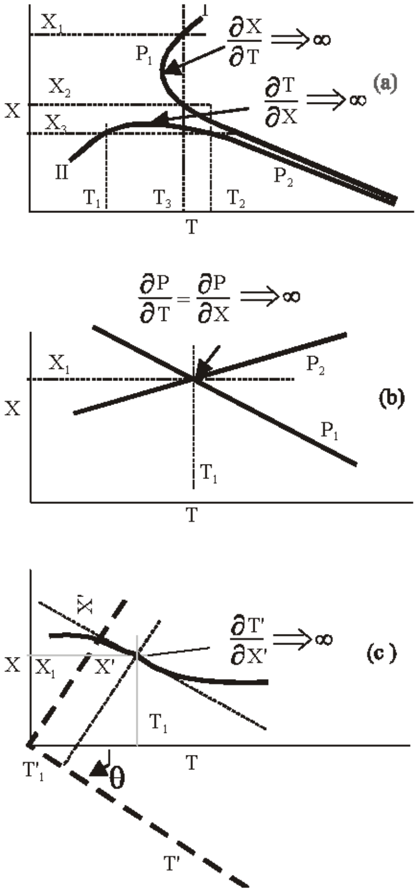

Fig. 2: Impermissible of a state function in a pure phase. a) multiple values, b) crossing of tendency and c) point of inflection, which is singular on rotating the axes by an angle θ[12]

From these properties of ideal gas, a relation between the heat capacity at constant P (C_P) and constant V (C_V) is derived as

$$C_P - C_V = R \tag{6}$$

The derivation of Eq. 6 exists in all the textbooks; however, there are some quarries about the characteristics of an ideal gas:

- According to Gibbs phase rule, a state function of a pure substance in a phase (ideal gas) should be a function of two thermodynamic variables (e.g. T and P). The equation (5) is in agreement with it. There are two independent variables among T, P and V. However, if we consider U as function of T only, then U is not an independent state function due to the following reasons:
- The characteristics of ideal gas cannot be defined considering T and U as independent variables.
- U can be expressed as a polynomial of T. A polynomial of a state function is not another independent state function.
- Validation of C_P- C_V= R at a given P and V: In this equation, C_P is at constant P and C_V is at constant V; therefore the equation is valid for constant P and V. However, it is never mentioned the values of P and V for the validation of this equation. If the equation is valid of all the values of P and V, then C_P and C_V of ideal gas are constant for all the range of P and V. For example, let us consider two values of P (P_1 and P_2) and one value of V (V_1). The equation should be valid for the two conditions of P and V (i.e. at (P_1, V_1) and (P_2, V_1)). In the both cases the values of V is same: therefore, C_V will have the same value. R is constant. In this manner C_P will also be same at P_1 and P_2. Similarly, we can demonstrate for different values of V. In summary, C_P and C_V of an ideal gas are constant of all the range of P and V. Similarly it is valid for any two independent thermodynamic variables.

EQUATION OF STATE

An equation of state is an empirical relation among state variables. The first equation of state (Eq. 5) was defined by combining Boyle's and Charles' gas laws (i.e. PV=RT, here number of moles is 1 since V is molar volume). The real gases obey this equation in a wide range of T and P. However, if we apply the second constraint of ideal gas behavior (i.e. U(T)), the real gases can be ideal only at very low T and P. This is a substantial limitation. One has to consider in developing an ideal behavior model of real systems.

The most important concept which is not discussed explicitly in the textbooks of thermodynamics is that all the three variables, P, T and V obey the state function conditions (i.e. Eqs. 1 and 2) in this equation of state. Therefore, any experimental data fitted to this equation will not violate any law of thermodynamics.

In 1879 van der Waals presented an equation of state for gas (vapor) and liquid region of a pure substance with including the volume of gas molecules and intermolecular attraction as following

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \tag{7}$$

where a and b are constants. The conditions of exact functions (Eq. 1 and 2) are fulfilled for P and T, but not for V. Fortunately, if the real data of liquid and vapor are fitted in this equation, the discontinuity and multiple values are either imaginary along the critical isochor or fall in the two phase region.

In 1901 H. Kamerlingh-Onnes proposed an equation of state for real gases called the virial Equation[13], which expresses the compressibility factor Z as

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + ... \tag{8}$$

where B and C are referred as the second and third virial coefficients, respectively and are function of T. In this equation P and V are state function but not T. Additionally, the values of B and C are relatively small compare to the volume of a real gas at a given temperature and B>>C and so on. Therefore, it can be considered as a modification of the ideal gas equation.

Benedict introduced an exponential term in the empirical equation for thermodynamic properties of light hydrocarbons and their mixtures. Recently, multi-parameter equations of state have been used for the development of empirical formulations for the thermodynamic properties[9].

There are two things which must be considered in formulating an equation of state and predicting the values of thermodynamic properties from it:

- The experimental data must be checked first for the thermodynamic consistency among them.
- All the equations of state are empirical relations. The values of any predicted thermodynamic property should be checked for consistency with the basic laws of thermodynamics.

STEAM TABLES OF PURE WATER

The International Association for the Properties of Water and Steam approved a formulation IAPWS-95 for the thermodynamic properties of pure water (Wagner and Proβ, 2002), which apparently provides more consistent values of the properties of water in comparison of the earlier formulations. Using the concepts presented in the sections 2 and 3 we will analyze the thermodynamic inconsistency in the formulation.

PVT characteristics of water: Figure 3 depicts the PT relationship for pure water according to the IAPWS-95 formulation. The critical isochor (i.e. total specific volume V= 0.003106 m^3 kg^{-1} or density = 322.0 kgm^{-3}) in the supercritical fluid region acts as a phase boundary between the liquid and vapor[10]. Water has many solid forms, depending on the conditions of P and T. All the Ice curves (I, III, V, VI and VII) define the melting curve. The supercritical fluid region exists at T and P higher than those of critical point, which does not represent a phase change but depends on an arbitrary definition of what constitutes the liquid and vapor phases. According to the IAPWS-95 formulation the supercritical fluid region also contains solid (ice) water.

It is well known that the variation of specific volume of liquid water with T at P=0.1 MPa has a minimum volume at T=~277 K. We know that P, T and V are state functions. If we consider P and V as independent state variables, there are two values of T at a given value of P and V. But according to the definition of state function, it should be uniquely defined, if T is a state function. This cannot be explained thermodynamically if we consider the whole liquid water region as a single phase. It was called as an anomalous behavior since the development of thermodynamics[3]. It is anomalous to the thermodynamic laws, if the whole liquid water is considered a single phase.

Recently,[14] presented the physics of liquid-liquid transition. A summary of the work of Sciortino et al. is on the webpage of Physics Review Letters as "A Tale of Two Liquids[15]. It says, Any liquid which eventually expands as it cools must have a liquid-liquid critical point." Thus there are two types of liquid water, which are represented by liquid and liquid I in Fig. 3. Additionally, there is an effect of hydrogen bonding on the molecular structure of water at low temperatures[16]. There are two types of structure: one is associated with hydrogen bonding (below 4°C) and other without hydrogen bonding. According to the definition of phase, a change in the structure of water molecule will produce a different phase. Therefore, there is a phase transition along the minimum volume curve (Fig. 3) and T is uniquely defined on fixing P and V in each liquid phase. It will be discussed later.

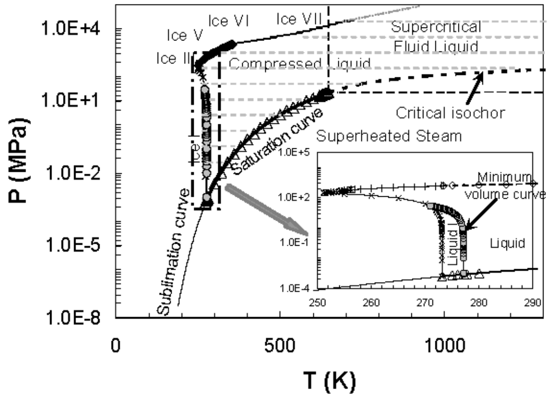

Fig. 3: PT-space of pure water according to the IAPWS-95 formulation, which is divided by six separation boundaries: (i) sublimation curve, (ii) saturation curve, (iii) critical isochor, (iv) ice I melting curve, (v) melting (Ice III to Ice VII) curve and (vi) minimum specific volume curve. The inserted figure depicts the location of liquid I and the minimum specific volume boundary

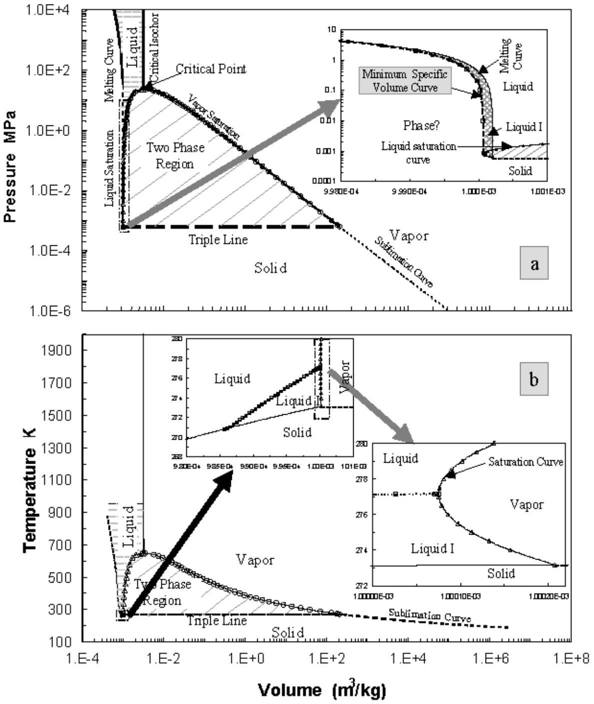

Fig. 4(a): P-V and (b) T-V spaces for pure water according to the IAPWS-95 formulation. The inserted figures illustrate the location of Liquid I phase

The inserted Figure in Fig. 3 shows that the minimum specific volume curve acts as a separation boundary between the liquid and liquid I phases of water. It is derived from the IAPWS-95 formulation, so its exactitude depends only on the formulation.

Figure 4a shows the P-V space for pure water. There is a triple line where liquid-vapor-solid (ice) coexists. The two phase region (liquid or liquid I and vapor) is bounded among the triple line, liquid saturation curve and vapor saturation curve. The vapor and liquid saturation curves meet at the critical point. The critical isochor, represented by a vertical line is the separation boundary between liquid and vapor. The liquid phase is up to the minimum specific volume curve. The liquid I phase will be bounded by the minimum specific volume curve, melting curve and triple line. The solid (ice) will be on the higher volume side at the melting curve. There may exist some solid phase in the region on the lower side of the minimum specific volume curve as shown in the inserted figure with a question mark on phase. Here we are not interested in the thermodynamic properties of solid (ice) water; therefore, we will not discuss it further. Figure 4b shows the VT-space. It is similar to VP-space. It also shows the location of Liquid I.

Thus the behaviors of P, T and V in the IAPWS-95 formulation for the water steam tables are thermodynamically consistent.

Behaviors of H, G and S of water: Figure 5 shows (a) isobaric behavior of H with T and (b) isothermal behavior of H with P. In the vapor region P increases with increasing T at constant H and vice versa. Similarly, H increases with T, while it decreases with P. Thus the behavior of H in the vapor phase is consistent with the definition of a state function.

The behavior of H in the liquid phase is inconsistent. In the low temperature range H increases with both T and P and is overlapping with the two phase region, whereas it increases with T and decreases with P in the high temperature range (Fig. 5a). The tendencies are crossing in the middle temperature range. If the increase of H with P and T is correct, it should exist in the whole liquid phase. Secondly, the values of H for the liquid region are also in the two phase region. It means that there could be only liquid or liquid-vapor at the same conditions of low T and P. This cannot be true. Thus the values of H in the low and middle temperature ranges are violating the definition of a state function.

Figure 5(b) shows the isothermal variation of H with P. There are two pressures for a given value of H in the compressed liquid region. For example, H=2000 kJ kg^{-1} for the 700 K isotherm is at P_1=63.458 MPa and P_2=456.356 MPa. If we consider T and H as independent variables, it is impossible to predict the right value of P. Similarly, the two values of P at a given value of T and H will not satisfy the Equation 1.

Figure 6 shows (a) isobaric behavior of G with T and (b) isothermal behavior of G with P. The behavior of G is consistent with the definition of state function. It increases with P, but it decreases with T. It has a discontinuity along the saturation curve and a point of inflection along the critical isochor. It means that there is a first order liquid-vapor phase transition along the saturation curve, while a second order liquid-vapor phase transition exists along the critical isochor.

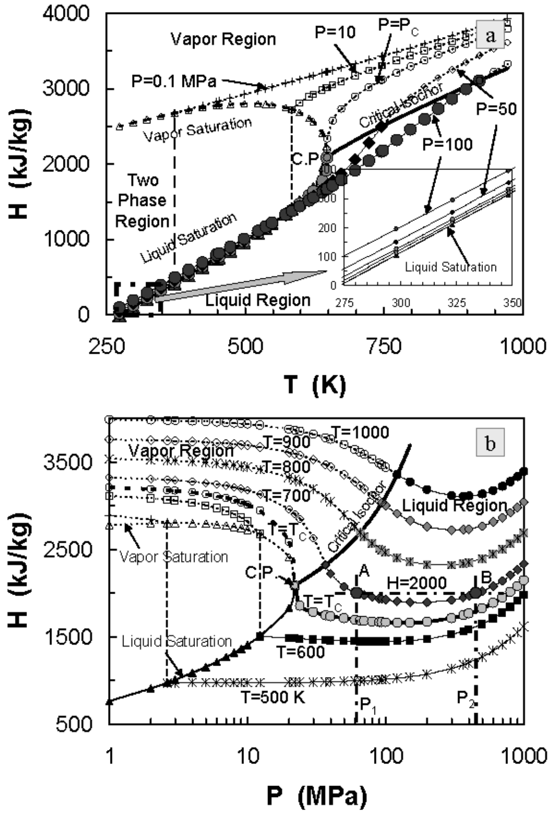

Fig. 5: (a)Isobaric and (b) Isothermal variations of Enthalpy (H). There is violation of the definition of state function in the liquid phase. For example, the values of H increases with T and P and overlapping with the two phase region in the low temperature range (see inserted figure in 4(a)). Similarly, in Figure 4(b) there are two values of pressure (P_1=63.458 and P_2=456.356 MPa) for a value of enthalpy (H=2000 kJ kg^{-1}) at T=700 K. It means that water can be pressurized without any expense energy (i.e. impossible)

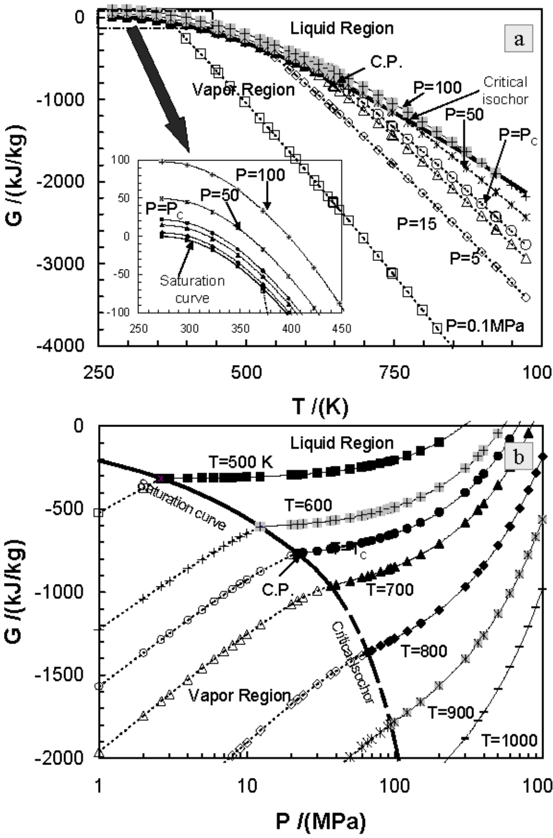

Fig. 6: (a) Isobaric and (b) Isothermal variations of Gibbs free energy (G). The behaviors of G are thermodynamically consistent. G increases with P, while it decreases with T. There are no multiple-values and crossovers in the tendencies

Figure 7 shows the V-G, V-S and S-G spaces for pure water according to the IAPWS-95 formulation. It covers the region corresponding to T (190 to 2000 K) and P (3.23×10^{-8} to 10000 MPa) for the liquid and vapor phases as shown in Figure 3. It can be observed that the V-G and V-G spaces do not overlap and are single valued. The compressed liquid region should be bounded between the melting, liquid saturation, critical isochor, maximum temperature and maximum pressure curves. The liquid region is overlapping to the two phase, vapor and solid regions in the case of S-G space. It means that there can be compressed liquid, superheated steam, liquid and steam, or solid ice at a given value of G and S in the liquid region. This cannot be explained thermodynamically.

Figure 8 shows the behavior of isotherms in the S-G space. For example, the isotherm at T=2000K is in the superheated steam region up to G≈-8000 kJ kg^{-1}. After this point there should be compressed liquid. However, the isotherm enters in the vapor region at G≈-3400 kJ kg^{-1}. It means that there may be vapor phase or liquid phase for the conditions of G and S. Then at G≈-500 kJ kg^{-1} it enters to two phase region. At G≈0, it crosses the triple and enters in the solid phase region. The overlapping of liquid region to the vapor, two phase and solid regions is not feasible.

Thus the values of U, H, G and S in the IAPWS-95 formulation are inconsistent thermodynamically. There is need to revise the procedure and experimental values, used in the development of the IAPWS-95 formulation.

Behaviors of C_P of water: The behaviors of P, V and T are consistent, while the behaviors of U, H, G and S are inconsistent thermodynamically in the IAPWS-95 formulation.

The values of U, H, G and S are calculated from the values of C_P and/or C_V. Therefore, to understand the thermodynamic inconsistencies in the behaviors of U, H, G and S, we will analyze the experimental data of C_p.

Figure 9 shows a comparison of experimental and calculated values of C_P at P=0.10, 2.55 and 12.26 MPa. There is a good correlation between the experimental and calculated values. There is a minimum in the behavior at each P. The heat capacity is not a state function; however, C_P is defined along a specific path. So, it should have some definite tendency. There are multiple values of C_P in the compressed liquid region between 273.16 and 400 K. C_P decreases first with T and then increases. It cannot be explained with the basic laws of thermodynamics.

According to the definition of phase transition, a minimum or maximum in the behavior of C_P is considered as a second or higher order phase transition[17]. This may be associated with the maximum density of water at 277 K. However, the minimum of C_P is at 300K. There are two possibilities for this difference in T: (a) a systematic analytical error in the values of C_P and (b) a broad phase boundary between liquid and liquid I.

Figure 10 shows the experimental values of C_p along saturation curve, in the compressed liquid region and in the superheated steam region, used in the derivation of the IAPWS-95 formulation. The values for the liquid and vapor phases along the saturation curve are shown by solid and dashed curves, respectively (Figure 10a). They are increasing with T for both the phases. The values of C_p are very high near to critical point (i.e., ~10^9 kJ kg^{-1} K). According to the behavior of C_P, the critical point acts as a heat sink.

C_P in the compressed liquid region increases with T while decreases with P (Fig. 10b). The variation of C_P for all the range of P and T up to 550 K is not very significant. There is drastic increase in the values of C_P above T=550 K and there are multiple values just near to the boundary with the vapor phase (i.e. saturation curve and critical isochor).

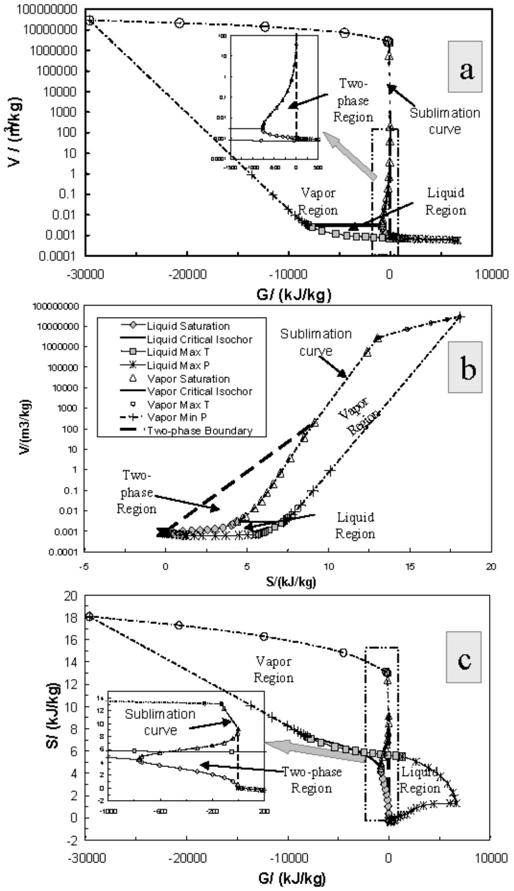

Fig. 7: V-G, V-S and G-S spaces for pure water according to the IAPWS-95 formulation. It shows the overall regions for the superheated steam and compressed liquid. The V-G and V-S spaces are consistent according to the definition of state function, but there is overlapping of the regions in the G-S space. Thus there are multiple values of S with G and vice versa at constant T, P or V

Thermodynamics deals only macroscopic properties of a system. If we fit any equation of state for C_P data up to T=550 K as a function of T and P, we cannot explain the drastic increase in C_P. Additionally, if we fit all the values in the compressed liquid region, we cannot explain the C_P values along the saturation curve. Similarly, the tendencies of C_P for vapor region are over-crossing and the values increase drastically near to the liquid-vapor separation boundary.

The C_P and C_V of water have been measured along the saturation curve; however, their physical significance has never been explained. For example, there is need to know a relation between the increase in T and amount of heat given to a system at constant P in order to measure C_P. There will be a change in P on changing T along the saturation curve. It is not possible to keep constant P. Thus, the measurement of C_P or C_V along the saturation curve is not feasible.

In summary, the development of the IAPWS-95 formulation is based on the thermodynamically inconsistent experimental data. Similarly, in creating the IAPWS-95 formulation the Holmholtz energy was divided in two parts: ideal and residual. The ideal behavior was considered in the whole range of T and P. Thus there is also need to revise the development procedure of a thermodynamic formulation of pure water or any system. However, the consistency is the first requirement.

Verma[12]discussed that the heat capacity at constant volume (C_V) can be measured more precisely than C_P in the compressed liquid and superheated steam region. Additionally, there are experimental difficulties in measuring C_V in the vapor phase at low pressure. Therefore, he defined the heat capacity along the saturation curve, C_{Sat} as the proportion of amount heat to the change in temperature. Thus, C_{Sat} is a function of only one independent variable (say T). Heat capacity is not a state function. Its value depends on the trajectory between two points. Therefore, one has to use the same trajectory (along the saturation curve and then the constant V path) for the calculation of the thermodynamic properties like U, H, G, S, etc.

Actually, the liquid I region is based only on the experimental data of T and V at P=0.1 MPa. There are no other experimental data for T and V at constant P in this region (Wagner and Proβ, 2002). There is still need to determine the PVT characteristics at higher P in this compressed region.

Any point can be considered as the reference point for calculating U, H, S and G from heat capacity data; however, the saturated liquid water at the triple point vapor-liquid-liquid I is a better option.

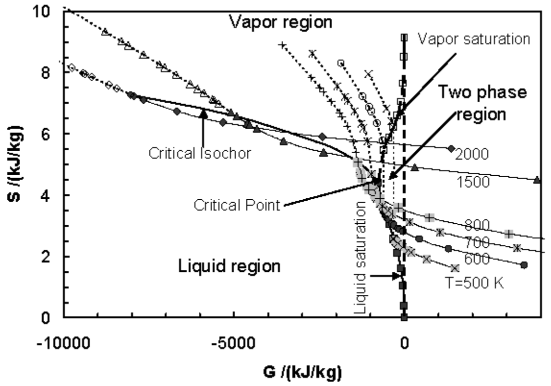

Fig. 8: Behavior of isotherms in the G-S space. The overlapping of liquid region to the vapor, two phase and solid regions is impermissible

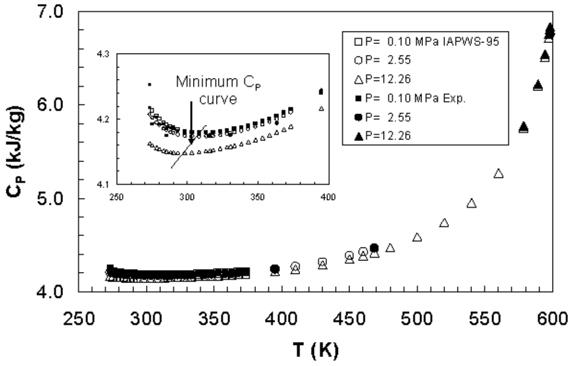

Fig. 9: Experimental and calculated values of C_P at a specified P. Same experimental data were used in the derivation of IAPWS-95 formation

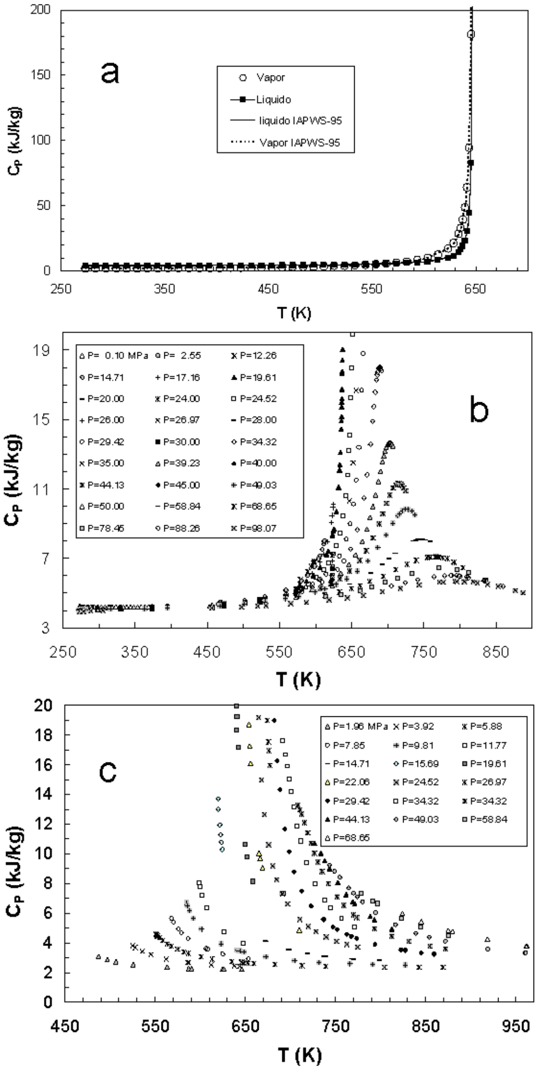

Fig. 10: Experimental values of C_P: (a) along the saturation curve, (b) in the compressed liquid region and (c) in the superheated steam region

The thermodynamic properties of water are calculated using the PVT characteristics, C_V and C_{Sat}. Accordingly, the internal energy for the compressed liquid and superheated steam are expressed as

$$\begin{aligned} U_{liq} &= \int_{T_{Sat}\ at\ V=V_1}^{T} C_{V,liq}dT + \int_{T_{ref}}^{T_{Sat}\ at\ V=V_1} C_{Sat,liq}dT \\ &\quad - \int_{V_{ref}}^{V_1} PdV \\ U_{vap} &= \int_{T_{Sat}\ at\ V=V_2}^{T} C_{V,vap}dT + \int_{T_{ref}}^{T_{Sat}\ at\ V=V_2} C_{Sat,vap}dT \\ &\quad - \int_{V_{ref,vap}}^{V_2} PdV - \int_{V_{ref}}^{V_{ref,vap}} PdV + L.H._{T_{ref},P_{ref}} \end{aligned} \tag{8}$$

where reference point (ref.) is the saturated liquid at the triple point (vapor-liquid-liquid I) and L.H. is the latent heat at ref. We are working to create new experimental data of the steam tables for pure water using this approach.

CONCLUSIONS

The laws of thermodynamics are well established and a formulation (equation of state) is an empirical relation among state variables. There are two prerequisites in creating a formulation: (a) thermodynamic consistency among the experimental values of state functions and (b) retaining the consistency in the predicted values through the formulation.

The IAPWS-95 formulation is thermodynamically inconsistent because it was creating through the incorrect experimental values of the thermodynamic properties of pure water. The experimental values of heat capacity at constant pressure (C_P) and at constant volume (C_V) along the saturation curve are measured through a physically incorrect concept. The measurement of C_V for liquid and vapor is more reliable and precise. It is unfeasible to measure C_V for all the conditions of temperature and pressure, required for calculating the thermodynamic properties of liquid or vapor. Therefore, the heat capacity along the saturation curve, C_{Sat} is defined as the proportion of amount heat to the change in temperature. Using the PVT characteristics, C_V and C_{Sat}, all the other thermodynamic properties of water can be calculated.

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