



Contents lists available at ScienceDirect

Deep-Sea Research I

journal homepage: www.elsevier.com/locate/dsrI

New equations for density, entropy, heat capacity, and potential temperature of a saline thermal fluid

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ARTICLE INFO

Article history:

Received 13 January 2008

Received in revised form

12 May 2008

Accepted 27 May 2008

Available online 1 June 2008

Keywords:

Thermal saline fluid

State equation

Density

Salinity

Entropy

Potential temperature

ABSTRACT

A set of fitted polynomial equations for calculating the physical variables density, entropy, heat capacity and potential temperature of a thermal saline fluid for a temperature range of 0–374 °C, pressure range of 0.1–100 MPa and absolute salinity range of 0–40 g/kg is established. The freshwater components of the equations are extracted from the recently released tabulated data of freshwater properties of Wagner and Pruß [2002]. The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. Journal of Physical and Chemical Reference Data 31, 387–535]. The salt water component of the equation is based on the near-linear relationship between density, salinity and specific heat capacity and is extracted from the data sets of Feistel [2003]. A new extended Gibbs thermodynamic potential of seawater. Progress in Oceanography 58, 43–114], Bromley et al. [1970. Heat capacities and enthalpies of sea salt solutions to 200 °C. Journal of Chemical and Engineering Data 15, 246–253] and Grunberg [1970. Properties of sea water concentrates. In: Third International Symposium on Fresh Water from the Sea, vol. 1, pp. 31–39] in a temperature range 0–200 °C, practical salinity range 0–40, and varying pressure and is also calibrated by the data set of Millero et al. [1981. Summary of data treatment for the international high pressure equation of state for seawater. UNESCO Technical Papers in Marine Science 38, 99–192]. The freshwater and salt water components are combined to establish a workable multi-polynomial equation, whose coefficients were computed through standard linear regression analysis. The results obtained in this way for density, entropy and potential temperature are comparable with those of existing models, except that our new equations cover a wider temperature—(0–374 °C) than the traditional (0–40 °C) temperature range. One can apply these newly established equations to the calculation of in-situ or onboard density, specific volume (therefore, the porosity), and potential temperature change that are usually measured on shipboard by the Ocean Drilling Project (ODP) and other hydrothermal-fluid studies.

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1. Introduction

Because of fundamental thermodynamic laws, a change in water pressure can bring a change in both temperature and other physical properties (such as density and specific volume) of the water. For example,

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when a high-pressure geothermal fluid or a regular seawater parcel from the bottom of the ocean is lifted to the surface, where atmospheric pressure prevails, the temperature of the thermal saline fluid will change even under adiabatic conditions when there is no exchange of heat of the fluid with its surroundings (Sun et al., 2007; Fig. 1). Density gradients arising from temperature and pressure variations can also drive the fluid movement. The change of various water properties due to pressure, temperature and salinity is described by the corresponding equation of state of seawater in geothermal fluid studies.

Traditionally, state equations of seawater have been established by empirical fitting to experiment data (cf. Millero et al., 1980, 1981; Fofonoff, 1985; Fofonoff and Millard, 1983; Bryden, 1973), in particular the International Equation of State of Seawater 1980 (EOS80). In these equations, the salinity of seawater is described by its “practical salinity”, defined on its 1978 scale (PSS-78), valid between 2 and 42. According to this, practical salinity, S , is a dimensionless number, approximately equal to the mass fraction of dissolved salt in grams in one kilogram of seawater. A new reference-composition salinity has recently been defined as a more accurate estimate for the absolute salinity of standard seawater (Millero et al., 2008). It is valid outside the validity range of PSS-78 and can be expressed in g/kg, i.e. as absolute salinity. Even though practical salinity is known to deviate from absolute salinity by about 0.5%, we will consider this difference as negligible in comparison to the further approximations made in this paper for estimating the equation of state of the thermal fluid. In particular, the dissolved salt found in abyssal thermal vents does not necessarily possess exactly the same

chemical composition as Atlantic surface water. With progress in thermodynamic theory, more recent studies (Feistel, 1993, 2003, 2008; Feistel and Hagen, 1995; McDougall et al., 2003; Jackett et al., 2006; Feistel and Marion, 2007) have focused on the consistent theoretical derivation and subsequent computation of various physical properties of seawater from a single, so-called thermodynamic potential function, in the temperature range 0–40 °C. Although the new formulation of Feistel and Marion (2007) covers high pressures and high salinities, it is restricted to a temperature below 25 °C. However, such a small temperature range rules out its application to most thermal fluids, whose temperatures are often higher than 40 °C. The most recent Gibbs function of seawater (Feistel, 2008) describes properties for up to 80 °C, but only at atmospheric pressure. For pure freshwater the well-established state-of-water equation of Wagner and Pruß (2002) has been the base of the 1995. Release of the International Association for the Properties of Water and Steam (IAPWS-95) as it is valid for high pressures and temperatures. There is also the Gibbs function available for pure water in the range 273–623 K, 0–100 MPa, the so-called IF-97 formulation (Wagner and Kretzschmar, 2008). The lack of salinity consideration in all freshwater equations limits their application to the geothermal fluids as well.

Recently, numerous studies of ODP holes have reported fluid temperatures above 40 °C and have fluid density reported, for example, ODP hole 858 and 1027C. Investigation of the Endeavor segment and the Pipe Organ vent of Juan de Fuca Ridge (Johnson and Tunncliffe, 1985; Schultz et al., 1992; Wetzler et al., 1998), the Middle Valley geothermal data in ODP holes 857D and 858G (Davis and Becker, 1999), the Cascadian Accretionary Prism (Davis et al., 1995, Nova Vent Program, 2002 at www.nova.gov), the Guaymas Basin of the Gulf of California (Little et al., 1988), the Rose Garden site of the East Pacific Rise, the southern East Pacific Rise (Jupp, 2000) and Taiwan Strait (Chen et al., 2005) all included the physical movement of thermal saline fluid. While treating the thermal dynamics of the saline thermal fluid with the physical properties of freshwater (Hayba and Ingebritsen, 1994) can provide basic understanding of fluid dynamics, lack of consideration of salinity-induced density-driven motion in these studies can introduce significant errors in some situations and make the results less reliable (Chen, 1981; Sun et al., 2007).

Therefore, this study attempts to combine the freshwater data at high temperatures (~374 °C, which is the approximate vapor saturation temperature of freshwater at 100 MPa) and pressure (100 MPa) from Wagner and Pruß (2002), the saline water data (salinity 40, pressure 0–100 MPa) from the model of Feistel (2003), the EOS80s experimental data of Millero et al. (1981) for temperatures 0–40 °C, and the data of Bromley et al. (1967, 1970), and Grunberg (1970) for temperatures 0–200 °C, absolute salinities 0–40 g/kg at saturation pressure to establish a set of equations that can be used to roughly estimate the density, entropy, heat capacity and potential temperature of saline thermal fluid for geothermal saline fluid studies. The results will be applicable for the temperature (T)

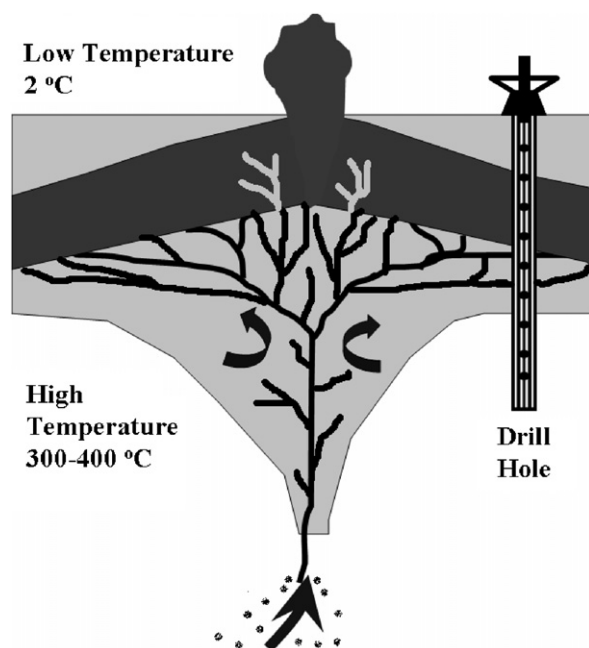


Fig. 1. Environmental contrasts between a deep borehole and the seafloor result in changes of the physical properties of the fluid.

range of 0–374 °C, pressure (*p*) range 0.1–100 MPa, and salinity (*S*) range 0–40 g/kg, which are the *T–P–S* ranges for most of geothermal saline fluids.

2. Density

The polynomial coefficients for the density of freshwater at temperatures of 0–374 °C and pressures of 0.1 (~atmospheric pressure) to 100 MPa were extracted from the data of Wagner and Pruß (2002), which is recommended by the IAPWS. The density of seawater for temperatures 0–40 °C, practical salinity 0–40 and pressures 0.1–100 MPa was calculated using equations of Feistel (2003). The density of the saline thermal fluid for temperatures 0–180 °C, absolute salinities 0–80 g/kg and vapor pressure was obtained from Grunberg (1970), though there is also a similar set of data by Higashi et al. (1931). The EOS80 experimental data by UNESCO (Joint panel on oceanographic tables and standards, Millero et al., 1981) were also used in the calibration of the density polynomial equation.

The density differences between fresh and saline water in this 0–180 °C temperature range were used in a multiple regression model to compute the polynomial coefficients of the saline part of the fourth-order polynomial equation. The logic behind extending the saline part of the coefficients based on the density difference at low temperature is the approximate linear relationship between density and salinity (Fig. 2) at saturation pressure. One notes from Fig. 2 that all the *R*² of regression coefficients for the linear fits of salinity vs. density are close to one, clearly indicating a straight-line relationship between salinity and density for the same temperature and pressure. This relationship implies that the density formulation given in Table 1 can theoretically be extended to a salinity level higher than 40 g/kg with no appreciable errors.

The density polynomial coefficients computed from the regression analysis listed in Table 1 are similar to the format of Fofonoff (1985) and McDougall et al. (2003). Here ρ is the density in kg/m³; *t* the in-situ temperature

in °C; *p* the pressure in MPa and *S* absolute salinity in g/kg. The goodness of the polynomial fit to the extracted data is indicated by the two multiple regression coefficients *R*² for the freshwater and salt water columns.

The density of a saline water sample is then calculated by subtracting the sum of the products of the two right columns which are the density differences between fresh and salt water, from the sum of the products of the two left columns which is the density of freshwater.

3. Specific entropy (σ) and specific heat capacity (*c_p*)

The polynomial coefficients of the freshwater entropy for temperatures ranging between 0 and 374 °C and pressures between 0.1 and 100 MPa were extracted from

Table 1
Density $\rho(t,p,S)$ (kg/m³) coefficients of thermal fluid

1	9.9920571E+02	<i>S</i>	-7.99992230E-01
<i>t</i>	9.5390097E-02	<i>St</i>	2.40936500E-03
<i>t</i> ²	-7.6186636E-03	<i>S</i> ²	-2.58052775E-05
<i>t</i> ³	3.1305828E-05	<i>S</i> ³	6.85608405E-08
<i>t</i> ⁴	-6.1737704E-08	<i>pS</i>	6.29761106E-04
<i>p</i>	4.3368858E-01	<i>p</i> ² <i>S</i>	-9.36263713E-07
<i>pt</i> ²	2.5495667E-05		
<i>pt</i> ³	-2.8988021E-07		
<i>pt</i> ⁴	9.5784313E-10		
<i>p</i> ²	1.7627497E-03		
<i>p</i> ² <i>t</i>	-1.2312703E-04		
<i>p</i> ² <i>t</i> ²	1.3659381E-06		
<i>p</i> ² <i>t</i> ³	4.0454583E-09		
<i>p</i> ³	-1.4673241E-05		
<i>p</i> ³ <i>t</i>	8.8391585E-07		
<i>p</i> ³ <i>t</i> ²	-1.1021321E-09		
<i>p</i> ³ <i>t</i> ³	4.2472611E-11		
<i>p</i> ³ <i>t</i> ⁴	-3.9591772E-14		

Units: *t*, °C; *p*, MPa; *S*, g/kg; *p*, MPa.

The density is calculated by subtracting the sum of the products of the two right columns from that of the two left columns.

Adjusted *R*², Left: 0.99992, Right: 0.99991.

Coefficients in left columns fitted from the density of freshwater.

Coefficients in right columns fitted from the density difference of fresh and salt water.

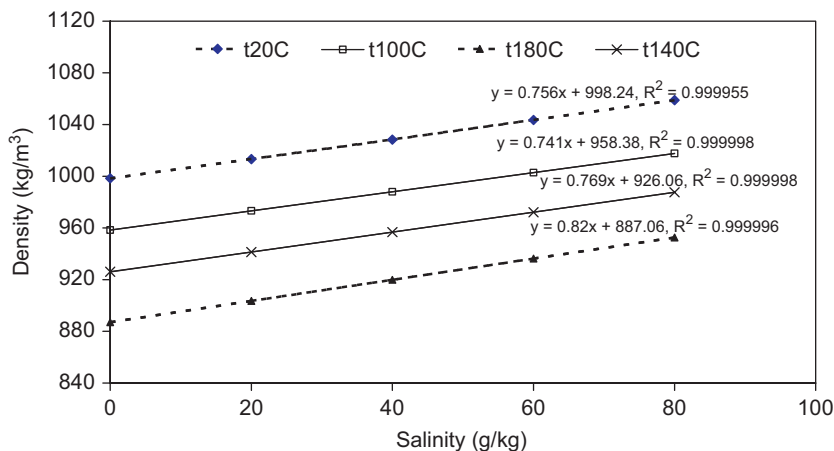


Fig. 2. Relationships between density and salinity for several temperatures based on the experimental data of Grunberg (1970). Legend t20C indicates at temperature 20 °C, etc.

the data of Wagner and Pruß (2002). The entropy of seawater at temperature 0–40 °C, pressure 0.101–100 MPa and practical salinity 0–40 were calculated from the model of Feistel (2003) which was derived from various sources including the EOS 80 experimental data of Millero et al. (1981). The entropy of saline water for temperatures ranging between 40 and 200 °C, absolute salinity between 0 and 120 g/kg and at vapor pressure were calculated using well-known thermodynamic formula:

$$\sigma(S, t, p) = \sigma_0(S, p) + \int_0^t \frac{c_p(S, t, p)}{t + 273.15K} dt \quad (1)$$

where c_p is the specific heat capacity in kJ/(kgK), calculated here through a polynomial equation fitted to the saline specific heat capacity data of Bromley et al. (1970), valid for temperatures between 40 and 200 °C, absolute salinities between 0 and 120 g/kg and vapor pressure. The quantity of $\sigma_0(S, p)$ is the specific value of σ that corresponds to the temperature independent terms and coefficients (1, p , p^2 , p^3 , p^4 , S , S^2 , S^3 , and S^4) in Table 2. Using the above-mentioned three sources, the polynomial coefficients of the entropy for the difference between freshwater and saline water are calculated. They are listed in the right two columns of Table 2. In a manner similar to that used to calculate density from the coefficients listed in Table 1, the entropy of a saline water sample from Table 2 is calculated by subtracting the sum of the products of the two right columns, which is the entropy difference of fresh and salt water, from the sum of the products of the left two columns, which is the entropy of freshwater in the corresponding table.

Table 2
Entropy $\sigma(t,p,S)$ coefficients of thermal fluid

1	7.71182883E-03	S	-4.67990975E-04
t	1.50117356E-02	S ²	2.84585789E-05
t ²	-2.37410293E-05	S ³	-3.50503953E-07
t ³	3.75444856E-08	S ⁴	1.35507185E-09
t ⁴	-1.52227969E-11	St	1.83889613E-05
t ⁵	6.07184558E-15	St ²	-8.13830857E-08
p	-1.43939529E-04	St ³	2.54724177E-10
pt	-5.01934525E-06	S ² t	-3.64880194E-08
pt ²	2.54031415E-09	S ³ t	2.49629547E-10
pt ³	-8.24948047E-11	pSt	4.34585798E-09
pt ⁴	-5.01693186E-15		
p ²	-1.21925066E-06		
p ² t	1.07139472E-08		
p ² t ²	7.97244635E-11		
p ² t ³	1.33489227E-13		
p ³	4.38423518E-09		
p ³ t	4.70876701E-11		
p ³ t ²	-1.68470164E-13		
p ³ t ³	-6.16079622E-17		
p ⁴	-6.28067181E-12		
p ⁴ t ²	8.18151132E-14		
p ⁴ t ³	8.89026362E-17		
p ⁵	2.94093673E-15		
p ⁵ t	-4.20129614E-17		

Units: t, °C; p, MPa; S, g/kg; p, MPa. σ , kJ/kg K. Adjusted R², left: 0.999973, right: 0.998594. Coefficients in the left two columns were fitted from entropy of freshwater of Wagner and Pruß (2002). Coefficients in the right two columns were fitted from the entropy difference of fresh and salt water.

For the fresh water portion of the coefficients of $c_p(S,t,p)$ in Table 3 (two left columns), they were fitted directly from Wagner and Pruß (2002) because of the availability of the data and improved accuracy. However, for the salt water portion of $c_p(S,t,p)$, they were the differentiation of the entropy function with respect to temperature given in Table 2 because of the lack of available large experimental data set at high temperature and high pressure. This approach makes the calculation of the c_p needing one more step than that of the entropy. If one lets $c_{p \text{ fresh}}$ denote the sum of products of two left columns in Table 3, and lets $c'_{p \text{ fresh-salt}}$ denote the sum of the products of fresh-salt water difference from the two right columns, then, the total $c_p(S,t,p)$ will be:

$$c_p(S, t, p) = c_{p \text{ fresh}} - (t + 273.15)c'_{p \text{ fresh-salt}} \quad (2)$$

The coefficients in Table 3 are valid for temperatures of 0–374 °C, pressures of 0–100 MPa and salinities of 0–40. Our approach is legitimate because of the near-linear relationship between specific heat and salinity as illustrated in Fig. 3, with R² values of the linear regression analysis that are close to one.

As an alternative to our fit of the freshwater data from Wagner and Pruß (2002), one could use the Gibbs function of the IF-97 formulation for pure water, which has 34 coefficients (Wagner and Kretzschmar, 2008) to calculate the entropy and specific heat of freshwater directly. The results can then be used to subtract the entropy and specific heat differences of the fresh-salt water given in Tables 2 and 3 to obtain the entropy and specific heat of saline water.

4. Potential temperature

The potential temperature θ is defined as the temperature that an element of seawater would have if it were moved adiabatically, and with no change of salinity from an initial pressure p to a reference pressure p_r . In relation to the entropy, the potential temperature $\theta(S, t, p, p_r)$ at pressure p , in reference to pressure p_r , is given implicitly by (Feistel, 2003)

$$\sigma(S, \theta, p_r) = \sigma(S, t, p) \quad (3)$$

where σ is the entropy in kJ/(kgK), θ , the potential temperature; t , the in-situ temperature in °C; p , the in-situ pressure; p_r , the reference pressure in MPa, and S , the salinity.

The calculation of the potential temperature followed McDougall et al. (2003) using the equation of entropy derived in Table 2. The potential temperature is given by

$$\theta(S, t, p, p_r) = t_0 + \int \Gamma(S, \theta[S_0, t_0, p_0, p_r], p) dp \quad (4)$$

where Γ is the adiabatic lapse rate calculated by

$$\Gamma = -g_{Tp}/g_{TT} = -\sigma_p/\sigma_t \quad (5)$$

where g_{Tp} , the same as $-\sigma_p$, and g_{TT} , the same as $-\sigma_t$, are the derivatives of entropy with respect to pressure p and temperature t , since entropy is defined by the Gibbs function, g , as, $\sigma = -(\partial g/\partial T_{S,p})$. The subscript in Eq. (4) refers to the initial state.

Table 3
Specific heat capacity $c_p(t,p,S)$ coefficients

1	4.19284306E+00	S	5.020186422E-03
t	-2.27325412E-04	S^2	-9.961229291E-06
t^2	2.36862694E-06	S^3	6.814886633E-08
t^4	1.67009248E-10	St	-2.604620356E-05
p	-3.97822834E-03	St^2	4.585292916E-08
pt	3.22914232E-05	St^3	7.641725299E-10
pt^3	-1.07252107E-09	S^2t	-3.648801938E-08
p^2	1.91296765E-05	S^3t	2.496295470E-10
p^2t	-4.17582927E-07	Sp	1.186419227E-06
p^2t^2	2.30627396E-09	Stp	4.345857976E-09

Units: t , °C; S , g/kg; p , MPa.

Adjusted R^2 . Left: 0.9974.

Coefficients in the left two columns are fitted from freshwater c_p . Coefficients in the right two columns are derived from the entropy difference of fresh-salt water of Table 2. Their products need to be multiplied by $(t+273.15)$ to match the products of the two left columns

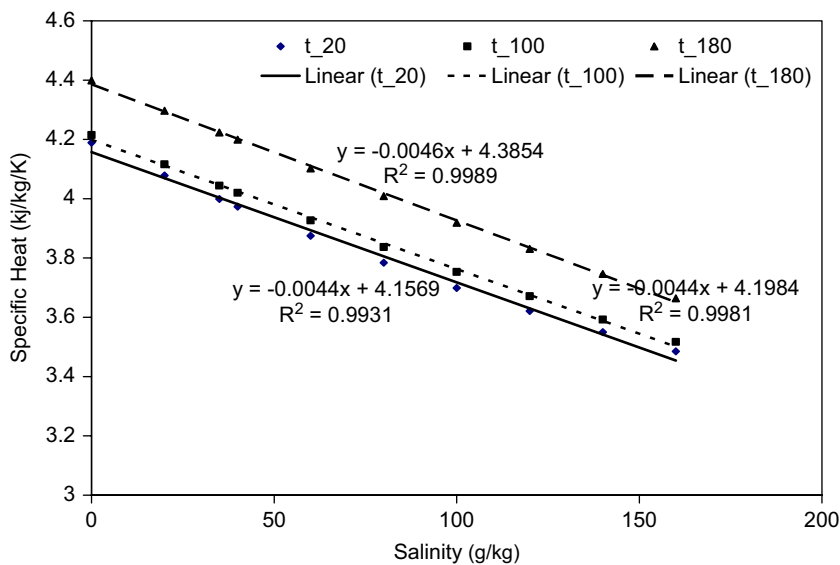


Fig. 3. Relationship of salinity vs. specific heat (c_p). t_{20} indicates temperature 20 °C. Data are from Grunberg (1970).

A FORTRAN program has been developed to calculate the potential temperature, by solving Eq. (3) following the algorithm of Fofonoff and Millard (1983), and using the entropy coefficients of Table 2. The calculations of density, entropy, and specific heat capacity based on the coefficients of Tables 1–3 are programmed in the same module as well. One can simply compile the FORTRAN code and produce a DOS executable file to run the calculation. A DOS executable file could be provided as electronic supplement. The parameters for the program input require in-situ pressure p , reference pressure p_r , temperature t , and salinity S . Outputs of the program are the density ρ , specific entropy σ , specific heat c_p and the potential temperature θ .

For users who have difficulty running a DOS program, an alternative method is to use the coefficients given in the four tables. However, concerning the potential temperature, because the coefficients in Table 4 were derived by fitting to the data calculated from the attached program, and only a limited number of coefficients are

Table 4
Potential temperature (θ) coefficients

t	9.9435332575E-01
St	3.4243232423E-04
St^2	-1.3242935873E-06
p	-2.2084562129E-02
pt^2	-2.7341841250E-06
p_r	1.6690215408E-02
$p_r t$	1.4543520913E-04
$p_r t^2$	2.7154565517E-06
pSt	-2.2042239069E-06

Units: θ , t , °C; p_r , MPa; S , g/kg; p , MPa.

Adjusted R^2 : 0.999975.

listed, its accuracy will not be as good as the one from the direct program calculation. Also, the potential temperature calculation using Table 4 is the direct sum of the products of the coefficients and variables in the two columns in Table 4, and this is different from using the coefficients of Tables 1–3.

5. Validity range of the equations

The equations established in this paper will be valid only for a liquid above the vapor saturation line, beyond the melting curve and underneath the critical point, i.e. within the area outlined in Fig. 4. This is because of the limitation of the data used in the derivation of the equations.

As the coefficients for the saline part for temperatures above 200 °C in the equations of this paper are extended from the regression of the saline data between 0 and 200 °C, assuming the near-linear relationship of density and specific heat capacity with the salinity, a precise estimation of the error range for the saline coefficients is difficult to make.

A comparison of the polynomial equations obtained in Tables 1–3 and the potential temperature calculated using

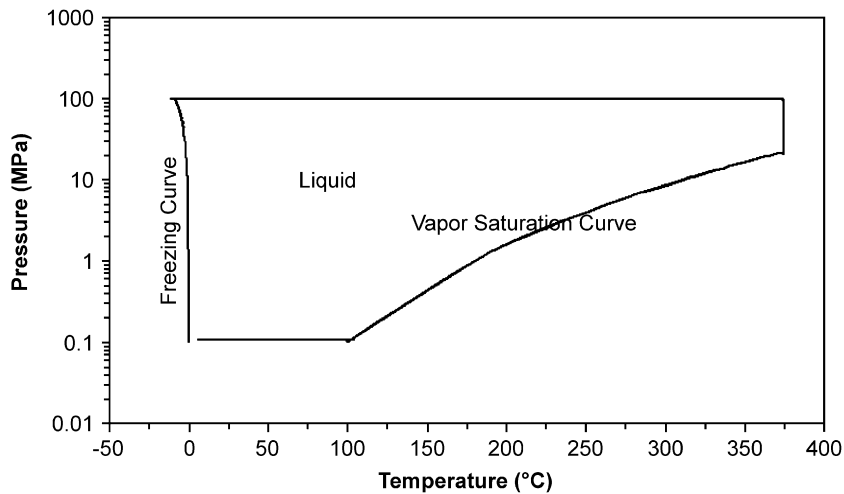


Fig. 4. Temperature and pressure validity range of the proposed equations (area confined by the solid lines).

Table 5

Residual standard errors compared to experiment and model data

Sources of the data	Parameters	Residual standard errors	Units	Data size
Bryden (1973)	Potential temperature	0.00942	°C	440
Fofonoff (1985)		0.00963	°C	440
McDougall et al. (2003)		0.00359	°C	440
	Data range: $T: 0-40, p: 0.11-54.1, S: 0-40$			
Wagner and Pruß (2002)	Entropy	0.00022	kJ/(kg K)	998
	Density	0.04638	kg/m ³	998
	Specific heat	0.00595	J/kg/°C	998
	Data range: $T: 0-375, p: 0.05-100, S: 0$			
Grunberg (1970)	Density	0.07541	kg/m ³	27
	Data range: $T: 0-180, p: 0.05-0.9838, S: 0-40$			
	Specific heat	0.00465	J/kg/°C	36
	Data range: $T: 0-180, p: 0.05-0.9647, S: 0-40$			
Feistel (2003)	Potential temperature	0.00173	°C	6909
	Entropy	0.00002	kJ/(kg K)	6909
	Density	0.00543	kg/m ³	6909
	Specific heat	0.00020	J/kg/°C	6909
	Data range: $T: 0-40, p: 0-100, S: 0-40$			
Millero et al. (1980, 1981)	Density	< 1E-06	kg/m ³	473
	Data range: $T: 0-40, p: 10-100, S: 0-40$			
Bromley et al. (1970)	Specific heat	0.00197	J/kg/°C	105
	Data range: $T: 0-200, p: 0-1.552, S: 0-40$			

Units: $t, ^\circ\text{C}; p, \text{MPa}; S, \text{g/kg}$.

the attached program with various other existing models is provided in Table 5. From the residual standard errors, one can get an approximate idea of how well the equations derived in this paper perform. Users are encouraged to use the program directly if possible because its coefficients for the parameters have more digits than the coefficients used in the tables. The equations from this project provide only a rough description of a saline thermal fluid and for higher accuracy one would need additional experimental saline thermal fluid data. Also, users need to be aware that the error tends to increase when the input data approach the vapor saturation curve in Fig. 4.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.dsr.2008.05.011](https://doi.org/10.1016/j.dsr.2008.05.011).

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