# The International Association for the Properties of Water and Steam

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## Revised Advisory Note No. 3
## Thermodynamic Derivatives from IAPWS Formulations



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This revised advisory note replaces the corresponding Advisory Note of 2008 and contains 14 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 Moscow, Russia, 22-27 June, 2014, for issue by its Secretariat. The members of IAPWS are: Britain and Ireland, Canada, the Czech Republic, Germany, Japan, Russia, Scandinavia (Denmark, Finland, Norway, Sweden), and the United States, and associate members Argentina & Brazil, Australia, France, Greece, Italy, New Zealand, and Switzerland.

The method provided in this advisory note is recommended for determining thermodynamic derivatives from the general and scientific formulation IAPWS-95 for water (Revision 2009) [1, 2], the industrial formulation IAPWS-IF97 for water (Revision 2007) [3, 4, 5], the IAPWS-1984 formulation for heavy water (Revision 2005) [6], the IAPWS equation of state 2006 for ice Ih (Revision 2009) [7, 8], and the IAPWS-2008 formulation for seawater [9, 10]. This revision adds formulae for the derivatives of the IAPWS formulation for computationally efficient calculations for liquid water for oceanographic use (2009) [11, 12] and the IAPWS industrial formulation for seawater (2013) [13, 14]. Further details of the method used in this advisory note can be found in the publication by W. Wagner and H.-J. Kretzschmar [15].

Further information concerning this advisory note, other releases, supplementary releases, guidelines, technical guidance documents, 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 $f = u - T s$
$\overline{f}$ Reduced Helmholtz free energy $\overline{f} = f\ \rho^* / p^*$ (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]
$\overline{T}$ Reduced Temperature $\overline{T} = T / T^*$ (heavy water)
$u$ Specific internal energy
$v$ Specific volume
$x$ Any property
$y$ Any property
$z$ Any property
$\alpha_p$ Relative pressure coefficient $\alpha_p = p^{-1}(\partial p/\partial T)_v$
$\alpha_v$ Isobaric cubic expansion coefficient $\alpha_v = v^{-1}(\partial v/\partial T)_p$
$\beta_p$ Isothermal stress coefficient $\beta_p = -p^{-1}(\partial p/\partial v)_T$
$\delta$ Reduced density, $\delta = \rho / \rho_c$
$\phi$ Reduced Helmholtz free energy $\phi = f /(RT)$
$\gamma$ Reduced Gibbs free energy $\gamma = g /(RT)$
$\kappa_T$ Isothermal compressibility $\kappa_T = -v^{-1}(\partial v/\partial p)_T$
$\pi$ Reduced pressure $\pi = p / p^*$
$\rho$ Density
$\overline{\rho}$ Reduced density $\overline{\rho} = \rho / \rho^*$ (heavy water)
$\tau$ 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 modeling non-stationary processes. When using the fundamental equations of the "Revised Release on the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use" (IAPWS-95, Revision 2009) [1], or of the "Revised Release on the IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam" (IAPWS-IF97, Revision 2007) [3], all of the partial derivatives of first and second order of various properties can be calculated analytically. This is also true for the fundamental equations of the "Revised Release on the IAPS Formulation 1984 for the Thermodynamic Properties of Heavy Water Substance" (IAPWS-84, Revision 2005) [6], the "Revised Release on an Equation of State 2006 for $H_2O$ Ice Ih" (Revision 2009) [7], the "Release on the IAPWS Formulation 2008 for the Thermodynamic Properties of Seawater" (IAPWS-2008) [9], the "Supplementary Release on a Computationally Efficient Thermodynamic Formulation for Liquid Water for Oceanographic Use" (2009) [11], and the "IAPWS Advisory Note No. 5: Industrial Calculation of the Thermodynamic Properties of Seawater" (2013) [13].

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

$\left(\frac{\partial z}{\partial x}\right)_y (v,T)$, from Helmholtz equations of IAPWS-95, of IAPWS-IF97 region 3, and of IAPWS-84 for heavy water,

$\left(\frac{\partial z}{\partial x}\right)_y (p,T)$, from Gibbs equations of IAPWS-IF97 regions 1, 2, 2 meta, 5, of the IAPWS formulation 2006 for ice, and of the IAPWS formulation 2009 for liquid water for oceanographic use,

$\left(\frac{\partial z}{\partial x}\right)_{y,S} (p,T,S)$, from Gibbs equations of the scientific formulation IAPWS-2008 for seawater and of the IAPWS industrial formulation 2013 for seawater, where $S$ 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 $T$ is

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

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 the "IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use" (IAPWS-95, Revision 2009) [1], the formulae for calculating the five properties $p$, $s$, $c_v$, $\alpha_p$, and $\beta_p$ of Table 1 from the dimensionless Helmholtz free energy equation $\phi(\delta,\tau)=\phi^{\mathrm{o}}(\delta,\tau)+\phi^{\mathrm{r}}(\delta,\tau)$ and its derivatives are

$$p=\rho RT\left(1+\delta\phi_{\delta}^{\mathrm{r}}\right), \qquad s=R\left[\tau\left(\phi_{\tau}^{\mathrm{o}}+\phi_{\tau}^{\mathrm{r}}\right)-\phi^{\mathrm{o}}-\phi^{\mathrm{r}}\right],$$

$$c_v=-R\tau^2\left(\phi_{\tau\tau}^{\mathrm{o}}+\phi_{\tau\tau}^{\mathrm{r}}\right), \qquad \alpha_p=\frac{1}{T}\left[1-\frac{\delta\tau\phi_{\delta\tau}^{\mathrm{r}}}{\left(1+\delta\phi_{\delta}^{\mathrm{r}}\right)}\right], \tag{2}$$

$$\beta_p=\rho\left[1+\frac{\left(\delta\phi_{\delta}^{\mathrm{r}}+\delta^2\phi_{\delta\delta}^{\mathrm{r}}\right)}{\left(1+\delta\phi_{\delta}^{\mathrm{r}}\right)}\right],$$

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

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

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

are given in [1] along with the associated values for $R$, $\rho_{\mathrm{c}}$, and $T_{\mathrm{c}}$.

### 3.3 Determination of Partial Derivatives for IAPWS-IF97 Region 3

The formulae for calculating $p$, $s$, $c_v$, $\alpha_p$, and $\beta_p$ 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, Revision 2007) [3] are

$$p=\rho RT\,\delta\phi_{\delta}, \qquad s=R\left(\tau\phi_{\tau}-\phi\right),$$

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

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

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

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

are given in [3] along with the associated values for $R$, $\rho_c$, and $T_c$.

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

The formulae for calculating $p$, $s$, $c_v$, $\alpha_p$, and $\beta_p$ 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) [6] are:

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

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

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

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

$$\bar{f}_{0,T} = \left(\frac{\partial\bar{f}_0}{\partial\bar{T}}\right)_{\bar{\rho}}, \;\; \bar{f}_{0,TT} = \left(\frac{\partial^2\bar{f}_0}{\partial\bar{T}^2}\right)_{\bar{\rho}}, \;\; \bar{f}_{0,\rho} = \left(\frac{\partial\bar{f}_0}{\partial\bar{\rho}}\right)_{\bar{T}}, \;\; \bar{f}_{0,\rho\rho} = \left(\frac{\partial^2\bar{f}_0}{\partial\bar{\rho}^2}\right)_{\bar{T}}, \;\; \bar{f}_{0,T\rho} = \left(\frac{\partial^2\bar{f}_0}{\partial\bar{T}\,\partial\bar{\rho}}\right)$$

$$\bar{f}_{1,T} = \left(\frac{\partial\bar{f}_1}{\partial\bar{T}}\right)_{\bar{\rho}}, \;\; \bar{f}_{1,TT} = \left(\frac{\partial^2\bar{f}_1}{\partial\bar{T}^2}\right)_{\bar{\rho}}, \;\; \bar{f}_{1,\rho} = \left(\frac{\partial\bar{f}_1}{\partial\bar{\rho}}\right)_{\bar{T}}, \;\; \bar{f}_{1,\rho\rho} = \left(\frac{\partial^2\bar{f}_1}{\partial\bar{\rho}^2}\right)_{\bar{T}}, \;\; \bar{f}_{1,T\rho} = \left(\frac{\partial^2\bar{f}_1}{\partial\bar{T}\,\partial\bar{\rho}}\right)$$

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:

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

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 $\kappa_T$ of Table 2 from the dimensionless Gibbs free energy equation $\gamma(\pi,\tau)$ and its derivatives of region 1 of the "IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam IAPWS-IF97" (IAPWS-IF97, Revision 2007) [3] are

$$v = \frac{RT}{p}\pi\gamma_\pi\,, \qquad s = R\left(\tau\gamma_\tau - \gamma\right),$$

$$c_p = -R\tau^2\gamma_{\tau\tau}\,, \qquad \alpha_v = \frac{1}{T}\left(1 - \frac{\tau\gamma_{\pi\tau}}{\gamma_\pi}\right), \tag{6}$$

$$\kappa_T = -\frac{1}{p}\frac{\pi\gamma_{\pi\pi}}{\gamma_\pi},$$

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

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

are given in [3] 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 $\kappa_T$ of Table 2 from the dimensionless Gibbs free energy equations $\gamma(\pi,\tau) = \gamma^{\mathrm{o}}(\pi,\tau) + \gamma^{\mathrm{r}}(\pi,\tau)$ and its derivatives of regions 2, 2 meta, and 5 of the "IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam" (IAPWS-IF97, Revision 2007) [3] are

$$v = \frac{RT}{p}\pi\left(\gamma_\pi^{\mathrm{o}} + \gamma_\pi^{\mathrm{r}}\right), \qquad s = R\left[\tau\left(\gamma_\tau^{\mathrm{o}} + \gamma_\tau^{\mathrm{r}}\right) - \left(\gamma^{\mathrm{o}} + \gamma^{\mathrm{r}}\right)\right],$$

$$c_p = -R\tau^2\left(\gamma_{\tau\tau}^{\mathrm{o}} + \gamma_{\tau\tau}^{\mathrm{r}}\right), \qquad \alpha_v = \frac{1}{T}\frac{\left(1+\pi\gamma_\pi^{\mathrm{r}} - \tau\pi\gamma_{\pi\tau}^{\mathrm{r}}\right)}{\left(1+\pi\gamma_\pi^{\mathrm{r}}\right)}, \tag{7}$$

$$\kappa_T = \frac{1}{p}\frac{\left(1-\pi^2\gamma_{\pi\pi}^{\mathrm{r}}\right)}{\left(1+\pi\gamma_\pi^{\mathrm{r}}\right)},$$

where $\gamma = g/(RT)$, $\pi = p/p^*$, and $\tau = T^*/T$ with the specific gas constant $R$ and the reducing parameters $p^*$ and $T^*$. The equations $\gamma^{\mathrm{o}}(\pi,\tau)$, $\gamma^{\mathrm{r}}(\pi,\tau)$, and their derivatives, which were abbreviated in Eq. (7) as follows:

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

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

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

### 4.4 Determination of Partial Derivatives for the IAPWS Computationally Efficient Thermodynamic Formulation for Liquid Water for Oceanographic Use

The formulae for calculating the properties $v = \rho^{-1}$, $s$, $c_p$, $\alpha_v = \alpha$, and $\kappa_T$ of Table 2 from the Gibbs free energy equation $g(T, p)$ and its derivatives of the IAPWS "Supplementary Release on a Computationally Efficient Thermodynamic Formulation for Liquid Water for Oceanographic Use" (2009) are directly given in [11].

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

The formulae for calculating the properties $v = \rho^{-1}$, $s$, $c_p$, $\alpha_v = \alpha$, and $\kappa_T$ of Table 2 from the Gibbs free energy equation $g(T, p)$ and its derivatives of the "IAPWS Revised Release on an Equation of State 2006 for $H_2O$ Ice Ih" (Revision 2009) are directly given in [7].

### 4.6 Determination of Partial Derivatives from the IAPWS Formulation 2008 for Seawater

The formulae for calculating the properties $v$, $s$, $c_p$, $\alpha_v$, and $\kappa_T$ of Table 2 from the "IAPWS Formulation 2008 for the Thermodynamic Properties of Seawater" [9] at constant salinity are

$$v = \frac{1}{\rho^{\mathrm{w}}} + g_p^{\mathrm{s}} , \qquad s = R^{\mathrm{w}} \left[ \tau \left( \phi_\tau^{\mathrm{o}} + \phi_\tau^{\mathrm{r}} \right) - \phi^{\mathrm{o}} - \phi^{\mathrm{r}} \right] - g_T^{\mathrm{s}} ,$$

$$c_p = -R^{\mathrm{w}} \left[ \tau^2 \left( \phi_{\tau\tau}^{\mathrm{o}} + \phi_{\tau\tau}^{\mathrm{r}} \right) - \frac{\left( 1 + \delta \phi_\delta^{\mathrm{r}} - \delta \tau \phi_{\delta\tau}^{\mathrm{r}} \right)^2}{\left( 1 + 2\delta \phi_\delta^{\mathrm{r}} + \delta^2 \phi_{\delta\delta}^{\mathrm{r}} \right)} \right] - T g_{TT}^{\mathrm{s}} , \tag{8}$$

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

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

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

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

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

represent the derivatives of the ideal-gas part $\phi^{\mathrm{o}}(\delta,\tau)$ and of the residual part $\phi^{\mathrm{r}}(\delta,\tau)$ of the dimensionless Helmholtz free energy equation $\phi(\delta,\tau) = \phi^{\mathrm{o}}(\delta,\tau) + \phi^{\mathrm{r}}(\delta,\tau)$ of the “IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use” (IAPWS-95) [1, 2]. The reduced parameters are $\phi = f/(R^{\mathrm{w}}\,T)$, $\delta = \rho^{\mathrm{w}}/\rho_{\mathrm{c}}$, and $\tau = T_{\mathrm{c}}/T$, where $R^{\mathrm{w}}$ is the specific gas constant and $\rho_{\mathrm{c}}$ and $T_{\mathrm{c}}$ are the critical parameters of IAPWS-95. The density of the pure water part $\rho^{\mathrm{w}}$ must be calculated iteratively from the equation

$$p = \rho^{\mathrm{w}} R^{\mathrm{w}}\, T\left(1 + \delta\, \phi^{\mathrm{r}}_{\delta}\right) \tag{9}$$

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

In Eq. (8), the abbreviations

$$g^{\mathrm{s}}_{T} = \left(\frac{\partial g^{\mathrm{s}}}{\partial T}\right)_{p,S},\ g^{\mathrm{s}}_{TT} = \left(\frac{\partial^2 g^{\mathrm{s}}}{\partial T^2}\right)_{p,S},\ g^{\mathrm{s}}_{p} = \left(\frac{\partial g^{\mathrm{s}}}{\partial p}\right)_{T,S},\ g^{\mathrm{s}}_{pp} = \left(\frac{\partial^2 g^{\mathrm{s}}}{\partial p^2}\right)_{T,S},\ g^{\mathrm{s}}_{Tp} = \left(\frac{\partial^2 g^{\mathrm{s}}}{\partial T\, \partial p}\right)_{S}$$

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

### 4.7 Determination of Partial Derivatives from the IAPWS Industrial Formulation 2013 for Seawater

The formulae for calculating the properties $v$, $s$, $c_p$, $\alpha_v$, and $\kappa_T$ of Table 2 from the Gibbs free energy equation $g(p,T,S)$ and its derivatives at constant salinity $S$ of the formulation described in the IAPWS Advisory Note on "Industrial Calculation of the Thermodynamic Properties of Seawater" (2013) are directly given in [13].

## 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:

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

According to Table 1, the partial derivatives are:

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

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

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

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

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

$\phi(\delta,\tau)$ of IAPWS-IF97 region 3 [3] 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:

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

According to Table 2, the partial derivatives are:

$$\left(\frac{\partial u}{\partial p}\right)_T = v\,(p\,\kappa_T - T\,\alpha_v) \qquad \left(\frac{\partial v}{\partial T}\right)_p = v\,\alpha_v$$

$$\left(\frac{\partial u}{\partial T}\right)_p = c_p - p\,v\,\alpha_v \qquad \left(\frac{\partial v}{\partial p}\right)_T = -v\kappa_T \tag{14}$$

$$\left(\frac{\partial p}{\partial p}\right)_T = 1 \qquad \left(\frac{\partial p}{\partial T}\right)_p = 0$$

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

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

The values of the properties $v$, $c_p$, $\alpha_v$, and $\kappa_T$ can be calculated from the dimensionless Gibbs free energy equations:

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

$\gamma(\pi,\tau) = \gamma^{\mathrm{o}}(\pi,\tau) + \gamma^{\mathrm{r}}(\pi,\tau)$ 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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