



ENAAČBA STANJA VODE IN VODNE PARE

SEMINARSKA NALOGA PRI PREDMETU JEDRSKA TEHNIKA IN ENERGETIKA

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Enačba stanja

- idealni plin: $pV = \frac{m}{M} RT$

p tlak, V prostornina, m masa, M molska masa, R splošna plinska konstanta, T temperatura

- Van der Waalsova: $\left(p + \frac{a}{V_M^2}\right)(V_M - b) = RT$ - približek

V_M volumen mola snovi, a , b konstanti, značilni za snov

- natančnost
- točnost ob kritični točki
- točnost ob faznih prehodih
- točnost v ekstremnih pogojih (T , p)

Pomembnost H₂O

- energetika (HE, pogon turbin, hladilo)
- industrija
- topilo
- vreme, klima
- geologija
- živa bitja
- ...



<http://www.flickr.com/photos/vattenfall/3581340677/sizes/m/in/photostream/>

Preučevanje lastnosti H₂O

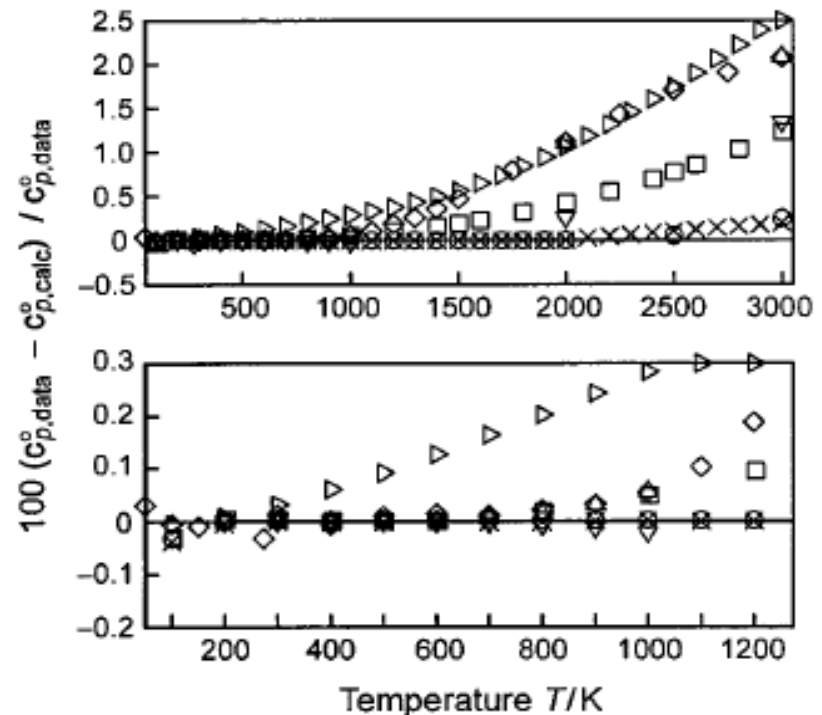


- IAPWS - International Association for the Properties of Water and Steam
- izmerjeni podatki => enačba stanja
- IAPWS-95 (The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use)
- IAPWS-IF97 (The IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam)
- računalniški programi (npr. <http://webbook.nist.gov/chemistry/fluid/>)
- parne tabele
- od tališča do 1273 K, do 1000 MPa, tudi do 0,0001 % natančno

<http://www.iapws.org/>

Eksperimentalni podatki

- izbrani izmed 20 000 podatkov, merjenih od l. 1928 dalje
- natančnost
- konsistenca z ostalimi podatki



- | | |
|---------------------------------|------------------------------------|
| ○ Woolley (1980) | ◇ TRC Tables (1988) |
| ▽ Woolley (1987) (1982 version) | ▷ Gurvich <i>et al.</i> (1989) |
| △ Woolley (1987) (1984 version) | × NIST-JANAF Tables [Chase (1998)] |
| | □ Vidler & Tennyson (2000) |

Eksperimentalni podatki

- po celem območju

TABLE 4.4. Information on the selected $p\rho T$ data

Authors	Temperature range T/K	Pressure range p/MPa	Uncertainty			Number of data	
			$\Delta T/\text{mK}^a$	Δp^a	$\Delta\rho$	Total	Selected
Tammann & Jellinghaus (1928)	259–273	49–147	$\pm 0.15\%$	257	28
Bridgman (1935)	253–268	98–490	$\pm 0.2\%$	129	22
Bridgman (1942)	348–448	980–3585	$\pm 0.5\%$	17	16
Vukalovich <i>et al.</i> (1961)	823–923	4.7–118	$\pm 0.2\%$	175	95
Vukalovich <i>et al.</i> (1962)	1022–1174	4.6–118	$\pm 0.25\%$	148	81
Rivkin & Akhundov (1962)	643–677	4.9–37	± 15	$\pm 0.01\%$	$\pm 0.05\%$	298	162
Rivkin & Akhundov (1963)	647–723	4.7–59	± 10	$\pm 0.01\%$	$\pm 0.05\%$	190	124
Rivkin & Troyanovskaya (1964)	643–653	9–27	± 10	$\pm 0.01\%$	$\pm 0.05\%$	316	82
Rivkin <i>et al.</i> (1966)	646–648	14.6–23	± 5	$\pm 0.01\%$	$\pm 0.04\%$	107	74
Grindley & Lind (1971)	298–423	100–800	± 20	...	$\pm 0.02\%$	560	112
Kell (1975)	236–268	0.101 325	...	$\pm 0.01\%$	$\pm 0.05\%$	120	21
Kell & Whalley (1975)	273–423	0.5–103	± 1	$\pm 0.01\%$	$\Delta\rho^b$	596	574
Kell <i>et al.</i> (1978)	448–623	1.3–103	± 1	$\pm 0.01\%$	$\Delta\rho^c$	196	145
Hilbert <i>et al.</i> (1981)	293–873	10–400	± 5	$\pm 0.01\%$	$\pm 0.2\%$	530	396
Hanafusa <i>et al.</i> (1984)	643–673	19.7–38.6	± 5	$\pm 0.003 \text{ MPa}$	$\pm 0.04\%$	123	93
Kell <i>et al.</i> (1985)	648–773	21–103	± 1	$\pm 0.01\%$	$\Delta\rho^d$	587	131
Kell <i>et al.</i> (1989)	473–773	0.1–36	± 2	$\pm 0.01\%$	$\pm 0.006 \text{ kg m}^{-3}$	630	509
Morita <i>et al.</i> (1989)	638–652	18.5–38	± 4	$\pm 0.02\%$	$\pm 0.04\%$	93	90
Takenaka & Masui (1990)	273–358	0.101 325	$\pm 1 \text{ ppm}$	79	18 ^{e,f}
Patterson & Morris (1994)	274–313	0.101 325	$\pm(0.6\text{--}1.4) \text{ ppm}$	13 ^f	... ^g
Masui <i>et al.</i> (1995)	273–358	0.101 325	$\pm(0.9\text{--}1.3) \text{ ppm}$	2 ^{h,i}	... ^g
Tanaka <i>et al.</i> (2001)	273–313	0.101 325	$\pm(0.84\text{--}0.87) \text{ ppm}$	41	... ^g

^aIf no uncertainty values are given, then these uncertainties are taken into account in the uncertainty in ρ .

^b $\Delta\rho = \pm(6 + 0.05 \cdot (T/K - 273 \text{ K}) + p/\text{MPa}) \times 10^{-4}$.

^c $\Delta\rho = \pm(7 + 0.1 p/\text{MPa}) \times 10^{-5} \rho + 0.04 \text{ kg m}^{-3}$; $T \geq 548 \text{ K}$: $\Delta\rho = \pm 0.1 \text{ kg m}^{-3}$.

^d $\Delta\rho = \pm(7 + 0.1 p/\text{MPa}) \times 10^{-5} \rho + 0.04 \text{ kg m}^{-3}$.

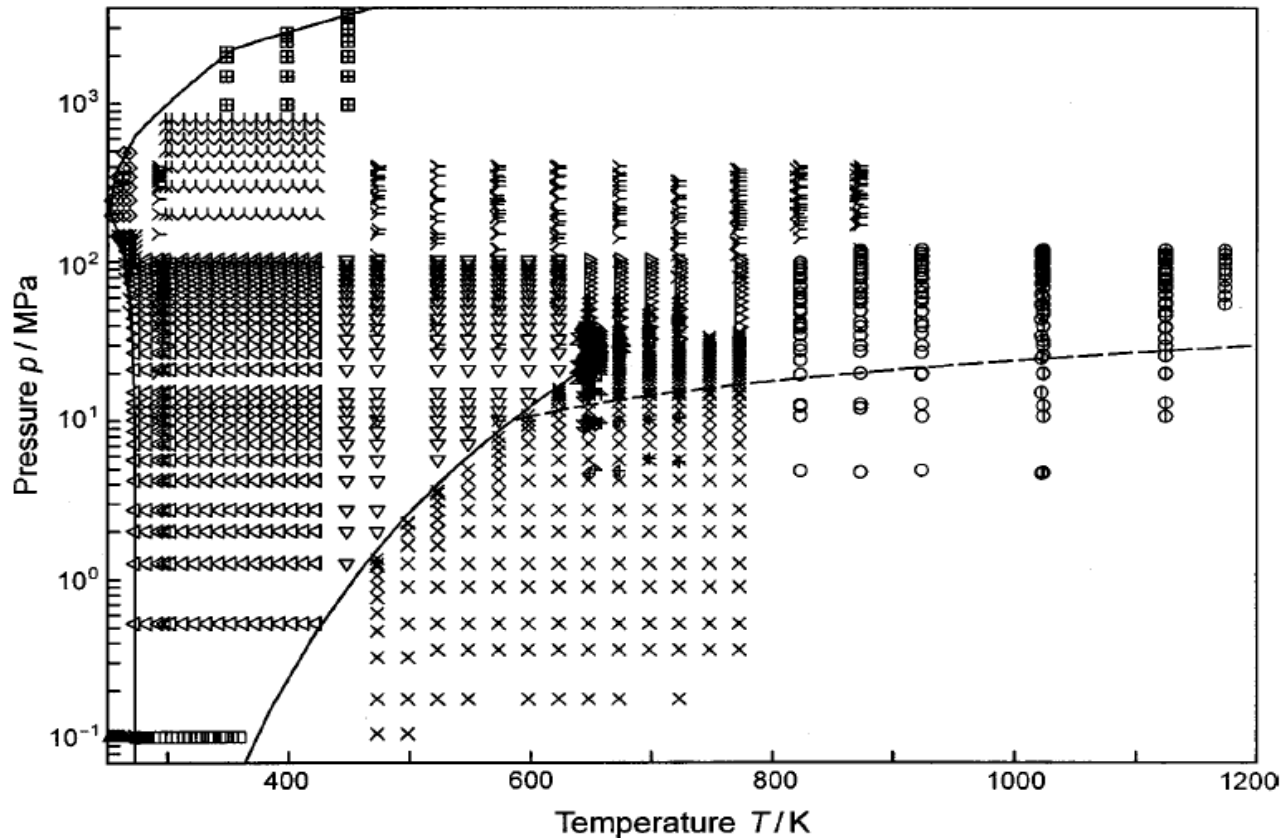
^eCalculated from their $\rho(T)/\rho_{\text{max}}$ equation, see text.

^fThe values correspond to VSMOW.

^gThese data were only available after the development of IAPWS-95 had been finished.

^hIn addition, a $\rho(T)$ equation is given valid for temperatures from 273.15 to 358.15 K.

Eksperimentalni podatki



Υ Tammann & Jellinghaus (1928)
 \diamond Bridgman (1935)
 \boxplus Bridgman (1942)
 \circ Vukalovich *et al.* (1961)
 \dagger Rivkin & Akhundov (1962)
 \oplus Vukalovich *et al.* (1962)
 \leftarrow Rivkin & Akhundov (1963)

\downarrow Rivkin & Troyanovskaya (1964)
 \rightarrow Rivkin *et al.* (1966)
 \wedge Grindley & Lind (1971)
 \triangle Kell (1975)
 \triangleleft Kell & Whalley (1975)
 ∇ Kell *et al.* (1978)
 \succ Hilbert *et al.* (1981)

\oplus Hanafusa *et al.* (1984)
 \triangleright Kell *et al.* (1985)
 \times Kell *et al.* (1989)
 \boxtimes Morita *et al.* (1989)
 \square Takenaka & Masui (1990)

— Phase boundaries

--- Isochore $\rho = 55 \text{ kg m}^{-3}$

Eksperimentalni podatki

- temperaturna lestvica ITS-90
- če ni meritev/ni mogoče meriti, izračunamo sintetične podatke
- če imamo meritve za količino preko območja, lahko testiramo kvaliteto ekstrapolacije

Krivulja nasičenja

- trojna točka
- kritična točka

$$T_t = 273.16 \text{ K}$$

$$p_t = 611.655 \text{ Pa}$$

$$\rho_t' = 999.793 \text{ kg m}^{-3}$$

$$\rho_t'' = 0.004 854 58 \text{ kg m}^{-3}$$

$$T_c = 647.096 \text{ K}$$

$$p_c = 22.064 \text{ MPa}$$

$$\rho_c = 322 \text{ kg m}^{-3}$$

ρ' gostota kapljevine, ρ'' gostota pare

- poznamo enačbe
- veljajo le v bližini faznega prehoda
- eksperimentalno določeni koeficienti

Krivulja nasičenja

- tlak pare, gostota kapljevine in pare:

Vapor–pressure equation and its derivative:

$$\ln\left(\frac{p_{\sigma}}{p_c}\right) = \frac{T_c}{T} (a_1 \vartheta + a_2 \vartheta^{1.5} + a_3 \vartheta^3 + a_4 \vartheta^{3.5} + a_5 \vartheta^4 + a_6 \vartheta^{7.5})$$

$$\frac{dp_{\sigma}}{dT} = -\frac{p_{\sigma}}{T} \left[\ln\left(\frac{p_{\sigma}}{p_c}\right) + a_1 + 1.5a_2 \vartheta^{0.5} + 3a_3 \vartheta^2 + 3.5a_4 \vartheta^{2.5} + 4a_5 \vartheta^3 + 7.5a_6 \vartheta^{6.5} \right], \quad (2.5a)$$

with $\vartheta = (1 - T/T_c)$, $T_c = 647.096$ K, $p_c = 22.064$ MPa, $a_1 = -7.859 517 83$, $a_2 = 1.844 082 59$, $a_3 = -11.786 649 7$, $a_4 = 22.680 741 1$, $a_5 = -15.961 871 9$, and $a_6 = 1.801 225 02$.

Saturated liquid density equation:

$$\frac{\rho'}{\rho_c} = 1 + b_1 \vartheta^{1/3} + b_2 \vartheta^{2/3} + b_3 \vartheta^{5/3} + b_4 \vartheta^{16/3} + b_5 \vartheta^{43/3} + b_6 \vartheta^{110/3}, \quad (2.6)$$

with $b_1 = 1.992 740 64$, $b_2 = 1.099 653 42$, $b_3 = -0.510 839 303$, $b_4 = -1.754 934 79$, $b_5 = -45.517 035 2$, and $b_6 = -6.746 944 50 \times 10^5$; for the definition of ϑ see Eq. (2.5).

Saturated vapor density equation:

$$\ln\left(\frac{\rho''}{\rho_c}\right) = c_1 \vartheta^{2/6} + c_2 \vartheta^{4/6} + c_3 \vartheta^{8/6} + c_4 \vartheta^{18/6} + c_5 \vartheta^{37/6} + c_6 \vartheta^{71/6}, \quad (2.7)$$

with $c_1 = -2.031 502 40$, $c_2 = -2.683 029 40$, $c_3 = -5.386 264 92$, $c_4 = -17.299 160 5$, $c_5 = -44.758 658 1$, and $c_6 = -63.920 106 3$; for the definition of ϑ see Eq. (2.5).

Krivulja nasičenja

- razlika notranje energije pri različnih temperaturah ($\Delta\alpha$), specifične entalpija (h), notranja energija (u), entropija (s)

$$\Delta\alpha = h' - \Delta^v h \frac{v'}{v'' - v'}$$

v specifični volumen
 $\Delta^v h$ izparilna toplota

Specific enthalpy

$$\frac{h'}{\text{kJ kg}^{-1}} = \frac{\alpha}{\alpha_0} + 10^3 \frac{T/\text{K}}{\rho' / (\text{kg m}^{-3})} \left(\frac{dp_\sigma}{dT} \right) \Big/ \left(\frac{\text{MPa}}{\text{K}} \right)$$

$$\frac{h''}{\text{kJ kg}^{-1}} = \frac{\alpha}{\alpha_0} + 10^3 \frac{T/\text{K}}{\rho'' / (\text{kg m}^{-3})} \left(\frac{dp_\sigma}{dT} \right) \Big/ \left(\frac{\text{MPa}}{\text{K}} \right)$$

Specific entropy

$$\frac{s'}{\text{kJ kg}^{-1} \text{K}^{-1}} = \frac{\psi}{\text{kJ kg}^{-1} \text{K}^{-1}} + 10^3 \frac{\left(\frac{dp_\sigma}{dT} \right) \Big/ \left(\frac{\text{MPa}}{\text{K}} \right)}{\rho' / (\text{kg m}^{-3})} \quad (2.14)$$

Specific internal energy

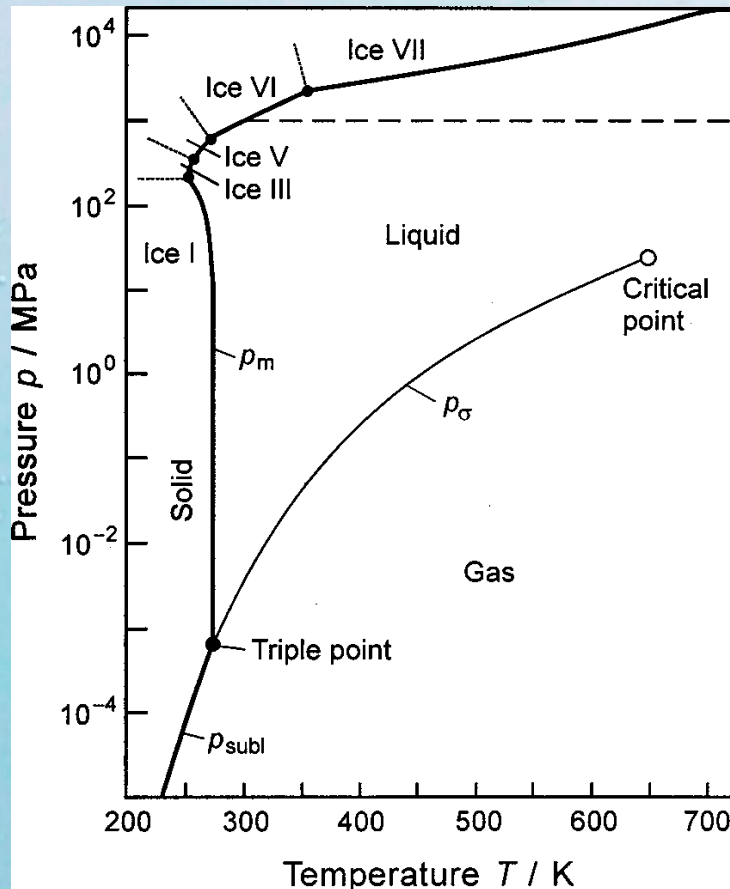
$$\frac{u'}{\text{kJ kg}^{-1}} = \frac{\alpha}{\alpha_0} + 10^3 \frac{\frac{T}{\text{K}} \left(\frac{dp_\sigma}{dT} \right) \Big/ \left(\frac{\text{MPa}}{\text{K}} \right) - \frac{p_\sigma}{\text{MPa}}}{\rho' / (\text{kg m}^{-3})}$$

$$\frac{u''}{\text{kJ kg}^{-1}} = \frac{\alpha}{\alpha_0} + 10^3 \frac{\frac{T}{\text{K}} \left(\frac{dp_\sigma}{dT} \right) \Big/ \left(\frac{\text{MPa}}{\text{K}} \right) - \frac{p_\sigma}{\text{MPa}}}{\rho'' / (\text{kg m}^{-3})}$$

$$\frac{s''}{\text{kJ kg}^{-1} \text{K}^{-1}} = \frac{\psi}{\text{kJ kg}^{-1} \text{K}^{-1}} + 10^3 \frac{\left(\frac{dp_\sigma}{dT} \right) \Big/ \left(\frac{\text{MPa}}{\text{K}} \right)}{\rho'' / (\text{kg m}^{-3})} \quad (2.15)$$

Krivulja nasičenja

- prehod led – voda ni vključen v IAPSW-95
- voda tvori 5 različnih struktur leda, le ena lahko sublimira



$$\ln\left(\frac{p_{\text{subl}}}{p_n}\right) = -13.928\,169(1 - \theta^{-1.5}) + 34.707\,823\,8(1 - \theta^{-1.25}), \quad (2.21)$$

with $\theta = T/T_n$, $T_n = 273.16$ K, and $p_n = 0.000\,611\,657$ MPa.

Plinska enačba

- izhodišče, ker se jo da delno razširiti na tekočo fazo
- tlak, temperatura, gostota, hitrost zvoka, specifična izobarna toplota, Joule-Kelvinov koeficient, ... - upošteva čez 1200 meritev
- velja med 273 in 1273 K ter do gostot 55 kg/m^3

Plinska enačba

$$\frac{f(\rho, T)}{RT} = \phi(\delta, \tau) = \phi^o(\delta, \tau) + \phi^r(\delta, \tau), \quad (3.2)$$

where $\delta = \rho/\rho_c$ and $\tau = T_c/T$ with $\rho_c = 322 \text{ kg m}^{-3}$, $T_c = 647.096 \text{ K}$, and $R = 0.461 518 05 \text{ kJ kg}^{-1} \text{ K}^{-1}$. The ideal-

$$\phi^r = \sum_{i=1}^7 n_i \delta^{d_i} \tau^{t_i}$$

where $\delta = \rho/\rho_c$ and $\tau = T_c/T$ with $\rho_c = 322 \text{ kg m}^{-3}$

TABLE 3.1. Coefficients and exponents of the residual part ϕ^r of the dimensionless Helmholtz free energy, Eq. (3.3)

i	d_i	t_i	n_i
1	1	0.25	0.474 865 925 9
2	1	1.25	$-0.112 437 055 3 \times 10^1$
3	1	3.5	$-0.811 862 740 1$
4	1	12	$-0.621 301 850 1 \times 10^{-3}$
5	2	1.5	0.192 443 099 3
6	2	13.5	$-0.832 286 766 2 \times 10^{-1}$
7	4	8.75	$0.139 105 223 0 \times 10^1$

Razvoj formulacije

- iščemo: $f(\rho, T) = f^o(\rho, T) + f^r(\rho, T)$
- brezdimenzijsko (delimo z RT):

$$\phi(\delta, \tau) = \phi^o(\delta, \tau) + \phi^r(\delta, \tau), \quad (5.2)$$

where $\delta = \rho/\rho_c$ is the reduced density and $\tau = T_c/T$ is the inverse reduced temperature with ρ_c and T_c the critical density and the critical temperature, respectively.

- prvi del za idealni plin, drugi del preostali efekti
- vse ostale količine se dajo izračunati iz tega

Razvoj formulacije

TABLE 6.3. Relations of thermodynamic properties to the ideal-gas part ϕ° , Eq. (6.5), and the residual part ϕ^r , Eq. (6.6), of the dimensionless Helmholtz free energy and their derivatives^a

Property	Relation
Pressure $p = \rho^2(\partial f/\partial \rho)_T$	$\frac{p(\delta, \tau)}{\rho RT} = 1 + \delta\phi_\delta^r$
Entropy $s = -(\partial f/\partial T)_\rho$	$\frac{s(\delta, \tau)}{R} = \tau(\phi_\tau^\circ + \phi_\tau^r) - \phi^\circ - \phi^r$
Internal energy $u = f + Ts$	$\frac{u(\delta, \tau)}{RT} = \tau(\phi_\tau^\circ + \phi_\tau^r)$
Enthalpy $h = u + pv$	$\frac{h(\delta, \tau)}{RT} = 1 + \tau(\phi_\tau^\circ + \phi_\tau^r) + \delta\phi_\delta^r$
Gibbs free energy $g = h - Ts$	$\frac{g(\delta, \tau)}{RT} = 1 + \phi^\circ + \phi^r + \delta\phi_\delta^r$
Isochoric heat capacity $c_v = (\partial u/\partial T)_\rho$	$\frac{c_v(\delta, \tau)}{R} = -\tau^2(\phi_{\tau\tau}^\circ + \phi_{\tau\tau}^r)$
Isobaric heat capacity $c_p = (\partial h/\partial T)_p$	$\frac{c_p(\delta, \tau)}{R} = -\tau^2(\phi_{\tau\tau}^\circ + \phi_{\tau\tau}^r) + \frac{(1 + \delta\phi_\delta^r - \delta\tau\phi_{\delta\tau}^r)^2}{1 + 2\delta\phi_\delta^r + \delta^2\phi_{\delta\delta}^r}$
Saturated liquid heat capacity $c_\sigma(T) = (\partial h/\partial T)_p + T(\partial p/\partial T)_\rho \cdot (dp_\sigma/dT)/(-\rho^2(\partial p/\partial \rho)_T) _{p=p_\sigma}$	$\frac{c_\sigma(\tau)}{R} = -\tau^2(\phi_{\tau\tau}^\circ + \phi_{\tau\tau}^r) + \frac{1 + \delta'\phi_\delta^r - \delta'\tau\phi_{\delta\tau}^r}{1 + 2\delta'\phi_\delta^r + \delta'^2\phi_{\delta\delta}^r} \cdot \left[(1 + \delta'\phi_\delta^r - \delta'\tau\phi_{\delta\tau}^r) - \frac{\rho_c}{R\delta'} \frac{dp_\sigma}{dT} \right]^b$

Razvoj formulacije

Speed of sound

$$w = (\partial p / \partial \rho)_s^{1/2}$$

$$\frac{w^2(\delta, \tau)}{RT} = 1 + 2\delta\phi_\delta^I + \delta^2\phi_{\delta\delta}^I - \frac{(1 + \delta\phi_\delta^I - \delta\tau\phi_{\delta\tau}^I)^2}{\tau^2(\phi_{\tau\tau}^\circ + \phi_{\tau\tau}^I)}$$

Joule–Thomson coefficient

$$\mu = (\partial T / \partial p)_h$$

$$\mu R \rho = \frac{-(\delta\phi_\delta^I + \delta^2\phi_{\delta\delta}^I + \delta\tau\phi_{\delta\tau}^I)}{(1 + \delta\phi_\delta^I - \delta\tau\phi_{\delta\tau}^I)^2 - \tau^2(\phi_{\tau\tau}^\circ + \phi_{\tau\tau}^I)(1 + 2\delta\phi_\delta^I + \delta^2\phi_{\delta\delta}^I)}$$

Isothermal throttling coefficient

$$\delta_T = (\partial h / \partial p)_T$$

$$\delta_T \rho = 1 - \frac{1 + \delta\phi_\delta^I - \delta\tau\phi_{\delta\tau}^I}{1 + 2\delta\phi_\delta^I + \delta^2\phi_{\delta\delta}^I}$$

Isentropic temperature-pressure coefficient

$$\beta_s = (\partial T / \partial p)_s$$

$$\beta_s \rho R = \frac{1 + \delta\phi_\delta^I - \delta\tau\phi_{\delta\tau}^I}{(1 + \delta\phi_\delta^I - \delta\tau\phi_{\delta\tau}^I)^2 - \tau^2(\phi_{\tau\tau}^\circ + \phi_{\tau\tau}^I)(1 + 2\delta\phi_\delta^I + \delta^2\phi_{\delta\delta}^I)}$$

Second virial coefficient

$$B(T) = \lim_{\rho \rightarrow 0} (\partial(p / (\rho RT)) / \partial \rho)_T$$

$$B(\tau) \rho_c = \lim_{\delta \rightarrow 0} \phi_\delta^I(\delta, \tau)$$

Third virial coefficient

$$C(T) = \lim_{\rho \rightarrow 0} \left[\frac{1}{2} (\partial^2(p / (\rho RT)) / \partial \rho^2)_T \right]$$

$$C(\tau) \rho_c^2 = \lim_{\delta \rightarrow 0} \phi_{\delta\delta}^I(\delta, \tau)$$

$$^a \phi_\delta^I = \left[\frac{\partial \phi^I}{\partial \delta} \right]_\tau, \quad \phi_{\delta\delta}^I = \left[\frac{\partial^2 \phi^I}{\partial \delta^2} \right]_\tau, \quad \phi_\tau^I = \left[\frac{\partial \phi^I}{\partial \tau} \right]_\delta, \quad \phi_{\tau\tau}^I = \left[\frac{\partial^2 \phi^I}{\partial \tau^2} \right]_\delta, \quad \phi_{\delta\tau}^I = \left[\frac{\partial^2 \phi^I}{\partial \delta \partial \tau} \right]_\tau, \quad \phi_\tau^\circ = \left[\frac{\partial \phi^\circ}{\partial \tau} \right]_\delta, \quad \phi_{\tau\tau}^\circ = \left[\frac{\partial^2 \phi^\circ}{\partial \tau^2} \right]_\delta.$$

$$^b \frac{dp_\sigma}{dT} = \frac{\rho'' \cdot \rho'}{\rho'' - \rho'} R \left[\ln \left(\frac{\rho''}{\rho'} \right) + \phi^I(\tau, \delta'') - \phi^I(\tau, \delta') - \tau(\phi_\tau^I(\tau, \delta'') - \phi_\tau^I(\tau, \delta')) \right].$$

Razvoj formulacije

- del za idealni plin:

$$f^\circ(\rho, T) = h^\circ(T) - RT - Ts^\circ(\rho, T)$$

- $h = h(T)$, $s = s(T, \rho) \Rightarrow$

$$f^\circ(\rho, T) = \left(\int_{T_0}^T c_p^\circ dT + h_0^\circ \right) - RT - T \left[\int_{T_0}^T \frac{c_p^\circ - R}{T} dT - R \ln \left(\frac{\rho}{\rho_0^\circ} \right) + s_0^\circ \right]$$

- c_p nam pove Planck-Einsteinova funkcija z eksperimentalno določenimi koeficienti:

$$\frac{c_p^\circ}{R} = 1 + n_3^\circ + \sum_{i=4}^8 n_i^\circ \frac{(\gamma_i^\circ \tau)^2 e^{-\gamma_i^\circ \tau}}{[1 - e^{-\gamma_i^\circ \tau}]^2}$$

Razvoj formulacije

- residualni del: minimiziramo funkcijo

$$\chi^2 = \sum_{j=1}^J \chi_j^2 = \sum_{j=1}^J \sum_{m=1}^{M_j} [[z_{\text{exp}} - z_{\text{calc}}(x_{\text{exp}}, y_{\text{exp}}, \bar{n})]^2]_{j,m} \cdot \sigma_{\text{tot},m}$$

J različnih količin z_j (npr. pritisk, hitrost zvoka, ...); M_j število eksperimentalnih vrednosti, uporabljenih za j -to količino.; x in y neodvisni spremenljivki, ki opredeljujeta vsako meritev – po navadi temperatura in tlak ali gostota

- obtežitev:

$$\sigma_{\text{tot}}^2 = \sigma_{\text{exp}}^2 / f_{\text{wt}}^2 ;$$

$$\sigma_{\text{exp}}^2 = \left[\frac{\partial \Delta z}{\partial x} \right]_{y,z}^2 \sigma_x^2 + \left[\frac{\partial \Delta z}{\partial y} \right]_{x,z}^2 \sigma_y^2 + \left[\frac{\partial \Delta z}{\partial z} \right]_{x,y}^2 \sigma_z^2$$

TABLE 5.1. Contribution of the several linear, nonlinear, and linearized data to the weighted sum of squares for the fitting and optimization

j	Type of data	Weighted sum of squares
Linear data		
1	$p(\rho, T)$	$\chi_1^2 = \sum_{m=1}^M \left[\frac{p - \rho RT}{\rho^2 RT} - \rho_c^{-1} \phi_\delta^r \right]_m^2 \cdot \sigma_m^{-2}$
2	$c_v(\rho, T)$	$\chi_2^2 = \sum_{m=1}^M \left[\frac{c_v}{R} + \tau^2 (\phi_{\tau\tau}^o + \phi_{\tau\tau}^r) \right]_m^2 \cdot \sigma_m^{-2}$
3	$B(T)$	$\chi_3^2 = \sum_{m=1}^M \left[B \cdot \rho_c - \lim_{\rho \rightarrow 0} \phi_\delta^r \right]_m^2 \cdot \sigma_m^{-2}$
Nonlinear data		
4	$w(p, T)$	$\chi_4^2 = \sum_{m=1}^M \left[\frac{w^2}{RT} - 1 - 2\delta\phi_\delta^r - \delta^2\phi_{\delta\delta}^r + \frac{(1 + \delta\phi_\delta^r - \delta\tau\phi_{\delta\tau}^r)^2}{\tau^2(\phi_{\tau\tau}^o + \phi_{\tau\tau}^r)} \right]_m^2 \cdot \sigma_m^{-2}$
5	$c_p(p, T)$	$\chi_5^2 = \sum_{m=1}^M \left[\frac{c_p}{R} + \tau^2(\phi_{\tau\tau}^o + \phi_{\tau\tau}^r) - \frac{(1 + \delta\phi_\delta^r - \delta\tau\phi_{\delta\tau}^r)^2}{1 + 2\delta\phi_\delta^r + \delta^2\phi_{\delta\delta}^r} \right]_m^2 \cdot \sigma_m^{-2}$
6	$h_2(p_2, T_2) - h_1(p_1, T_1)$	$\chi_6^2 = \sum_{m=1}^M \left[\frac{h_2}{RT_2} - \frac{h_1}{RT_1} - [\tau(\phi_\tau^o - \phi_\tau^r) + \delta\phi_\delta^r]_2 \right. \\ \left. + [\tau(\phi_\tau^o - \phi_\tau^r) + \delta\phi_\delta^r]_1 \right]_m^2 \cdot \sigma_m^{-2}$

7	$\mu(p, T)$	$\chi_7^2 = \sum_{m=1}^M \left[\mu R \rho + \frac{(\delta \phi_\delta^r + \delta^2 \phi_{\delta\delta}^r + \delta \tau \phi_{\delta\tau}^r)}{(1 + \delta \phi_\delta^r - \delta \tau \phi_{\delta\tau}^r)^2 - \tau^2 (\phi_{\tau\tau}^o + \phi_{\tau\tau}^r)(1 + 2 \delta \phi_\delta^r + \delta^2 \phi_{\delta\delta}^r)} \right]_m^2 \cdot \sigma_m^{-2}$
8	$\delta_T(p, T)$	$\chi_8^2 = \sum_{m=1}^M \left[\delta_T \rho - 1 + \frac{1 + \delta \phi_\delta^r - \delta \tau \phi_{\delta\tau}^r}{1 + 2 \delta \phi_\delta^r + \delta^2 \phi_{\delta\delta}^r} \right]_m^2 \cdot \sigma_m^{-2}$
9	$p_\sigma(T)$	$\chi_9^2 = \sum_{m=1}^M \left[\frac{p_{\sigma,m} - p_\sigma}{RT_c \rho_c} \right]_m^2 \cdot \sigma_m^{-2}$
10	$\rho'(T)$	$\chi_{10}^2 = \sum_{m=1}^M \left[\frac{\rho'_m - \rho'}{\rho_c} \right]_m^2 \cdot \sigma_m^{-2}$
11	$\rho''(T)$	$\chi_{11}^2 = \sum_{m=1}^M \left[\frac{\rho''_m - \rho''}{\rho_c} \right]_m^2 \cdot \sigma_m^{-2}$
12	$u'_2(T_2) - u'_1(T_1)$	$\chi_{12}^2 = \sum_{m=1}^M \left[\frac{u'_2}{RT_2} - \frac{u'_1}{RT_1} - [\tau(\phi_\tau^o + \phi_\tau^r)]_2 + [\tau(\phi_\tau^o + \phi_\tau^r)]_1 \right]_m^2 \cdot \sigma_m^{-2}$
13	$u''(T) - u'(T)$	$\chi_{13}^2 = \sum_{m=1}^M \left[\frac{u'' - u'}{RT} - \tau \left[\ln \frac{\delta'}{\delta} + \phi_\tau^r(\delta', \tau) - \phi_\tau^r(\delta, \tau) \right] \right]_m^2 \cdot \sigma_m^{-2}$
Linearized data		
4*	$w(\rho^p, T)$	$\chi_{4*}^2 = \sum_{m=1}^M \left[\frac{w^2}{RT} - \gamma^p \cdot (1 + 2 \delta \phi_\delta^r + \delta^2 \phi_{\delta\delta}^r) \right]_m^2 \cdot \sigma_m^{-2}$
5*	$c_p(\rho^p, T)$	$\chi_{5*}^2 = \sum_{m=1}^M \left[\frac{c_p}{R} + \tau^2 (\phi_{\tau\tau}^o + \phi_{\tau\tau}^r) - \epsilon^p \right]_m^2 \cdot \sigma_m^{-2}$
6*	$h_2(\rho_2^p, T_2) - h_1(\rho_1^p, T_1)$	$\chi_{6*}^2 = \sum_{m=1}^M \left[\frac{h_2}{RT_2} - \frac{h_1}{RT_1} - [\tau(\phi_\tau^o - \phi_\tau^r) + \delta \phi_\delta^r]_2 + [\tau(\phi_\tau^o - \phi_\tau^r) + \delta \phi_\delta^r]_1 \right]_m^2 \cdot \sigma_m^{-2}$

12*	$u'_2(\rho_2^{\text{p}}, T_2) - u'_1(\rho_1^{\text{p}}, T_1)$	$\chi_{12}^2 = \sum_{m=1}^M \left[\frac{u'_2}{RT_2} - \frac{u'_1}{RT_1} - [\tau(\phi_\tau^\circ + \phi_\tau^{\text{r}})]_2 + [\tau(\phi_\tau^\circ + \phi_\tau^{\text{r}})]_1 \right]_m^2 \cdot \sigma_m^{-2}$
13*	$u''(\rho^{\text{p}}, T) - u'(\rho^{\text{p}}, T)$	$\chi_{13}^2 = \sum_{m=1}^M \left[\frac{u'' - u'}{RT} - \tau \left[\ln \frac{\delta'}{\delta} + \phi_\tau^{\text{r}}(\delta'', \tau) - \phi_\tau^{\text{r}}(\delta', \tau) \right] \right]_m^2 \cdot \sigma_m^{-2}$
14	$p(\rho^{\text{p}}, T)$	$\chi_{14}^2 = \sum_{m=1}^M \left[\frac{p_\sigma - \rho' RT}{(\rho')^2 RT} - \rho_c^{-1} \phi_\delta^{\text{r}}(\delta', \tau) \right]_m^2 \cdot \sigma_m^{-2}$
15	$p(\rho^{\text{p}}, T)$	$\chi_{15}^2 = \sum_{m=1}^M \left[\frac{p_\sigma - \rho'' RT}{(\rho'')^2 RT} - \rho_c^{-1} \phi_\delta^{\text{r}}(\delta'', \tau) \right]_m^2 \cdot \sigma_m^{-2}$
16	Maxwell criterion	$\chi_{16}^2 = \sum_{m=1}^M \left[\frac{p_\sigma}{RT} \cdot \left[\frac{1}{\rho''} - \frac{1}{\rho'} \right] - \ln \left[\frac{\rho'}{\rho''} \right] - [\phi^{\text{r}}(\delta', \tau) - \phi^{\text{r}}(\delta'', \tau)] \right]_m^2 \cdot \sigma_m^{-2}$

Explanations

For the relations between the several properties and ϕ° and ϕ^{r} and their derivatives see Table 6.3.

For the weighted sum of squares the following abbreviations and definitions are used:

$$(1) \quad \phi_\delta^{\text{r}} = \left[\frac{\partial \phi^{\text{r}}}{\partial \delta} \right]_\tau, \quad \phi_{\delta\delta}^{\text{r}} = \left[\frac{\partial^2 \phi^{\text{r}}}{\partial \delta^2} \right]_\tau, \quad \phi_\tau^{\text{r}} = \left[\frac{\partial \phi^{\text{r}}}{\partial \tau} \right]_\delta, \quad \phi_{\tau\tau}^{\text{r}} = \left[\frac{\partial^2 \phi^{\text{r}}}{\partial \tau^2} \right]_\delta, \quad \phi_{\delta\tau}^{\text{r}} = \left[\frac{\partial^2 \phi^{\text{r}}}{\partial \delta \partial \tau} \right]_\delta, \quad \phi_\tau^\circ = \left[\frac{\partial \phi^\circ}{\partial \tau} \right]_\delta, \quad \phi_{\tau\tau}^\circ = \left[\frac{\partial^2 \phi^\circ}{\partial \tau^2} \right]_\delta.$$

(2) The weight σ_m corresponds to the quantity σ_{tot} according to Eq. (5.9).

(3) The subscript p means precorrelated. The precorrelation factors γ^{p} and ϵ^{p} are defined by the relations:

$$\gamma^{\text{p}} = \frac{c_p(\rho^{\text{p}}, T)}{c_v(\rho^{\text{p}}, T)}$$

$$\epsilon^{\text{p}} = c_p - c_v = \left[\frac{(1 + \delta \phi_\delta^{\text{r}} - \delta \tau \phi_{\delta\tau}^{\text{r}})^2}{1 + 2 \delta \phi_\delta^{\text{r}} + \delta^2 \phi_{\delta\delta}^{\text{r}}} \right]_{\tau, \delta}$$

All precorrelated quantities are calculated from a preliminary equation of state.

Razvoj formulacije

- nimamo podatkov o strukturi residualnega dela
- banka členov
- s statistično-stohastičnimi metodami izberemo ustrezno kombinacijo
- optimizacija je rekurzivna – potrebujemo enačbo stanja (oz. ustrezen približek)

Razvoj formulacije

- banka členov, odvisnih od reducirane gostote in inverzne reducirane temperature
- členi 4 tipov:
- polinomi $\phi_i^r = n_i \delta^{d_i} \tau^{t_i}$
- polinomi in eksponenti $\phi_i^r = n_i \delta^{d_i} \tau^{t_i} e^{-\delta^{c_i}}$
- podobni Gaussu $\phi_i^r = n_i \delta^{d_i} \tau^{t_i} e^{-\alpha_i(\delta - \epsilon_i)^2 - \beta_i(\tau - \gamma_i)^2}$
- neanalitični $\phi_i^r = n_i \Delta^{b_i} \delta \psi,$

$$\Delta = \theta^2 + B_i [(\delta - 1)^2]^{a_i},$$

$$\theta = (1 - \tau) + A_i [(\delta - 1)^2]^{1/(2\beta_i)},$$

$$\psi = e^{-C_i(\delta - 1)^2 - D_i(\tau - 1)^2}.$$

Razvoj formulacije

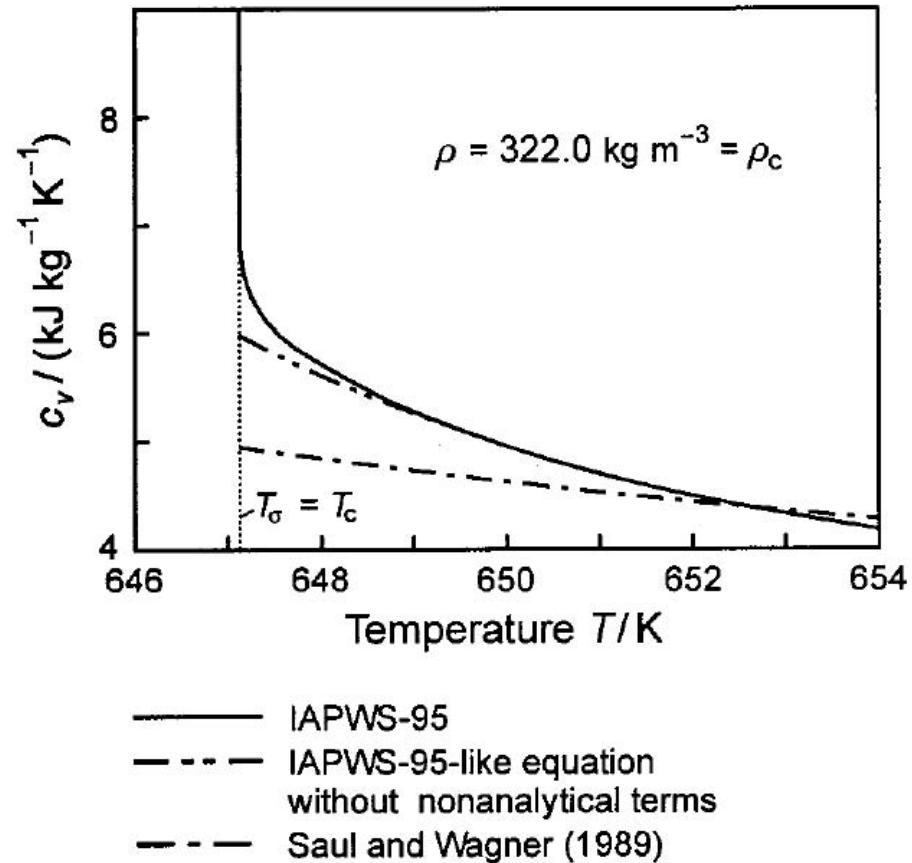
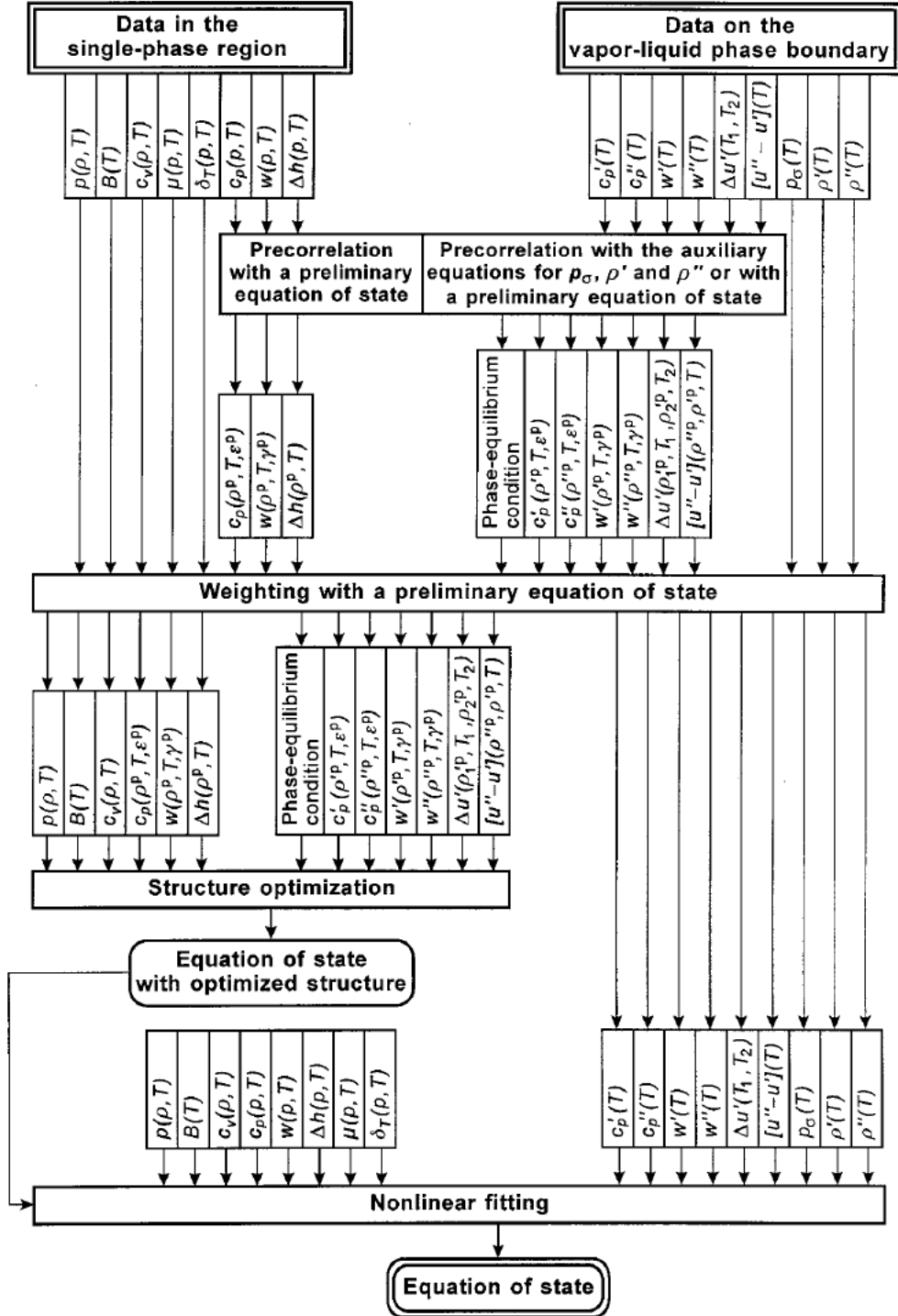


FIG. 6.5. Isochoric heat capacity in the critical region as a function of temperature (on the critical isochore of the single-phase region) calculated from IAPWS-95, Eq. (6.4), an IAPWS-95-like equation but without nonanalytical terms, and the equation of Saul and Wagner (1989).

Razvoj formulacije

- izbranih 745 členov => splošna oblika za kapljevinski del enačbe stanja:

$$\begin{aligned}
 \phi^r = & \sum_{i=1}^5 \sum_{j=-4}^8 n_{ij} \delta^i \tau^{j/8} + e^{-\delta} \sum_{i=1}^{15} \sum_{j=1}^{16} n_{ij} \delta^i \tau^j \\
 & + e^{-\delta^2} \sum_{i=1}^{12} \sum_{j=1}^{10} n_{ij} \delta^i \tau^j + e^{-\delta^3} \sum_{i=1}^5 \sum_{j=10}^{23} n_{ij} \delta^i \tau^j \\
 & + e^{-\delta^4} \sum_{i=1}^9 \sum_{j=10}^{20} n_{ij} \delta^{2i} \tau^j + e^{-\delta^6} \sum_{i=3}^7 \sum_{j=12}^{25} n_{ij} \delta^i \tau^{2j} \\
 & + \sum_{i=1}^{45} n_i \delta^{d_i} \tau^{t_i} e^{-\alpha_i(\delta - \epsilon_i)^2 - \beta_i(\tau - \gamma_i)^2} \\
 & + \sum_{i=1}^1 \sum_{j=1}^4 \sum_{k=1}^3 \sum_{l=1}^1 \sum_{m=1}^3 n_{ijklm} \Delta^{b_j} \delta \psi,
 \end{aligned}$$



Razvoj formulacije

- enačba stanja vode in vodne pare:

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

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

$$\phi^\circ = \ln \delta + n_1^\circ + n_2^\circ \tau + n_3^\circ \ln \tau + \sum_{i=4}^8 n_i^\circ \ln[1 - e^{-\gamma_i^\circ \tau}]$$

TABLE 6.1. Coefficients of Eq. (6.5)^a

i	n_i°	γ_i°	i	n_i°	γ_i°
1	-8.320 446 482 01	...	5	0.973 15	3.537 342 22
2	6.683 210 526 8	...	6	1.279 50	7.740 737 08
3	3.006 32	...	7	0.969 56	9.244 377 96
4	0.012 436	1.287 289 67	8	0.248 73	27.507 510 5

^aThe values of the coefficients n_3° to n_8° and γ_i° are also valid for Eq. (5.6).

$$\begin{aligned} \phi^r = & \sum_{i=1}^7 n_i \delta^{d_i} \tau^{t_i} + \sum_{i=8}^{51} n_i \delta^{d_i} \tau^{t_i} e^{-\delta^c} \\ & + \sum_{i=52}^{54} n_i \delta^{d_i} \tau^{t_i} e^{-\alpha_i(\delta - \epsilon_i)^2 - \beta_i(\tau - \gamma_i)^2} + \sum_{i=55}^{56} n_i \Delta^{b_i} \delta \psi \end{aligned}$$

i	c_i	d_i	t_i	n_i
1	...	1	-0.5	$0.125\ 335\ 479\ 355\ 23 \times 10^{-1}$
2	...	1	0.875	$0.789\ 576\ 347\ 228\ 28 \times 10^1$
3	...	1	1	$-0.878\ 032\ 033\ 035\ 61 \times 10^1$
4	...	2	0.5	0.318 025 093 454 18
5	...	2	0.75	-0.261 455 338 593 58
6	...	3	0.375	$-0.781\ 997\ 516\ 879\ 81 \times 10^{-2}$
7	...	4	1	$0.880\ 894\ 931\ 021\ 34 \times 10^{-2}$
8	1	1	4	-0.668 565 723 079 65
9	1	1	6	0.204 338 109 509 65
10	1	1	12	$-0.662\ 126\ 050\ 396\ 87 \times 10^{-4}$
11	1	2	1	-0.192 327 211 560 02
12	1	2	5	-0.257 090 430 034 38
13	1	3	4	0.160 748 684 862 51
14	1	4	2	$-0.400\ 928\ 289\ 258\ 07 \times 10^{-1}$
15	1	4	13	$0.393\ 434\ 226\ 032\ 54 \times 10^{-6}$
16	1	5	9	$-0.759\ 413\ 770\ 881\ 44 \times 10^{-5}$
17	1	7	3	$0.562\ 509\ 793\ 518\ 88 \times 10^{-3}$
18	1	9	4	$-0.156\ 086\ 522\ 571\ 35 \times 10^{-4}$
19	1	10	11	$0.115\ 379\ 964\ 229\ 51 \times 10^{-8}$
20	1	11	4	$0.365\ 821\ 651\ 442\ 04 \times 10^{-6}$
21	1	13	13	$-0.132\ 511\ 800\ 746\ 68 \times 10^{-11}$
22	1	15	1	$-0.626\ 395\ 869\ 124\ 54 \times 10^{-9}$
23	2	1	7	-0.107 936 009 089 32
24	2	2	1	$0.176\ 114\ 910\ 087\ 52 \times 10^{-1}$
25	2	2	9	0.221 322 951 675 46
26	2	2	10	-0.402 476 697 635 28
27	2	3	10	0.580 833 999 857 59
28	2	4	3	$0.499\ 691\ 469\ 908\ 06 \times 10^{-2}$



29	2	4	7	$-0.313\ 587\ 007\ 125\ 49 \times 10^{-1}$
30	2	4	10	-0.743 159 297 103 41
31	2	5	10	0.478 073 299 154 80
32	2	6	6	$0.205\ 279\ 408\ 959\ 48 \times 10^{-1}$
33	2	6	10	-0.136 364 351 103 43
34	2	7	10	$0.141\ 806\ 344\ 006\ 17 \times 10^{-1}$
35	2	9	1	$0.833\ 265\ 048\ 807\ 13 \times 10^{-2}$
36	2	9	2	$-0.290\ 523\ 360\ 095\ 85 \times 10^{-1}$
37	2	9	3	$0.386\ 150\ 855\ 742\ 06 \times 10^{-1}$
38	2	9	4	$-0.203\ 934\ 865\ 137\ 04 \times 10^{-1}$
39	2	9	8	$-0.165\ 540\ 500\ 637\ 34 \times 10^{-2}$
40	2	10	6	$0.199\ 555\ 719\ 795\ 41 \times 10^{-2}$
41	2	10	9	$0.158\ 703\ 083\ 241\ 57 \times 10^{-3}$
42	2	12	8	$-0.163\ 885\ 683\ 425\ 30 \times 10^{-4}$
43	3	3	16	$0.436\ 136\ 157\ 238\ 11 \times 10^{-1}$
44	3	4	22	$0.349\ 940\ 054\ 637\ 65 \times 10^{-1}$
45	3	4	23	$-0.767\ 881\ 978\ 446\ 21 \times 10^{-1}$
46	3	5	23	$0.224\ 462\ 773\ 320\ 06 \times 10^{-1}$
47	4	14	10	$-0.626\ 897\ 104\ 146\ 85 \times 10^{-4}$
48	6	3	50	$-0.557\ 111\ 185\ 656\ 45 \times 10^{-9}$
49	6	6	44	-0.199 057 183 544 08
50	6	6	46	0.317 774 973 307 38
51	6	6	50	-0.118 411 824 259 81

i	c_i	d_i	t_i	n_i	α_i	β_i	γ_i	ϵ_i
52	...	3	0	$-0.313\ 062\ 603\ 234\ 35 \times 10^2$	20	150	1.21	1
53	...	3	1	$0.315\ 461\ 402\ 377\ 81 \times 10^2$	20	150	1.21	1
54	...	3	4	$-0.252\ 131\ 543\ 416\ 95 \times 10^4$	20	250	1.25	1

i	a_i	b_i	B_i	n_i	C_i	D_i	A_i	β_i
55	3.5	0.85	0.2	-0.148 746 408 567 24	28	700	0.32	0.3
56	3.5	0.95	0.2	0.318 061 108 784 44	32	800	0.32	0.3

Veljavnost

- velja za celotno območje od tališča ledu (najnižja temperatura 251,156 K pri 209,9 MPa) do 1273 K in pritiska do 1000 MPa
- v območju stabilne kapljevine se da ekstrapolirati do 100 GPa in do 5000 K (vsaj za gostoto in entalpijo)
- ustrezno se ekstrapolira tudi v območje podhlajene in pregrete tekočine, ne pa podhlajene pare

Napake

- odvisne od količine

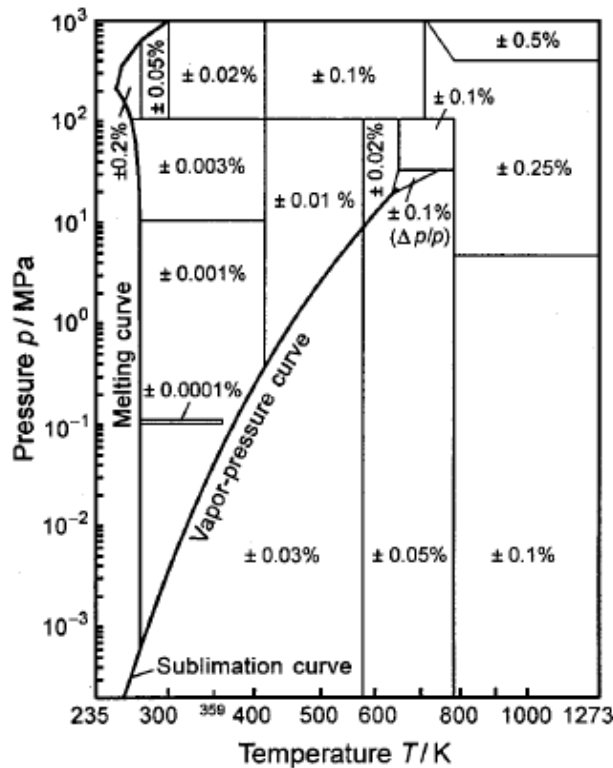


FIG. 6.1. Percentage uncertainties in density estimated for IAPWS-95, Eq. (6.4). In the enlarged critical region (triangle), the uncertainty is given as percentage uncertainty in pressure. This region is bordered by the two isochores 527 and 144 kg m⁻³ and by the 30 MPa isobar. The positions of the lines separating the uncertainty regions are approximate.

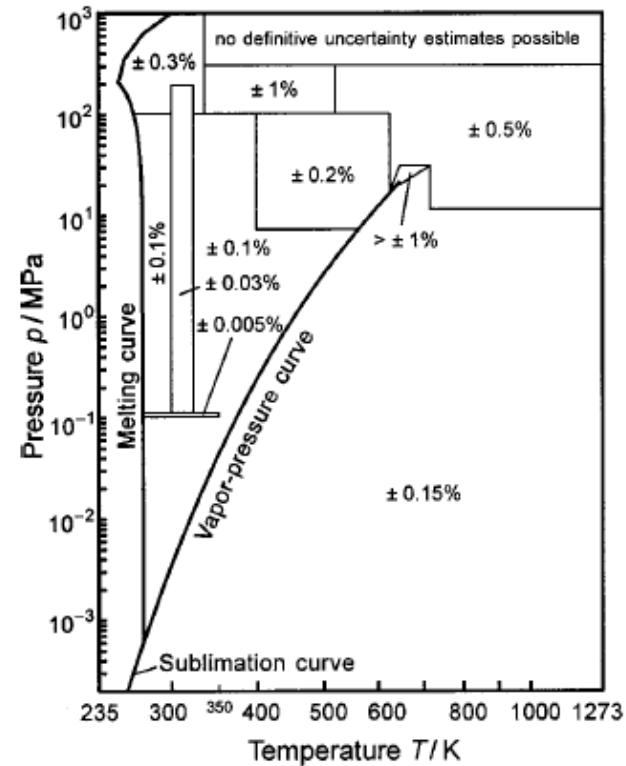


FIG. 6.2. Percentage of uncertainties in speed of sound estimated for IAPWS-95, Eq. (6.4). For the uncertainty in the triangle around the critical point, see the text; for the definition of this region, see Fig. 6.1. The positions of the lines separating the uncertainty regions are approximate.

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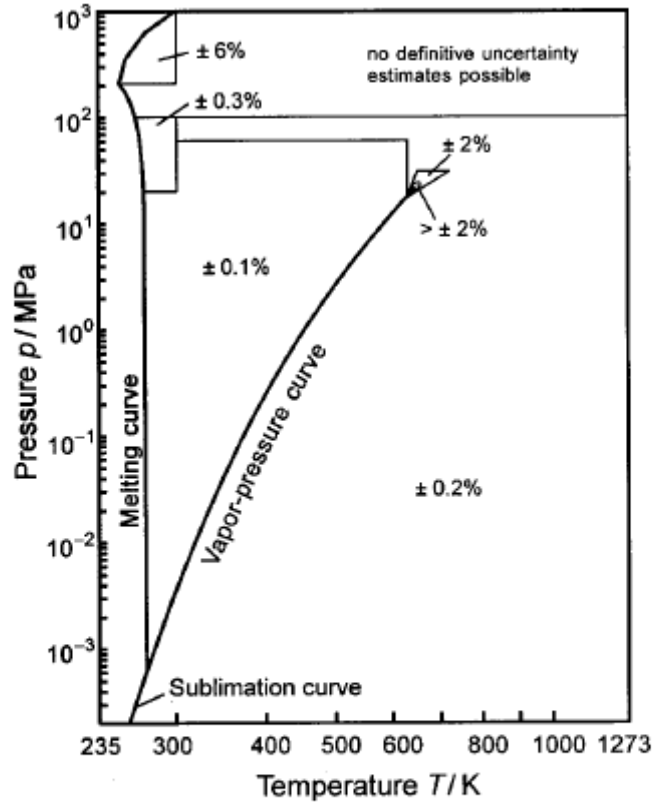


FIG. 6.3. Percentage uncertainties in specific isobaric heat capacity estimated for IAPWS-95, Eq. (6.4). For the uncertainty in the immediate vicinity of the critical point, see the text; for the definition of the triangle around the critical point, see Fig. 6.1. The positions of the lines separating the uncertainty regions are approximate.

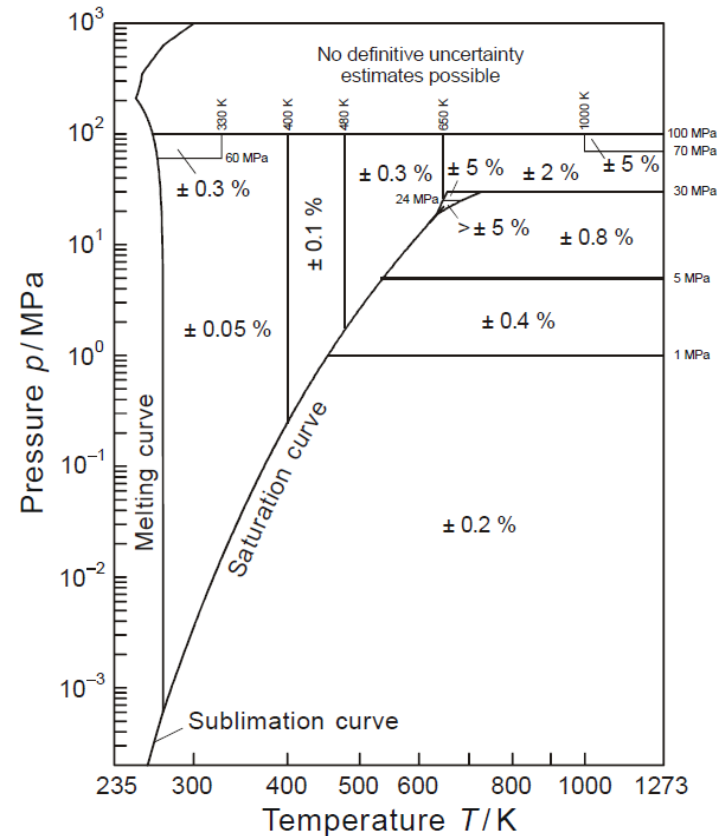


Figure 3 Percentage uncertainties $\Delta(\Delta h)/\Delta h$ in adiabatic enthalpy differences Δh estimated for IAPWS-95. The uncertainty values given relate to enthalpy differences along adiabatic reversible (isentropic) and adiabatic irreversible paths (steam turbines, boiler feed pumps, and hydroturbines). In the gas region, the uncertainty values correspond to enthalpy differences of $10 \leq \Delta h / (\text{kJ kg}^{-1}) \leq 1000$, whereas in the liquid region, the uncertainty values correspond to enthalpy differences of $1 \leq \Delta h / (\text{kJ kg}^{-1}) \leq 10$. The positions of the lines separating the uncertainty regions, marked by the given values of temperature and pressure, are approximate. For the definition of the enlarged critical region, see Fig. 1.

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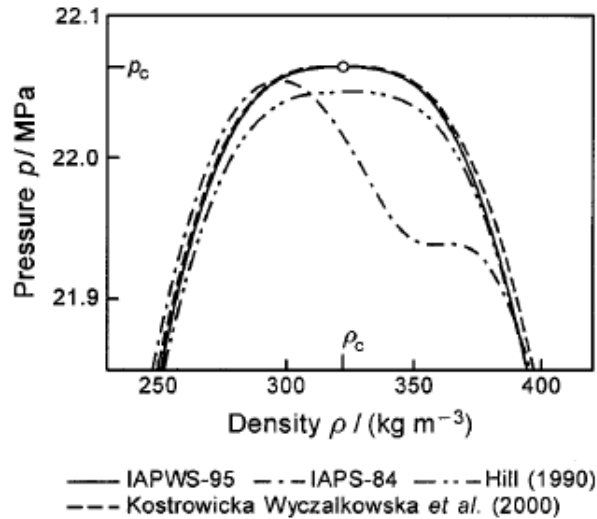


FIG. 7.4. The vapor–liquid phase boundary in the critical region of the p – ρ diagram calculated from IAPWS-95, Eq. (6.4), IAPS-84, the equation of Hill (1990), and the crossover equation of Kostrowicka Wyczalkowska et al. (2000).

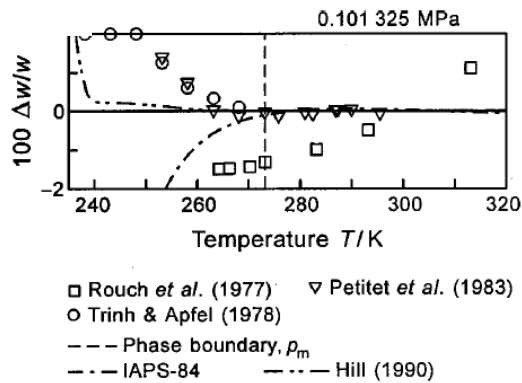


FIG. 7.5. Percentage deviations $100\Delta w/w = 100(w_{\text{exp}} - w_{\text{calc}})/w_{\text{exp}}$ between experimental data of the speed of sound w in the subcooled liquid along the isobar $p = 0.101\,325$ MPa and values calculated from IAPWS-95, Eq. (6.4). Values calculated from IAPS-84 and the equation of Hill (1990) are plotted for comparison.

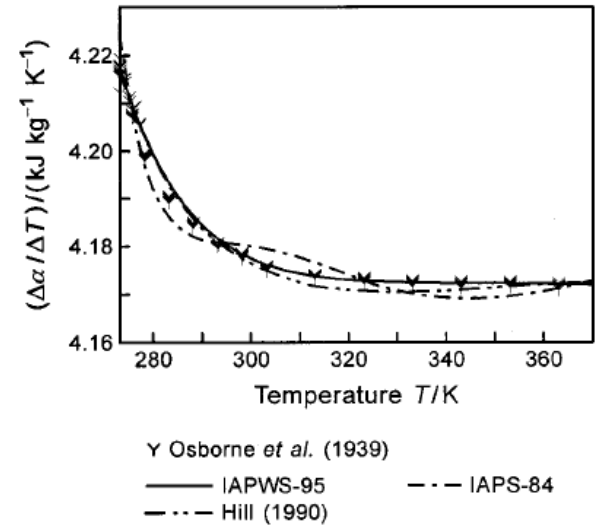


FIG. 7.8. The caloric difference quantity $\Delta\alpha$ related to ΔT (with $\Delta T = 1$ K) as a function of temperature calculated from IAPWS-95, Eq. (6.4), IAPS-84, and the equation of Hill (1990). The experimental data $\Delta\alpha/\Delta T$ of Osborne et al. (1939) are plotted for comparison.



Viri

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- če ni drugače označeno, so vse slike iz članka Wagnerja in Prußa