NEW EQUATIONS OF STATE FOR INDUSTRIAL APPLICATION

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Summary: *The overview article characterizes briefly the main types of equations of state, namely, the cubic, virial, Benedict Webb Rubin equation, its modifications and the multiparameter equations. Their forms, methods of their derivation, accuracy and their applicability are mentioned. In the next chapter are shortly discussed the optimization methods of the multiparameter equations of state. The semifinal chapter deals with the new engineering equations, and the last chapter indicates the databases for computation of the thermodynamic properties of fluids*

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1. EQUATION of STATE

The equation of state (EOS) is a functional relation between the dependent variable and two independent variables expressed in an analytical form. The relation is unambiguous, and continuous, but its derivatives need not to be continuous. Equation of state holds for the system in the equilibrium state, only. The equation of state is determined in an experimental way from measured thermodynamic properties, or on the base of molecular theory models and modern statistical-thermodynamic theories.

The importance of EOS consists in a condensed and easily mathematically treatable form, enabling analytical computation of another thermodynamic quantities. It serves for process and equipment design calculations, thermodynamic analysis of power cycles and their optimization. The equations of state for pure fluids are the starting point for computation of mixtures.

The motivation for the development of EOS is twofold: scientific for the understanding of behavior of fluids and condensed matter, and industrial need for accurate process and design calculations.

The level of equations of state depends on the quantity, accuracy, range and kind of experimental data, on the state of computation techniques, on the knowledge of mathematical and statistical methods, and the experience of the correlator.

Hereafter the six notable groups of equations of state, namely cubic, virial, Benedict-Webb-Rubin, modified BWR, multiparametr and new engineering/technical EOS are characterized and their application for industrial computations are shortly discussed.

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1.1 CUBIC EOS

are not the most appropriate models for representation of pure-fluid properties, their theoretical background is usually insufficiently rigorous. However, they are the most frequently used EOS, especially in petroleum and chemical industry, due to the best balance between accuracy, reliability, simplicity and speed of computation. They are successfully used to describe the state behavior of mixtures.

Their advantages and drawbacks are: They yield the density roots without iteration. They are not capable of accurate representing properties over a wide range of pressures and temperatures. Derived properties such as heat capacity and speed of sound have substantial errors. They can be used with good accuracy for V-L equilibrium calculations. Good results are attained as far as the range of interest is limited and the fit of the EOS has been optimized to data in this region. The region around the critical point is one where the cubic equations are inherently inaccurate.

The most important types of cubic equations are:

Van der Waals equation (1873) [1]. It is the first equation of state that was capable of expressing the continuity from gaseous to liquid state

$$p = RT /(V - b) - a/V^2$$

or rewritten in cubic form

$$V^3 - (b - RT / p)V^2 + (a / p)V - ab / p = 0.$$

A number of investigators modified the van der Waals equation to improve its accuracy.

Clausius equation (1881) [2], replaced the volume in the attractive term of the van der Waals equation by $(v + c)$, and thus created the three-parameter equation, a precursor of a modern cubic EOS

$$p = RT /(V - b) - a/(V + c)^2.$$

Several decades later, the concept of the temperature-dependent attractive parameter proved to be essential for the practical success of cubic equations for phase equilibrium calculations.

Redlich-Kwong equation (RK EOS) (1949) [3]

$$p = \frac{RT}{v - b} - \frac{a}{T^{1/2}v(v + b)},$$

parameter a and b were calculated from critical point conditions

$$a = \Omega_a R^2 T_c^{2.5} / p_c \text{ and } b = \Omega_b RT_c / p_c \quad \text{with} \quad \Omega_a = 0.42747 \text{ and } \Omega_b = 0.0867.$$

Soave-Redlich-Kwong equation (SRK-EOS) (1972) [4] introduced temperature dependence α in the a parameter in RK EOS, and let it be a function of the acentric factor of the fluid:

$$\alpha = [1 + (0.48 + 1.57\omega - 0.176\omega^2)(1 - T_r^{0.5})]^2.$$

This equation resulted in accurate vapor pressure for light hydrocarbons and an important tool for the prediction of V-L equilibria at moderate and high pressures for nonpolar fluids.

Peng-Robinson equation (PR EOS) (1976) [5]

$$p = \frac{RT}{v - b} - \frac{a_c \alpha}{v(v - b) + b(v - b)}$$

with $b = 0.0077796 \, RT_c/p_c$; $\quad a = a_c\alpha;$ $\quad a_c = 0.457235(RT_c)^2 / p_c$

$$\alpha = \left[1 + \left(0.37464 + 1.54226\omega - 0.26992\omega^2\right)\left(1 - T_r^{0.5}\right)\right]^2.$$

offered better liquid density prediction than the Soave equation using different volume dependence to give slightly improved liquid volumes, and changed the temperature dependence of α to give accurate vapor pressure prediction for higher hydrocarbons.

Presently, SRK and PR equations are the most frequently used cubic EOS in the petroleum and chemical industry.

Anderko (1990) [6] characterized the state-of-the-art of cubic equations as follows:

For pure components they have reached maturity and no substantial progress can be expected in this area. Reliable techniques have been established to represent vapor pressure of both polar and nonpolar or associating compounds. The representation of volumetric properties has been improved within the limits imposed by the cubic form. The only exception is the representation of properties of heavy hydrocarbons and ill-defined compounds, which is still an area of active research.

1.2 VIRIAL EQUATIONS of STATE

were firstly proposed as empirical equations, however, they have a rigorous theoretical foundation in the statistical thermodynamics. Basic thesis of virial EOS from the viewpoint of the classical and quantum mechanics summarized Mason and Spurling [7].

Virial equations occur in two forms, as the **infinite Taylor power series expansion in inverse volume** (Leiden form) about the ideal gas state in which each term is a correction to the sum of the preceding terms

$$z = \frac{pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \ldots\ldots$$

and as the **Taylor series expansion in pressure** (Berlin type)

$$z = 1 + B'(T)p + C'(T)p^2 + \ldots.$$

Its advantage is in using the well-measurable quantities p and T as independent variables. But a simple theoretical interpretation cannot be given to the coefficients in this equation.

The virial coefficients B, C, D, etc, from the statistical mechanics represent the simultaneous interaction between molecules, for pure fluids they are functions of temperature only. The 2nd virial coefficient is by far the most well known, the 3rd virial coefficient is known with less accuracy for a number of fluids, but the value of D and higher virial coefficient is not well established experimentally but theoretical evaluation for model systems is possible.

The truncated virial EOS has a limited number of terms/coefficients, depending on the extent of the pressure or on the volume range. The two- or three-term virial equations are used successfully for the description of the gaseous phase at low and moderate pressures.

Truncated virial equations of state are used in the form $p = p(v,T)$ or $v = v(p,T)$. The second form is used rarely because with the same number of coefficients as at the first one, it represents the behavior of gas less successfully.

Empirical virial equations of state can be written in the form

$$\frac{pv}{RT} - 1 = \rho \sum_{j=0}^{J} \sum_{i=0}^{I} b_{ij} \rho^i T^j \ .$$

They are always with limited number of terms and occur with a regular or irregular row of exponents. The particular coefficients are not identical with virial coefficients. The majority of equations due to practical reasons instead of ρ and T use reduced quantities $\tau = T_c/T$ and $\omega = \rho/\rho_c$. Virial equations of state represent the gas phase with relatively small number of terms very well. They are able to describe the liquid phase within the limits of experimental accuracy but they need higher number of terms or experience in the selection of suitable terms.

Empirical modifications of virial EOS are capable to provide reliable description of *pvT* properties of fluids and fluid mixtures in a wide range of parameters. In the neighborhood of the critical point their accuracy is lower like at all analytical equations.

Virial equations are used for correlation of the thermodynamic properties of various fluids. They usually treat varied sets of experimental data (thermal, caloric and acoustic), assigned with weights, over various ranges of parameters with or without constraints. The constants are determined by the application of generalized method of the least squares. The method of compiling a unified virial EOS and computation of tables of thermodynamic properties of technically important fluids has been described e.g. in the book on thermodynamic properties of nitrogen [8] prepared by the State Service for Standard Reference Data (GSSSD-USSR). The last mentioned equations belong already to the sort of multiparameter equations. Their accuracy is practically the same as that of modified BWR EOS of that time.

Computation of thermodynamic properties of fluids is carried out usually from a unified virial EOS in the form

$$z = 1 + \sum_{i=1}^{r} \sum_{j=0}^{s} b_{ij} \omega^i \tau^{-j}$$

with the aid of the ancillary equations for vapor pressure, density of saturated liquid and heat capacity in the ideal-gas state.

Conclusion: The truncated virial EOS with real virial coefficients is applicable only in gaseous phase. In the case that the coefficients are only fitting parameters it is applicable to all states. The virial EOS has been successfully used to describe single-phase regions of a number of technically important fluids.

1.3 BENEDICT-WEBB-RUBIN EQUATION of STATE and its MODIFICATIONS

Benedict-Webb-Rubin equation (1940) [9] with eight adjustable constants to each substance is applicable to vapor and liquid phases

$$p = \frac{RT}{V} + \frac{B_0 RT - A_0 - C_0/T^2}{V^2} + \frac{bRT - a}{V^3} + \frac{a\alpha}{V^6} + \frac{C}{T^2 V^2}\left(1 + \frac{\gamma}{V^2}\right)\exp\left(\frac{-\gamma}{V^2}\right).$$

The contribution of the exponential term is very large in the high-density range, in the liquid phase, and in the critical region. The original equation was intended for 12 hydrocarbons, but later the set of constants has been successfully expanded on other substances. Fifty-two fluids with individual sets of coefficients for the reduced form of the BWR EOS including non-hydrocarbons compiled Cooper and Goldfranck [10].

The BWR EOS describes *p-v-T-x* data, isothermal change of enthalpy and entropy with pressure, latent heats of vaporization and heat of mixing, fugacity and L-V equilibria. It facilitates interpolation and extrapolation, calculations involving integration and differentiation and provides concise summary of a large mass of data. The equation gives

reliable pressures (within 0.5 % of the true values) for densities up to 1.8 times the critical density.

Modified (or extended) BWR equations of state (M-BWR EOS)

To improve the overall accuracy of the BWR EOS, the number of constants has been increased by adding additional temperature-dependent and/or volume-dependent terms.

The M-BWR reads

$$\frac{p}{\rho RT} - 1 = \sum_{i=1}^{r}\sum_{j=0}^{s} a_{ij}\rho^i\tau^{-j} + e^{-\gamma}\sum_{l=0}^{L}\sum_{k=0}^{K} a_{kl}\rho^{ki}\tau^{-l}$$

where $\gamma = (\rho/\rho_c)^2$ and some of the a_{ij} and a_{kl} may be zero.

A wide range of parameters can be covered with a reasonable number of coefficients; particular modifications can be characterized by the number of coefficients and by maximum values of exponents at density and by the extent of exponents at the thermal functions.

Here are some developing types of M-BWR EOS in pressure explicit form:

Strobridge (1962) [11] introduced the 16-constant M-BWR EOS

$$p = RT\rho + \left(C_1 RT + C_2 + \frac{C_3}{T} + \frac{C_4}{T^2} + \frac{C_5}{T^4}\right)\rho^2 + (C_6 RT + C_7)\rho^3 + C_8 T\rho^4 + C_{15}\rho^6 +$$

$$\left[\left(\frac{C_9}{T^2} + \frac{C_{10}}{T^3} + \frac{C_{11}}{T^4}\right) + \left(\frac{C_{12}}{T^2} + \frac{C_{13}}{T^3} + \frac{C_{14}}{T^4}\right)\rho^2\right]\rho^3 \exp(-\gamma\rho^2),$$

This equation became the pattern for others.

Bender (1970) [12] proposed a 20-constant M-BWR EOS in the form

$$p = \rho TR + \left(n_1 + n_2/T + n_3/T^2 + n_4/T^3 + n_5/T^4\right)\rho + \left(n_6 + n_7/T + n_8/T^2\right)\rho^2$$

$$+ \left(n_9 + n_{10}/T\right)\rho^3 + \left(n_{11} + n_{12}/T\right)\rho^4 + \left(n_{13}/T\right)\rho^5 +$$

$$\left[n_{14}/T^3 + n_{15}/T^4 + n_{16}/T^5 + (n_{17}/T^3 + n_{18}/T^4 + n_{19}/T^5)\rho^2\right]\rho^2 \cdot \exp(-n_{20}\rho^2).$$

The coefficients n_1 through n_{20} were found by a linear least squares fit to the selected pvT data and conditions of phase equilibrium. The best fit of the whole pvT surface was found when the product $n_{20}\rho_c^2 = 1$. The equation represents accurately pvT behavior both in vapor and liquid range up to 500 bar and in the whole temperature range where experimental data are available. The coefficients of the Bender type EOS were determined for a number of technically important fluids.

Bender [12] and Wagner [13] independently introduced the rigorous procedure using the three conditions for two-phase equilibrium, namely the equality of temperature, pressure and values of Gibbs function for both phases at the bubble point and at the dew point (so called Maxwell-rule/criterion), what enabled to calculate the vapor pressure and the orthobaric densities directly from the EOS from the triple point up to critical point.

Consideration of phase equilibrium data during the development of the EOS was the precondition for the development of more accurate EOS.

Starling's M-BWR equation (1973) [14] frequently used in petroleum industry includes 11 constant

$$p = RT\rho + \left(B_0 RT - A_0 - \frac{C_0}{T^2} + \frac{D_0}{T_3} - \frac{E_0}{T^4} \right)\rho^2 + \left(bRT - a - \frac{d}{T} \right)\rho^3 + \alpha\left(a + \frac{d}{T} \right)\rho^6 +$$

$$\frac{c\rho^3}{T^2}\left(1 + \gamma\rho^2\right)\exp\left(-\gamma\rho^2\right).$$

Jacobsen and Stewart 32-constant M-BWR (1973) [15] has following form

$$p = RT\rho + \left(A_1 T + A_2 + \frac{A_3}{T} + \frac{A_4}{T^2} \right)\rho^2 + \left(A_6 T + A_7 + \frac{A_8}{T} + \frac{A_9}{T^2} \right)\rho^3 + \left(A_{10} + A_{11} + \frac{A_{12}}{T} \right)\rho^4 + A_{13}\rho^5 + c +$$

$$\frac{A_{16}}{T}\rho^7 + \left(\frac{A_{17}}{T} + \frac{A_{18}}{T^2} \right)\rho^8 + \frac{A_{19}}{T^2}\rho^9 + \left[\left(\frac{A_{20}}{T^2} + \frac{A_{21}}{T^3} \right)\rho^3 + \left(\frac{A_{22}}{T^2} + \frac{A_{23}}{T^4} \right)\rho^5 + \left(\frac{A_{24}}{T^2} + \frac{A_{25}}{T^3} \right)\rho^7 \right]\exp\left(-\rho_r^2\right) +$$

$$\left[\left(\frac{A_{26}}{T^2} + \frac{A_{27}}{T^4} \right)\rho^9 + \left(\frac{A_{28}}{T^2} + \frac{A_{29}}{T^3} \right)\rho^{11} + \left(\frac{A_{30}}{T^2} + \frac{A_{31}}{T^3} + \frac{A_{32}}{T^4} \right)\rho^{13} \right]\exp\left(-\rho_r^2\right).$$

This type of M-BWR is sufficiently accurate to satisfy advanced technical and scientific demands. This model has been adopted in the NBS/NIST for description of a number of fluids including refrigerants.

Equations in terms $p(T, \rho)$ and $z(T, \rho)$ need to be integrated to calculate caloric properties and supplemented by an independent formulation of ideal gas heat capacity $c_p^0(T)$. As far as phase equilibrium condition (Maxwell criterion) is not considered during the development of the EOS, ancillary equations for vapor pressure and saturated densities need to be used.

Equation in Helmholtz energy $a = a(T, \rho)$ enables calculation of all thermodynamic properties by combining derivatives of a with respect to T and ρ. In fact, the EOS in terms of the Helmholtz energy is always split into one part, which describes the ideal gas contribution a^0 (the equivalent to the formulation of c_p^0) and a residual part a^r (the equivalent to pressure explicit equation). The first EOS exclusively formulated in the Helmholtz energy was that by Keenan, Keyes, Hill and Moore [16] for water and steam followed with EOS by Pollak [17] and Haar & Gallagher [18, 19].

Determination of the coefficients in the equation is always done from the assembly of input data by least-squares techniques, that is, by minimizing the sums of squares of the difference between each datum and its value as calculated from the equation in such a way as to give numerical values to the unknown coefficients of the equation.

The accuracy of equations of state has been improved before all by increasing the number of terms without regard to the physical meaning and complexity of calculation. The most spread empirical virial equations and the modified BWR equations according the extent of the treated region and requested accuracy included from 20 to 100 coefficients, which were determined by the least square method.

The real breakthrough came when the flexibility of functional forms of pressure explicit and the Helmholtz energy equations has been combined with the use of optimization algorithms.

1.4 MULTIPARAMETER EQUATIONS of STATE (MP-EOS)

are accurate equations of state composed of pure polynomial terms and polynomial terms combined with exponential function in density with the inverse reduced temperature τ and reduced density δ as independent variables. They are a special sort of M-BWR EOS, which differs rather with processing of multiproperty data and application of sophisticated optimization methods used for their construction.

Setting up a MP-EOS for pure substances requires accurate experimental multiproperty data, with assigned weight, knowledge of linear and nonlinear fitting procedures, functional form of the EOS, defined bank of terms (with 300 to 1000 terms), mathematical algorithm based on objective statistical criteria for selection the best combination of 20 to 40 terms from the bank of terms and suitable regression analysis-optimization procedure.

For the construction of MP-EOS are considered following experimental data: vapor pressure, saturated liquid densities, ideal-gas heat capacity as function of temperature, *pvt* and speed of sound data in all regions of the thermodynamic surface. Saturated vapor density data, experimental or derived from other data using theoretical models, are essential if linearized phase-equilibrium data are used in linear algorithm during the development of an EOS. The accuracy of calculated energies and caloric properties can be improved if isochoric heat capacity (c_v-ρ-T), isobaric heat capacity (c_p-p-T), enthalpy differences (Δh-p-T), and Joule-Thompson coefficients are used. Several fixed points (critical- and triple point data), reference state enthalpy and entropy and molecular data, are used too.

MP-EOS

a) in the pressure explicit form

$$\frac{p}{\rho RT} = 1 + \sum_{I_{pol}} n_i \delta^{d_i} \tau^{t_i} + \sum_{I_{exp}} n_i \delta^{d_i} \tau^{t_i} \exp\left(-\delta^2\right),$$

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

For a complete description of the energy quantities (entropy, enthalpy, internal energy and heat capacity at various state points), like all pressure explicit EOS, needs to be combined with the ideal-gas heat capacity equation. Representation of properties is continuously integrated through the two-phase region to calculate properties in the liquid phase. This procedure is valid if the equation has been developed using procedures including the conditions for the two-phase equilibrium in the least square determination of the coefficients in the equation of state.

The pressure explicit equations combined with ideal-gas heat capacity are entirely equivalent to equation of state expressed in the Helmholtz energy. The accuracy of these formulations is usually 0.04 % for densities, 0.05 % for vapor pressure and 0.75 % for heat capacity.

b) in the Helmholtz energy

Fundamental equation of state contains calorimetric and reference state information, and thus the absolute values of specific properties may be calculated directly by differentiation without additional information. It gives a complete description of the thermodynamic properties. The formulation of the Helmholtz energy with independent variables T and v (or ρ), or their nondimensional equivalents τ and δ are the only fundamental relations suitable for description the whole fluid region.

The functional form for a fundamental EOS explicit in nondimensional Helmholtz energy: is usually split into one part describing the behavior of hypothetical ideal-gas at given values of T and ρ, and a second part which describes the residual behavior of the real fluid:

$$\alpha(\delta,\tau) = \frac{a(T,\rho)}{RT} = \alpha^0(\tau,\delta) + \alpha^r(\tau,\delta)$$

α^0 is the reduced ideal-gas contribution, α^r is the reduced real-fluid contribution. In general, equation for α^r still depends on an empirical representation of experimental data.

The common formulations for the residual Helmholtz energy is expressed by the relation

$$a^r(\tau,\delta) = \sum_{i=1}^{I_{Pol}} n_i \tau^{t_i} \delta^{d_i} + \sum_{i=I_{Pol}+1}^{I_{Pol}+I_{Exp}} n_i \tau^{t_i} \delta^{d_i} \exp\left(-\gamma_i \delta^{p_i}\right).$$

The density exponents d_i and p_i have to be positive integer values to make sure that a^r and all its derivatives vanish in the limit of zero density. For p_i values up to 8 have been used and higher values are common for d_i. Because the Helmholtz free energy cannot be measured directly, the information about it must be obtained from other thermodynamic properties accessible to measurement and related to the free energy by rigorous thermodynamic relations. Fitting an EOS to different thermodynamic property data is called a **multiproperty fit**. The aim of any optimization procedure is to minimize a sum of squares of a weighted form of the least square sum. The linear fitting procedure could be used only with experimental data, which linearly depend on the independent variables δ and τ. They are (p,ρ,T) values, differences of internal energy, isochoric heat capacity, virial coefficients and vapor-liquid phase equilibrium conditions. The non-linear experimental data, such as speed of sound, enthalpy, isobaric heat capacity, Joule-Thomson coefficient and vapor pressure can be used after the linearization of the non-linear data or by means of the non-linear optimization procedure.

To improve the **description of properties in the critical region** (the extended critical region is defined by limits $0.98 \leq T/T_c \leq 1.1$ and $0.7 \leq \rho/\rho_c \leq 1.3$ but with respect to temperature it is too large. At advanced equations of states the critical region is in the limits $0.998 \leq T/T_c \leq 1.01$ and $0.75 \leq \rho/\rho_c \leq 1.25$), so-called two-dimensional Gaussian bell shaped terms were introduced. Setzmann and Wagner [20] reformulated the Gaussian bell shaped terms by introducing one additional parameter. The modified Gaussian bell shaped term has the form

$$a_{GBS}^r = \sum n_i \tau^{t_i} \delta^{d_i} \exp\left(-\eta_i(\delta-\varepsilon_i)^2 - \beta(\tau-\gamma_i)^2\right)$$

where η, β, ε and γ are additional internal parameters. The modified Gaussian bell shaped term has been used also for nitrogen [21], CO_2 [22], water [23], argon [24] and ethylene [25].

Equation with Gaussian bell shaped terms are able to represent even the most accurate experimental data in the critical region within their experimental uncertainty, except for isochoric heat capacity and speed of sound very close to the critical point, within $|T-T_c|/T_c < \approx 0.002$ and $|\rho-\rho_c|/\rho_c < \approx 0.025$, where these properties cannot be described by an analytical formulation. To overcome this problem Span proposed in 1993 nonanalytical terms, which enabled to represent steep increase of the isochoric heat capacity and steep decrease of speed of sound when approaching the critical point.

Relations for the calculation of thermodynamic properties from the Helmholtz energy in the homogenous region, at the vapor-liquid equilibrium phases and in the two-phase region can be found, e.g., in [20, 26].

The reference MP-EOS are equations highly accurate in the technically and scientifically most important regions, V-L phase boundary and homogeneous fluid at temperatures up to 500 K and 30 MPa, in the critical region and are able of the reasonable extrapolation. Nevertheless, some of them do not satisfy the demands on description of the critical region and do not warrant reasonable extrapolation due to restricted data availability.

The empirical multiparameter equations have been the most important source of accurate thermodynamic property data for more than 30 years now. They are also the bases for printed property charts and tables, and with appropriate software (interactive programs) they are used for accurate computerized calculations. Dynamic Link Libraries in combination with Microsoft Excel® sheets are often used for direct process calculations.

2. OPTIMIZING PROCEDURES

In most cases, the virial and M-BWR equations have not been optimized with respect to their structure. Primarily the terms in these equations have been determined subjectively by experience or by trial and error.

Optimization of the structure of an empirical EOS means the development of effective functional expressions of the relationship between experimental data established by selection of combination of general functional expressions, the bank of terms, which yield the best description of the physical relationship with minimum number of terms.

Ahrendts and Baehr [27, 28] presented the theoretical foundation for minimization of the sum of squares, which include experimental values of any variable of state including their inaccuracies of measurement and relevant mathematical procedures. The procedures can be used in the regression regardless of whether the experimental data are explicit or implicit, linear or nonlinear functions of the EOS-parameters.

The stepwise regression analysis for the optimization of formulations describing the two-dimensional problems such as vapor pressure equations developed Wagner [29]. Its special version, de Reuck and Armstrong applied to the construction of the EOS for propylene [30]. Although the terms in a proposed "bank of terms" are empirical, only the statistically most important terms are selected. The stepwise multiple regression procedure is a refinement of the least squares method, which allows to eliminate the highly correlated terms from the functional form and provides for an optimal representation by the sequential selection of terms on the bases of the magnitude of the correlation coefficient of the fit to measured data. The computer program denoted SEEQ, developed de Reuck and is described in [31].

The regression analysis selects the optimum combination of terms using statistical criteria. This method is purely deterministic; it is fast and has been used internationally for years, especially for the establishment of vapor pressure equations and equations of state. The bank of terms did not contain more than 100 terms.

The evolutionary optimization method EOM, using some principles from biological evolution and a teachable random search strategy has been developed by Ewers and Wagner [32] to achieve a greater flexibility, which is necessary for the development of effective wide-range equations of state, with a large bank of terms (up to 1000 terms). In contrast to the stepwise regression analysis, which determines a single equation out of the bank of terms, the EOM optimizes simultaneously a population of formulations, each represented by a parameter vector identifying the corresponding terms out of the bank. As in the biological evolution, the

EOM requires a large population and many generations for the determination of the optimum. Therefore it requires a lot of computer time. Because of its complexity, others have not used this method. Another disadvantage is that the method is able to optimize the structure only for a predetermined number of terms in the final equation. Schmidt and Wagner [33] used this method for establishing a 32-constant EOS for oxygen [34], representing the residual Helmholtz free energy as a function of reduced temperature and density.

OPTIM algorithm developed Setzmann and Wagner [35]. This method combines the most effective elements of the EOM and the stepwise regression analysis into a new concept allowing the optimization of the functional structure for all problems accessible to the linear-least squares technique. The resulting EOS has at least the same quality as an equation determined by using the EOM, the structure and the length of the equation are optimized simultaneously and the program consumes much less computer time than the EOM. In their paper is discussed construction of the regression matrix, a new algorithm, constraints, convergence criterion, control parameters. Examples for establishing a vapor pressure equation and EOS explicit in the Helmholtz energy are given. The method was verified on the equation for methane [19].

NLREG nonlinear stepwise regression analysis and NLOPT optimization algorithm. The Setzmann-Wagner's algorithm OPTIM was restricted to linear optimization problems. However the implicit nonlinear relation to the Helmholtz energy and its derivatives could be used in linearized form. A cyclic process could eliminate the influence of the approximation implied by this linearization. But it does not work on highly accurate speed of sound data from spherical resonator measurements. Therefore, Tegeler et al. [36] used nonlinear optimization algorithm (NLOPT). The speeding up the nonlinear stepwise regression analysis (NLREG) and the nonlinear optimization algorithm (NLOPT) as well as the automated optimization algorithms, discussed in [26], are designed for use by experienced experts only.

3. NEW ENGINEERING EQUATIONS

In preceding chapters some EOS were presented, which has been used for industrial calculations in process and equipment design. A reasonable accuracy, a simpler mathematical structure and fixed functional form are desirable features for the engineering EOS. This can be reached under some degree of compromise.

Span, Collmann and Wagner [37] described developing of a new algorithm for the simultaneous optimization as a method to establish generalized functional forms for empirical EOS, which meet the typical technical requirements on the accuracy, short functional form, and proved it on a set of nonpolar fluids.

Span and Wagner applied this method to the development of new functional form for the multiparameter technical/engineering equations of state for nonpolar, weekly polar and polar fluids, and presented detailed results and comparison for 22 technically important fluids in a set of three articles [38]. The new **simultaneous optimization algorithm, SIMOPT**, considers data sets for different substances simultaneously. The chosen functional form yields in average the best results for a set of a certain group of fluids. Equations of state using the simultaneously optimized functional form can be fitted to data sets for different fluids of the same group without significant disadvantage. They are numerically very stable, and their substance-specific coefficients can be easily fitted to restricted data sets. Equations developed

by this manner yield thermal properties, derived caloric properties and speed of sound with reasonable accuracy for technical applications. The uncertainties of this new class of technical equations of states is summarized below:

Pressure range	Uncertainty in					
	$\rho(p,T)$	$w(p,T)$	$c_p(p,T)$	$p(T)$	$\rho'(T)$	$\rho''(T)$
$p \leq 30$ MPa	0.2 %	1-2 %	1-2 %	0.2 %	0.2 %	0.4 %
$p > 30$ MPa	0.5 %	2 %	2 %	-	-	-

In the first article they discuss the residual form of the reduced Helmholtz EOS, necessity of weighing experimental data (it is mandatory for EOS based on data for various properties, since deviations in various properties cannot be compared each other unless they are normalized in a suitable way), constrain to critical parameters, and accuracy versus numerical stability.

Based on selected data for 15 non- or weekly polar fluids (Ar, O_2, N_2, C_2H_4, i-C_4H_{10}, cyclohexane C_6H_{12}, SF_6, normal alkanes from methane through octane (CH_4, C_2H_6, C_3H_8, n-C_4H_{10}, n-C_5H_{12}, n-C_6H_{14}, n-C_7H_{16}, and n-C_8H_{18}), and the bank of 583 polynomial and exponential terms, the simultaneous optimization algorithm resulted in functional form with total of 12 polynomial and exponential terms for engineering (technical) EOS:

$$\alpha(\tau,\delta) = \alpha^0(\tau,\delta) + n_1\delta\tau^{0.250} \qquad + n_2\delta\tau^{1.125} \qquad + n_3\delta\tau^{1.500}$$
$$+ n_4\delta^2\tau^{1.375} \qquad + n_5\delta^3\tau^{0.250} \qquad + n_6\delta^7\tau^{0.875}$$
$$+ n_7\delta^2\tau^{0.625}e^{-\delta} \quad + n_8\delta^5\tau^{1.750}e^{-\delta} + n_9\delta\tau^{3.625}e^{-\delta^2}$$
$$+ n_{10}\delta^4\tau^{3.625}e^{-\delta^2} + n_{11}\delta^3\tau^{14.5}e^{-\delta^3} + n_{12}\delta^4\tau^{12.0}e^{-\delta^3}$$

The reduced Helmholtz energy is defined in the inverse reduced temperature, $\tau = T_c/T$, and the reduced density $\delta = \rho/\rho_c$. The substance-specific parameters T_c, ρ_c, R and n_i, which are needed to evaluate the technical equation of state for non- and weakly polar fluids, and the sources of the correlation used for the ideal-gas contribution, $\alpha^0(\tau,\delta)$ are given in [38] the second part.

Analogously, the technical EOS for 13 typical polar fluids (CO_2, NH_3, CFC-11, CFC-12. HCFC-22. HFC-32, CFC-113, HCFC-123, HFC-125, HFC-134a, HFC-143a, and HFC-152a) has been derived using selected data by the simultaneous optimization algorithm. The result was the functional form again with total of 12 polynomial and exponential terms but with different set of coefficients n_i and exponents. The substance-specific parameters T_c, ρ_c, R and n_i, which are needed to evaluate the technical equation of state for polar fluids, and the sources of the correlation used for the ideal-gas contribution, $\alpha^0(\tau,\delta)$ are given in [38] part three. Moreover, the second and third parts include statistical and graphical comparisons with experimental data.

Recently Lemon and Span [39] successfully applied the simultaneous optimization method to develop short fundamental EOS for 20 industrial fluids with different polarities and reduced availability of experimental data. At the University of Paderbon, Germany, a research program is underway to develop a new category of short form equations describing associated fluids.

Sun and Ely [40] developed as well a universal EOS suitable for engineering applications. Their **simultaneous optimization algorithm MULTIREG** is proposed to develop an

accurate and compact engineering EOS for broad range of fluids with one single functional form in the Helmholtz free energy equation of state. The algorithm is based on **simulated annealing** method, a stochastic algorithm, and operates on different fluids at the same time to achieve the best average results. Simulated annealing (SA) has been used in variety of applications in combinatorial optimization problems. Its potential advantage is that it can find global minima and it can be easily combined with parallel regression to develop a universal EOS. SA was first developed to optimize circuit design by Kirkpatrick et al. [41], and independently by Cerny [42]. Schubert K.B., and Ely J.F. [43] applied the SA method to develop reference EOS for refrigerants R-134a and R-123.

In the article beside others, is the flow diagram of the MULTIREG algorithm. The proposed 14-term EOS in the Helmholtz energy has a good accuracy for 13 selected non- and weekly polar fluids (CH_4, C_2H_6, C_3H_8, n-C_4H_{10}, n-C_5H_{12}, n-C_6H_{14},, C_2H_4, i-C_4H_{10}, N_2, cyclohexane C_6H_{12}, C_6H_6 and $C_7H_{8)}$, five polar fluids (CO_2, NH_3, HFC-32, HFC-125, HFC-134a), and four associating fluids (methanol CH_3OH, ethanol C_2H_5OH, propanol C_3H_7OH, and H_2O). The equation gives also good predictions for some associating fluids such as alcohols and water. Comparisons of proposed equations and those by Span and Wagner [38] are included as well as with the selected experimental data. The validity range of proposed equation is practically the same as at Span-Wagner's technical equations; details are in L. Sun Ph.D. Dissertation, Dept. Chem. Engineering, Colorado School of Mines, Golden, 2003.

In the next article, Sun and Ely [44] present a four-parameter corresponding states model (CSP) to generalize the universal technical EOS, based on available information on reference fluids as propane, n-octane, and water. This model is in the form of the Helmholtz free energy and takes four parameters as independent variables, namely, the critical density and temperature, acentric factor (ω) and polarity factor (β) as variables. They applied it to 22 fluids. This CSP model shows good accuracy and offers the flexibility to be extended to other fluids, compared to other generalized EOS such as Span and Wagner [38] for nonpolar fluids and those by Platzer and Maurer [45] and by Wilding and Rowley [46] for polar fluids.

In addition, they have successfully developed a correlation model for the polarity factor β by using quantitative structure activity relationship (QSAR) molecular descriptors. This model enabled to estimate the polarity factor from molecular level information of a given fluid and eliminated the need of fitting experimental data.

The polarity factor β reflects microscopic information about a molecule; correlation models should relate the values of β to certain types of molecular descriptors. They used the modern molecule simulation software Accelrys, Cerius^2 Ver.0.4, which enables to model a molecule at a quantum mechanical and statistical mechanical level. The selected molecular descriptors used in this work are spatial descriptors: molecular surface area (*A*), volume (*V*), radius of gyration (*G*) and the dipole moment (*D*). Descriptors are combined in power forms put in a bank of terms.

4. **Databases for Computation of Thermodynamic Properties of Fluids**

New formulations/equations of thermodynamic properties of fluids are published in specialized technical journals as Fluid Phase Equilibrium, Journal of Chemical Thermodynamics, Journal of Chemical Engineering Data, Journal of Thermophysics and Journal of Physical and Chemical Reference Data. It is necessary to tell, for its exploitation the user must oneself prepare the computer-program. Excepting formulations for water substance and ammonia-water substance prepared by the IAPWS, no published formulations

include the values to assist the user in computer-program verification. In the case that the user whishes to get without programming reliable values, it is better to buy suitable, attested databases or software, for instance:

NIST Standard Reference Database 12: Thermodynamic and Transport Properties of Pure Fluids including 32 fluids: NH_3, Ar, Kr, Ne, Xe, He, F_2, CO_2, CO, n-H_2, p-H_2, D_2, CH_4, C_2H_6, C_3H_6, n-C_4H_{10}, iso-C_4H_{10}, C_5H_{12}, C_6H_{14}, C_2H_4, N_2, O_2, NF_3, R-22, R-32, R-123, R-124, R-125, R-134a, R-143a, and R-152a (details on www.nist.gov/srd/nist12.htm), or

NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties Database (REFPROP) Version 7, which includes refrigerants HFCs: R-23, R-32, R-41, R-123, R-134a, R-143a, R-152a, R-227ea, R-236fa, R-245ca, and R-245fa; HCFCs: R-22, R-123, R-124, R-141b and R-142b; traditional CFCs: R-11, R-12, R-13, R-113, R-114, and R-115; fluorocarbons: R-14, R-116, R-218 and RC-318; natural refrigerants: NH_4, CO_2, C_3H_8, iso-C_4H_{10}, and C_3H_6; main air constituents: N_2, O_2, and Ar; light natural gas constituents: CH_4 up to iso-C_4H_{10}; H_2O and H_2O-NH_3, and 35 predefined mixtures from air, over R-401A through R-509a (more details are on www.nist.gov/srd/nist23.htm).

Extensive software packages have been developed at the Chair of Thermodynamics, Ruhr-University Bochum, Germany, based on highly accurate equations of state, which in many cases, have been considered as international references for the properties of the corresponding substances. They provide easily calculating thermodynamic properties for users in industry and research:

Software FLUIDICAL for the calculation of thermodynamic properties of 69 substances from the fundamental equations of state in the form of Helmholtz energy in three versions. See: http://www.ruhr-uni-bochum.de/thermo/software. The program enables to calculate more than 20 different thermodynamic properties. For a large number of substances the transport properties can be also calculated. As input values, every possible combination of the properties temperature, pressure, density, specific enthalpy and specific entropy can be used. Calculable properties are: *T, p, ρ, h, s, c_p, c_v, w, u, f, g, fugacity,* $(\partial p / \partial T)_\rho, (\partial p / \partial \rho)_T, (\partial \rho / \partial T)_p$, *$\mu$, δ_T, κ, B, C, η, v,* and *λ*. The **interactive program ThermoFluids** has been developed for users who occasionally need to calculate thermodynamic properties and who prefer to work with predefined Windows based program. This software package is available from Springer Verlag under ISBN: 3-540-21408-9.

Software for the scientific formulation of thermodynamic properties of ordinary water substance IAPWS-95,

Software for the industrial formulation IAPWS-IF97 for water and steam
(Wagner W., Overhoff U.: Extended IAPWS-IF97 Steam Tables, Springer-Verlag, Berlin, 2006. ISBN 3-540-21412-7).

Software for the reference equation of state GERG-2004 for natural gases and mixtures of natural-gas components [47] is based on the new reference equation of state for natural gases, comprising a number of thermodynamic properties of binary and multicomponet mixtures consisting of any of the 18 natural gas components (CH_4, N_2, CO_2, C_2H_4, C_3H_8, n-C_4H_{10}, iso- C_4H_{10}, n-C_5H_{12}, iso-C_5H_{12}, n-C_6H_{12}, n-C_7H_{16}, n-C_8H_{18}, H_2, O_2, CO, H_2O, He and Ar). The software enables calculation of thermodynamic properties in the gaseous, liquid and supercritical region, allows carrying out extensive VLE calculations, including flash, phase envelope, dew point and bubble point calculations, for any binary and multi-

component mixture. The equation of state GERG-2004 has been adopted by the Groupe Européen de Recherche Gazières (GERG) as the international reference equation of state for natural gases. Kunz, Wagner and Jaeschke reported at the 16th STP about a new extended version of previously developed GERG-2004 wide-range reference equation of state for natural gases. The extended equation covers 21 specific natural gas components. The range of validity covers temperatures from 90 to 450 K and pressures up to 35 MPa.

5. Acknowledgement

6. References

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