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Proposal for an Advisory Note for Calculating Thermodynamic Derivatives for Water and Steam from the IAPWS Formulations

Contents

1 Introduction

► Thermodynamic differential quotients such as

$$\left(\frac{\partial h}{\partial p}\right)_v, \left(\frac{\partial u}{\partial p}\right)_v, \left(\frac{\partial s}{\partial p}\right)_v, \left(\frac{\partial T}{\partial p}\right)_h, \left(\frac{\partial T}{\partial p}\right)_s, \left(\frac{\partial v}{\partial h}\right)_p, \left(\frac{\partial v}{\partial s}\right)_p \ldots$$

are required for:

- Calculating non-stationary processes
- Solving equation systems of stationary heat cycle calculations.

► All thermodynamic differential quotients can be determined from IAPWS-95 and IAPWS-IF97.

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IAPWS should show the way how to calculate any differential quotient from IAPWS-95 and IAPWS-IF97.

2 Determination of any Differential Quotient from IAPWS-95

► Fundamental equation of IAPWS-95:

Helmholtz equation $f(\rho,T)$

$\rho = 1/v$ and T are the input variables.

► All thermodynamic properties and derivatives can be formed as a function of v and T from $f(v,T)$ and from its derivatives

$$\left(\frac{\partial f}{\partial T}\right)_v, \left(\frac{\partial^2 f}{\partial T^2}\right)_v, \left(\frac{\partial f}{\partial v}\right)_T, \left(\frac{\partial^2 f}{\partial v^2}\right)_T, \left(\frac{\partial^2 f}{\partial T\, \partial v}\right).$$

⟶ but only with respect to v and T !

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Differential quotients derived with respect other properties have to be formed.

► Common expression for forming any differential quotient $\left(\frac{\partial z}{\partial x}\right)_y$ from derivatives with respect to v and T

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

where x, y, z can represent one of the properties: p, T, v, h, u, s, g, or f

► Derivatives of these properties with respect to v and T

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	$p\left(T\alpha_p - 1\right)$	c_v
h	$p\left(T\,\alpha_p - v\,\beta_p\right)$	$c_v + p\,v\,\alpha_p$
s	$p\,\alpha_p$	$\frac{c_v}{T}$
g	$-pv\,\beta_p$	$p\,v\,\alpha_p - s$
f	$-p$	$-s$

Required quantities:

Pressure p

Specific entropy s

Specific isochoric heat capacity c_v

Relative pressure coefficient

$$\alpha_p = p^{-1}\left(\partial p/\partial T\right)_v$$

Isothermal stress coefficient

$$\beta_p = -p^{-1}\left(\partial p/\partial v\right)_T$$

► Determination of these 5 quantities from the Helmhotz equation of IAPWS-95

Dimensionless form of the Helmholtz equation

$$\frac{f(\rho,T)}{RT} = \phi(\delta,\tau) = \phi^{\text{o}}(\delta,\tau) + \phi^{\text{r}}(\delta,\tau) \quad ,$$

where $\delta = \rho / \rho_{\text{c}} \qquad \tau = T_{\text{c}} / T$

Determination from the Helmholtz equation

$$p = \rho R T \left(1 + \delta \phi^{\text{r}}_{\delta}\right) \qquad s = R \left(\tau \left(\phi^{\text{o}}_{\tau} + \phi^{\text{r}}_{\tau}\right) - \phi^{\text{o}} - \phi^{\text{r}}\right)$$

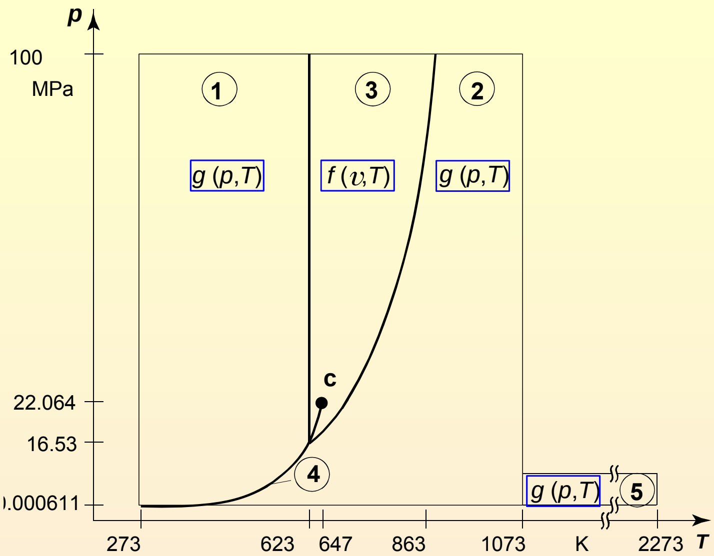
$$c_v = -R \tau^2 \left(\phi^{\text{o}}_{\tau\tau} + \phi^{\text{r}}_{\tau\tau}\right) \qquad \alpha_p = \frac{1}{T}\left(1 - \frac{\tau \phi^{\text{r}}_{\delta\tau}}{\phi^{\text{r}}_{\delta}}\right)$$

$$\beta_p = \rho \left(2 + \frac{\delta \phi^{\text{r}}_{\delta\delta}}{\phi^{\text{r}}_{\delta}}\right)$$

The procedure allows to determine any differential quotient from IAPWS-95

3 Determination of any Differential Quotient from IAPWS-IF97

► Fundamental equations of IAPWS-IF97:



Regions 1, 2 and 5
Gibbs Equations $g(p,T)$

Region 3
Helmholtz Equation $f(v,T)$

All thermodynamic properties and derivatives can be formed

with respect to p and T — with respect to v and T

3.1 Differential Quotients for Regions 1, 2, and 5

► Common expression for forming any differential quotient $\left(\frac{\partial z}{\partial x}\right)_y$ from derivatives with respect to p and T

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

where

x, y, z can represent one of the properties: p, T, v, h, u, s, g, or f

► Derivatives of these properties with respect to p and T

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

Required quantities:

Specific volume v

Specific entropy s

Specific isobaric heat capacity c_p

Isobaric cubic expansion coefficient
$\alpha_v = v^{-1}(\partial v/\partial T)_p$

Isothermal compressibility
$\kappa_T = -v^{-1}(\partial v/\partial p)_T$

► **Determination of these 5 quantities from the Gibbs equations**

Region 1

Dimensionless form of the Gibbs equation

$$\frac{g(p,T)}{RT} = \gamma(\pi,\tau) \quad ,$$

where $\pi = p/p^*$ $\quad \tau = T^*/T$

Calculation from the Gibbs equation

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

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

Regions 2, 2meta, and 5

Dimensionless form of the Gibbs equation

$$\frac{g(p,T)}{RT} = \gamma(\pi,\tau) = \gamma^{\mathrm{o}}(\pi,\tau) + \gamma^{\mathrm{r}}(\pi,\tau) \quad ,$$

where $\pi = p/p^*$ $\quad \tau = T^*/T$

Calculation from the Gibbs equation

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

$$c_p = -R\tau^2\left(\gamma^{\mathrm{o}}_{\tau\tau} + \gamma^{\mathrm{r}}_{\tau\tau}\right) \qquad \alpha_v = \frac{1}{T}\left(\frac{1 + \pi\gamma^{\mathrm{r}}_\pi - \tau\pi\gamma^{\mathrm{r}}_{\pi\tau}}{1 + \pi\gamma^{\mathrm{r}}_\pi}\right) \qquad \kappa_T = \frac{1}{p}\left(\frac{1 - \pi^2\gamma^{\mathrm{r}}_{\pi\pi}}{1 + \pi\gamma^{\mathrm{r}}_\pi}\right)$$

3.2 Differential Quotients for Region 3

► Common expression for forming any differential quotient $\left(\frac{\partial z}{\partial x}\right)_y$ from derivatives with respect to v and T

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

where

x, *y*, *z* can represent one of the properties: *p*, *T*, v, *h*, *u*, *s*, *g*, or *f*

► Derivatives of these properties with respect to *p* and *T*

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	$p\,\alpha_p$	$\frac{c_v}{T}$
g	$-pv\,\beta_p$	$p\,v\,\alpha_p - s$
f	$-p$	$-s$

Required quantities:

Pressure *p*

Specific entropy *s*

Specific isochoric heat capacity c_v

Relative pressure coefficient

$\alpha_p = p^{-1}(\partial p/\partial T)_v$

Isothermal stress coefficient

$\beta_p = -p^{-1}(\partial p/\partial v)_T$

► **Determination of these 5 quantities from the Helmholtz equation**

Region 3

Dimensionless form of the Helmholtz equation

$$\frac{f(\rho,T)}{RT} = \phi(\delta,\tau) \quad ,$$

where $\delta = \rho/\rho_c \qquad \tau = T_c/T$

Calculation from the Helmholtz equation

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

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

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

4 Example: Calculation of the differential quotient $\left(\frac{\partial u}{\partial p}\right)_v$ for IAPWS-IF97 Region 2

Comparison of $\left(\frac{\partial u}{\partial p}\right)_v$ with $\left(\frac{\partial z}{\partial x}\right)_y$ $\Rightarrow$ $z = u$, $x = p$, $y = v$

Common Formula $\left(\frac{\partial z}{\partial x}\right)_y (p,T)$

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

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

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

$z = u$, $x = p$, $y = v$

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	$\frac{c_p}{T}$	$-v\,\alpha_v$
g	$-s$	v
f	$-p\,v\,\alpha_v - s$	$p\,v\,\kappa_T$

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

$\left(\frac{\partial p}{\partial p}\right)_T = 1$

$\left(\frac{\partial v}{\partial T}\right)_p = v \cdot \alpha_v$

$\left(\frac{\partial v}{\partial p}\right)_T = -v \cdot \kappa_T$

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

$\left(\frac{\partial u}{\partial T}\right)_p = c_p - p \cdot v \cdot \alpha_v$

Insertion into (a)

$$\left(\frac{\partial u}{\partial p}\right)_v = \frac{v \cdot (p \cdot \kappa_T - T \cdot \alpha_v) \cdot (v \cdot \alpha_v) - (c_p - p \cdot v \cdot \alpha_v) \cdot (-v \cdot \kappa_T)}{1 \cdot (v \cdot \alpha_v) - 0 \cdot (-v \cdot \kappa_T)}$$

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

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

Calculation from the Gibbs equation of region 2

$$v = \frac{R\,T}{p}\,\pi\left(\gamma_\pi^{\mathrm{o}} + \gamma_\pi^{\mathrm{r}}\right)$$

$$\alpha_v = \frac{1}{T}\left(\frac{1+\pi\gamma_\pi^{\mathrm{r}} - \tau\pi\gamma_{\pi\tau}^{\mathrm{r}}}{1+\pi\gamma_\pi^{\mathrm{r}}}\right)$$

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

$$c_p = -R\,\tau^2\left(\gamma_{\tau\tau}^{\mathrm{o}} + \gamma_{\tau\tau}^{\mathrm{r}}\right)$$

$$s = R\left(\tau\left(\gamma_\tau^{\mathrm{o}} + \gamma_\tau^{\mathrm{r}}\right) - \left(\gamma^{\mathrm{o}} + \gamma^{\mathrm{r}}\right)\right)$$

The procedure can be applied easily by the user

5 Summary

- Common procedure for calculating any differential quotient $\left(\frac{\partial z}{\partial x}\right)_y$,

  where x, y, z can represent p, T, v, u, h, s, g, or f,

  using the fundamental equations of
  - the Scientific Formulation IAPWS-95
  - the new Industrial Formulation IAPWS-IF97

- Procedure can be used without knowledge of the thermodynamic differential equations

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Proposal: Preparation of an IAPWS Guideline

by the IAPWS meeting, 2006