

PROPERTIES OF WATER AND STEAM

**Proceedings of the 11th International
Conference**

Edited by

M. Píchal

O. Šifner

Institute of Thermomechanics
Czechoslovak Academy of Sciences

● **HEMISPHERE PUBLISHING CORPORATION**

A member of the Taylor & Francis Group

New York Washington Philadelphia London

An Alternative Method for the Numerical Calculation of the Maxwell Criterion in Vapour Pressure Computations

H.-J. KRETZSCHMAR

Zentrum für Forschung und Technik

Institut für Energieversorgung Dresden des Kombiniertes Verbundnetze

Energie, Zeunerstrasse 83, Dresden 8027, DDR

T. ZSCHUNKE, J. KLINGER, and A. DITTMAN

Technische Universität Dresden

Mommsenstrasse 13, Dresden 8027, DDR

INTRODUCTION

The origin of the paper presented was the necessity of applying the MAXWELL rule for water substance in connection with the HGK-equation (IAPS 1984 Formulation [1-3]) in our function type computer program package PROLIB [4-7].

VAPOUR-LIQUID EQUILIBRIUM AND MAXWELL RULE

In equations of state, temperature and volume are mainly used as independent quantities. So does the IAPS formulation, too. For these physical formulated equations of state, the following relations are to be taken as the basis for calculating of the phase equilibrium:

	$f = f_{EOS}(T, v)$	$p = p_{EOS}(T, v)$
MAXWELL Criterion	$p_s = - \frac{f_{EOS}(T, v_v) - f_{EOS}(T, v_l)}{v_v - v_l} \equiv p_m$	$p_s = \frac{v_l \int_{v_l}^{v_v} \rho_{EOS}(T, v) dv_T}{v_v - v_l} \equiv p_m$ (1)
boiling water	$p_s = - \left[\frac{\partial f_{EOS}}{\partial v}(T, v_l) \right]_T \equiv p_l$	$p_s = p_{EOS}(T, v_l) \equiv p_l$ (2)
saturated vapour	$p_s = - \left[\frac{\partial f_{EOS}}{\partial v}(T, v_v) \right]_T \equiv p_v$	$p_s = p_{EOS}(T, v_v) \equiv p_v$ (3)

On the left the MAXWELL rule is written for the canonical equation of state, while the right hand side shows these relations as a transformation for a thermal equation of state. The index EoS means equation of state.

The vapour pressure can also be determined, by using the equation of state for both the boiling liquid and saturated vapour. Therefore equations (2) and (3) must also be valid. Equations (1), (2) and (3) can be used for the calculation of three unknown variables p_s , v_l , v_v .

DISCUSSION OF KNOWN METHODS AND CONCLUSIONS

In order to determine the saturation pressure p_s at a given

temperature T , the right or left equation system (1), (2), (3) is to be solved. All methods to calculate the MAXWELL rule departing from physical formulated equations of state are variations of the solution of this task.

The following algorithms are used in computer codes of different authors: For a given temperature T , at first the starting value for the saturation pressure p_s is formed. Then the corresponding volumes v_l and v_v are determined with the equation of state (relations (2) and (3)). By using equation (1), these volumes allow to calculate an improved saturation pressure p_s . It is used again in the next step to determine new saturation volumes. The iteration process is repeated until the saturation pressure cannot be improved considerably. In further variations of the above-mentioned method of substitution, the three equations are calculated in another sequence. Other authors apply onedimensional iteration methods (for instance NEWTON, REGULA FALSI or half of difference) to determine the pressure correction. It is also the case with the algorithm used by HAAR et al. [1].

From the preceding considerations, the following aspects can be outlined for the development of a new method:

1. By using the equation of state, the volumes are determined within the pressure iteration in all the methods mentioned. This is always an iterative procedure apart from the cubic equation of state. That means, two further iterations are interlocked in the external iteration cycle. Therefore a method which excludes these volume calculations should be looked for.
2. The functioning of the described methods is depending on the accuracy of the starting value for the saturation pressure. A very exact starting value is required, when the critical state is approached. In any case an initial pressure with three real volume solutions based on the equation of state is required. An algorithm independent of errors in the starting values would bring about considerable ease for practical use.

PRESENTATION OF THE NEW METHOD

In the developed algorithm [8-10], the improved saturation volumes of both phases are directly determined in each iteration step. So neither the laborious internal iterations nor the internal cubic solutions are not required. Next the equations for the volume corrections Δv_l and Δv_v in the $(k+1)$ iteration step

$$v_l^{(k+1)} = v_l^{(k)} + \Delta v_l^{(k+1)} \quad (4)$$

$$v_v^{(k+1)} = v_v^{(k)} + \Delta v_v^{(k+1)} \quad (5)$$

will be derived. The algorithm of these corrections is the main result of the work presented here. For this purpose, the thermal equation of state is replaced by separate approximations on and close to the boiling liquid curve and to the saturated vapour curve. Here the tangents to the given isotherme in the saturated volumes of the k -th step are being used:

saturated liquid:

$$\rho_{l\Delta}^{(k+1)}(T,v) = \rho_{EOS}(T,v_l^{(k)}) + \alpha_l^{(k)}(v - v_l^{(k)}) \quad \text{where} \quad \alpha_l^{(k)} = \left[\frac{\partial \rho_{EOS}}{\partial v}(T, v_l) \right]_T^{(k)} \quad (6)$$

saturated vapour:

$$\rho_{v\Delta}^{(k+1)}(T,v) = \rho_{EOS}(T,v_v^{(k)}) + \alpha_v^{(k)}(v - v_v^{(k)}) \quad \text{where} \quad \alpha_v^{(k)} = \left[\frac{\partial \rho_{EOS}}{\partial v}(T, v_v) \right]_T^{(k)} \quad (7)$$

Before we can incorporate these replacement functions into the transformed MAXWELL rule

$$\rho_{EOS}(T, v_l^{(k+1)}) = \rho_{EOS}(T, v_v^{(k+1)}) ; \quad \rho_{EOS}(T, v_l^{(k+1)}) = \frac{\int_{v_l^{(k+1)}}^{v_v^{(k+1)}} \rho_{EOS}(T, v) dv_T}{v_v^{(k+1)} - v_l^{(k+1)}} \quad (8)$$

the integral of the second equation has to be decomposed, as seen in the equation

$$\int_{v_l^{(k+1)}}^{v_v^{(k+1)}} \rho_{EOS}(T, v) dv_T = \int_{v_l^{(k+1)}}^{v_v^{(k)}} \rho_{EOS}(T, v) dv_T - \int_{v_l^{(k)}}^{v_l^{(k+1)}} \rho_{EOS}(T, v) dv_T + \int_{v_v^{(k)}}^{v_v^{(k+1)}} \rho_{EOS}(T, v) dv_T \quad (9)$$

The equation system

$$\begin{aligned} \rho_l^{(k)} + \alpha_l^{(k)} \cdot (v_l^{(k+1)} - v_l^{(k)}) &= \rho_v^{(k)} + \alpha_v^{(k)} \cdot (v_v^{(k+1)} - v_v^{(k)}) \\ [\rho_l^{(k)} + \alpha_l^{(k)} \cdot (v_l^{(k+1)} - v_l^{(k)})] \cdot (v_v^{(k+1)} - v_l^{(k+1)}) &= \rho_m^{(k)} \cdot (v_v^{(k)} - v_l^{(k)}) - \rho_l^{(k)} \cdot (v_l^{(k+1)} - v_l^{(k)}) - \\ &\quad - \frac{1}{2} \alpha_l^{(k)} \cdot (v_l^{(k+1)} - v_l^{(k)})^2 + \rho_v^{(k)} \cdot (v_v^{(k+1)} - v_v^{(k)}) + \frac{1}{2} \alpha_v^{(k)} \cdot (v_v^{(k+1)} - v_v^{(k)})^2 \end{aligned} \quad (10)$$

is obtained finally. By eliminating the saturation vapour volume and thus transforming system (10), one obtains the quadratic equation (11) for the correction of the boiling liquid volume with the coefficients A, B and C:

$$A \cdot (\Delta v_l^{(k+1)})^2 + B \cdot (\Delta v_l^{(k+1)}) + C = 0$$

where $A = \frac{1}{2} \cdot \alpha_l^{(k)} \cdot (\alpha_l^{(k)} - \alpha_v^{(k)})$ (11)

$$B = \alpha_l^{(k)} \cdot [\rho_l^{(k)} - \rho_v^{(k)} - \alpha_v^{(k)} \cdot (v_l^{(k)} - v_v^{(k)})]$$

$$C = \alpha_v^{(k)} \cdot (v_l^{(k)} - v_v^{(k)}) \cdot (\rho_m^{(k)} - \rho_l^{(k)}) + \frac{1}{2} (\rho_l^{(k)} - \rho_v^{(k)})^2$$

The final solution formula for the correction of the boiling liquid volume, which is to be used in the (k+1) iteration step, is represented by equation

$$\Delta v_l^{(k+1)} = -\frac{B}{2A} + \text{sign} \left\{ \frac{\alpha_l^{(k)} - \alpha_v^{(k)}}{\alpha_v^{(k)}} \right\} \cdot \sqrt{\frac{B^2}{4A^2} - \frac{C}{A}} \quad (12)$$

The correct sign of the solution results from the fact, that the difference of the vapour volume and liquid volume must be positive. Using relation (12), one also obtains the result for the correction of the saturation vapour volume

$$\Delta v_v^{(k+1)} = \frac{\rho_l^{(k)} - \rho_v^{(k)} + \alpha_l^{(k)} \cdot \Delta v_l^{(k+1)}}{\alpha_v^{(k)}} \quad (13)$$

The ascents of the auxiliary tangents are approximately calculated by using the known values from the k-th and (k-1) iteration step. Thus, equations

$$\alpha_l^{(k)} = \frac{\rho_l^{(k)} - \rho_l^{(k-1)}}{v_l^{(k)} - v_l^{(k-1)}} \quad \text{where } v_l^{(0)} = 0,999 \cdot v_l^{(1)}$$

$$\alpha_v^{(k)} = \frac{\rho_v^{(k)} - \rho_v^{(k-1)}}{v_v^{(k)} - v_v^{(k-1)}} \quad \text{where } v_v^{(0)} = 1,001 \cdot v_v^{(1)}$$

(14)

with: $v_l^{(1)}, v_v^{(1)}$ - starting values of iteration

are obtained. In the first iteration step, the written formal corrections have proved true. The volumes marked with pointer (1) represent the iteration starting values. Now we can test the new volumes by calculating the pressures p_m, p_l and p_v with the equations (1), (2) and (3). The MAXWELL rule is fulfilled, if the three pressures correspond to each other. In practice the iteration is interrupted, when the relative change of the middle pressure p_m is small enough between two iteration steps. In fig. 1 the algorithm is illustrated.

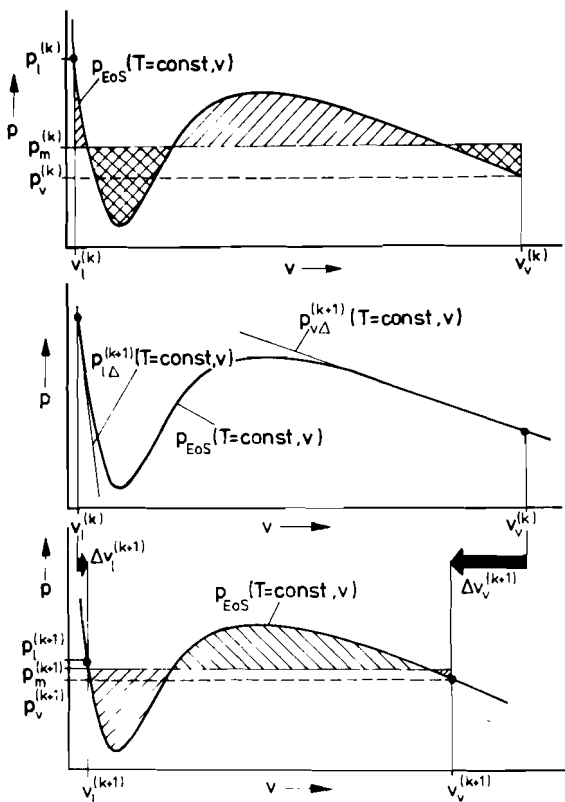


FIGURE 1. Graphical illustration of the new method

The upper p,v-diagram shows, that in the k-th iteration step the values of p_M , p_l and p_v , calculated on the saturated volumes v_l and v_v , are not corresponding. Now the isotherm T is substituted by the tangents $p_{l\Delta}$ and $p_{v\Delta}$ at the boiling liquid curve and at the saturated vapour curve, as shown in the middle diagram. In the lower diagram the resulting volume corrections Δv_l and Δv_v of the (k+1) iteration step have been marked. Now the values of the three pressures p_M , p_l and p_v based on the new volumes correspond more accurately to each other.

ITERATION STARTING VALUES

The ranges of the initial volumes $v_l^{(1)}$ and $v_v^{(1)}$, required for the new method, are shown in the p,v-diagram of fig. 2. In principle, these volumes must be situated in the ranges marked with stripes out of the spinodals of the equation of state. Starting values are required for the saturated volumes only. The range marked with points is required for the starting pressure needed in other methods. In order to apply the method to different substances or equations of state, simple laws are used for the determination of starting volumes. Such laws are the models of the ideal fluid state and of the ideal gas state (tab. 1). For the vapour pressure needed in the ideal gas equation, the AUGUST-equation can be used. These approximations guarantee the convergence of the method for the whole range of phase equilibrium. For cubic equations of state a special and simpler algorithm is presented in [8,9].

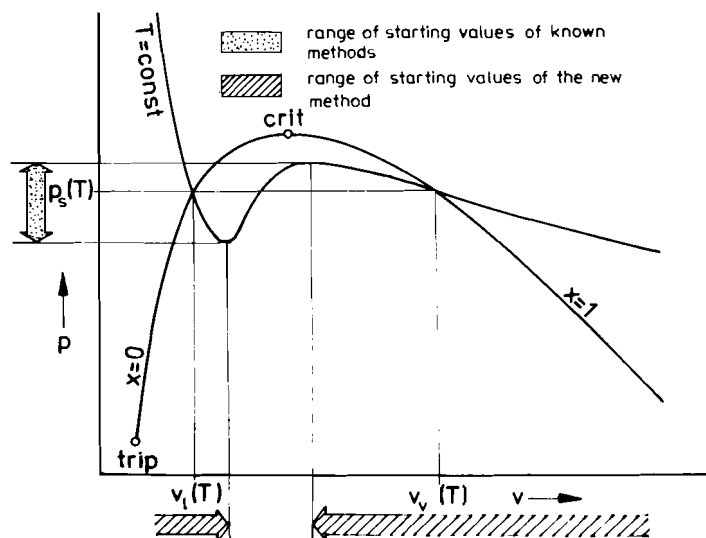


FIGURE 2. Ranges of starting values

TABLE 1. Iteration starting values

relation of starting values	model taken as a basis according to [4,5]	
$p_s^{(1)} = p_s(T)$	<p>AUGUST-equation</p> $\frac{1}{T} - \frac{1}{T_{crit}} = \frac{\ln p_s - \ln p_{crit}}{\ln p_s - \ln p_{trip}}$ <p>with $T_{crit} = 647,27 \text{ K}$ $T_{trip} = 273,16 \text{ K}$ $p_{crit} = 22,115 \text{ M Pa}$ $p_{trip} = 6,1 \cdot 10^4 \text{ M Pa}$ for water</p>	
$v_l^{(1)} = v_l(T)$	<p>ideal liquid</p> $v_l - v_{l,trip} = K(T - T_{trip})$ <p>with $K = 4,8 \cdot 10^{-7} \text{ m}^3/(\text{kg}\cdot\text{K})$ for water</p>	
$v_v^{(1)} = v_v(p_s, T)$	<p>ideal gas</p> $p v_v = R \cdot T$ $\left(\log \frac{p}{p_{crit}} + \log \frac{v_v}{v_{crit}} \right) = \log \frac{R \cdot T}{p_{crit} v_{crit}}$ <p>with $R = 0,462 \text{ kJ}/(\text{kg}\cdot\text{K})$ for water</p>	

APPLICATION TO THE EQUATION OF STATE IAPS 84

In order to test the efficiency of the developed method, direct comparison calculations were carried out with the numerical algorithm used by HAAR et al. [1]. We made a comparison calculating the saturation pressure by using the equation of state IAPS 84 for water. We found, that by using our method at least 30 % of calculation time had been saved. Approaching the triple temperature even 60 % of CPU time was saved.

Tab. 2 shows a numerical example calculated for the reduced temperature $\bar{T}=0.9$ and an iteration precision of 0.000 001. The different times when the reduced pressure \bar{p}_s achieved the prescribed iteration accuracy are of interest. In the algorithm used by HAAR et al. three steps are calculated in the \bar{p} -iteration. But in every step the reduced volumes \bar{v}_l and \bar{v}_v are to be iterated. Therefore 24 computations of the equation of state $\bar{p}=\bar{p}(\bar{T}, \bar{v})$ are carried out.

In the new algorithm seven iteration steps are required. But here in every step the equation of state is calculated two times for boiling liquid and saturation vapour only. So total 14 computations are necessary to achieve the same accuracy.

TABLE 2. Comparison of the calculation alternatives by means of a numerical example

Algorithm by HAAR et al. [1]			Algorithm of this work		
\bar{P}_s	\bar{V}_l	\bar{V}_v	$\bar{P}_s = \bar{P}_m$ [by equ. (1)]	\bar{V}_l	\bar{V}_v
0.442 156 19 ⁽¹⁾	0.362 336 64 ⁽¹⁾	8.736 974 5 ⁽¹⁾	0.525 377 18	0.363 255 55 ⁽¹⁾	9.058 147 4 ⁽¹⁾
	0.404 715 14	6.403 450 7	0.437 318 35	0.404 676 12	8.152 332 7
	0.435 715 91	5.954 970 5	0.437 358 58	0.436 298 88	7.337 099 4
	0.452 646 99	5.894 905 5	0.440 568 19	0.453 862 17	6.603 389 5
	0.458 050 25	5.889 038 7	0.442 182 01	0.458 676 03	5.943 050 5
	0.458 897 29	5.888 501 4	0.442 193 38	0.458 988 55	5.887 394 5
	0.458 982 65	5.888 452 5	<u>0.442 193 38</u>	0.458 989 78	5.887 548 7
	0.458 990 50	5.888 448 1			
	0.458 991 21	<u>5.888 447 7</u>			
	<u>0.458 991 28</u>				
0.442 193 42	0.458 991 28 ⁽¹⁾	5.888 447 7 ⁽¹⁾			
	0.458 989 93	5.887 629 7			
	0.458 989 81	5.887 555 2			
	<u>0.458 989 80</u>	5.887 548 5			
<u>0.442 193 38</u>		<u>5.887 547 8</u>			
24 computations of the equation of state $\bar{P}(\bar{T}, \bar{V})$			14 computations of the equation of state $\bar{P}(\bar{T}, \bar{V})$		
reduced properties: $\bar{P} = p/22.115 \text{ MPa}$; $\bar{T} = T/647.27 \text{ K}$; $\bar{V} = v/0.003147 \text{ m}^3/\text{kg}$					
(1) iteration starting value					

Because the computation of the equation of state needs the most CPU time we can estimate, that the new method requires 60 % of the calculation time. Indeed, it is the case in this example. The strong convergence of the new method especially noticeable at high demands of accuracy should be underlined. The last two values for \bar{P}_m demonstrate this fact. The application of the new method to cubic equations of state and an additional example can be found in [8,9].

CONCLUSIONS

The direct comparison with other methods showed a decrease in the calculation time on an average to 50 % for equations implicit in volume. For cubic equations of state we reached a decrease to 70 %. Both the internal iterations and the cubic solutions of the equation of state are not necessary. For this method only a single iteration cycle has to be calculated. The algorithm guarantees some convergence and numerical stability of the iteration up to reduced temperatures of 0.999 and with a modification even up to the critical point. This modification consists in a controlled slow-down of the convergence [8,9].

The method presented here is relatively independent of inaccurate starting values for the saturation volumes. An initial value for the saturation pressure is not needed.

REFERENCES

1. Haar, L., Gallagher, I. S., Kell, G. S., Steam Tables, Hemisphere, Washington, D.C., 1984
2. Grigull, U., NBS/NRC-Wasserdampfatafeln, Springer, Berlin, 1988
3. Dittmann, A., Klinger, J., Kretzschmar, H.-J., Neue international verbindliche Rahmentafeln und eine genaue Zustandsgleichung für die thermodynamischen Eigenschaften von Wasser und Wasserdampf, Energietechnik, vol. 38, no. 1, pp. 1-5, and no. 2, pp. 48-68, 1988
4. Kretzschmar, H.-J., Klinger, J., Zur stoffunabhängigen Berechnung von impliziten Zustandfunktionen - ein Beitrag zur effektiven Bereitstellung von Stoffdaten in thermodynamischen Prozeßberechnungen der Energieanlagen-technik, Energietechnik, vol. 34, no. 6, pp. 210-215, 1984
5. Kretzschmar, H.-J., Näherungen fuer thermodynamische Zustandfunktionen beliebiger Variabler - angewendet als Iterationsstartwertgleichungen, Wiss. Z. TU Dresden, vol. 33, no. 4, pp. 139-146, 1984
6. Dittmann, A., Klinger, J., Kretzschmar, H.-J., in The Properties of Steam, ed. V. V. Sychev and A. A. Aleksandrov, vol 1, pp. 284-293, Mir, Moscow, 1986
7. Kretzschmar, H.-J., Klinger, J., Schneider, S., Dittmann, A., Zur Bereitstellung thermophysikalischer Stoffdaten für die Modellierung energiewandelnder Prozesse auf Personalcomputer, Wiss. Ber. IH Zittau, vol. 709, no. VI/5, pp. 16-22, 1987
8. Zschunke, T., Kretzschmar, H.-J., Klinger, J., Ein alternatives Verfahren zur numerischen Realisierung des MAXWELL-Kriteriums in Phasengleichgewichtsberechnungen, Chemische Technik, vol. 40, no. 5, pp. 199-205, 1988
9. Kretzschmar, H.-J., Klinger, J., Zschunke, T., Ein alternatives Verfahren zur numerischen Realisierung des MAXWELL-Kriteriums in Phasengleichgewichtsberechnungen, Report and FORTRAN-progr., TU Dresden, WB Thermodynamik, 1986
10. Dittmann, A., Zschunke, T., Klinger, J., Kretzschmar, H.-J., An Alternative Method for the Numerical Realization of the MAXWELL-Criterion in Phase Equilibrium Calculations, 10th IUPAC Conf. on Chemical Thermodynamics, Prague, 1988