EPJ Web of Conferences **114**, 02133 (2016)
DOI: 10.1051/epjconf/201611402133

Dependence of the isobaric specific heat capacity of water vapor on the pressure and temperature

Magda Vestfálová[1,a], Pavel Šafařík[2]

[1] *KEZ, TU Liberec, Studentská 1402/2, 461 17 Liberec 1, Czech Republic*
[2] *U12112, CTU Prague, Technická 4, 166 07 Praha 6, Czech Republic*

Abstract. The fundamental base for the calculation of the thermodynamic properties of substances is the thermal equation of state and the dependence of some of the basic specific heat capacities on temperature. Dependence of isobaric specific heat capacity on the pressure can already be deduced from these relations. International standards of the properties of water and steam are based on the new scientific formulation IAPWS-95. The equation is in the form of Helmholtz dimensionless function with very much parameters. The aim of this paper is to design the simple dependence of the isobaric specific heat capacity of water vapor on the pressure and temperature in the range in which the steam occurs in the atmospheric moist air.

1 Introduction

Water and water vapor plays an important role in many natural phenomena. They are also the usual work media or process media in various industrial sectors, especially in technical or chemical fields. Therefore, their properties are explored in detail, measured and tabulated.

Since 1929, research and standardization of the properties of water and steam has been organized internationally. The aim was to provide a reliable and uniform thermophysical data. At first, it was a loose association of professionals engaged in measuring, describing, or using thermophysical properties of water and steam. Since 1972, a loose association has been replaced by of a permanent organization, the International Association for the Properties of Water and Steam - IAPWS. One of the member countries of IAPWS is also Czech Republic.

During a period of international cooperation to standardization the properties of water and steam, IAPWS has published a series of documents based on a thorough verification of the available experimental data on the properties of water [1], on the analysis of variance of data files, on data classification according to plausibility, on interpolation of the data [2] and on appropriate expression of the properties of water vapor, especially thermodynamic properties and transport properties.

In 1995, the Pruß-Wagner equation [3] was adopted as an international formulation of thermodynamic properties of water and steam for scientific purposes IAPWS-95. It was evaluated as the best equation of state for water and steam for a wide range of parameters, which represents the available experimental data very well. The equation is in the form of Helmholtz dimensionless function according on temperature and reduced density in the form of a uniform state equation valid for the liquid phase and gas phase too. International standards of the properties of water and steam are based on the new scientific formulation IAPWS-95 and they are available for example in [4]. Document IAPWS-95 was recently revised in 2014 [5].

In 1997, it was received a document stating the properties of water and steam in the formulation for industrial purposes - IAPWS IF-97. Its importance lies in the fact that it is binding international basis for energy (particularly for tenders and guarantee tests). Formulation of the properties of water and steam for industrial purposes is compatible with scientific standards with sufficient accuracy and reduces significantly the computational time to achieve the values of thermodynamic parameters of water and steam in five defined areas of parameters. In these areas, fundamental equations are defined - in three fields these are specific equations for the Gibbs free energy, in one area this is the equation for the Helmholtz free energy and in one area it is implicit quadratic equation as a relationship between the pressure and temperature of saturation. International Standards of properties of water and steam based on the industrial formulation IAPWS IF-97 are available for example in the form of tables in [6]. Document IAPWS IF-97 is gradually completed [7], for example by the reverse functions to further reducing the computational time required values of thermodynamic parameters of water and steam, and by other cues from the current industrial applications.

The aim of the presented paper is to derive the simple dependence of the isobaric specific heat capacity of water

---

[a] Corresponding author: pavel.safarik@fs.cvut.cz

vapor on the pressure and temperature in the range in which the steam occurs in the atmospheric moist air. The dependence is based on the tabulated data according to formulation for scientific purposes IAPWS-95 and it was derived for using in calculations of the properties of the atmospheric moist air.

2 Specific heat capacity at constant pressure of real gases

Let dependency of states parameters (pressure p, temperature T and the specific volume v) of real gas is expressed by some thermal equation of state

$$f(p,T,v)=0\,. \tag{1}$$

Let the isobaric specific heat capacity of a real gas depends on the temperature and pressure

$$c_p=\left(\frac{\partial q}{\partial T}\right)_p=\left(\frac{\partial h}{\partial T}\right)_p=c_p(T,p), \tag{2}$$

where q is the specific heat and h is the specific enthalpy.

The full differential of isobaric specific heat capacity is expressed

$$d c_p=\left(\frac{\partial c_p}{\partial T}\right)_p dT+\left(\frac{\partial c_p}{\partial p}\right)_T dp\,. \tag{3}$$

The dependence of the specific heat capacity on the pressure can be derived from thermal state equation (1) (see further). Its temperature dependence can not be deduced from other properties of the substance and thus it belongs (together with the thermal equation of state) to the necessary initial foundations for building computational relationships of thermodynamic properties of substances.

In the theory of ideal gas, specific heat capacity has a constant value. For model of partly ideal gas, it is usually worked with dependency of specific heat capacity on temperature in the polynomial form

$$c_p=A+BT+CT^2+DT^3+\dots\,. \tag{4}$$

where $A\ (J\cdot kg^{-1}\cdot K^{-1})$, $B\ (J\cdot kg^{-1}\cdot K^{-2})$, $C\ (J\cdot kg^{-1}\cdot K^{-3})$, $D\ (J\cdot kg^{-1}\cdot K^{-4})$, ... are constants of polynomial. In the calculations taking into account the real properties of substances, the relationship (4) expresses the limit approximation of the real gas for $p\rightarrow 0$, it is dependence of the isobaric specific heat capacity on the temperature in an idealized state of gas.

The dependence of the isobaric specific heat capacity on the pressure can be obtained from the thermal state equation by the following procedure:

Equation (2) is differentiated by pressure at a constant temperature

$$\left(\frac{\partial c_p}{\partial p}\right)_T=\left[\frac{\partial}{\partial p}\left(\frac{\partial h}{\partial T}\right)_p\right]_T=\left[\frac{\partial}{\partial T}\left(\frac{\partial h}{\partial p}\right)_T\right]_p\,. \tag{5}$$

The derivative of enthalpy can be obtained by differentiating of the Gibbs equation ($dh=T\,ds+v\,dp$, where s is the specific entropy)

$$\left(\frac{\partial h}{\partial p}\right)_T=T\left(\frac{\partial s}{\partial p}\right)_T+v\,. \tag{6}$$

Substituting the Maxwell equation

$$\left(\frac{\partial h}{\partial p}\right)_T=-T\left(\frac{\partial v}{\partial T}\right)_p+v\,. \tag{7}$$

Substituting equation (7) into equation (5)

$$\left(\frac{\partial c_p}{\partial p}\right)_T=\left[\frac{\partial}{\partial T}\left\{-T\left(\frac{\partial v}{\partial T}\right)_p+v\right\}\right]_v=-T\left(\frac{\partial^2 v}{\partial T^2}\right)_p\,. \tag{8}$$

If the thermal equation of state of technical type (it is in the form $v=v(p,T)$) is available (and it describes the properties of steam with sufficient accuracy) then it would be possible to obtain a derivative $\left(\frac{\partial v}{\partial T}\right)_p$ and to solve the equation (8) and to obtain the dependence of the isobaric specific heat capacity at pressure.

3 Specific heat capacity of water vapor - regression of IAPWS-95 data

Another way to obtaining the functional dependence of the specific heat capacity on pressure and temperature, is the simple regression of data, for example from IAPWS-95.

The paper is focused on the properties of water vapor occurring in the unsaturated moist air at "normal" temperatures, it is at temperatures of *0°C* to *200°C*. The values of isobaric specific heat capacity of water vapor by IAPWS-95 under these conditions are shown in Table 1 [4]. Graphical dependence of the isobaric specific heat capacity on the temperature with parameter - pressure is shown in Figure 1. It is evident that the course of this dependence is not monotonic. But the dependence of the isobaric specific heat capacity on the pressure with parameter - temperature, as it is shown in Figure 2, appears to be linear. Therefore, the relationship for dependence of isobaric specific heat capacity on the pressure in the shape

$$c_p=E+F\,x\,, \tag{9}$$

Table 1. The isobaric specific heat capacity of water vapor in $kJ \cdot kg^{-1} \cdot K^{-1}$ - dependence on pressure and temperature by IAPWS-95 - selected values [4].

p [Pa] **t [°C]**	**611.657**	**1000**	**2000**	**5000**	**10000**	**20000**	**50000**	**101325**
5	1.875							
10	1.872	1.884						
15	1.87	1.878						
20	1.87	1.875	1.896					
25	1.87	1.874	1.888					
30	1.871	1.874	1.884					
40	1.872	1.875	1.881	1.905				
50	1.874	1.876	1.881	1.896	1.928			
60	1.877	1.878	1.882	1.894	1.914			
70	1.880	1.881	1.884	1.893	1.909	1.942		
80	1.883	1.884	1.887	1.894	1.906	1.931		
90	1.887	1.888	1.890	1.895	1.905	1.925	1.991	
100	1.891	1.891	1.893	1.898	1.906	1.922	1.974	2.080
120	1.899	1.900	1.901	1.904	1.910	1.921	1.956	2.021
140	1.909	1.909	1.910	1.912	1.916	1.924	1.949	1.994
160	1.919	1.919	1.919	1.921	1.924	1.930	1.948	1.980
180	1.929	1.929	1.930	1.931	1.933	1.938	1.951	1.976
200	1.940	1.940	1.941	1.942	1.943	1.947	1.957	1.976

where *E* and *F* are the parameters of linear dependence will be investigated.

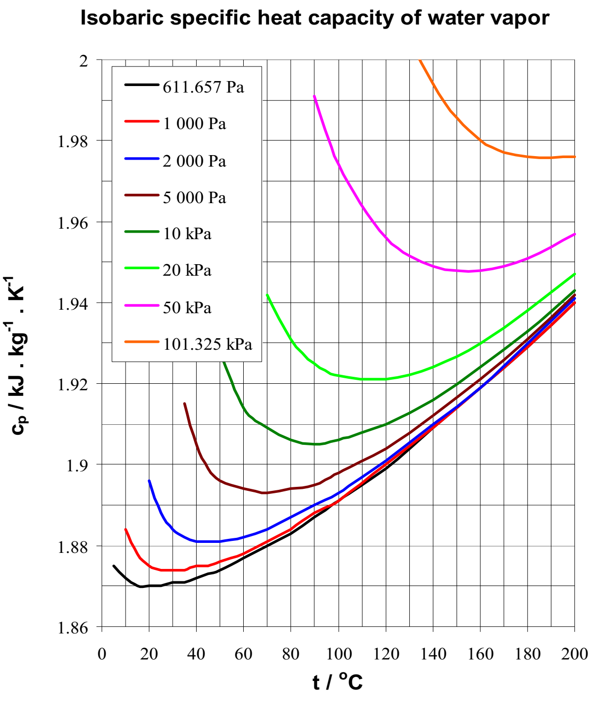

Figure 1. The isobaric specific heat capacity of water vapor - dependence on pressure and temperature by IAPWS-95 [4] (parameter - pressure).

Parameter *E* (it is the value of the isobaric specific heat capacity c_p at the lowest "known" pressure) depends on

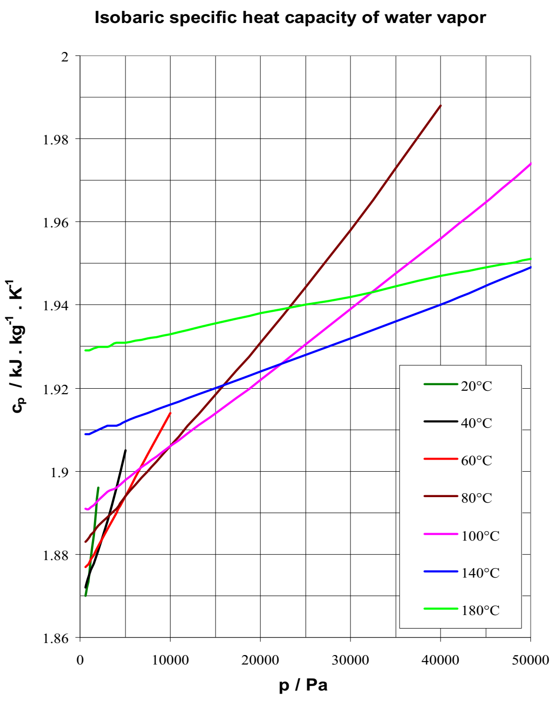

Figure 2. The isobaric specific heat capacity of water vapor - dependence on pressure and temperature by IAPWS-95 [4] (parameter - temperature).

the temperature (see Figure 2). As low "known" pressure is adopted pressure *611.657 Pa* (the pressure of the triple point of water). Therefore parameter *E* corresponds with the isobaric specific heat capacity at a pressure equal to the pressure of the triple point of water. In the linear dependence (9) will not be direct the value of the pressure, but the value of difference between the pressure and the pressure of the triple point of water. The pressure of the triple point can be considered as the pressure "very low", so, it can be assumed that this is an idealized state of water vapor, it is water vapor acts as an ideal gas at this pressure. Dependence of the parameter *E* on temperature is therefore for us the dependence of isobaric specific heat capacity in an idealized state of the gas on temperature according to equation (4)

$$E = E(t) = \left(c_p\right)_{p\,=\,611.657\ Pa} = A_E + B_E\,t + C_E\,t^2 + D_E\,t^3 + \ldots\,, \qquad (10)$$

where *t (°C)* is a temperature, A_E, B_E, C_E, D_E, ... are the coefficients of polynomial regression.

By regression of data IAPWS-95 by 2nd order polynomial, we obtained the course of the isobaric specific heat capacity c_p at a pressure of *611.657 Pa* with a deviation less than *0.1 %* (Figure 3).

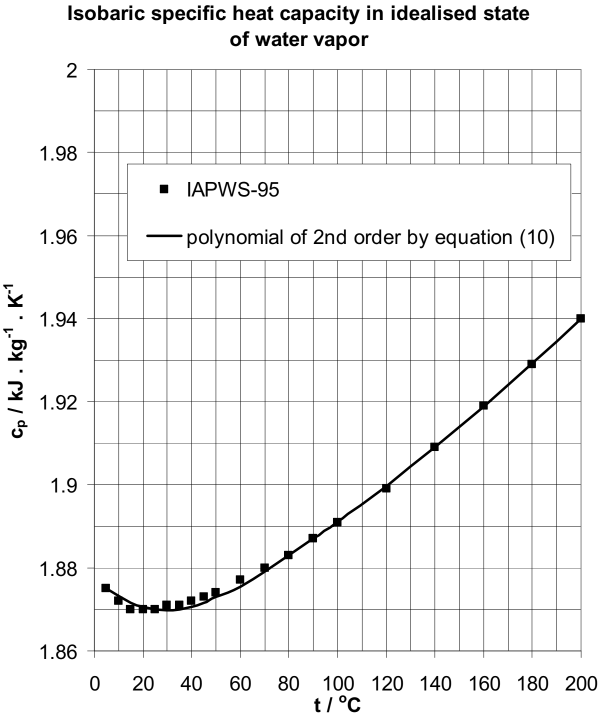

Figure 3. The isobaric specific heat capacity of water vapor at low pressure (p_{tr}) according IAPWS-95 [4], and by regression polynomial, equation (10).

The parameter F is a slope of the growth of the isobaric specific heat capacity c_p when the pressure increases. It is temperature-dependent function. It decreases with temperature (the higher is the temperature, the slower is the growth of c_p when the pressure increases, as Figure 2 shows).

Polynomial dependence of inverted value of slope *F* in linear relationship in equation (9) has the form

$$\frac{1}{F} = \frac{1}{F(t)} = A_F + B_F\,t + C_F\,t^2 + D_F\,t^3 + \ldots\,. \qquad (11)$$

It is achieved the compliance with data IAPWS - 95 (see Figure 4) already using 2nd order polynomial in equation (11).

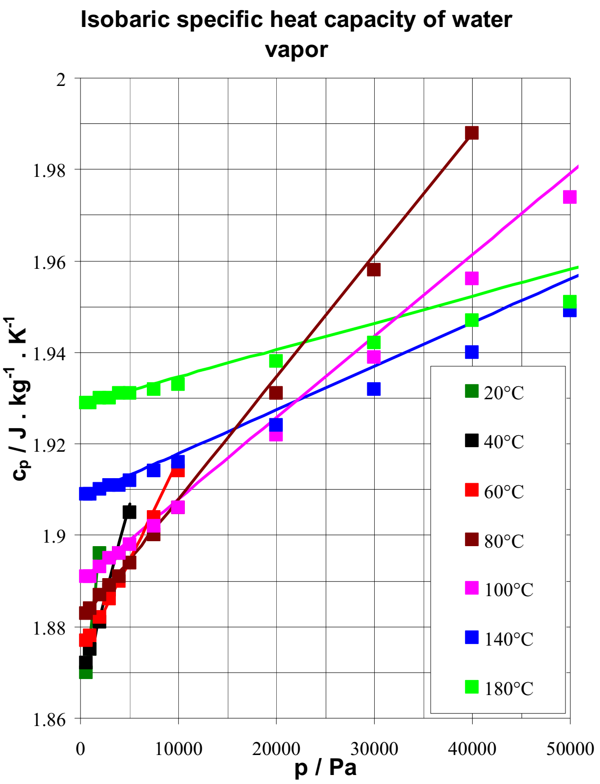

Figure 4. The isobaric specific heat capacity of water vapor in dependence on pressure and temperature (parameter - temperature) according IAPWS-95 [4], and by regression polynomial (11).

Figure 5 shows the dependence of isobaric specific heat capacity c_p on the temperature and on the pressure determined by a simplified relationship using equation (10) and (11) in the form

$$c_p(p,t) = E(t) + F(t)(p - p_{tr}) = A_E + B_E\,t + C_E\,t^2 + \frac{1}{A_F + B_F\,t + C_F\,t^2}(p - p_{tr}). \qquad (12)$$

Table 2. Coefficients of polynomials regression of isobaric specific heat capacity c_p of water vapor for the temperature range *0°C - 200°C* and pressures to *200 kPa.*

	t < 50°C	**t > 50°C**
A_E **[m² . s⁻² . K⁻¹]**	1877.2	1856.1
B_E **[m². s⁻². K⁻²]**	-0.49545	0.28056
C_E **[m². s⁻². K⁻³]**	$8.1818 \cdot 10^{-3}$	$6.9444 \cdot 10^{-4}$
A_F **[kg . K . m⁻³]**	22.537	22.537
B_F **[kg . m⁻³]**	0.49321	0.49321
C_F **[kg . K⁻¹. m⁻³]**	0.048927	0.048927

Table 3. Variations of the isobaric specific heat capacity c_p of water vapor calculated by the regression polynomial (12) from the values IAPWS-95 in *%* in the temperature range *0°C - 200°C* and pressures to *200 kPa* .

p [Pa] t [°C]	**611.657**	**1000**	**2000**	**5000**	**10000**	**20000**	**50000**	**100000**	**101325**	**200000**
5	$2\cdot10^{-13}$									
10	0.061	0.060								
15	0.090	0.169								
20	0.034	0.166	0.071							
25	$1\cdot10^{-13}$	0.103	0.170							
30	0.066	0.029	0.150							
40	0.078	0.066	0.056	0.102						
50	0.056	0.040	0.008	0.150	0.018					
60	0.083	0.046	0.025	0.035	0.134					
70	0.045	0.029	0.009	0.050	0.093	0.128				
80	$5\cdot10^{-14}$	0.002	0.016	0.037	0.106	0.191				
90	0.001	0.010	0.001	0.077	0.118	0.199	0.131			
100	0.006	0.042	0.031	0.049	0.097	0.191	0.260	0.422	0.452	
120	0.041	0.014	0.029	0.071	0.090	0.179	0.337	0.356	0.340	
140	$9\cdot10^{-14}$	0.019	0.017	0.062	0.101	0.180	0.360	0.583	0.545	0.421
160	0.012	0.003	0.042	0.053	0.089	0.160	0.372	0.615	0.665	0.881
180	0.006	0.018	0.004	0.036	0.085	0.131	0.370	0.643	0.631	1.068
200	$1\cdot10^{-13}$	0.010	0.017	0.006	0.078	0.120	0.346	0.649	0.631	1.136

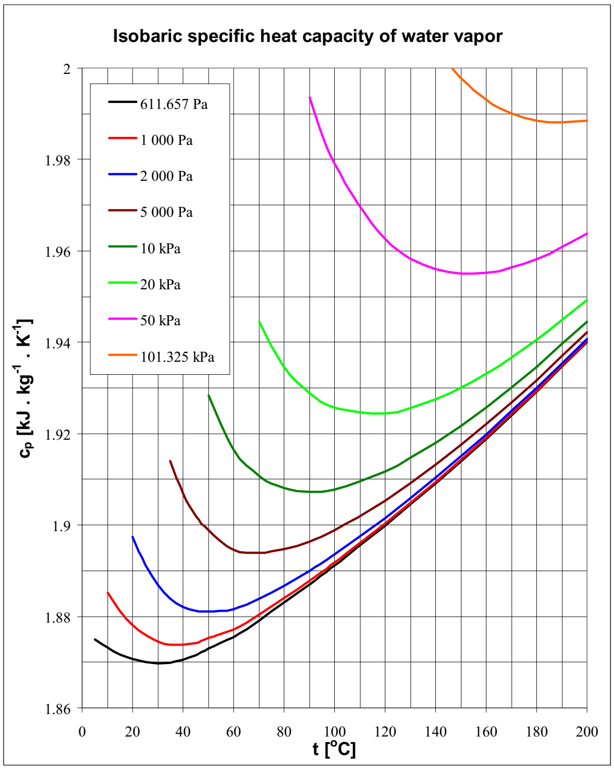

Figure 5. Dependence of the isobaric specific heat capacity of water vapor on the pressure and on the temperature (parameter - pressure) calculated according to the regression equation (12).

To calculation, the coefficients of polynomial regression according to Table 2 were used.

The values shown in Figure 5 are compared with the data IAPWS-95 (see Figure 1) for temperatures up to *200°C* and pressures up to *200 kPa* and differences are less than *1.2 %* (see Table 3).

4 Conclusion

The relationship for calculation the isobaric specific heat capacity of water vapor in the states in which the water vapor founds in humid atmospheric air under normal conditions, is derived, equation (12). Values obtained with derived relationship deviates from the values IAPWS-95 by less than *1.2 %* (while this deviation for isobaric specific heat capacity of water vapor as an ideal gas reaches for example at a temperature of 200^oC and a pressure of *200 kPa* values around *35%*). Such variation is acceptable for most engineering calculations in the humid air.

Acknowledgements

The first author, M.Vestfálová, express his gratitude for the support of project SGS No.21000 „Experimental and Numerical Investigation in Fluid Mechanics, Thermodynamics and Heat Transfer“ .

The second author, P. Šafařík, expresses his gratitude for the support of research from TAČR Competence

Centre, "Advanced Technologies for the Production of Heat and Electricity," Reg. No. TE01020036.

References

1. H. Sato, K. Watanabe, J.M.H. Levelt Sengers, J.S. Gallagher, P.G. Hill, J. Straub, W. Wagner, Sixteen Thousands Evaluated Experimental Thermodynamic Property Data for Water and Steam, Journal of Physical and Chemical Reference Data, **20**, 1023-1044 (1991)
2. J. Straub, K. Scheffler, *Water and Steam, Their Properties and Current Industrial Applications* (1980)
3. W. Wagner, A. Pruß, The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use, Journal of Physical and Chemical Reference Data, **31**, 387-535 (2002)
4. O. Šifner, J. Klomfar, *International Standards of Thermophysical Properties of Water and Steam* (1996)
5. Revised Release on the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use (2014)
6. R. Mareš, O. Šifner, J. Kadrnožka, *Tables of Properties of Water and Steam* (1999)
7. Revised Release on the IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam (2007)