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Representation of Data on Thermodynamic Properties of Substances for Computerized Calculation of Technical Processes

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The paper discusses the experience gained in multipurpose application of the generalized system of the programmes for representing the thermodynamic properties of substances and their derivatives. The values of all the equations of state not explicitly formulated are calculated iteratively ensuring their precise adjustment of consistency, where the initial iteration values are independent of a certain substance and are thermodynamically based relations.

Especially, the results of using different equations of state for water in thermodynamic process calculations are dealt with.

1. INTRODUCTION

In algorithms to calculate thermodynamic processes, the retrievals of the properties of substances determine the extent of computing time. Therefore, for a long period of time, the authors have been seeking for an effective method of representation of the thermodynamic properties for such calculations. Further we shall discuss the experience gained in solving this problem, especially in applying the different statements describing the thermodynamic properties of water and water steam.

First of all, it should be especially taken into consideration that most of the equations of state occurring in the process algorithms because of their complexity cannot be introduced evidently. The authors think that in developing new equations of state, their applicability in the thermodynamic process calculations should be first taken into account.

2. DESCRIPTION OF THE PROGRAMME SET FOR CALCULATING PROPERTY VALUES OF SUBSTANCES

2.1. WORKING SUBSTANCES

At present, the state parameters of almost 30 working substances may be determined with the help of the actual programme set for calculating property values of substances (see Table 1). As the mathematical procedures are principally carried out independent of a substance, when the equation of state belonging to the respective substance is used, in addition for several variants for water, other substances relevant to process calculations in energetics are also offered.

Table 1. Equations of state for water in the material characteristics programme set of the Department of Thermodynamics

Substance	Equation of state	Source of literature
Water	The 1968 IFC formulation for scientific and general use	[1]
	The 1967 IFC formulation for industrial use	[2]
	Formulation by Rivkin and Kremenevskaya, 1977	[3]
	VDI steam tables, 1960	[4]
	Formulation by Haar and Gallagher, 1982	[5]

Other substances:

- 9 Refrigerants
 - Carbondioxide
 - Helium
 - Sodium
- 15 Ideal gases

Because of the complexity of the IFC formulations, the VDI formulation of 1960 and the reduced equations of Rivkin and Kremenevskaya (for a limited field of applications) have been introduced. First test calculations were made with the characteristic equations of Haar, Gallagher and Kell.

2.2. FUNCTIONS OF THE PROPERTIES OF SUBSTANCES

The wide range of thermodynamic equations of state, transport parameters and differential coefficients (cf. Table 2) in our programme

set arises from the requirements of different process calculations in the field of power engineering.

Table 2. Functions of the thermodynamic properties of substances in the programme set of the Department of Thermodynamics

$\rho_s = \rho_s(T_s)$	$\eta = \eta(\rho, T, v^*, x)$
$T_s = T_s(\rho_s)$	$\lambda = \lambda(\rho, T, v^*, x)$
$v = v(\rho, T, x)$	$\sigma_s = \sigma_s(T)$
$\rho, x = \rho, x(T, v)$	
$T, x = T, x(\rho, v)$	
$s = s(\rho, T, v^*, x)$	$c_p = c_p(\rho, T, v^*, x)$
$h = h(\rho, T, v^*, x)$	$a_s = a_s(\rho, T, v^*, x)$
$\rho, v, x = \rho, v, x(T, s)$	$\left(\frac{\partial \rho}{\partial T}\right)_v = \left(\frac{\partial \rho}{\partial T}\right)_v(\rho, T, v^*, x)$
$\rho, v, x = \rho, v, x(T, h)$	
$T, v, x = T, v, x(\rho, s)$	$\left(\frac{\partial T}{\partial v}\right)_\rho = \left(\frac{\partial T}{\partial v}\right)_\rho(\rho, T, (v^*, x)$
$T, v, x = T, v, x(\rho, h)$	
$\rho, T, x = \rho, T, x(v, s)$	$\left(\frac{\partial v}{\partial \rho}\right)_T = \left(\frac{\partial v}{\partial \rho}\right)_T(\rho, T, v^*, x)$
$\rho, T, x = \rho, T, x(s, h)$	
$\rho, T, x = \rho, T, x(v, u)$	
$\rho, T, v, x = \rho, T, v, x(s, h)$	$\left(\frac{\partial s}{\partial T}\right)_v = \left(\frac{\partial s}{\partial T}\right)_v(\rho, T, v^*, x)$

* There is no necessity of the input of v as a given quantity.

First of all, the inverse functions required for the given pairs of parameters ρ, T, v, s and h are calculated. From this, each additional parameter may be determined by a single or double call of subprograms arranged in series. The variable v included additionally in the straight-through calculations in this case regardless whether there is a technical $f(\rho, T)$ or physical $f(T, v)$ formulation, allows one to make an efficient calculation. The percentage of vapour included in the functional relations indicates the applicability of the subprograms in the fluid one-phase and two-phase region (water/vapour).

The user disposes of the set of programmes as "black box" available as subprograms developed for each of the functions pointed out in Table 2. He selects the desired function by an index as an additional parameter.

2.3. PROCEDURE OF CALCULATION

To prepare the functional dependences shown in Table 2, the following procedure is applied.

Proceeding from reduced specific equations of state $\chi, \sigma, \epsilon = \chi, \sigma, \epsilon(\beta, \theta, x)$ for technical formulation or $\beta, \sigma, \epsilon = \beta, \sigma, \epsilon(\theta, \chi)$ for physical formulation and from the function of the vapour pressure

$\beta_s = \beta_s(\theta_s)$ the thermodynamic functions and differential coefficients are calculated by iterations and by forming the numerical difference quotients (exceptions are λ , η and σ_s , for these separate equations are present). This procedure stood the test, in contrast to other methods [6]; the thermodynamic consistency of the calculated parameters is immediately directed by the selectable error limits in the iterations and the prescribed distances in the numerical differentiations. As for the required memory capacity, this procedure offers considerable economy, anyway. And if the sufficient initial parameters and effective methods of iteration and differentiation are applied, the computing time required is also justified [17].

The internal procedure of calculation may be illustrated by an example. As seen from Fig. 1, firstly, it is tested in the algorithms, whether there is a one-phase or two-phase region. In the example of the functions, $T, v, x = T, v, x(p, s)$ illustrated, proceeding from the pressure, the border curve entropies are determined and compared with the given one. Secondly, the actual calculations in the one-phase and two-phase regions are performed. In order to avoid ineffective interlocked iterations, the calculations are executed separately for technical and physical formulations of the specific state equations. That means that a way of calculation is adopted on the base of the parameters given in a specific instance (here β and σ) separately. As the algorithm in Fig. 1 is independent of a certain substance, all the operations are carried out by the parameters reduced to the critical state (following the IFC formulations).

2.4. INITIAL EQUATIONS OF ITERATION

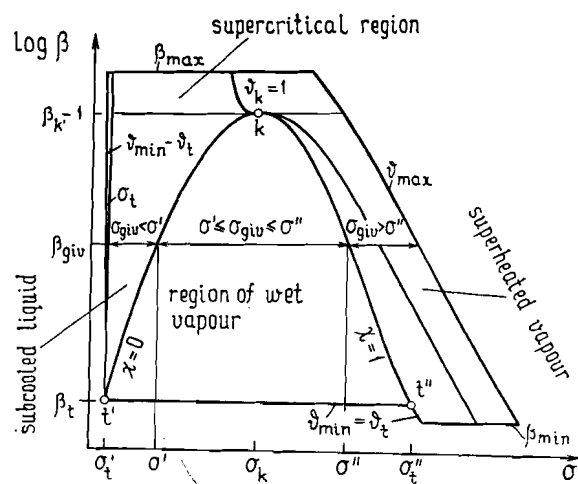
Due to the fact that all the functions whose variables coincide with the indicated parameters of the stored equations of state are determined iteratively, there arises a question concerning the kind of initial values the accuracy of which defines the efficiency of the iterations. In [8] for the functional dependences compiled in Table 3 approximations independent of materials were prepared. The solution described more closely in [9] and [10] is based on a modification of the Redlich-Kwong equation of state and on a linear approximation of the vapour pressure function in the $\ln \beta_s, 1/\theta_s$ plane.

3. EXPERIENCE GAINED IN APPLYING DIFFERENT CHARACTERISTIC EQUATIONS FOR WATER

3.1. THE ACCURACY

The known formulations of IFC 68, IFC 67, Rivkin and Kremenevskaya (R+K), VDI 60 and other reduced equations of state are discussed from the standpoint of their fitness to determine the thermodynamic processes in this and in the following sections.

Of course, the IFC 68 provides the most accurate values, especially close to the critical point, but for the calculations in power engineering



physical formulation
 $[\beta, \sigma, \varepsilon = \beta, \sigma, \varepsilon(\theta, \chi)]$

technical formulation
 $[\chi, \sigma, \varepsilon = \chi, \sigma, \varepsilon(\beta, \theta, x)]$

Test of phases

$\beta_{giv} < \beta_t$	— vapour
$\beta_{giv} \geq 1$	— supercritical
$\sigma_{giv} < \sigma'_t$	— liquid
$\sigma_{giv} > \sigma''_t$	— vapour
$\beta_{giv} < 1 \wedge \sigma_{giv} < \sigma'$	— liquid
$\wedge \sigma_{giv} > \sigma''$	— vapour
$\wedge \sigma'' \leq \sigma_{giv} \leq \sigma''$	— wet vapour
with $\theta_s = \theta_s(\beta_{giv})$	

- one-dimensional iteration of χ' and χ'' out of $\beta = \beta(\theta_s, \chi)$, compensation to β_{giv}
- $\sigma' = \sigma'(\theta_{it}, \chi')$ $\sigma'' = \sigma''(\theta_{it}, \chi'')$
- $\sigma', \sigma'' = \sigma', \sigma''(\beta_{giv}, \theta_s)$

One-phase region

- two-dimensional iteration of θ_{it} and χ_{it} out of $\beta = \beta(\theta, \chi)$, compensation to β_{giv} ; $\sigma = \sigma(\theta, \chi)$, compensation to σ_{giv}
- one-dimensional iteration of θ_{it} out of $\sigma = \sigma(\beta_{giv}, \theta)$, compensation to σ_{giv}
- $\chi_{it} = \chi(\beta_{giv}, \theta_{it})$

Two-phase region

$$\theta_{it} = \theta_s(\beta_{giv}) \quad x_{it} = \frac{\sigma_{giv} - \sigma'}{\sigma'' - \sigma'} \quad \chi_{it} = \chi + x_{it}(\chi'' - \chi')$$

with

- χ', χ'' and σ', σ'' out of the test of phases
- σ', σ'' out of the test of phases
- $\chi', \chi'' = \chi', \chi''(\beta_{giv}, \theta_{it})$

Fig. 1. Illustration of the iterate calculation of thermodynamic functions of state in case of $T, v, x = T, v, x(p, s)$

Table 3. Tabulation of initial equations required for the iterate calculation of thermodynamic functions of state

Thermodynamic functions of state	Iterate initial equations needed					
	One-phase region		Wet vapour region		Test of phases	
	PF	TF	PF	TF	PF	TF
$T_s = T_s(p_s)$	—	—	$\phi_s = \phi_s(\beta_s)$	$\phi_s = \phi_s(\beta_s)$	—	—
$v = v(p, T, x)$	$x = x(\beta, \phi)$	—	$x' = x'(\beta_s, \phi_s)$ $x'' = x''(\beta_s, \phi_s)$	—	—	—
$p, x = p, x(T, v)$ $T, x = T, x(p, v)$	$\phi = \phi(\beta, x)$	$\beta = \beta(\phi, x)$ $\phi = \phi(\beta, x)$	—	—	—	—
$p, v, x = p, v, x(T, s)$ $p, v, x = p, v, x(T, h)$	$x = x(\phi, \sigma)$ $x = x(\phi, \epsilon)$	$\beta = \beta(\phi, \sigma)$ $\beta = \beta(\phi, \epsilon)$	—	—	—	—
$p, T, x = p, T, x(v, s)$	$\phi = \phi(X, \sigma)$	$\phi = \phi(X, \sigma)$ $\beta = \beta(X, \sigma)$	$\phi_s = \phi_s(X, \sigma)$ $x'' = x''(X, \sigma)$	$\phi_s = \phi_s(X, \sigma)$	$\phi_s = \phi_s(X')$ $\phi_s = \phi_s(X'')$	$\phi_s = \phi_s(X')$ $\phi_s = \phi_s(X'')$
$p, T, x = p, T, x(v, h)$	$\phi = \phi(X, \epsilon)$	$\phi = \phi(X, \epsilon)$ $\beta = \beta(X, \epsilon)$	$\phi_s = \phi_s(X'' \epsilon)$ $x'' = x''(X, \epsilon)$	$\phi_s = \phi_s(X, \epsilon)$	$\phi_s = \phi_s(X')$ $\phi_s = \phi_s(X'')$	$\phi_s = \phi_s(X')$ $\phi_s = \phi_s(X'')$
$T, v, x = T, v, x(p, s)$	$\phi = \phi(\beta, \sigma)$	$\phi = \phi(\beta, \sigma)$	—	—	—	—
$T, v, x = T, v, x(p, h)$	$x = x(\beta, \sigma)$ $\phi = \phi(\beta, \epsilon)$ $x = x(\beta, \epsilon)$	$\phi = \phi(\beta, \epsilon)$	—	—	—	—
$p, T, v, x = p, T, v, x(s, h)$	$\phi = \phi(\sigma, \epsilon)$ $x = x(\sigma, \epsilon)$	$\phi = \phi(\sigma, \epsilon)$ $\beta = \beta(\sigma, \epsilon)$	$\phi_s = \phi_s(\sigma, \epsilon)$ $x'' = x''(\sigma'', \epsilon)$	$\phi_s = \phi_s(\sigma, \epsilon)$	$\phi_s = \phi_s(\sigma')$ $x'' = x''(\sigma')$ $x'' = x''(\sigma'')$	$\phi_s = \phi_s(\sigma')$ $\phi_s = \phi_s(\sigma'')$

$\beta = \frac{p}{p_k} \quad \phi = \frac{T}{T_k} \quad x$ } formulation
 v_k PF — physical
 v_k TF — technical

$\sigma = \frac{s \cdot T_k}{p_k \cdot v_k} \quad \epsilon = \frac{h}{p_k \cdot v_k}$
 s — saturation curve
 ' — boiling curve; '' — dew curve

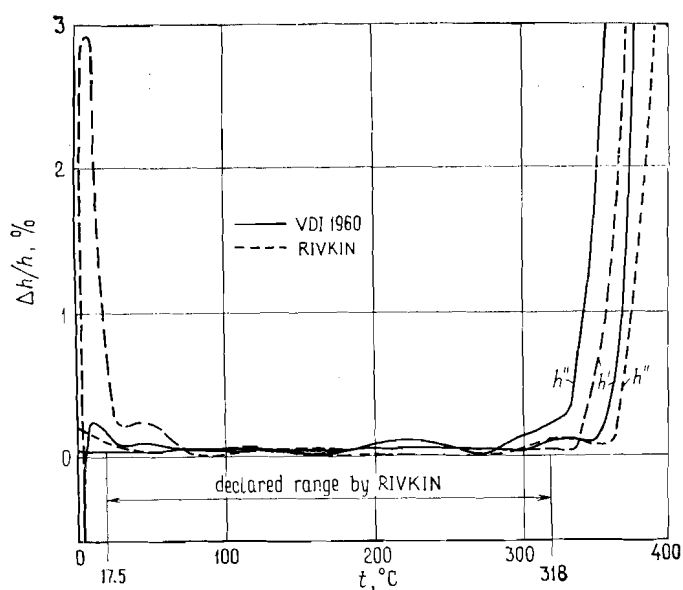


Fig. 2. Relative errors of equations of state of enthalpy by VDI 60 and RK on the dew line and boiling line in comparison with IFC 68

it is not so important. The inconsistency between the equations of state for the subregions on the border curves and a separate function of vapour pressure is disadvantageous. When neither p nor T are given parameters, the solution by means of the equations of Clausius and Clapeyron in iterating T from s and h in the two-phase region results in relative errors of 0.001-0.01%, regardless of a more precise iteration accuracy. This is also valid for IFC 67, VDI 60 and RK. In using the Maxwell's criterion to calculate the vapour pressure relation as it is provided by Haar, Gallagher and Kell, the error described does not occur. However, the proportional increase of the computing time is of such an extent that we consider that it is not well to apply in the long run the concept last named in thermodynamic calculations.

As to the accuracy in process calculations, IFC 68 and IFC 67 equations are equal, and the formulation HGK results in improving the accuracy at high pressures. If VDI 60 or the formulation RK is applied, the errors quickly increase beyond the range of validity mentioned. (Fig. 2 shows a comparison of the saturation and the dewing line. As the actual equations in using VDI 60 become very inaccurate, in the border curves they should be replaced by statements according to Tratz, Vesper, Mayinger, Schmidt.) In addition, greater deviations should be determined in the overheated vapour region.

3.2. THE REQUIREMENTS FOR MEMORY LOCATIONS

For the comparison, with respect to the process calculations it is insufficient to compare only the different equations of state. The differences are considerably levelled by the iterating subprograms independent of substances.

In Table 4, the differences for individual equations of state and for the total set of programmes are specified.

Table 4. Comparison of equations of state for water on their application in thermodynamic calculations of processes

	IFC 68	IFC 67	Rivkin	VD 160	Haar
1. Calculation time					
— equations of state	100%	84%	26%	49%	≈ 315%
— calculations of processes	100%	60%	15%	25%	≈ 400%
2. Storage capacity needed					
— equations of state	100%	90%	25%	30%	50%
— programme set	100%	98%	91%	93%	95%

3.3. THE COMPUTING TIME

The comparison of the periods of time required for computing the equations of state (Table 4) reflects the scope and complexity of different formulations and shows that among the formulations so far applied, the IFC 68 requires the longest period of computing time.

These differences become still more apparent in process calculations. Since in the IFC 68 the total superheated steam range is formulated from the physical point of view, that results in two-dimensional iteration cycles as compared with IFC 67, the period of computing time is considerably longer, though the complexity of the equations of state used in computations is practically the same. Due to more simple algorithms, the periods of computing time becomes considerably shorter for VDI 60 and RK, as compared with IFC 67.

The algorithm according to HGK is more comprehensive that results in a longer computing time. This arises, above all, from the required calculations twofold accurate. However, these statements are valid for the computer BESM 6.

3.4. THE APPLICABILITY FOR PROCESS CALCULATIONS

IFC 68. Being now the most accurate formulation, it is still not convenient for use. Due to many subregions, the problems of consistency arise at the borders. There are additional problems in the

two-phase region, as in the technically interesting area the border curves are differently formulated.

IFC 67. As known, this formulation is more suitable for computer-aided calculations, as the conventional superheated steam region is technically predetermined.

VDI 60. The continuous technical formulation is in its favour, but there are inaccuracies in the critical region which should not be tolerated.

RK. In the region described a sufficient accuracy is achieved. However, this formulation can only be applied to calculate steam expansion in turbines, as the maximum pressure in the two-phase region is insufficient to describe modern power station cycles.

Comparison. Enthalpy differences are mainly relevant in algorithms for stationary processing. The differences in accuracy of the individual formulations are principally so insignificant that they are inferior to the inaccuracies in modelling of machine elements. As for computational time (see Table 4) almost similar packet programs are fed into the computer memory, the GDR industry still uses the VDI 60 system to solve conventional tasks; IFC 68 is employed for commercial delivery calculations. But as for instationary enterprise calculations, thermodynamic differential coefficients are required. Satisfactory numerical results in these cases can be achieved only by applying IFC 68 and HGK.

The reduced equations to describe the process calculations of frequently occurring thermodynamic functions for definite state regions developed by Dohrendorf, Schwindt, Meyer-Pitroff, Vesper, Grigull, Magerfleisch and others were tested and used in experiments. However, it was impossible to insert them into the universally applicable programme set because of some difficulties when changing to the IFC 68 and IFC 67. Besides, the inconsistency in the domain of definition increases and additional memory location is required.

We welcome IAPS efforts lasting for years to obtain a uniform equation of state. Thus, the disadvantages described adhering to the IFC 68 and IFC 67 are omitted. In addition, less memory location is required. By the use of the Maxwell criterion of vapour pressure relation also their inconsistency is guaranteed. However, it should not be neglected that the computing time is considerably increased when each physically formulated equation of state for process calculations of open systems is applied, because they are oriented to pressure and temperature as independent variables and again to the Maxwell criterion. Therefore, it should be investigated whether this economic aspect allows one to steadily apply such equations in process calculations.

4. UTILIZATION AND APPLICATION

The programme set of thermodynamic properties of substances was drawn up to effectively represent characteristics parameters of substances for thermodynamic process calculations with the use of computers. Also at present, this utilization is still in the forefront. However, by the further development of the electronic data processing and the introduction

of the engineer's interactive operation, new practical demands should be taken into consideration.

The main results are the programme systems for process calculations [7] and [11], the water vapour chart computed directly according to IFC 68 [14] in contrast to [12] and [13] and a system to make optional state diagrams [15].

At present, a data file programme is being developed with access to the property values programme set. The increasing interest of the industry to the use of reduced equations of state, not only for water, induces us to start the investigation of this problem.

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