

The International Association for the Properties of Water and Steam

Berlin, Germany

September 2008

Revised Advisory Note No. 3 Thermodynamic Derivatives from IAPWS Formulations

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This advisory note contains 13 pages, including this cover page.

This revised advisory note has been authorized by the International Association for the Properties of Water and Steam (IAPWS) at its meeting in Berlin, Germany, 07-12 September, 2008, for issue by its Secretariat. The members of IAPWS are: Argentina and Brazil, Britain and Ireland, Canada, the Czech Republic, Denmark, France, Germany, Greece, Italy, Japan, Russia, and the United States of America, and associate member Switzerland.

The method provided in this advisory note is recommended for determining thermodynamic derivatives from “The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use” (IAPWS-95) [1, 2] and from “The IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam” (IAPWS-IF97) [3, 4, 5]. The revision adds formulae for the derivatives of “The IAPWS Formulation 1984 for the Thermodynamic Properties of Heavy Water Substance” (Revision 2005) [6], “The IAPWS Equation of State for H₂O Ice Ih” (2006) [7, 8], and “The IAPWS Formulation 2008 for the Thermodynamic Properties of Seawater” [9, 10]. Further details of this advisory note can be found in the corresponding article by H.-J. Kretzschmar *et al.* [11].

Further information concerning this advisory note, IAPWS-95, IAPWS-IF97, and other releases, supplementary releases, guidelines, and advisory notes issued by IAPWS can be obtained from the Executive Secretary of IAPWS or from <http://www.iapws.org>.

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1 Nomenclature

Thermodynamic quantities:

- c_p Specific isobaric heat capacity $c_p = (\partial h / \partial T)_p$
 c_v Specific isochoric heat capacity $c_v = (\partial u / \partial T)_v$
 f Specific Helmholtz free energy $f = u - T s$
 \bar{f} Reduced Helmholtz free energy $\bar{f} = f \rho^* / p^*$ (heavy water)
 g Specific Gibbs free energy $g = h - T s$
 h Specific enthalpy $h = u + p v$
 p Pressure
 R Specific gas constant
 s Specific entropy
 S Salinity of seawater
 T Absolute temperature^a
 \bar{T} Reduced Temperature $\bar{T} = T / T^*$ (heavy water)
 u Specific internal energy
 v Specific volume
 x Any property
 y Any property
 z Any property
 α_p Relative pressure coefficient $\alpha_p = p^{-1} (\partial p / \partial T)_v$
 α_v Isobaric cubic expansion coefficient $\alpha_v = v^{-1} (\partial v / \partial T)_p$
 β_p Isothermal stress coefficient $\beta_p = -p^{-1} (\partial p / \partial v)_T$
 δ Reduced density, $\delta = \rho / \rho_c$
 ϕ Reduced Helmholtz free energy $\phi = f / (RT)$
 γ Reduced Gibbs free energy $\gamma = g / (RT)$
 κ_T Isothermal compressibility $\kappa_T = -v^{-1} (\partial v / \partial p)_T$
 π Reduced pressure $\pi = p / p^*$
 ρ Density
 $\bar{\rho}$ Reduced Density $\bar{\rho} = \rho / \rho^*$ (heavy water)
 τ Inverse reduced temperature $\tau = T^* / T$

Subscripts:

- 0 Ideal-gas part
 1 Residual Part
 c Critical point
 p at constant pressure
 S at constant salinity
 T at constant temperature
 v at constant specific volume
 y at constant property y

Superscripts:

- o Ideal-gas part
 r Residual part
 s Salinity part
 w Water part
 * Reducing quantity

^a Note: T denotes absolute temperature on the International Temperature Scale 1990 (ITS-90).

2 Background

Partial derivatives of thermodynamic properties of water and steam are used for many purposes. In particular, they are required for solving equation systems in power-cycle, boiler, or turbine calculations, and particularly for modelling non-stationary processes. When using the fundamental equations of “The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use” (IAPWS-95) [1, 2] or of “The IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam” (IAPWS-IF97) [3, 4, 5], all of the partial derivatives of first and second order of various properties can be calculated correctly. This is also true for the fundamental equations of “The IAPS Formulation 1984 for the Thermodynamic Properties of Heavy Water Substance” (Revision 2005) [6], “The IAPWS Equation of State for H₂O Ice Ih” (2006) [7, 8] and “The IAPWS Formulation 2008 for the Thermodynamic Properties of Seawater” [9, 10].

This advisory note provides the formulae for the determination of partial derivatives such as

$$\left(\frac{\partial z}{\partial x}\right)_y (v, T), \text{ from Helmholtz equations of IAPWS-95, of IAPWS-IF97 region 3, and of}$$

heavy water,

$$\left(\frac{\partial z}{\partial x}\right)_y (p, T), \text{ from Gibbs equations of IAPWS-IF97 regions 1, 2, 2 meta, 5, and of ice, and}$$

$$\left(\frac{\partial z}{\partial x}\right)_{y,S} (S, T, p), \text{ from the Gibbs equation of seawater, where } S \text{ is the salinity.}$$

The variables x , y , z can represent any thermodynamic properties. The formulae for the properties pressure p , temperature T , specific volume v , specific internal energy u , specific enthalpy h , specific entropy s , specific Gibbs free energy g , and specific Helmholtz free energy f are given in this document.

Two examples shall serve to illustrate the application of the method.

3 Partial Derivatives from Fundamental Helmholtz Free Energy Equations

3.1 General Procedure for Helmholtz Free Energy Equations

The general expression for the determination of any partial derivative $(\partial z / \partial x)_y$ from an equation of state as a function of the specific volume v and temperature T reads

$$\left(\frac{\partial z}{\partial x}\right)_y = \frac{\left(\frac{\partial z}{\partial v}\right)_T \left(\frac{\partial y}{\partial T}\right)_v - \left(\frac{\partial z}{\partial T}\right)_v \left(\frac{\partial y}{\partial v}\right)_T}{\left(\frac{\partial x}{\partial v}\right)_T \left(\frac{\partial y}{\partial T}\right)_v - \left(\frac{\partial x}{\partial T}\right)_v \left(\frac{\partial y}{\partial v}\right)_T}. \quad (1)$$

The variables x, y, z can represent any thermodynamic property. Table 1 contains the formulae for calculating the partial derivatives of the properties $p, T, v, u, h, s, g,$ and f with respect to v and T that are needed in Eq. (1).

Table 1. Derivatives of x, y, z with respect to v at constant T and vice versa, where x, y, z are any of the quantities $p, T, v, u, h, s, g,$ and f

x, y, z	$\left(\frac{\partial x}{\partial v}\right)_T, \left(\frac{\partial y}{\partial v}\right)_T, \left(\frac{\partial z}{\partial v}\right)_T$	$\left(\frac{\partial x}{\partial T}\right)_v, \left(\frac{\partial y}{\partial T}\right)_v, \left(\frac{\partial z}{\partial T}\right)_v$
p	$-p\beta_p$	$p\alpha_p$
T	0	1
v	1	0
u	$p(T\alpha_p - 1)$	c_v
h	$p(T\alpha_p - v\beta_p)$	$c_v + p v \alpha_p$
s	$p\alpha_p$	c_v/T
g	$-p v \beta_p$	$p v \alpha_p - s$
f	$-p$	$-s$

For example, for the variable $z = p$ the expression $(\partial z/\partial v)_T$ means $(\partial p/\partial v)_T$ which is equal to $-p\beta_p$ according to Table 1. As can be seen in Table 1, in addition to the values of the variables v and T , the values of the five quantities pressure p , specific entropy s , specific isochoric heat capacity c_v , relative pressure coefficient $\alpha_p = p^{-1}(\partial p/\partial T)_v$, and isothermal stress coefficient $\beta_p = -p^{-1}(\partial p/\partial v)_T$ are required. These quantities contain the first and second derivatives of the Helmholtz free energy f with respect to v at constant T and vice versa.

3.2 Determination of Partial Derivatives from IAPWS-95

For IAPWS-95, the formulae for calculating the five properties $p, s, c_v, \alpha_p,$ and β_p from the dimensionless Helmholtz free energy equation $\phi(\delta, \tau) = \phi^o(\delta, \tau) + \phi^r(\delta, \tau)$ and its derivatives are

$$\begin{aligned}
 p &= \rho RT \left(1 + \delta \phi_\delta^r\right), & s &= R \left[\tau \left(\phi_\tau^o + \phi_\tau^r\right) - \phi^o - \phi^r \right], \\
 c_v &= -R \tau^2 \left(\phi_{\tau\tau}^o + \phi_{\tau\tau}^r\right), & \alpha_p &= \frac{1}{T} \left[1 - \frac{\delta \tau \phi_{\delta\tau}^r}{\left(1 + \delta \phi_\delta^r\right)} \right], \\
 \beta_p &= \rho \left[1 + \frac{\left(\delta \phi_\delta^r + \delta^2 \phi_{\delta\delta}^r\right)}{\left(1 + \delta \phi_\delta^r\right)} \right], & &
 \end{aligned} \tag{2}$$

where $\phi = f/(RT)$, $\delta = \rho/\rho_c$, and $\tau = T_c/T$ with the specific gas constant R and the critical parameters ρ_c, T_c . The equations $\phi^o(\delta, \tau)$, $\phi^r(\delta, \tau)$ and their derivatives which were abbreviated in Eq. (2) as follows:

$$\phi_\tau^o = \left(\frac{\partial \phi^o}{\partial \tau} \right)_\delta, \quad \phi_{\tau\tau}^o = \left(\frac{\partial^2 \phi^o}{\partial \tau^2} \right)_\delta,$$

$$\phi_\delta^r = \left(\frac{\partial \phi^r}{\partial \delta} \right)_\tau, \quad \phi_{\delta\delta}^r = \left(\frac{\partial^2 \phi^r}{\partial \delta^2} \right)_\tau, \quad \phi_\tau^r = \left(\frac{\partial \phi^r}{\partial \tau} \right)_\delta, \quad \phi_{\tau\tau}^r = \left(\frac{\partial^2 \phi^r}{\partial \tau^2} \right)_\delta, \quad \phi_{\delta\tau}^r = \left(\frac{\partial^2 \phi^r}{\partial \delta \partial \tau} \right),$$

are given in [1, 2] along with the associated values for R , ρ_c , and T_c .

3.3 Determination of Partial Derivatives for IAPWS-IF97 Region 3

The formulae for calculating p , s , c_v , α_p , and β_p of Table 1 from the dimensionless Helmholtz free energy equation $\phi(\delta, \tau)$ and its derivatives of region 3 of the ‘‘IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam’’ (IAPWS-IF97) are

$$p = \rho RT \delta \phi_\delta, \quad s = R(\tau \phi_\tau - \phi),$$

$$c_v = -R \tau^2 \phi_{\tau\tau}, \quad \alpha_p = \frac{1}{T} \left(1 - \frac{\tau \phi_{\delta\tau}}{\phi_\delta} \right), \quad (3)$$

$$\beta_p = \rho \left(2 + \frac{\delta \phi_{\delta\delta}}{\phi_\delta} \right),$$

where $\phi = f/(RT)$, $\delta = \rho/\rho_c$, $\tau = T_c/T$ with the specific gas constant R and the critical parameters ρ_c , T_c . The equation $\phi(\delta, \tau)$ and its derivatives which were abbreviated in Eq. (3) as follows:

$$\phi_\delta = \left(\frac{\partial \phi}{\partial \delta} \right)_\tau, \quad \phi_{\delta\delta} = \left(\frac{\partial^2 \phi}{\partial \delta^2} \right)_\tau, \quad \phi_\tau = \left(\frac{\partial \phi}{\partial \tau} \right)_\delta, \quad \phi_{\tau\tau} = \left(\frac{\partial^2 \phi}{\partial \tau^2} \right)_\delta, \quad \phi_{\delta\tau} = \left(\frac{\partial^2 \phi}{\partial \delta \partial \tau} \right),$$

are given in [3, 4] along with the associated values for R , ρ_c , and T_c .

3.4 Determination of Partial Derivatives from the IAPS Formulation 1984 for Heavy Water

The formulae for calculating p , s , c_v , α_p , and β_p of Table 1 from the dimensionless Helmholtz free energy equation $\bar{f}(\bar{T}, \bar{\rho}) = \bar{f}_0(\bar{T}, \bar{\rho}) + \bar{f}_1(\bar{T}, \bar{\rho})$ and its derivatives of the ‘‘IAPS Formulation 1984 for the Thermodynamic Properties of Heavy Water’’ (Revision 2005) are:

$$p = p^* \bar{\rho}^2 (\bar{f}_{0,\rho} + \bar{f}_{1,\rho}), \quad s = -\frac{p^*}{T^* \rho^*} (\bar{f}_{0,T} + \bar{f}_{1,T}),$$

$$c_v = -\frac{p^*}{T^* \rho^*} \bar{T} (\bar{f}_{0,TT} + \bar{f}_{1,TT}), \quad \alpha_p = \frac{1}{T^*} \frac{(\bar{f}_{0,T\rho} + \bar{f}_{1,T\rho})}{(\bar{f}_{0,\rho} + \bar{f}_{1,\rho})}, \quad (4)$$

$$\beta_p = \rho^* \left[2\bar{\rho} + \bar{\rho}^2 \frac{(\bar{f}_{0,\rho\rho} + \bar{f}_{1,\rho\rho})}{(\bar{f}_{0,\rho} + \bar{f}_{1,\rho})} \right],$$

where $\bar{f} = f \rho^* / p^*$, $\bar{T} = T / T^*$, $\bar{\rho} = \rho / \rho^*$ with the reference constants p^* , T^* , and ρ^* . In Eq. (4), the derivatives were abbreviated as follows:

$$\begin{aligned} \bar{f}_{0,T} &= \left(\frac{\partial \bar{f}_0}{\partial \bar{T}} \right)_{\bar{\rho}}, \quad \bar{f}_{0,TT} = \left(\frac{\partial^2 \bar{f}_0}{\partial \bar{T}^2} \right)_{\bar{\rho}}, \quad \bar{f}_{0,\rho} = \left(\frac{\partial \bar{f}_0}{\partial \bar{\rho}} \right)_{\bar{T}}, \quad \bar{f}_{0,\rho\rho} = \left(\frac{\partial^2 \bar{f}_0}{\partial \bar{\rho}^2} \right)_{\bar{T}}, \quad \bar{f}_{0,T\rho} = \left(\frac{\partial^2 \bar{f}_0}{\partial \bar{T} \partial \bar{\rho}} \right) \\ \bar{f}_{1,T} &= \left(\frac{\partial \bar{f}_1}{\partial \bar{T}} \right)_{\bar{\rho}}, \quad \bar{f}_{1,TT} = \left(\frac{\partial^2 \bar{f}_1}{\partial \bar{T}^2} \right)_{\bar{\rho}}, \quad \bar{f}_{1,\rho} = \left(\frac{\partial \bar{f}_1}{\partial \bar{\rho}} \right)_{\bar{T}}, \quad \bar{f}_{1,\rho\rho} = \left(\frac{\partial^2 \bar{f}_1}{\partial \bar{\rho}^2} \right)_{\bar{T}}, \quad \bar{f}_{1,T\rho} = \left(\frac{\partial^2 \bar{f}_1}{\partial \bar{T} \partial \bar{\rho}} \right) \end{aligned}$$

The equations $\bar{f}_0(\bar{T}, \bar{\rho})$ and $\bar{f}_1(\bar{T}, \bar{\rho})$ are given in [6].

4 Partial Derivatives from Fundamental Gibbs Free Energy Equations

4.1 General Procedure for Gibbs Free Energy Equations

The general expression for the determination of any partial derivative $(\partial z / \partial x)_y$ from an equation of state as a function of pressure p and temperature T is:

$$\left(\frac{\partial z}{\partial x} \right)_y = \frac{\left(\frac{\partial z}{\partial p} \right)_T \left(\frac{\partial y}{\partial T} \right)_p - \left(\frac{\partial z}{\partial T} \right)_p \left(\frac{\partial y}{\partial p} \right)_T}{\left(\frac{\partial x}{\partial p} \right)_T \left(\frac{\partial y}{\partial T} \right)_p - \left(\frac{\partial x}{\partial T} \right)_p \left(\frac{\partial y}{\partial p} \right)_T} \quad (5)$$

In all of the partial derivatives, the variables x , y , z can represent any thermodynamic property. Table 2 comprises the formulae for calculating the partial derivatives of the properties p , T , v , u , h , s , g , and f with respect to p and T that are needed in Eq. (5). As can be seen, in addition to the values of the variables p and T , values of the five quantities specific volume v , specific entropy s , specific isobaric heat capacity c_p , isobaric cubic expansion coefficient $\alpha_v = v^{-1}(\partial v / \partial T)_p$, and isothermal compressibility $\kappa_T = -v^{-1}(\partial v / \partial p)_T$ are required. These quantities contain the first- and second-order derivatives of the Gibbs free energy g with respect to p at constant T and vice versa.

Table 2. Derivatives of x, y, z with respect to p at constant T and vice versa, where x, y, z are any of the quantities $p, T, v, u, h, s, g,$ and f

x, y, z	$\left(\frac{\partial x}{\partial T}\right)_p, \left(\frac{\partial y}{\partial T}\right)_p, \left(\frac{\partial z}{\partial T}\right)_p$	$\left(\frac{\partial x}{\partial p}\right)_T, \left(\frac{\partial y}{\partial p}\right)_T, \left(\frac{\partial z}{\partial p}\right)_T$
p	0	1
T	1	0
v	$v \alpha_v$	$-v \kappa_T$
u	$c_p - p v \alpha_v$	$v(p \kappa_T - T \alpha_v)$
h	c_p	$v(1 - T \alpha_v)$
s	c_p/T	$-v \alpha_v$
g	$-s$	v
f	$-p v \alpha_v - s$	$p v \kappa_T$

4.2 Determination of Partial Derivatives for IAPWS-IF97 Region 1

The formulae for calculating the properties $v, s, c_p, \alpha_v,$ and κ_T of Table 2 from the dimensionless Gibbs free energy equation $\gamma(\pi, \tau)$ and its derivatives of IAPWS-IF97 region 1 are

$$\begin{aligned}
 v &= \frac{RT}{p} \pi \gamma_\pi, & s &= R(\tau \gamma_\tau - \gamma), \\
 c_p &= -R \tau^2 \gamma_{\tau\tau}, & \alpha_v &= \frac{1}{T} \left(1 - \frac{\tau \gamma_{\pi\tau}}{\gamma_\pi} \right), \\
 \kappa_T &= -\frac{1}{p} \frac{\pi \gamma_{\pi\pi}}{\gamma_\pi}, & &
 \end{aligned} \tag{6}$$

where $\gamma = g/(RT)$, $\pi = p/p^*$, and $\tau = T^*/T$ with the specific gas constant R and the reducing parameters p^*, T^* . The equation $\gamma(\pi, \tau)$ and its derivatives which were abbreviated in Eq. (6) as follows:

$$\gamma_\pi = \left(\frac{\partial \gamma}{\partial \pi} \right)_\tau, \quad \gamma_{\pi\pi} = \left(\frac{\partial^2 \gamma}{\partial \pi^2} \right)_\tau, \quad \gamma_\tau = \left(\frac{\partial \gamma}{\partial \tau} \right)_\pi, \quad \gamma_{\tau\tau} = \left(\frac{\partial^2 \gamma}{\partial \tau^2} \right)_\pi, \quad \gamma_{\pi\tau} = \left(\frac{\partial \gamma}{\partial \pi \partial \tau} \right),$$

are given in [3, 4] along with the associated values for $R, p^*,$ and T^* .

4.3 Determination of Partial Derivatives for IAPWS-IF97 Regions 2, 2 meta, and 5

The formulae for calculating the properties $v, s, c_p, \alpha_v,$ and κ_T of Table 2 from the dimensionless Gibbs free energy equations $\gamma(\pi, \tau) = \gamma^0(\pi, \tau) + \gamma^1(\pi, \tau)$ and its derivatives of IAPWS-IF97 region 2, 2 meta, and 5 are

$$\begin{aligned}
v &= \frac{RT}{p} \pi \left(\gamma_{\tau}^{\circ} + \gamma_{\tau}^{\text{r}} \right), & s &= R \left[\tau \left(\gamma_{\tau}^{\circ} + \gamma_{\tau}^{\text{r}} \right) - \left(\gamma^{\circ} + \gamma^{\text{r}} \right) \right], \\
c_p &= -R \tau^2 \left(\gamma_{\tau\tau}^{\circ} + \gamma_{\tau\tau}^{\text{r}} \right), & \alpha_v &= \frac{1}{T} \frac{\left(1 + \pi \gamma_{\pi}^{\text{r}} - \tau \pi \gamma_{\pi\tau}^{\text{r}} \right)}{\left(1 + \pi \gamma_{\pi}^{\text{r}} \right)}, \\
\kappa_T &= \frac{1}{p} \frac{\left(1 - \pi^2 \gamma_{\pi\pi}^{\text{r}} \right)}{\left(1 + \pi \gamma_{\pi}^{\text{r}} \right)},
\end{aligned} \tag{7}$$

where $\gamma = g/(RT)$, $\pi = p/p^*$, and $\tau = T^*/T$ with the specific gas constant R and the reducing parameters p^* , T^* . The equations $\gamma^{\circ}(\pi, \tau)$, $\gamma^{\text{r}}(\pi, \tau)$ and their derivatives which were abbreviated in Eq. (8) as follows:

$$\begin{aligned}
\gamma_{\tau}^{\circ} &= \left(\frac{\partial \gamma^{\circ}}{\partial \tau} \right)_{\pi}, & \gamma_{\tau\tau}^{\circ} &= \left(\frac{\partial^2 \gamma^{\circ}}{\partial \tau^2} \right)_{\pi}, \\
\gamma_{\pi}^{\text{r}} &= \left(\frac{\partial \gamma^{\text{r}}}{\partial \pi} \right)_{\tau}, & \gamma_{\pi\pi}^{\text{r}} &= \left(\frac{\partial^2 \gamma^{\text{r}}}{\partial \pi^2} \right)_{\tau}, & \gamma_{\tau}^{\text{r}} &= \left(\frac{\partial \gamma^{\text{r}}}{\partial \tau} \right)_{\pi}, & \gamma_{\tau\tau}^{\text{r}} &= \left(\frac{\partial^2 \gamma^{\text{r}}}{\partial \tau^2} \right)_{\pi}, & \gamma_{\pi\tau}^{\text{r}} &= \left(\frac{\partial^2 \gamma^{\text{r}}}{\partial \pi \partial \tau} \right),
\end{aligned}$$

where the value for R and the values for p^* , and T^* for each of the regions 2, 2 meta, and 5 are given in [3, 4, 5].

4.4 Determination of Partial Derivatives from the IAPWS Formulation 2006 for Ice Ih

The formulae for calculating the properties v , s , c_p , α_v , and κ_T of Table 2 from the Gibbs free energy equation $g(T, p)$ and its derivatives of the ‘‘IAPWS Release on an Equation of State for H₂O Ice Ih’’ (2006) are given in [7, 8].

4.5 Determination of Partial Derivatives from the IAPWS Formulation 2008 for Seawater

The formulae for calculating the properties v , s , c_p , α_v , and κ_T of Table 2 from the ‘‘IAPWS Formulation 2008 for the Thermodynamic Properties of Seawater’’ at constant salinity are

$$\begin{aligned}
v &= \frac{1}{\rho^{\text{w}}} + g_p^{\text{s}}, & s &= R^{\text{w}} \left[\tau \left(\phi_{\tau}^{\circ} + \phi_{\tau}^{\text{r}} \right) - \phi^{\circ} - \phi^{\text{r}} \right] - g_T^{\text{s}}, \\
c_p &= -R^{\text{w}} \left[\tau^2 \left(\phi_{\tau\tau}^{\circ} + \phi_{\tau\tau}^{\text{r}} \right) - \frac{\left(1 + \delta \phi_{\delta}^{\text{r}} - \delta \tau \phi_{\delta\tau}^{\text{r}} \right)^2}{\left(1 + 2 \delta \phi_{\delta}^{\text{r}} + \delta^2 \phi_{\delta\delta}^{\text{r}} \right)} \right] - T g_{TT}^{\text{s}},
\end{aligned} \tag{8}$$

$$\alpha_v = \frac{\frac{1}{T \rho^w} \left(\frac{1 + \delta \phi_\delta^r - \delta \tau \phi_{\delta\tau}^r}{1 + 2\delta \phi_\delta^r + \delta^2 \phi_{\delta\delta}^r} \right) + g_{Tp}^s}{\left(\frac{1}{\rho^w} + g_p^s \right)},$$

$$\kappa_T = \frac{\frac{1}{(\rho^w)^2} R^w T \left(\frac{1}{1 + 2\delta \phi_\delta^r + \delta^2 \phi_{\delta\delta}^r} \right) - g_{pp}^s}{\left(\frac{1}{\rho^w} + g_p^s \right)}.$$

Because all these formulas are for constant salinity, the subscript S is not explicitly written. For the pure water part, the abbreviations used in the release

$$\phi_\tau^o = \left(\frac{\partial \phi^o}{\partial \tau} \right)_\delta, \quad \phi_{\tau\tau}^o = \left(\frac{\partial^2 \phi^o}{\partial \tau^2} \right)_\delta,$$

$$\phi_\delta^r = \left(\frac{\partial \phi^r}{\partial \delta} \right)_\tau, \quad \phi_{\delta\delta}^r = \left(\frac{\partial^2 \phi^r}{\partial \delta^2} \right)_\tau, \quad \phi_\tau^r = \left(\frac{\partial \phi^r}{\partial \tau} \right)_\delta, \quad \phi_{\tau\tau}^r = \left(\frac{\partial^2 \phi^r}{\partial \tau^2} \right)_\delta, \quad \phi_{\delta\tau}^r = \left(\frac{\partial^2 \phi^r}{\partial \delta \partial \tau} \right)$$

represent the derivatives of the ideal-gas part $\phi^o(\delta, \tau)$ and of the residual part $\phi^r(\delta, \tau)$ of the dimensionless Helmholtz free energy equation $\phi(\delta, \tau) = \phi^o(\delta, \tau) + \phi^r(\delta, \tau)$ of the ‘‘IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use’’ (IAPWS-95). The reduced parameters are $\phi = f / (R^w T)$, $\delta = \rho^w / \rho_c$, and $\tau = T_c / T$, where R^w is the specific gas constant and ρ_c , T_c are the critical parameters of IAPWS-95. The density of the pure water part ρ^w must be calculated iteratively from the equation

$$p = \rho^w R^w T \left(1 + \delta \phi_\delta^r \right) \quad (9)$$

for given pressure p and given temperature T . The equations $\phi^o(\delta, \tau)$, $\phi^r(\delta, \tau)$ and their derivatives are given in [1, 2] along with the associated values for R^w , ρ_c , and T_c .

In Eq. (8), the abbreviations

$$g_T^s = \left(\frac{\partial g^s}{\partial T} \right)_{p,S}, \quad g_{TT}^s = \left(\frac{\partial^2 g^s}{\partial T^2} \right)_{p,S}, \quad g_p^s = \left(\frac{\partial g^s}{\partial p} \right)_{T,S}, \quad g_{pp}^s = \left(\frac{\partial^2 g^s}{\partial p^2} \right)_{T,S}, \quad g_{Tp}^s = \left(\frac{\partial^2 g^s}{\partial T \partial p} \right)_S$$

represent the partial derivatives at constant salinity S of the saline part $g^s(S, T, p)$ of the Gibbs free energy equation. The equation $g^s(S, T, p)$ is given in [9, 10].

5 Examples for Determining Partial Derivatives

As examples, the partial derivative $(\partial u/\partial p)_v$ is to be determined from the fundamental equation $f(\rho, T)$ of IAPWS-95 or IAPWS-IF97 region 3 and from the fundamental equation $g(p, T)$ of IAPWS-IF97 regions 1, 2, 2meta, or 5.

5.1 Determination of $(\partial u/\partial p)_v$ from a Helmholtz Free Energy Equation

The fundamental equations for IAPWS-95 and for region 3 of IAPWS-IF97 are Helmholtz equations in the form $f(\rho, T)$, so Eq. (1) and Table 1 must be used for determining the required partial derivative. A comparison of the required partial derivative $(\partial u/\partial p)_v$ with the general expression for the partial derivative of Eq. (1) results in $z = u$, $x = p$, and $y = v$. With these assignments, Eq. (1) formally reads:

$$\left(\frac{\partial u}{\partial p}\right)_v = \frac{\left(\frac{\partial u}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_v - \left(\frac{\partial u}{\partial T}\right)_v \left(\frac{\partial v}{\partial v}\right)_T}{\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_v - \left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial v}\right)_T}. \quad (10)$$

According to Table 1, the partial derivatives are:

$$\begin{aligned} \left(\frac{\partial u}{\partial v}\right)_T &= p(T\alpha_p - 1) & \left(\frac{\partial v}{\partial T}\right)_v &= 0 \\ \left(\frac{\partial u}{\partial T}\right)_v &= c_v & \left(\frac{\partial v}{\partial v}\right)_T &= 1 \\ \left(\frac{\partial p}{\partial v}\right)_T &= -p\beta_p & \left(\frac{\partial p}{\partial T}\right)_v &= p\alpha_p \end{aligned} \quad (11)$$

The insertion of these results into Eq. (10) yields

$$\left(\frac{\partial u}{\partial p}\right)_v = \frac{c_v}{p\alpha_p}. \quad (12)$$

The values of the properties p , c_v , and α_p are calculated from the dimensionless Helmholtz free energy equation:

$\phi(\delta, \tau) = \phi^o(\delta, \tau) + \phi^r(\delta, \tau)$ of IAPWS-95 [1, 2] with Eq. (2), or

$\phi(\delta, \tau)$ of IAPWS-IF97 region 3 [3, 4] with Eq. (3).

Any other partial derivative can be determined analogously.

5.2 Determination of $(\partial u/\partial p)_v$ from a Gibbs Free Energy Equation

Since the basic equations of regions 1, 2, 2meta, and 5 are Gibbs equations in the form $g(p, T)$, Eq. (5) and Table 2 must be used for determining the required derivative. A comparison of

$(\partial u / \partial p)_v$, with the general expression for the partial derivative of Eq. (5) results in $z = u$, $x = p$, and $y = v$. With these assignments, Eq. (5) formally reads:

$$\left(\frac{\partial u}{\partial p}\right)_v = \frac{\left(\frac{\partial u}{\partial p}\right)_T \left(\frac{\partial v}{\partial T}\right)_p - \left(\frac{\partial u}{\partial T}\right)_p \left(\frac{\partial v}{\partial p}\right)_T}{\left(\frac{\partial p}{\partial p}\right)_T \left(\frac{\partial v}{\partial T}\right)_p - \left(\frac{\partial p}{\partial T}\right)_p \left(\frac{\partial v}{\partial p}\right)_T} \quad (13)$$

According to Table 2, the partial derivatives are:

$$\begin{aligned} \left(\frac{\partial u}{\partial p}\right)_T &= v(p \kappa_T - T \alpha_v) & \left(\frac{\partial v}{\partial T}\right)_p &= v \alpha_v \\ \left(\frac{\partial u}{\partial T}\right)_p &= c_p - p v \alpha_v & \left(\frac{\partial v}{\partial p}\right)_T &= -v \kappa_T \\ \left(\frac{\partial p}{\partial p}\right)_T &= 1 & \left(\frac{\partial p}{\partial T}\right)_p &= 0 \end{aligned} \quad (14)$$

The insertion of these results into Eq. (13) yields

$$\left(\frac{\partial u}{\partial p}\right)_v = -v T \alpha_v + \frac{c_p \kappa_T}{\alpha_v} . \quad (15)$$

The values of the properties v , c_p , α_v , and κ_T can be calculated from the dimensionless Gibbs free energy equations:

$\gamma(\pi, \tau)$ for IAPWS-IF97 region 1 [3, 4] with Eq. (6), or

$\gamma(\pi, \tau) = \gamma^0(\pi, \tau) + \gamma^f(\pi, \tau)$ for IAPWS-IF97 regions 2, 2meta, or 5 with Eq. (7).

Any other partial derivative can be determined analogously.

6 References

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