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SteamTablesIIE: An ActiveX to Calculate the Thermodynamic Properties of Water

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ABSTRACT

The thermodynamic properties of water are of fundamental importance to perform geochemical, reservoir and production engineering calculations in the geothermal industry. Using the IAPWS-95 formulation an ActiveX component, *SteamTablesIIE* is developed to calculate thermodynamic properties of pure water as a function of two independent intensive variables: (1) temperature (T) or pressure (P) and (2) T, P, volume (V), internal energy (U), enthalpy (H), entropy (S) or Gibbs free energy (G). The second variable cannot be same as variable 1. Additionally, it calculates the properties along the separation boundaries (i.e., sublimation, saturation, critical isochor, ice I melting, ice III to ice VII melting and minimum volume curves) considering the input parameter as T or P for the variable 1.

SteamTablesIIE takes into account the following 27 intensive properties: *T, P, fraction, state, V, density (Den), compressibility factor (Z_0), U, H, G, Helmholtz free energy (A), S, heat capacity at constant pressure (C_p), heat capacity at constant volume (C_v), coefficient of thermal expansion (CTE), isothermal compressibility (Z_{iso}), speed of sound (VelS), partial derivative of P with T at constant V (dPdT), partial derivative of T with V at constant P (dTdV), partial derivative of V with P at constant T (dVdP), Joule-Thomson coefficient (JTC), isothermal throttling coefficient (IJTC), viscosity (Vis), thermal conductivity (ThrmCond), surface tension (SurfTen), Prandtl number (PrdNum) and dielectric constant (DielCons).* The use of *SteamTablesIIE* requires certain precautions because there may be multiple values.

1. INTRODUCTION

Water plays a fundamental role in the process of transformation of our planet, Earth. It is well established that water is an essential component for the existence of life.

In the electricity production industry the different types of fuels (heat sources) like coal, petroleum, natural gas, nuclear fuel, geothermal heat, etc. are used to convert water into vapor which moves turbines. To understand the process and efficiency of energy conversion at different stages of electricity generation the thermodynamic properties of water are required. In the geothermal industry the reservoir engineering and geochemistry cannot be dealt without the thermodynamic properties of water.

Consequently, the water is the most studied substance on the Earth. However, our knowledge on its thermodynamic properties is still very limited.

The International Association for the Properties of Water and Steam (IAPWS) has compiled all the literature on the thermodynamic properties of water and developed a formulation (IAPWS-95) for the steam tables (i.e. thermodynamic properties of water). Using this formulation Verma (2003) developed an ActiveX component *SteamTables* for the properties of water as a function of temperature (T) and pressure (P).

Most of the scientific and engineering problems may be solved by considering T and P as independent variables, but in some cases we need to consider other variables as independent parameters like the pressure-enthalpy chart, which is of extreme importance for electricity production engineers. Additionally, all the thermodynamic properties of a pure substance may be defined as a function of any two independent state variables.

In this work an ActiveX component, *SteamTablesIIE* is developed to extend the application of *SteamTables* to calculate the thermodynamic properties of pure water as a function of two state variables: (1) T or P and (2) T, P, volume (V), internal energy (U), enthalpy (H), entropy (S), or Gibbs free energy (G). The second variable cannot be same as variable 1. Additionally, the calculation of the properties along the separation boundaries (i.e., sublimation, saturation, critical isochor, ice I melting, ice III to ice VII melting and minimum volume curves) considering the input parameter as T or P for the variable 1 is included. The limitations of *SteamTablesIIE* are also discussed. Similarly, an analysis of experimentally measured thermodynamic properties of water is presented.

2. THERMODYNAMICS: A SUMMARY

Verma (2006) summarized the thermodynamic concepts used for understanding the relations among the state properties of a substance. T, P, V, U, H, S, G, Helmholtz free energy (A) including conductivity, solubility, equilibrium constant of a chemical reaction, etc. are state variables. Any two state variables are sufficient and necessary to define completely a pure homogeneous system in a phase. If Z is a dependent state function of two state variables X and Y, it should fulfill the following relations of a mathematical exact function.

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

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

If one independent variable (say Y) is constant, we are looking for the behavior of X with Z and vice versa. In this case the equation 2 reduces to

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

The variation of a state function between two points is independent of trajectory (path) and the past history of the substance. There cannot be any maximum or minimum in the behavior of a state function with an independent state variable in a pure phase when the other independent state variable is constant. In other words, a state function (or an exact function) cannot be a multi-valued function unless a phase transition exists.

3. PROGRAM DESCRIPTION

Verma (2003) explained the basic aspects associated with the programming of an ActiveX component and its use in MS-Excel. An ActiveX component is a server application that exposes its functionality through an interface consisting of properties, methods and events. The procedure for employing an ActiveX component in MS-Excel is described in details by Verma (2003). The properties of an ActiveX, which can be modified by the user, are considered as write only and serve as input parameters. Similarly, the read only properties serve as output parameters and the user cannot change them. The value of read and write properties can be modified and obtained after calculations by the user.

SteamtablesIIE has 8 write only properties: SepBoundry, Variable1, Value1, Variable2 Value2, NPhs, NProp and NDataset. These parameters are separation boundary, variable 1, value of variable 1, variable 2, value of variable 2, number of phase, number of property, and number of dataset, respectively. Similarly, it has six read only properties: Liquid, Liquid 1, Liquid2, Vapor, Vapor1 and Vapor2 and a public method: UpDate. The user can only access the public methods of an ActiveX component like Update. The properties Liquid, Liquid 1, Liquid2, Vapor, Vapor1 and Vapor2 are objects of phase type. A phase type object contains 27 properties: *T, P, fraction, state, V, density (Den), compressibility factor* (Z_0)*, U, H, G, A, S, heat capacity at constant pressure* (C_p)*, heat capacity at constant volume* (C_v)*, coefficient of thermal expansion (CTE), isothermal compressibility* (Z_{iso})*, speed of sound (VelS), partial derivative of P with T at constant V (dPdT), partial derivative of T with V at constant P (dTdV), partial derivative of V with P at constant T (dVdP), Joule-Thomson coefficient (JTC), isothermal throttling coefficient (IJTC), viscosity (Vis), thermal conductivity (ThrmCond), surface tension (SurfTen), Prandtl number (PrdNum) and dielectric constant (DielCons).*

SteamTablesIIE uses internally *SteamTables* to perform the calculations. It calculates first the corresponding values of T and P for the input parameters. For example, if the input variables are T and P, it determines first the state of water and then inputs the value of T and P in *SteamTables* to calculate the properties of water. The procedure is complex when one of the variables is not T or P. To illustrate the calculation (see Figure 4) let us consider the variable 1 is T (=500 K) and variable 2 is H (=2000 kJ/kg). The first step is to identify the possible ranges of P corresponding to T=500K: (i) the superheated steam region which may have any value of pressure within 3.23×10^{-8} to 2.639 MPa, (ii) along saturation curve at P= 2.639 MPa and (iii) the compressed liquid region (P=2.639 to 4695.585 MPa). The second step is to find any extremum point for enthalpy in these ranges in order to further subdivide the ranges. Fortunately, there is no extremum point in the case. The third step to calculate the values of enthalpy for the temperature and the end values of pressure ranges: (i) for the superheated steam region the range of H is 2932.348 to 2802.478 kJ/kg, (ii) along saturation curve the range of H is 280.478 to 975.431 kJ/kg and (iii) for the compressed liquid region the range of H is 975.431 to 4006.728 kJ/kg. The fourth step is to identify the H ranges which have the given input value of H (=2000 kJ/kg). In this case it can be along the saturation curve and in the compressed liquid region. The fifth step is to find the values of T and P which have H=2000kJ/kg. It is simply balance the enthalpy for a vapor fraction along the saturation curve. In the case of compressed liquid region it performs numerical calculations using the trial and error method. The tolerance is generally order of 10^{-8}. It internally sets the value of tolerance depending of the region; however, the accuracy of the calculated values is always within the analytical uncertainty in the IAPWS-95. If the input values of the parameters are out of range, it assigns -1 to all the parameters. Thus it never crashes.

Table 1. The Content of Library File, MyLib2009

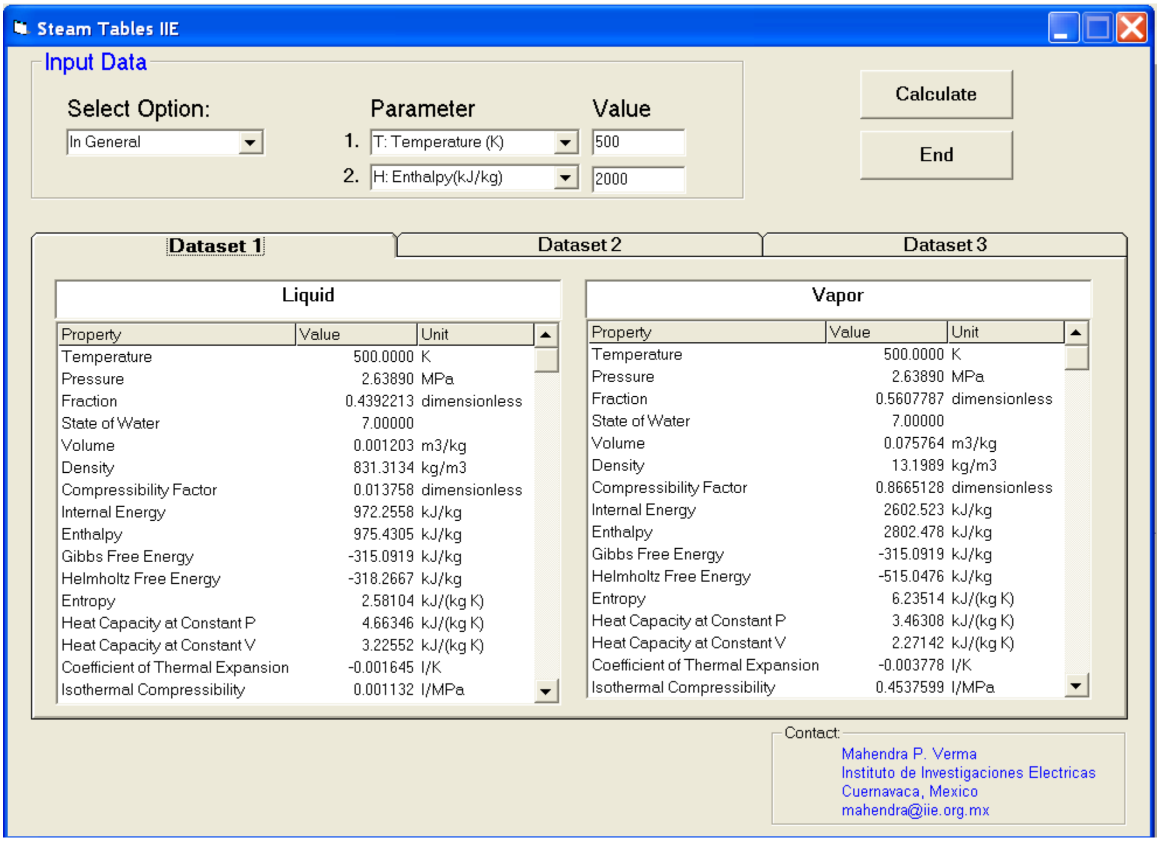
ActiveX	Description
SteamTables	Thermodynamic properties of water as function of T and P using the IAPWS-95 formulation
SteamTablesIIE	Thermodynamic properties of water based on the multiple variable sets.
Phase	This is used internally by *SteamTablesIIE*
QrtzGeotherm	Geothermal reservoir temperature and vapor fraction from quartz geothermometery
MoodyChart	Frictional factor for fluid flow in a pipeline
OrificeMeter	Steam flow rate in a geothermal pipeline with a differential head orifice flow meter

We are working to include all the ActiveX components required to simulate the steam flow in a geothermal pipeline network in the library MyLib2009.dll. MyLib2009 is available for scientific use from the author. Presently, the library has the ActiveX components which are given in Table 1.

3.1 Demonstration Program

Using the ActiveX *SteamTablesIIE* a demonstration of program *StmTblIIE* is written in Visual Basic 6.0. The program package can be installed on a computer in the Windows environment with running setup program and following the instructions. The graphic user interface of *StmTblIIE* is given in Figure 1. The user provides the values of parameters given in the input data frame. In the select option combo box, the default is to calculate the thermodynamic properties of water in general. If one selects a separation boundary, the combo box and textbox for variable 2 are cleared. So, the value of temperature or pressure can be typed in the textbox for variable 1.

To perform the calculation one has to provide the values of all input parameters in the input frame and press the button “Calculate”. The calculation of thermodynamic properties of pure water at T=500 K and H=2000 kJ/kg is shown in Figure 1. The first dataset is along the saturation curve (state=7), which is shown in the figure. If we press the tab “Dataset 2”, it shows the values of second dataset. The second dataset is in the compressed liquid region at T=500K and P=1557.039 MPa. It shows all the values of vapor as -1, which means that there is no vapor for the conditions. There is no possible third dataset in this case; therefore, the values of all the parameters are -1 in the tab “Dataset 3”.



Select Option: In General

Parameter / Value

1. T: Temperature (K) 500

2. H: Enthalpy(kJ/kg) 2000

Liquid

Property	Value	Unit
Temperature	500.0000	K
Pressure	2.63890	MPa
Fraction	0.4392213	dimensionless
State of Water	7.00000	
Volume	0.001203	m3/kg
Density	831.3134	kg/m3
Compressibility Factor	0.013758	dimensionless
Internal Energy	972.2558	kJ/kg
Enthalpy	975.4305	kJ/kg
Gibbs Free Energy	-315.0919	kJ/kg
Helmholtz Free Energy	-318.2667	kJ/kg
Entropy	2.58104	kJ/(kg K)
Heat Capacity at Constant P	4.66346	kJ/(kg K)
Heat Capacity at Constant V	3.22552	kJ/(kg K)
Coefficient of Thermal Expansion	-0.001645	l/K
Isothermal Compressibility	0.001132	l/MPa

Vapor

Property	Value	Unit
Temperature	500.0000	K
Pressure	2.63890	MPa
Fraction	0.5607787	dimensionless
State of Water	7.00000	
Volume	0.075764	m3/kg
Density	13.1989	kg/m3
Compressibility Factor	0.8665128	dimensionless
Internal Energy	2602.523	kJ/kg
Enthalpy	2802.478	kJ/kg
Gibbs Free Energy	-315.0919	kJ/kg
Helmholtz Free Energy	-515.0476	kJ/kg
Entropy	6.23514	kJ/(kg K)
Heat Capacity at Constant P	3.46308	kJ/(kg K)
Heat Capacity at Constant V	2.27142	kJ/(kg K)
Coefficient of Thermal Expansion	-0.003778	l/K
Isothermal Compressibility	0.4537599	l/MPa

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Figure 1: Interface form for the demonstration program *StmTblIIE* to display properties of ActiveX *SteamTablesIIE*. It shows the calculation of the thermodynamic properties of liquid and vapor at T=500 K and H=2000 kJ/kg. The first dataset is along the saturation curve, which is shown in the figure. The second dataset is in the compressed liquid region, which can be seen by pressing tab "Dataset 2". There is no possible third dataset in this case; therefore the values of all the parameters are -1 in the tab "Dataset 3".

3.2 Using *SteamTablesIIE* in MS-Excel

Verma (2003) described in details to write a macro in the personal workbook of Excel, which permits to use the macro in any workbook. Once the demonstration program, *StmTblIIE* is installed, it installs automatically the dynamic link library ("MyLib2009.dll") in the directory "C:\Windows\System32". MyLib2009 contains the objects, *SteamTablesIIE*, *Steamtables* *Phase* and others. *SteamtablesIIE* uses internally the objects, *SteamTables* and *Phase*.

If we do not want to install the above demonstration program, we should extract the DLL file "MyLib2009.dll" from the compressed file "StmTblIIE.Cab" and use the registration procedure in the Windows environment as described by Verma (2008). Now, the reference in MS-Excel is created as described (Verma, 2003, 2008). *SteamTables* calculates faster the thermodynamic properties of water if the independent variables are T and P, and there is no interest in knowing the state of water. The listing of excel functions is not given here, but it is available from the author.

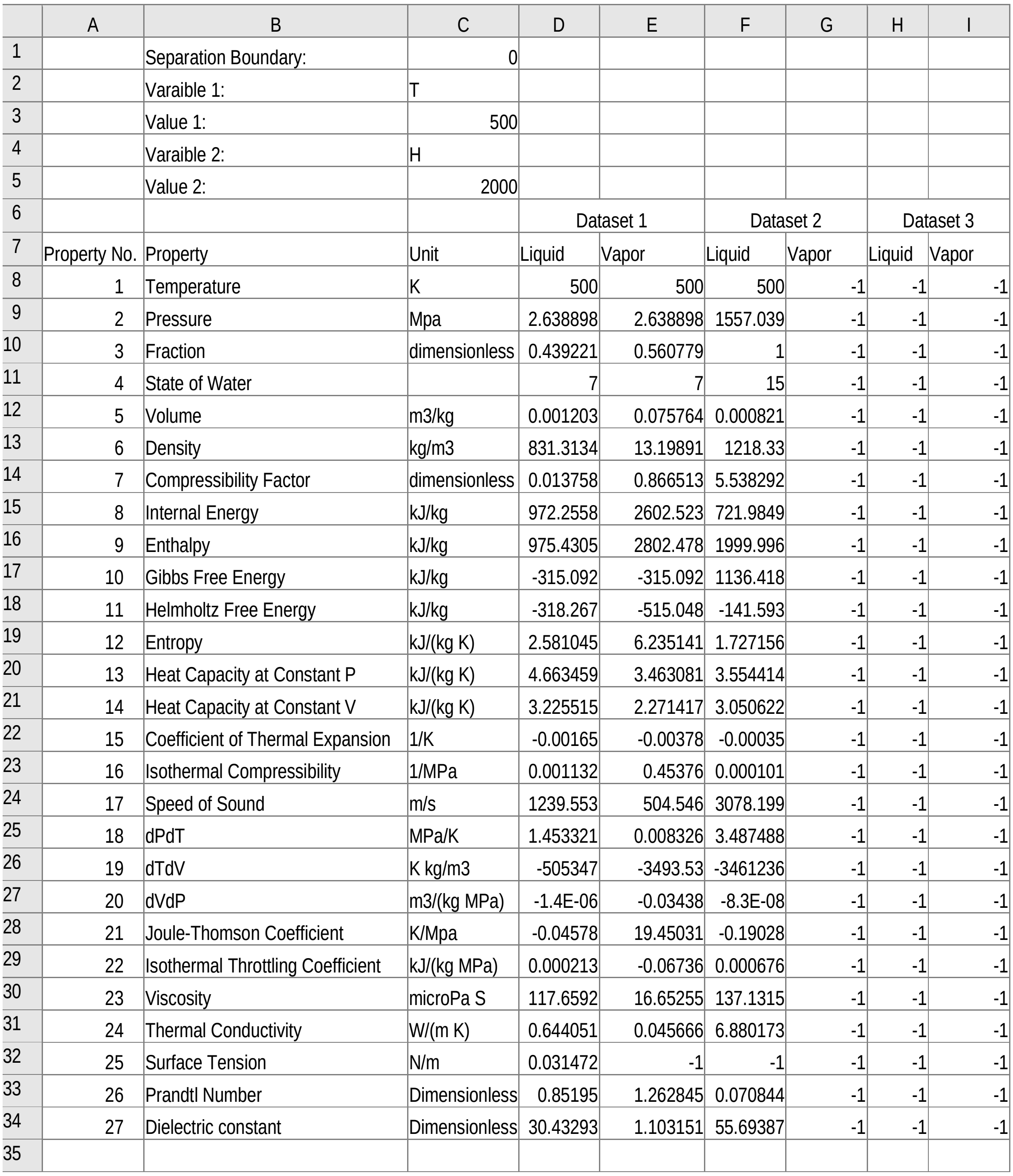
Using the function WtrStmTblIIE (SepBndry, Vari1, Valu1, Vari2, Valu2, NPhs, NProp, NDataset) the calculation of thermodynamic properties of water for T=500 K and H=2000 kJ/kg in a MS-Excel worksheet is shown in Figure 2. The first five lines have the values of separation boundary (SepBndry), variable 1 (Vari1), value 1 (Valu1), variable 2 (Vari2), and value 2 (Valu2), respectively. These data together with phase number (NPhs), property number (NProp) and dataset number (NDataset) are the input parameters for the function WtrStmTblIIE. Thus one can consult in a glance whole steam tables in an excel worksheet.

4. THERMODYNAMIC PROPERTIES OF WATER

SteamTablesIIE provides the values of 27 thermodynamic properties of water; however, we will only analyze the properties which are of interest to the geothermal industry.

4.1 PVT Characteristics

Verma (2003) presented the TP relationship for pure water according to the IAPWS-95 formulation (Figure 3). The saturation curve is the locus of T and P values where liquid and vapor coexist in equilibrium: it starts from the ice-water-vapor triple point and terminates at the critical point. Water has many solid forms, depending on the conditions of pressure and temperature. All the ice curves (I, III, V, VI and VII) define the melting curve. The supercritical fluid region, existing at T and P higher than those of critical point, is shown by diagonal lines, which do not represent phase changes but depend on an arbitrary definition of what constitutes liquid and vapor phases. The critical isochor (i.e. total specific volume V= 0.003106 m^3/kg or density = 322.0 kg/m^3) in the supercritical fluid region acts as a phase boundary between the liquid-like and vapor-like fluid. The



	A	B	C	D	E	F	G	H	I
1		Separation Boundary:	0						
2		Varaible 1:	T						
3		Value 1:	500						
4		Varaible 2:	H						
5		Value 2:	2000						
6				Dataset 1		Dataset 2		Dataset 3	
7	Property No.	Property	Unit	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor
8	1	Temperature	K	500	500	500	-1	-1	-1
9	2	Pressure	Mpa	2.638898	2.638898	1557.039	-1	-1	-1
10	3	Fraction	dimensionless	0.439221	0.560779	1	-1	-1	-1
11	4	State of Water		7	7	15	-1	-1	-1
12	5	Volume	m3/kg	0.001203	0.075764	0.000821	-1	-1	-1
13	6	Density	kg/m3	831.3134	13.19891	1218.33	-1	-1	-1
14	7	Compressibility Factor	dimensionless	0.013758	0.866513	5.538292	-1	-1	-1
15	8	Internal Energy	kJ/kg	972.2558	2602.523	721.9849	-1	-1	-1
16	9	Enthalpy	kJ/kg	975.4305	2802.478	1999.996	-1	-1	-1
17	10	Gibbs Free Energy	kJ/kg	-315.092	-315.092	1136.418	-1	-1	-1
18	11	Helmholtz Free Energy	kJ/kg	-318.267	-515.048	-141.593	-1	-1	-1
19	12	Entropy	kJ/(kg K)	2.581045	6.235141	1.727156	-1	-1	-1
20	13	Heat Capacity at Constant P	kJ/(kg K)	4.663459	3.463081	3.554414	-1	-1	-1
21	14	Heat Capacity at Constant V	kJ/(kg K)	3.225515	2.271417	3.050622	-1	-1	-1
22	15	Coefficient of Thermal Expansion	1/K	-0.00165	-0.00378	-0.00035	-1	-1	-1
23	16	Isothermal Compressibility	1/MPa	0.001132	0.45376	0.000101	-1	-1	-1
24	17	Speed of Sound	m/s	1239.553	504.546	3078.199	-1	-1	-1
25	18	dPdT	MPa/K	1.453321	0.008326	3.487488	-1	-1	-1
26	19	dTdV	K kg/m3	-505347	-3493.53	-3461236	-1	-1	-1
27	20	dVdP	m3/(kg MPa)	-1.4E-06	-0.03438	-8.3E-08	-1	-1	-1
28	21	Joule-Thomson Coefficient	K/Mpa	-0.04578	19.45031	-0.19028	-1	-1	-1
29	22	Isothermal Throttling Coefficient	kJ/(kg MPa)	0.000213	-0.06736	0.000676	-1	-1	-1
30	23	Viscosity	microPa S	117.6592	16.65255	137.1315	-1	-1	-1
31	24	Thermal Conductivity	W/(m K)	0.644051	0.045666	6.880173	-1	-1	-1
32	25	Surface Tension	N/m	0.031472	-1	-1	-1	-1	-1
33	26	Prandtl Number	Dimensionless	0.85195	1.262845	0.070844	-1	-1	-1
34	27	Dielectric constant	Dimensionless	30.43293	1.103151	55.69387	-1	-1	-1
35									

Figure 2: An example MS-Excel worksheet for calculating the properties of water at T=500 K and H=2000 kJ/kg. The values are same as shown in Figure 1. All the three datasets are shown here. The impermissible values are shown with -1

ice VII curve is extended up to the maximum pressure as shown with a solid black line in the Figure 3. Thus according to the IAPWS formulation the supercritical fluid region also contains solid (ice) water.

It was observed in late 19th century that the water had maximum density at T=277.127 K (~4ºC) and P=0.1 MPa. It was called an anomalous behavior. It is anomalous to the thermodynamic laws, if the whole liquid water is considered a single phase. Recent works suggest that there is the effect of hydrogen bonding on the molecular structure of water at low temperatures. There are two types of structure: *one associated with hydrogen bonding (below 4ºC) and other is 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 (Figure 3) and the water density behavior is consistent with the laws of thermodynamics.

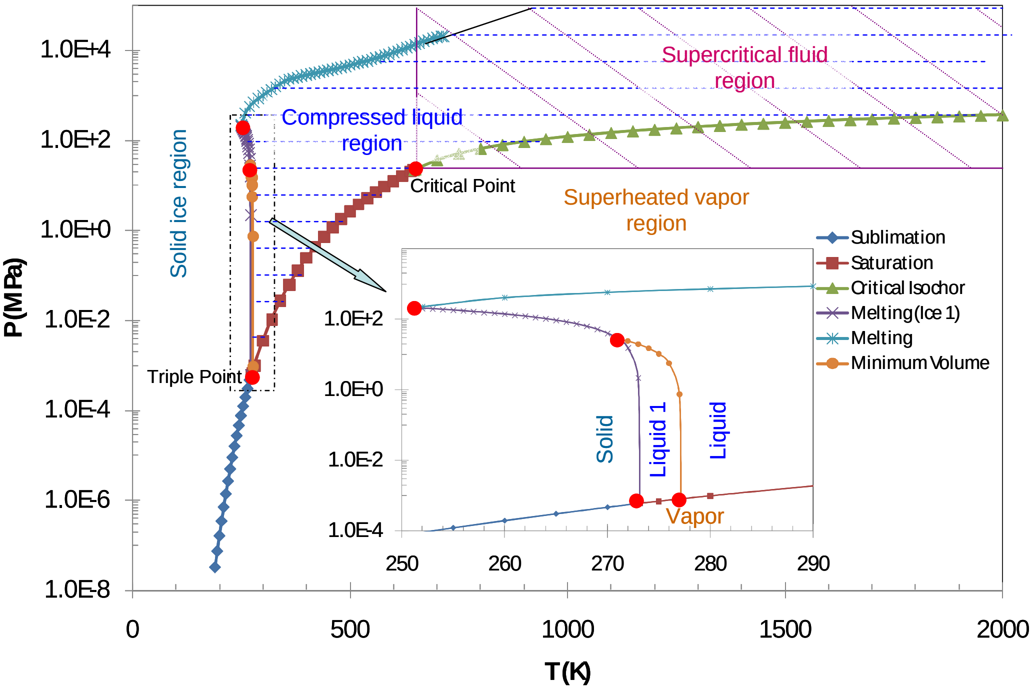


Figure 3: TP characteristic of pure water (Verma, 2003). The inserted figure shows the location of liquid 1 region. The supercritical fluid region is formed of superheated steam, compressed liquid and ice as shown by diagonal lines at T and P higher than the values of critical point. There are four triple points which as shown with red dots.

4.2 Characteristics of Other State Functions

The other important state variables are U, H, S, G and A. Figure 4 shows a PH diagram for pure water. The critical isochor curve is a separation boundary for the compressed liquid and superheated steam in the fluid region. Three isotherms at T=300, 500 and 700 K are plotted. If we consider T and H as independent variables, there may be two points of intersection. For example, if T=300 K and H=2000 kJ/kg, there is only one intersection (denoted by x) between the isotherm at 300 K and H=2000 kJ/kg line within the two phase region. The water state is along the saturation curve at P=3.5x10^{-3} MPa and the vapor fraction is 0.774. If T=500 K and H=2000 kJ/kg, there are two values: a) along the saturation curve at P=2.64 MPa with vapor fraction 0.561 and b) in the compressed liquid at P=1557.0 MPa. Similarly, If T=700 K and H=2000 kJ/kg, there are two values in the compressed liquid region: first at P=63.5 and second at P=459.4 MPa. It is against the basic definition of state function.

5. GEOTHERMAL CALCULATIONS

To understand the consequences of inconsistency in the thermodynamic data of water in the geothermal calculations, let us consider a simple example. In a deep geothermal exploration project, three reservoirs were found with same characteristics except different pressure

A. *T=700 K and P= 63.5 MPa*
B. *T=700 K and P=180.0 MPa*
C. *T=700 K and P=456.4 MPa*

Which one is the best geothermal reservoir for electricity generation?

In the geothermal industry we flash the deep geothermal brines in a separator at a specified T (say 450 K) or P and use the vapor to move the turbines for the generation of electricity. So, we use only the concept of mass and energy balance (a simplification).

$$H_R = yH_v + (1-y)H_l \qquad (4)$$

Where H_R is the reservoir enthalpy (liquid), y is the fraction of vapor, and H_v and H_l are the enthalpy of liquid and vapor at the separator, respectively.

Using the steam tables we can write the enthalpy of liquid in the reservoirs

A.	*T=700 K and P= 63.5 MPa,*	*H=2000 kJ/kg*
B.	*T=700 K and P=180.0 MPa*	*H=1894 kJ/kg*
C.	*T=700 K and P=456.4 MPa*	*H=2000 kJ/kg*

The enthalpies of vapor and liquid at the separator at T=450 K and P= 0.93 MPa are

H_v *=2774.4 kJ/kg* H_l*=749.2 kJ/kg*

Thus the fraction of vapor in the three cases is

A. *y=0.62*
B. *y=0.56*
C. *y=0.62*

It is clear that the reservoirs A and C will produce same electricity, while the reservoir B will produce slightly less electricity. So, the right answer could be A or C. But our scientific quest enforces us to think. A simple reasoning says that there should be some systematic variation in the electricity production with changing only the reservoir pressure. In our calculation every parameter is same expect the reservoir enthalpy of liquid. Thus it is a problem of steam tables (i.e. thermodynamic data of water).

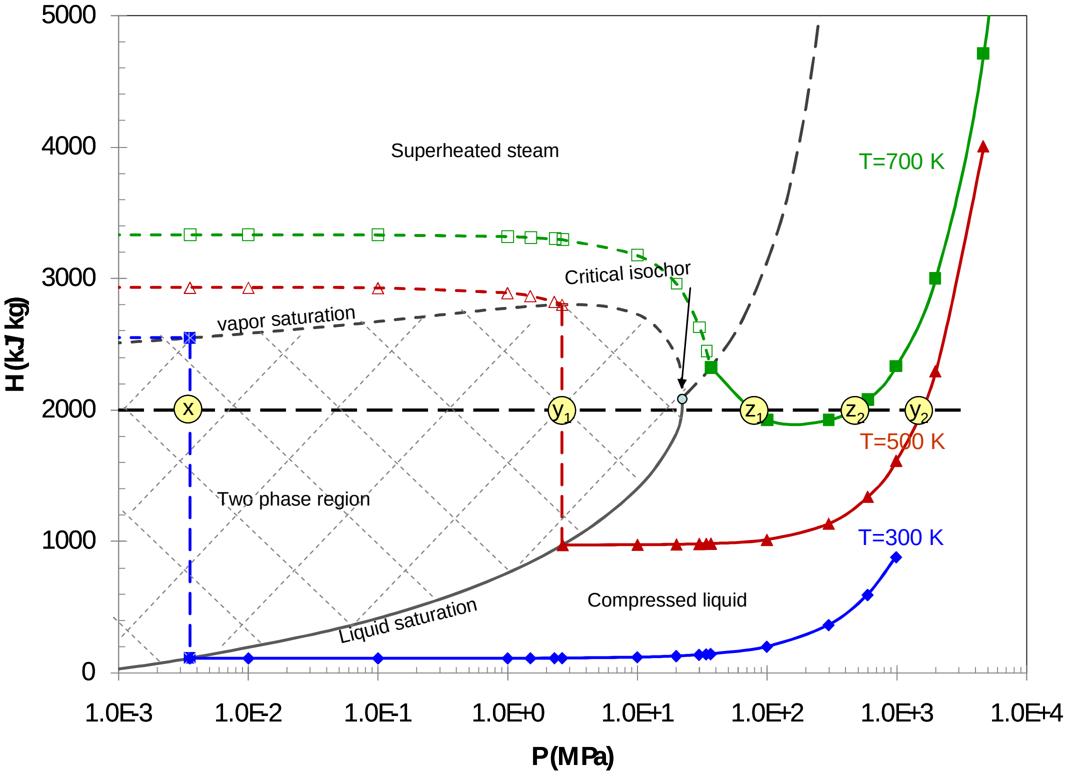


Figure 4: H-P diagram for pure water. Three isotherms at T=300, 500 and 700 K and their intersections with the line H=2000 kJ/kg are shown with x, y and z, respectively. There is only one intersection for isotherm T=300 K, whereas there are two intersections for isotherms T=500 and 700 K.

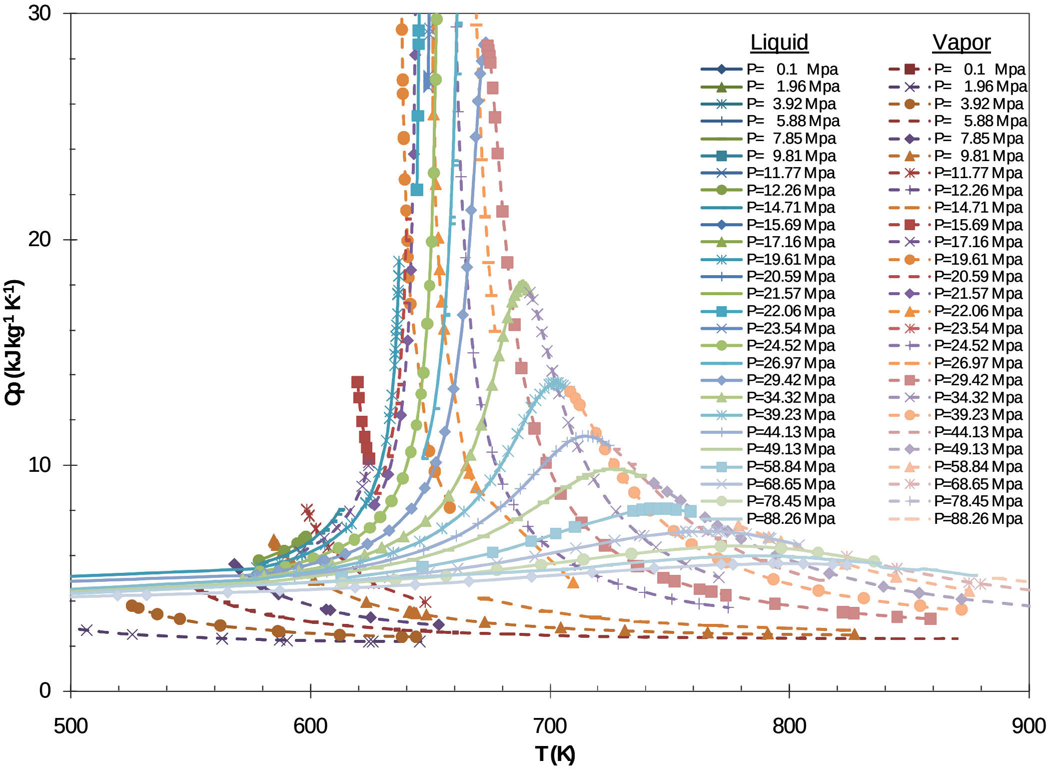


Figure 5: Experimental data for the heat capacity at constant pressure (C_p) of water. The values are divided in two groups: (a) for the compressed liquid region and (b) for superheated steam region.

6. EXPERIMENTAL MEASUREMENT OF STATE FUNCTION

The state functions U, H, S, G and A cannot be measured directly. There are calculated from the PVT characteristics and heat capacity data (Verma, 2005).

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.

Similarly, there is inconsistency in the measured values of C_p (or C_v) in the compressed liquid and superheated steam regions, discussed later. In summary, the development of the IAPWS-95 formulation is based on the thermodynamically inconsistent experimental data. In creating the IAPWS-95 formulation the Helmholtz energy was divided in two parts: ideal and residual. The ideal behavior was considered in the whole range of T and P. Verma (2006) shows that the ideal gas concept is only valid at high temperature and low pressure for steam phase. Thus there is also need to revise the development procedure of a thermodynamic formulation of pure water or any system. However, the consistency in the experimental data is the first requirement.

Verma (2005) 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 (see webpage of IAPWS for the database). 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. 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

$$\begin{aligned} U_{liq} &= \int_{T_{Sat}\ at\ V=V_1}^{\mathrm{T}} C_{V,liq}\,dT + \int_{T_{ref}}^{T_{Sat}\ at\ V=V_1} C_{Sat,liq}\,dT - \int_{V_{ref}}^{V_1} PdV \\ U_{vap} &= \int_{T_{Sat}\ at\,V=V_2}^{\mathrm{T}} C_{V,vap}dT + \int_{T_{ref}}^{T_{Sat}\ at\,V=V_2} C_{Sat,vap}dT - \int_{V_{ref,vap}}^{V_2} PdV - \int_{V_{ref}}^{V_{ref,vap}} PdV + L.H._{T_{ref},P_{ref}} \end{aligned} \tag{5}$$

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 still working to create new experimental data of the steam tables for pure water using this approach.

6.1 Heat Capacity at Constant Pressure

The behaviors of P, V and T are consistent, while the behaviors of U, H, G, S and A are inconsistent thermodynamically in the IAPWS-95 formulation. The values of U, H, G, S and A 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 5 shows the variation of experimental data of C_p with T. The data are taken from the webpage of IAPWS. The values are divided in two groups: (a) for the compressed liquid region and (b) for superheated steam region. The boundary is considered as the saturation curve or critical isochor.

The behavior of C_P in the compressed liquid region increases with T while decreases with P. 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). There is a maximum near to the liquid-vapor separation boundary.

There is also drastic behavior the values of C_P in the vapor phase region near the liquid-vapor separation boundaries for the corresponding pressure. It is clear that C_P increases with P while decreases with T. It is contrary to its behavior in the liquid phase region, but both the behaviors of C_P in the liquid and vapor phase region are consistent thermodynamically.

It is difficult to measure the C_p near to the critical point. However, according to the IAPWS formulation the value of C_p is very high near to critical point (i.e., ~10^9 kJ/kg K). The critical point acts as a heat sink. In other word there is tremendous amount of energy in the water near the critical point. A geothermal reservoir with such conditions will be a perfect system, but it is not observed in practice.

The most of the experimental values of C_P were measured in 1956-70 (see database of IAPWS). The experimental details for the measurement of C_P are not stayed clearly in the literature. It is difficult to state precisely the reasons for such inconsistent values. It is also amazing that there are no significant affords to reproduce the experimental values of C_P since 1970. The liquid-vapor kinetics can explain the maximum of C_P in the liquid phase region.

The surface temperature of our earth is quite less than the normal boiling point of water at 0.1 MPa (1 atm). It means that the water is in the compressed liquid region and there should not be any vapor in the atmosphere according to the thermodynamic equilibrium. Thus the formation of atmospheric vapor is a consequence of kinetic processes.

Let us consider the heating of different amount of water in a constant volume vessel and the pressure is applied with some inert gas. The amount of water is filled such that the pressure is higher than the saturated pressure at corresponding T throughout the experiment. The calculations are performed with the following considerations: (i) the constant values of C_P for the liquid and vapor water corresponding to the extreme conditions of P and T, (ii) the 5% volume of vapor phase is filled with saturated vapor and (iii) the heat of vaporization is considered as the enthalpy difference along the saturation curve. There are many limitations in these calculation; however, it demonstrates successful the reason of existing maximum in the C_P in the compressed liquid region.

Figure 6 presents the theoretical variation of heat capacity in two cases, (a) 0.2 kg of water at 30 MPa and (b) 0.35 kg of water at 10 MPa in a reaction vessel $V=0.5\times10^{-3}$ m^3. The amount of water are considered with taking care that the whole liquid does not convert to vapor phase and the reaction vessel does not fill completely with liquid phase in the temperature range. The values of C_P are considered as constant for the liquid and vapor phases, although there will be some variation of C_P with T at constant P. For example, the C_P values are taken as 4.091 kJ/kg K of liquid water at T = 273.16 K and 2.787 kJ/kg K for vapor water at 1000 K for the curve at 30 MPa. There is a maximum at T=629 K in the curve a.

The curve b corresponds to heating 0.350 kg of water in the container of 0.5×10^{-3} m^3 at 10 MPa. In this case the maximum is at T=529 K. Thus the mechanism explains successfully the existence of maximum in the experimental data of C_P at temperature below and near the critical point.

CONCLUSIONS

The ActiveX *SteamTablesIIE* calculates the 27 thermodynamic properties of water: temperature *(T), pressure (P), fraction, state, volume (V), density (Den), compressibility factor (Z_0), internal energy (U), enthalpy (H) Gibbs free energy (G), Helmholtz free energy (A), entropy (S), heat capacity at constant pressure (C_p), heat capacity at constant volume (C_v), coefficient of thermal expansion (CTE), isothermal compressibility (Z_{iso}), speed of sound (VelS), partial derivative of P with T at constant V (dPdT), partial derivative of T with V at constant P (dTdV), partial derivative of V with P at constant T (dVdP), Joule-Thomson coefficient (JTC), isothermal throttling coefficient (IJTC), viscosity (Vis), thermal conductivity (ThrmCond), surface tension (SurfTen), Prandtl number (PrdNum) and dielectric constant (DielCons)* as a function of two independent intensive variables: (1) T or P and (2) T, P, V, U, H, S or G. The second variable cannot be same as variable 1. Additionally, it calculates the properties along the separation boundaries (i.e., sublimation, saturation, critical isochor, ice I melting, ice III to ice VII melting and minimum volume curves) considering the input parameter as T or P for the variable 1.

There exist multiple values of the thermodynamic properties of water. For example, in case of T and H as independent variables there is only one value for the all the thermodynamic parameters at T=300 K and H=2000 kJ/k g. The water state is along the saturation curve at $P=3.5x10^{-3}$ MPa and the vapor fraction is 0.774. At T=500 K and H=2000 kJ/kg there are two values: a) along the saturation curve at P=2.64 MPa with vapor fraction 0.561 and b) in the compressed liquid at P=1557.0 MPa. Similarly, at T=700 K and H=2000 kJ/kg there are two values in the compressed liquid region: first at P=63.5 and second at P=459.4 MPa.

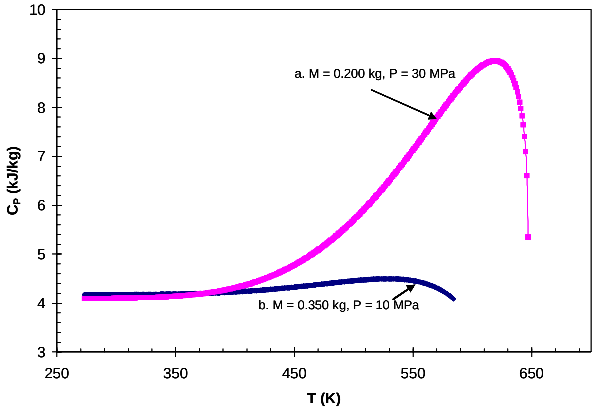


Figure 6: Calculated values of C_P for two cases: (a) 0.2 kg of water at 30 MPa and (b) 0.35 kg of water at 10 MPa in a reaction vessel of $V=0.5\times10^{-3}$ m^3

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The values of the state functions U, H, S, G and A are calculated from the PVT characteristics and heat capacity data. The values of heat capacity are incorrect and consequently there is thermodynamic inconsistency in the steam tables.

REFERENCES

Verma, M.P.: Steam Tables for pure water as an ActiveX component in Visual Basic 6.0. Computers & Geosciences 29, (2003), 1155-1163.

Verma, M.P.: Verma Procedure for the determination of heat capacity of liquids. *Proceedings,* 30th Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, CA (2005).

Verma, M.P.: Thermodynamics, equations of state and experimental data: a review. Journal of Engineering and Applied Sciences, **1**, (2006) 35-43.

Verma, M.P.: QrtzGeotherm: An ActiveX component for the quartz solubility geothermometers. Computers & Geosciences 34, (2008), 1918-1925.