

Thermal equation of state BWR for water and water steam

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Abstract. The fundamental bases for the calculation of the thermodynamic properties of substances are the thermal equation of state and the dependence of some of the basic specific heat capacities on temperature. Any other thermodynamic properties of a substance can already be deduced from these relations. The aim of this paper is to design the simple thermal equation of state for water steam based on original BWR thermal equation of state, which describes the behavior of H₂O in the gaseous phase in region of usual pressures and temperatures with sufficient accuracy.

1 Introduction

Water and water vapor plays an important role in many phenomena occurring in nature. They are also the customary working substances in various industrial fields (for example in engineering industry, chemistry field, food industry, ...). Therefore, their properties are explored, measured and tabulated in detail. [1] Research of properties of water and water steam began to organize on an international level since 1929 to provide reliable and consistent data on their properties. In 1972 there was founded the International Association for the Properties of Water and Steam - IAPWS which deals with verification and interpolation of experimental data and with expressing of the thermodynamic and transport properties of water and steam. In 1995, there was accepted Pruß - Wagner equation as the international formulation of thermodynamic properties of water and steam for scientific purposes IAPWS-95. [2]. The equation is in the form of Helmholtz dimensionless function depending on temperature and reduced density. The equation is valid for the liquid and gas in a wide range of temperatures and pressures. It contains a large number of constants. International Standards properties of water and steam for example [3] are based on Scientific formulation IAPWS-95.

In many cases, there is necessary to use some "simple" equation for calculation of thermodynamic properties of water steam. "Simple" form of thermal equation of state will be applicable only on a limited range of temperatures and pressures, and it will have less accuracy. The aim of this paper is to present, if possible, a "simple" thermal equation of state and to define its application area, where agreed accuracy is maintained.

In 1940 Manson Benedict, G. B. Webb and L. C. Rubin constructed "quite simple" so called original

Benedict - Webb - Rubin thermal equation of state (hereinafter BWR) [4].

$$p = rT\rho + rT\rho^2 B_0 + rT\rho^3 b - A_0\rho^2 - a\rho^3 + a\alpha\rho^6 - \frac{\rho^2 C_0}{T^2} + \frac{c\rho^3}{T^2} (1 + \gamma\rho^2) e^{-\gamma\rho^2}. \quad (1)$$

Equation has some physical basics in the state behavior of gases. It contains an addition to the specific constant r still eight parameters: A_0 , B_0 , C_0 , a , b , c , α and γ that characterize the individual properties of the gas. They must be determined from experimental dates by regression. So, as well as other multi-parameter equations, BWR equation can be only used to description of properties of substances for which there is sufficient amount of experimental data in wide range of pressures and temperatures. This requirement is fulfilled for water and water steam undoubtedly.

In 1973 modification of the Benedict–Webb–Rubin equation of state by Starling was made [5]

$$p = rT\rho + rT\rho^2 B_0 + rT\rho^3 b - A_0\rho^2 - a\rho^3 + a\alpha\rho^6 + \frac{\alpha d\rho^6}{T} - \frac{\rho^2 C_0}{T^2} + \frac{\rho^2 D_0}{T^3} + \frac{\rho^2 E_0}{T^4} + \frac{c\rho^3}{T^2} (1 + \gamma\rho^2) e^{-\gamma\rho^2}. \quad (2)$$

Values of the various parameters for 15 substances can be found in work [5].

Another modification of the Benedict–Webb–Rubin equation of state was made in 1987 by Jacobsen and Stewart [6], it is noted as mBWR

$$p = \sum_{n=1}^9 a_n \rho^n + \sum_{n=10}^{15} a_n \rho^{2n-17} e^{-\gamma\rho^2}. \quad (3)$$

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The mBWR equation subsequently evolved into a 32 term version with numerical parameters determined by fitting the equation to empirical data for a reference fluid [7].

At first BWR equation was suggested for calculation of behavior of hydrocarbons. For these substances values obtained from BWR equation are very close to the experimental data [8]. For these substances BWR equation describes the behavior of materials in single phase areas (it is in superheated steam and in the super cooled liquid) very well. In heterogeneous areas (below the limit curve), as expected, there is a local maximum and a local minimum and the results are totally unrealistic. Parameters of BWR equation for hydrocarbons are presented for example in work [9] too.

We want to obtain a "simple" equation of state for water and water steam, so we try to use the original BWR equation.

In [10] there was shown the using of BWR thermal equation of state for H_2O . There was described derivation of the isochoric specific heat capacity and enthalpy from the thermal equation BWR. It has been shown that in the area where the error of p - v - T values obtained from BWR thermal state equations is small, the values of enthalpy, calculated from the relation derived using equation BWR are sufficiently precise too. The disadvantage was that the application area (the area with small errors) is very small.

The aim of this paper is to provide the values of constants of BWR equation $A_0, B_0, C_0, a, b, c, \alpha$ and γ so that this BWR equation describes with a "sufficient" accuracy the behavior of water steam, it means H_2O in gas phase in commonly used ranges of pressures and temperatures, and if possible till to limit curve. A "reasonable" accuracy we will consider the deviation of the values obtained from the solution BWR and tabulated data according to formulation for scientific purposes IAPWS-95 was less than 1 %.

2 Model of ideal gas

The first term on the right side of BWR equation (1) - $(r \cdot T \cdot \rho)$, which is proportional to the first power of density, corresponds to the state equation of ideal gas. Other members, proportional to the higher powers of density, represent the correction on the real behavior of gas. Obviously, the higher is the density, the greater is the influence of correction terms on the calculated pressure value.

In the "bigger" distances from the limit curve, it means in a state of much diluted gases (at "high" temperatures and "low" pressures, it means the "big" specific volumes, respectively "small" densities) the behavior of real materials approaches to the behavior of ideal gases. Correction terms in the BWR equation with higher power of density is unlikely to be strongly applied. In the case of water vapor we can illustrate this fact on several isotherms: error to 1 % is for temperature $1000^\circ C$ to the pressure 15 MPa, for temperature $500^\circ C$ to the pressure 1 MPa, for temperature $200^\circ C$ to the pressure 0.1 MPa, for temperature $100^\circ C$ to the pressure 0.05 MPa

(in Figure 1. - red line). For temperature $50^\circ C$ is the pressure of saturated steam very low - 0.012351 MPa. In this point (on the limit curve) we obtain values with accuracy 0.4 % by using the model of ideal gas. The accuracy to 1 % is maintained on the limit curve until the temperature $80^\circ C$. In triple point (temperature $0.01^\circ C$, pressure 0.000611657 MPa), the state of saturated steam is calculated with accuracy 0.07 % using the model of ideal gas.

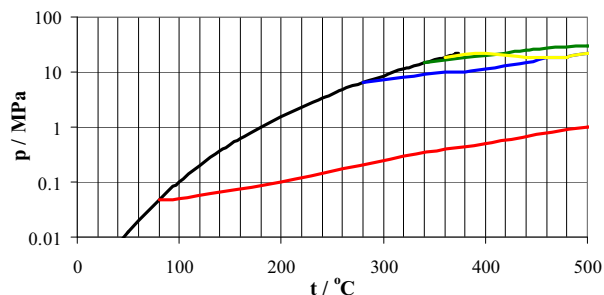


Figure 1. Field of application of the different models with the accuracy to 1 %: thick line - the limit curve; red line - limit of applicability of ideal gas model; blue line - limit of applicability of model with correction A_0, B_0 and C_0 ; green line - limit of applicability of model with correction A_0, B_0, C_0, a and b ; yellow line - limit of application of BWR equation.

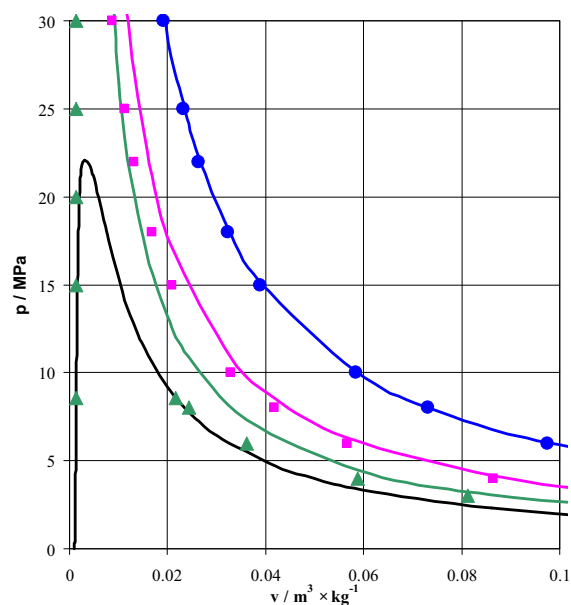


Figure 2. Comparison of isotherms of an ideal gas with real isotherms: thick line - the limit curve; green - isotherm $300^\circ C$; pink - isotherm $500^\circ C$; blue - isotherm $1000^\circ C$; lines - ideal gas isotherms; points - real values.

Figure 2. shows the real isotherms $300^\circ C$, $500^\circ C$ and $1000^\circ C$ and corresponding isotherms calculated using the ideal gas model. With increasing specific volume is the ideal isotherms and the real isotherms close to each other, conversely a decreasing specific volume increases the difference between the ideal and the real isotherm. We obtain higher pressure using the model of ideal gas than its actual value at low specific volumes.

Table 1. Specific volume $10^3 \cdot v / m^3 \text{ kg}^{-1}$ of water steam depending on the pressure and temperature; yellow highlighted numbers - accuracy of model of ideal gas less than 1 %; pink highlighted numbers - accuracy of model with correction A_0 , B_0 and C_0 less than 1 %; green highlighted numbers - accuracy of model with correction A_0 , B_0 , C_0 , a and b less than 1 %.

p / MPa	18	15	10	8	6	4	2	1	0.5	0.1	0.01
1000	32.282	38.808	58.390	73.079	97.560	146.52	293.42	587.21	1174.80	5875	58757
500	16.810	20.827	32.811	41.767	56.671	86.44	175.68	354.11	710.94	3565	35679
480	15.990	19.923	31.627	40.362	54.891	83.90	170.85	344.66	692.26	3473	34736
460	15.116	18.973	30.407	38.926	53.083	81.34	165.98	335.19	673.56	3380	33833
440	14.171	17.694	29.144	37.451	51.240	78.74	161.09	325.69	654.84	3288	32909
420	13.122	16.874	27.826	35.928	49.355	76.11	156.17	316.17	636.09	3195	31986
400	11.915	15.671	26.436	34.344	47.419	73.43	151.21	306.61	617.30	3103	31063
380	10.419	14.289	24.950	32.681	45.418	70.70	146.21	297.00	598.47	3010	30139
360	8.111	12.582	23.325	30.912	43.333	67.90	141.15	287.35	579.60	2917	29216
340			21.487	28.992	41.135	65.02	136.03	277.64	560.67	2824	28292
320			19.270	26.840	38.780	62.02	130.82	267.86	541.68	2732	27369
300				24.279	36.189	58.87	125.51	257.98	522.61	2639	26445
280					33.199	55.50	120.05	248.00	503.42	2546	25521
260						51.78	114.41	237.88	484.12	2453	24598
240							108.50	227.30	464.66	2360	23674
220							102.18	216.98	444.96	2266	22749
200								206.02	425.03	2172	21825
180								194.44	404.63	2078	20901
160									383.66	1984	19976
140										1889	19050
120										1793	18124
100										1696	17196
50											14866

In Table 1., the area in which the ideal gas model gives accuracy to 1 % is "highlighted" in yellow.

3 Correction using members proportional to the square of density

If the state of gas comes "near" to the limit curve, it is (due to the independent variables in the BWR equation) if specific volume decreases (resp. density increases), the deviation of the ideal gas model from the fair value increases. In the BWR equation, the influence of the correction members with higher power density grows. The second, the fourth and the seventh term on the right side are proportional to the square of density (other members depend on even higher powers of density) their effects are thus manifested first. The fourth member - $(-A_0 \cdot \rho^2)$ is directly proportional only to the square of the density and it corresponds to the absolute deviation between the ideal and the real isotherm apparently. Whereas it is necessary to make such a correction, which

"reduce" the ideal pressure in the BWR equation this member is subtracted. Deviation between ideal and real isotherm is not the same for all temperatures. At high temperatures (the substance is closer to the model of an ideal gas) the deviation is less, therefore the first correction (reduction of the ideal pressure due to fourth member) is "mitigated" due to the second member - $(r \cdot T \cdot \rho^2 \cdot B_0)$, which depends directly proportional to temperature, it is its influence increases with increasing of temperature. In the temperature range where the substance is describable due to ideal gas model, the fourth and the second member are mutually compensated. Conversely, at low temperatures, where the substance approaches the limit of liquefaction, is the absolute difference between the ideal and actual pressure greater - correction from ideal behavior is reinforced due to seventh member - $\left(-\frac{\rho^2 \cdot C_0}{T^2}\right)$, which is inversely proportional to the square of the temperature and therefore it significantly increases if the temperature falls.

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To estimate the coefficients A_0 , B_0 , C_0 was used IAPWS-95 data of water steam at different temperatures and such densities at which the maximum error of the model of an ideal gas from real data was 5 % approximately.

If the thermodynamic properties of water vapor was calculated from the ideal gas state equation adjusted to the real behavior of water steam through the 2nd, 4th and 6th member in BWR equation, the area, where the error of calculated values was less than 1%, significantly increased: for temperature 1000°C to the pressure 50 MPa , for temperature 500°C to the pressure 22 MPa . On the limit curve, the accuracy 1 % is maintained at temperatures up to 290°C . In Table 1. the region is indicated by a pink color, in the Figure 1. by blue color.

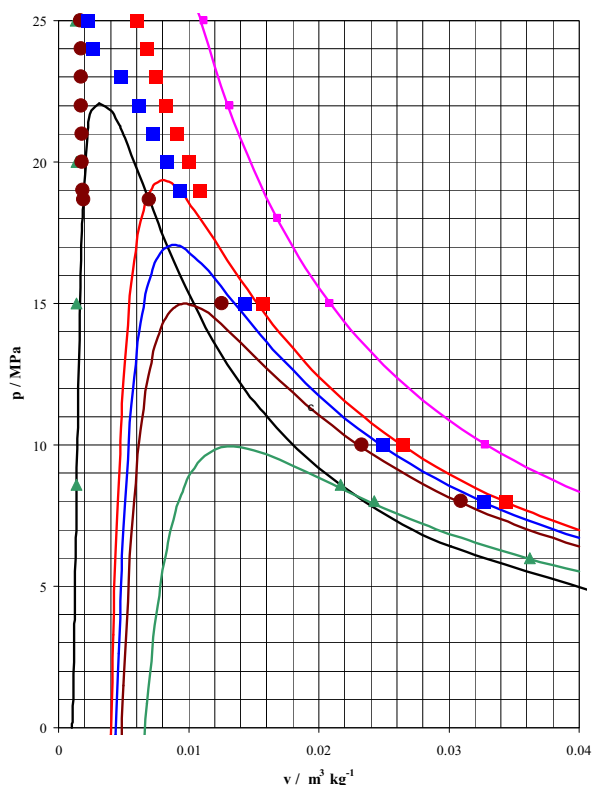


Figure 3. Comparison of isotherms of model with correction A_0 , B_0 and C_0 with real isotherms: thick line - the limit curve; green - isotherm 300°C ; brown - isotherm 360°C ; bleu - isotherm 380°C ; red - isotherm 400°C ; pink - isotherm 500°C ; lines - model with correction A_0 , B_0 and C_0 isotherms; points - real values.

4 Correction using members proportional to the third power of density

At low values of specific volume, however, the error is still too big in gaseous state too, see Figure 3. At low specific volumes, the model gives the lower value of pressure than its real value. Obviously this is the area in which begin to apply the correcting members with higher than the square power of the density. The third and the fifth member are proportional to the third power of density. The fifth member $(-a \cdot \rho^3)$ is directly

proportional only to the third power of density and apparently corresponds to the absolute deviation between the calculated and real isotherm. Whereas it is necessary to make such a correction that "increases" calculated pressure, in BWR equation that member will be added (negative value of a). The deviation of calculated pressures from the real values of pressure is not the same for all temperatures - the higher the temperature, the smaller the difference between the actual and the calculated pressure. The original correction (fifth member) is therefore necessary to "alleviate" (decrease) by correction using the third member $(T \cdot \rho^3 \cdot b)$, whose influence is greater the higher the temperature of the gas. To estimate the coefficients a and b was used IAPWS-95 data of steam water at different temperatures and such densities at which the maximum error of the model of an ideal gas with the previous correction (2nd, 4th and 7th member in a BWR equation) from the real data was approximately 5 %.

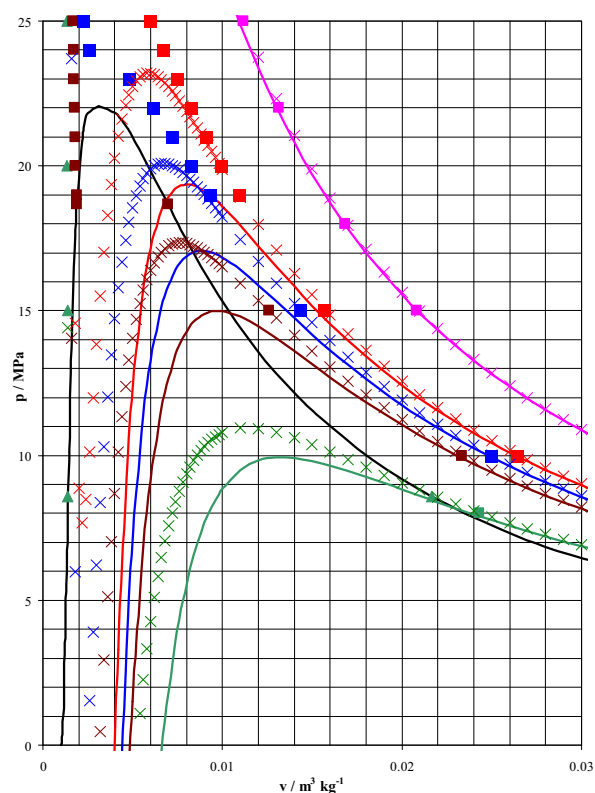


Figure 4. Comparison of isotherms of model with correction A_0 , B_0 , C_0 , a and b (lines) with isotherms of model with correction only A_0 , B_0 and C_0 (crosses) and with real isotherms (points): thick line - the limit curve; green - isotherm 300°C ; brown - isotherm 360°C ; bleu - isotherm 380°C ; red - isotherm 400°C ; pink - isotherm 500°C .

If the thermodynamic properties of water vapor was calculated from the ideal gas state equation adjusted to the real behavior of water steam through the 2nd, 3rd, 4th, 5th and 6th member in BWR equation, the area, where the error of calculated values was less than 1 %, increased again: on the limit curve, the accuracy 1 % is maintained at temperatures up to 340°C . In Table 1., the

region is indicated by a green color, in the Figure 1. by green color too.

5 Correction using members with special dependence on density

Isotherms calculated using such equations have already the known shape of Van der Waals isotherm (with the local maximum and minimum in the area of wet steam), see Figure 4. The big mistake, however, still occurs near the critical point, it is at much lower levels of specific volume. Obviously, this is the area where it would be needed used further correction in the state equation.

The third power density is found in the eighth member $\left(\frac{c \cdot \rho^3}{T^2} (1 + \gamma \cdot \rho^2) e^{-\gamma \cdot \rho^2}\right)$, but the dependence of

this correction term on the density is more complicated. To illustrate the effect of the eighth member look at

Figure 5., where dependence $\frac{\rho^3}{T^2} (1 + \rho^2) e^{-\rho^2}$ on $\frac{1}{\rho}$ (it is

on specific volume) is plotted for two different temperatures. It is evident, that this member neither monotonically decreases nor monotonically increases with increasing density (it is with decreasing specific volume), but its influence is reflected only in a certain range of densities. Its dependence has a marked maximum for concretely value of density. This member is inversely proportional to the square of temperature. His influence, therefore, probably will decrease significantly with increasing temperature. This member is significantly exhibit to correcting the shape of isotherms in the occurrence of local maxima and minima; it is below the limit curve (area of phase change). The constant γ should be determined so that the region of influence of the eighth member coincides to the densities corresponds with the start and end of the phase transformation of water vapor.

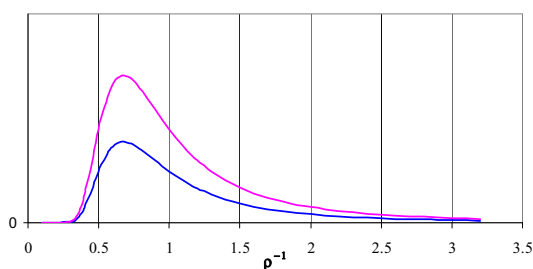


Figure 5. Dependence of $\frac{\rho^3}{T^2} (1 + \rho^2) e^{-\rho^2}$ on $\frac{1}{\rho}$ for temperature 500°C (blue line) and for temperature 300°C (pink line).

The last unused member of the BWR equation is the 7th member - $(a \cdot \alpha \cdot \rho^6)$. It is proportional to the sixth power of density and thus it has influence only at significantly high densities. This member does not depend on the temperature, which means that adjusts value of pressure independently on the temperature - for the some density it add to the calculated values of pressure (see the previous correction) still the same value.

When parameter c and parameter α are estimated, we need for small values of specific volumes (where correction using the 7th member and the 8th member may have effect on the calculated value of pressure) to ensure: the applicability of the equation on the saturation line to the higher temperatures, refinement of equation near the critical point, the existence of a critical point - the inflection point on the critical isotherm, maintaining sufficient accuracy equation at high temperatures.

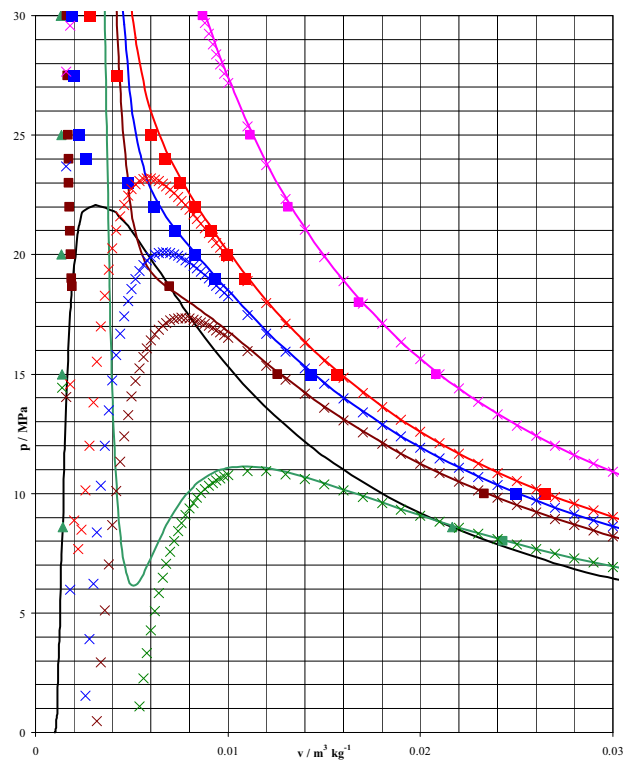


Figure 6. Comparison of isotherms of model with correction A_0, B_0, C_0, a, b, c and α (lines) with isotherms of model with correction only A_0, B_0, C_0, a and b (crosses) and with real isotherms (points): thick line - the limit curve; green - isotherm 300°C ; brown - isotherm 360°C ; bleu - isotherm 380°C ; red - isotherm 400°C ; pink - isotherm 500°C .

It turns out that it is not possible to satisfy simultaneously these requirements for H_2O using the original BWR equation. It is possible to extend the application area of the equation on the limit curve to higher temperatures, but at the cost of a reduced pressure into which an equation is usable in gas phase at high temperatures (see the yellow line in Figure 1.). Figure 6. shows some isotherms calculated by equation with correcting members with A_0, B_0, C_0, a and b (crosses) and same isotherms calculated using the BWR equation with such choice of parameters c and α , that we obtained the good accuracy on the limit curve to the high temperatures (see isotherm 360°C). We see that for this temperature and pressure of saturation, BWR equation gives a more accurate value, but the shape of this isotherm is bad - it looks like supercritical isotherms (no inflection point). If we use such combination of correction parameters that on the critical isotherm (it is on the isotherm 373.946°C) is an inflection point, we get the critical point shifted

significantly to the left (to higher values of specific volumes than corresponds with data IAPWS-95) and the error of calculated values on the boundary curve is much more even for lower temperatures.

It turns out that if we want to calculate the thermodynamic properties of steam using "simple" equation of state based on the original BWR equation, it is useless to use its full form - 7th and 8th correction terms have not brought any significant refinement of calculated values of pressure. For routine engineering calculations of water vapor it is thus possible to use a simplified BWR equation of the form

$$p=rT\rho+rT\rho^2B_0+rT\rho^3b-A_0\rho^2-a\rho^3-\frac{\rho^2C_0}{T^2} \quad (4)$$

This equation gives sufficiently accurate results. When we use simplified BWR equation with coefficients, which we obtained by shown procedure, we can calculate the properties of water vapor to a state of beginning of condensation to the pressure *15 MPa* (temperature *340°C*). For high temperature, equation can be used for even higher pressures (see Figure 1.), but pressures up to *30 MPa*.

6 Conclusions

Simplified BWR equation using coefficients derived in this paper, is less accurate than the equations used in IAPWS, near the critical point and in liquid areas even is not usable at all. The great advantage is the simplicity of equation, and thus easier possibility of calculating of the properties of the water vapor. Another advantage is the possibility of derivation of the relationship for other thermodynamic properties (isobaric specific heat capacity c_p , enthalpy h , ...) [10] and thus the simple possibility of calculating of the thermodynamic processes in the superheated steam without the using of thermodynamic tables of water and steam.

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