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Revised Advisory Note No. 3
Thermodynamic Derivatives from IAPWS Formulations

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Summary

The method provided in this Revised Advisory Note is recommended for determining thermodynamic derivatives from IAPWS formulations, in particular from the Scientific Formulation IAPWS-95 for Ordinary Water [1], the Industrial Formulation IAPWS-IF97 for Water and Steam [3], the Computationally Efficient Thermodynamic Formulation for Liquid Water for Oceanographic Use [6], the IAPWS Equation of State 2006 for Ice Ih [8], the IAPWS Scientific Formulation 2008 for Seawater [12], and the IAPWS Industrial Formulation 2013 for Seawater [14].

In this 2018 revision of Advisory Note No. 3, the formulae of the IAPS Formulation 1984 for Heavy Water have been replaced by the formulae of the IAPWS Formulation 2017 [10].

Further details of the method used in this Advisory Note can be found in the publication by H.-J. Kretzschmar and W. Wagner [16].

This Advisory Note contains 14 pages, including this cover page.

Further information about this Advisory Note and other documents issued by IAPWS can be obtained from the Executive Secretary of IAPWS (Dr. R.B. Dooley, bdooley@iapws.org) or from http://www.iapws.org.

Contents

1 Nomenclature

Thermodynamic quantities:

a	Molar Helmholtz energy (heavy water, Sec. 3.4)
c_p	Specific isobaric heat capacity $c_p = \left(\partial h/\partial T\right)_p$
c_v	Specific isochoric heat capacity $c_v = \left(\partial u/\partial T\right)_v$
f	Specific Helmholtz energy
g	Specific Gibbs energy
h	Specific enthalpy
M	Molar mass M (heavy water, Sec. 3.4)
p	Pressure
R	Molar gas constant (heavy water formulation, Sec. 3.4)
R	Specific gas constant (ordinary water, Secs. 3.2 and 3.3)
s	Specific entropy
S	Salinity of seawater
T	Absolute temperature[a]
u	Specific internal energy
v	Specific volume
x	Any property
y	Any property
z	Any property
α	Reduced Helmholtz energy (heavy water) $\alpha = a/(RT)$
α_p	Relative pressure coefficient $\alpha_p = p^{-1}\left(\partial p/\partial T\right)_v$
α_v	Isobaric cubic expansion coefficient $\alpha_v = v^{-1}\left(\partial v/\partial T\right)_p$
β_p	Isothermal stress coefficient $\beta_p = -p^{-1}\left(\partial p/\partial v\right)_T$
δ	Reduced density, $\delta = \rho/\rho_\mathrm{c}$
ϕ	Reduced Helmholtz energy $\phi = f/(RT)$
γ	Reduced Gibbs energy $\gamma = g/(RT)$
κ_T	Isothermal compressibility $\kappa_T = -v^{-1}\left(\partial v/\partial p\right)_T$
π	Reduced pressure $\pi = p/p^*$
ρ	Density
ρ	Molar density (heavy water, Sec. 3.4)
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

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[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

"Revised Release on the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use" (IAPWS-95, Revision 2016) [1, 2, 3], or of

"Revised Release on the IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam" (IAPWS-IF97, Revision 2012) [3, 4, 5],

all of the partial derivatives of first and second order of various properties can be calculated analytically. This is also true for fundamental equations of

"Supplementary Release on a Computationally Efficient Thermodynamic Formulation for Liquid Water for Oceanographic Use" (2009) [6, 7],

"Revised Release on the Equation of State 2006 for H_2O Ice Ih" (Revision 2009) [8, 9],

"Release on the IAPWS Formulation 2017 for the Thermodynamic Properties of Heavy Water" (IAPWS-2017) [10, 11],

"Release on the IAPWS Formulation 2008 for the Thermodynamic Properties of Seawater" (IAPWS-2008) [12, 13], and

"Advisory Note No. 5: Industrial Calculation of the Thermodynamic Properties of Seawater" (2013) [14, 15].

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 and IAPWS-IF97 region 3 for water and steam, and of the IAPWS formulation 2017 for heavy water,

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

$\left(\frac{\partial z}{\partial x}\right)_{y,S} (p,T,S)$, from Gibbs equations of the IAPWS scientific formulation 2008 for seawater and of the IAPWS industrial formulation 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 energy g, and specific Helmholtz energy f are given in this document.

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

3 Partial Derivatives from Fundamental Helmholtz Energy Equations

3.1 General Procedure for Helmholtz 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 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, 2016) [1], the formulae for calculating the five properties *p*, *s*, c_v, α_p, and β_p of Table 1 from the dimensionless Helmholtz energy equation $\phi(\delta,\tau)=\phi^{\mathrm{o}}(\delta,\tau)+\phi^{\mathrm{r}}(\delta,\tau)$ and its derivatives are

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

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

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

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 ρ_{c} and T_{c}. The equations $\phi^{\mathrm{o}}(\delta,\tau)$, $\phi^{\mathrm{r}}(\delta,\tau)$ and their derivatives which were abbreviated in Eq. (2) as follows:

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

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

are given in [1] 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 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, 2012) [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 ρ_{c} and T_{c}. The equation $\phi(\delta,\tau)$ and its derivatives which were abbreviated in Eq. (3) as follows:

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

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

3.4 Determination of Partial Derivatives from the IAPWS Formulation 2017 for Heavy Water

The formulae for calculating p, s, c_v, α_p, and β_p of Table 1 from the dimensionless Helmholtz energy equation $\alpha(\delta,\tau) = \alpha^\mathrm{o}(\delta,\tau) + \alpha^\mathrm{r}(\delta,\tau)$ and its derivatives of the "IAPWS Formulation 2017 for the Thermodynamic Properties of Heavy Water" [10] are:

$$p = \rho R T\left(1+\delta\alpha_\delta^\mathrm{r}\right), \qquad s = \frac{R}{M}\left[\tau\left(\alpha_\tau^\mathrm{o}+\alpha_\tau^\mathrm{r}\right)-\alpha^\mathrm{o}-\alpha^\mathrm{r}\right],$$

$$c_v = -\frac{R}{M}\tau^2\left(\alpha_{\tau\tau}^\mathrm{o}+\alpha_{\tau\tau}^\mathrm{r}\right), \qquad \alpha_p = \frac{1}{T}\left[1-\frac{\delta\,\tau\,\alpha_{\delta\tau}^\mathrm{r}}{\left(1+\delta\,\alpha_\delta^\mathrm{r}\right)}\right], \tag{4}$$

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

where $\alpha = a/(RT)$, $\delta = \rho/\rho_\mathrm{c}$, and $\tau = T_\mathrm{c}/T$ with the molar density ρ, the temperature T, the molar Helmholtz energy a, the molar gas constant R, the molar mass M, and the critical parameters molar density ρ_c and temperature T_c. The equations $\alpha^\mathrm{o}(\delta,\tau)$, $\alpha^\mathrm{r}(\delta,\tau)$ and their derivatives which were abbreviated in Eq. (4) as follows:

$$\alpha_\tau^\mathrm{o} = \left(\frac{\partial\alpha^\mathrm{o}}{\partial\tau}\right)_\delta, \quad \alpha_{\tau\tau}^\mathrm{o} = \left(\frac{\partial^2\alpha^\mathrm{o}}{\partial\tau^2}\right)_\delta,$$

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

are given in [10] along with the associated values for molar gas constant R, molar mass M, molar critical density ρ_c, and critical temperature T_c.

4 Partial Derivatives from Fundamental Gibbs Energy Equations

4.1 General Procedure for Gibbs 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 $\alpha_v = v^{-1}\left(\partial v/\partial T\right)_p$, and isothermal compressibility $\kappa_T = -v^{-1}\left(\partial v/\partial p\right)_T$ are required. These quantities contain the first- and second-order derivatives of the Gibbs 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, α_v, and κ_T of Table 2 from the dimensionless Gibbs 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, 2012) [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, 2meta, and 5

The formulae for calculating the properties v, s, c_p, α_v, and κ_T of Table 2 from the dimensionless Gibbs energy equations $\gamma(\pi,\tau) = \gamma^{\mathrm{o}}(\pi,\tau) + \gamma^{\mathrm{r}}(\pi,\tau)$ and its derivatives in regions 2, 2 meta, and 5 of the “IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam" (IAPWS-IF97, 2012) [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 κ_T of Table 2 from the Gibbs energy equation $g(T,p)$ and its derivatives of the "Supplementary Release on a Computationally Efficient Thermodynamic Formulation for Liquid Water for Oceanographic Use" (2009) are directly given in [6].

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 κ_T of Table 2 from the Gibbs energy equation $g(T, p)$ and its derivatives of the "Revised Release on an Equation of State 2006 for H_2O Ice Ih" (2009) are directly given in [8].

4.6 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" [12] 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 formulae are for constant salinity, the subscript S is not explicitly written.
For the pure water part, the abbreviations used in the release

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

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

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 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]. The reduced quantities are $\phi = f/(R^{\mathrm{w}}\,T)$, $\delta = \rho^{\mathrm{w}}/\rho_{\mathrm{c}}$, and

$\tau = T_\mathrm{c}/T$, where R^w is the specific gas constant and ρ_c and 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

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

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] along with the associated values for R^w, ρ_c, and T_c.

In Eq. (8), the abbreviations

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

represent the partial derivatives at constant salinity S of the saline part $g^\mathrm{s}(S,T,p)$ of the Gibbs energy equation. The equation $g^\mathrm{s}(S,T,p)$ is given in [12].

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

The formulae for calculating the properties v, s, c_p, α_v, and κ_T of Table 2 from the Gibbs energy equation $g(p,T,S)$ and its derivatives at constant salinity S of the formulation described in the Advisory Note on “Industrial Calculation of the Thermodynamic Properties of Seawater" (2016) are given in [14].

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 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:

$$\left(\frac{\partial u}{\partial v}\right)_T = p\left(T\alpha_p - 1\right) \qquad \left(\frac{\partial v}{\partial T}\right)_v = 0$$

$$\left(\frac{\partial u}{\partial T}\right)_v = c_v \qquad \left(\frac{\partial v}{\partial v}\right)_T = 1 \tag{11}$$

$$\left(\frac{\partial p}{\partial v}\right)_T = -p\,\beta_p \qquad \left(\frac{\partial p}{\partial T}\right)_v = p\,\alpha_p$$

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 α_p are calculated from the dimensionless Helmholtz 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 Energy Equation

Since the basic equations of regions 1, 2, 2meta, and 5 of IAPWS-IF97 [3] 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, α_v, and κ_T can be calculated from the dimensionless Gibbs 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 [3] with Eq. (7).

Any other partial derivative can be determined analogously.

6 References

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