Thermodynamic properties of dissociated steam

R Z Aminov, A A Gudym
Saratov Scientific Center of the Russian Academy of Sciences,
410054 Saratov, ul. Politekhnicheskaya 77

E-mail: oepran@inbox.ru

Abstract. In connection with the development of hydrogen technologies and the generation of dissociated steam as a result of the oxidation of hydrogen in an oxygen environment, it became necessary to determine the calorific parameters of dissociated steam. In the existing tables, the caloric parameters of dissociated steam are presented at a reference temperature of 0 K. By contrast, the authors have developed tables of dissociated steam using a reference temperature of 0°C, within the pressure range 0.01–20.0 MPa and the temperature range 1250–4000 K, along with a system of equations for the industrial calculation of the properties of dissociated steam within the temperature range 1250–2300 K and pressure range 0.01–10.0 MPa, followed by a temperature range of 2200–3600 K. During the dissociation of steam, a mixture of eight components is formed including hydrogen H, oxygen O, radicals OH and HO₂, molecules of hydrogen H₂, oxygen O₂, steam H₂O, and hydrogen peroxide H₂O₂. All existing tables of the properties of dissociated steam are based on a mixture of six components: H₂, O₂, OH, H, O, and H₂O. For evaluate whether this is an oversimplification, the composition of the mixture comprising all eight components was calculated, taking into account additional chemical reactions for the formation of HO₂ and H₂O₂. At a pressure of 0.01 MPa, the maximum mole fraction of HO₂ was 2.8·10⁻⁵ at a temperature of 3000 K, and at a pressure of 10 MPa, the maximum mole fraction was 5·10⁻⁵ at a temperature of 4000 K. The mole fraction of H₂O₂ was much lower. Thus at temperatures up to 3000 K, calculations of the properties of dissociated steam are restricted to six components.

1. Introduction
When the temperature of water steam exceeds 1250–1450 K it undergoes dissociation. Decreased pressure and increased temperature leads to an increase in the degree of dissociation.

In terms of elementary chemical reactions, the dissociation of steam results in the formation of a chemical reaction mixture comprising atoms, radicals, and molecules. In previous studies [1, 2], this mixture has been reported to comprise 14 elementary reactions, in other studies 20 elementary reactions have been proposed. All of these reactions involved only eight component atoms, namely hydrogen H, oxygen O, radicals OH and HO₂, hydrogen H₂, oxygen O₂, water steam H₂O, and hydrogen peroxide H₂O₂.

To determine the properties of high temperature dissociated steam within the temperature range 2000–6000 K, previous reports [3–6] limited the number of components considered to be participating in chemical reactions to six, namely H₂, O₂, OH, H, O, and H₂O.

On this basis, a table was constructed for dissociated water steam starting from 0 K [3, 4], with the reference starting from 0°C [5, 6].
2. Calculation of the properties of dissociated steam

To study the effect on the thermodynamic properties of dissociated steam for each of the eight components involved in the elementary reactions, including HO₂ and H₂O₂, which were not previously taken into account, the quantitative composition of all of the components of the mixture was calculated. The six major types of independent reactions were as follows:

\[
\begin{align*}
H_2O &\rightleftharpoons H_2 + 1/2O_2; \\
H_2O &\rightleftharpoons OH + 1/2H_2; \\
O_2 &\rightleftharpoons 2O; \\
H_2 &\rightleftharpoons 2H; \\
1/2H_2 + O_2 &\rightleftharpoons HO_2; \\
H_2 + O_2 &\rightleftharpoons H_2O_2;
\end{align*}
\]

(1)

Calculation of the equilibrium composition at given values of pressure and temperature is carried out using the equilibrium constants of the components of the gas mixture:

\[
\begin{align*}
K_{p1} &= \frac{x_{H_2}x_{O_2}^{0.5}}{p^{0.5}}; \\
K_{p2} &= \frac{x_{OH}x_{H_2}^{0.5}}{p}; \\
K_{p3} &= \frac{x_{O_2}^{2}}{p}; \\
K_{p4} &= \frac{x_{H_2}^{2}}{p}; \\
K_{p5} &= \frac{x_{HO_2}}{x_{H_2}^{0.5}x_{O_2}}; \\
K_{p6} &= \frac{x_{H_2O_2}}{x_{H_2}^{2}x_{O_2}}.
\end{align*}
\]

(2)

Here \(K_{p1}, K_{p2}, K_{p3}, K_{p4}, K_{p5}, K_{p6}\) – equilibrium constants of the components of the gas mixture; \(x_{H_2}, x_{O_2}, x_{OH}, x_{H_2O_2}\) – mole fraction of mixture components: molecules of hydrogen, oxygen, water steam, hydroxyl group OH, atoms oxygen and hydrogen, radicals HO₂; hydrogen peroxide H₂O₂; \(p\) – gas mixture pressure, MPa; 9,869.

To determine the solution of this system, two equations were augmented, the law of mass action and the balance of atoms, which were determined using the initial correction of atoms of O and H and then the products of H₂O dissociation.

The solution of the system was determined by the equilibrium composition at given values of pressure \(p\) and temperature \(T\). The calculated mole fractions of the components of the mixture of dissociated steam at a pressure of 1 MPa are shown in figure 1.

![Figure 1. The composition of the mixture of the components of dissociated steam at a pressure of 1 MPa](image)

1 – O₂, 2 – O, 3 – H₂, 4 – OH, 5 – H, 6 – H₂O₂

Because the relatively small values of the mole fraction of components HO₂ and H₂O₂ are not presented in figure 1, the mole fractions of components HO₂ and H₂O₂ in the mixture that are dependent on the pressure and temperature are shown in figure 2.
The mole fractions of \( \text{HO}_2 \) and \( \text{H}_2\text{O}_2 \) in the mixture increased with increasing temperature and pressure. At a pressure of 100 MPa, the mole fraction of \( \text{HO}_2 \) was 0.002 (0.2%) at a temperature of 5500 K, and for \( \text{H}_2\text{O}_2 \) it was 0.0004 (0.04%) at a temperature of 5000 K.

The mole fractions of \( \text{HO}_2 \) and \( \text{H}_2\text{O}_2 \) in the mixture significantly affected the properties of dissociated steam at temperatures above the maximum temperature of burning hydrogen in oxygen, i.e. 3980 K at a pressure of 100 MPa, and 3600 K at 10 MPa. The temperature of combustion of hydrogen was determined by the heat of formation of \( \text{H}_2\text{O} \) (heat of combustion of \( \text{H}_2 \)).

A temperature of dissociated steam greater than the temperature of combustion is achieved by additional heating of the combustion products of hydrogen from an external source. The maximum mole fraction during the combustion of hydrogen at a pressure of 100 MPa was 0.0007, of which \( \text{H}_2\text{O}_2 \) was 0.0002, and at a pressure of 10 MPa, 0.0002 was \( \text{HO}_2 \) and 0.00005 was \( \text{H}_2\text{O}_2 \). Thus the uncertainty of the composition of the mixture was previously presented in tables [4], and at a pressure of 100 MPa without consideration of the components and without an additional heat supply it was 0.0009 (0.09%), and at a pressure of 10 MPa it was less than 0.00025 (0.025%). During the chemical reactions and the formation of components \( \text{HO}_2 \) and \( \text{H}_2\text{O}_2 \), the mixture diminish the fractions of \( \text{O}_2 \), \( \text{H}_2 \), and \( \text{H}_2\text{O} \). Furthermore, due to insignificant differences in the properties of these components and the heat of formation of \( \text{H}_2\text{O} \) and \( \text{H}_2\text{O}_2 \) the changes in the thermodynamic properties of dissociated steam for the specified changes in the composition of the mixture were more than one order of magnitude smaller.

As shown by calculations, the uncertainty (error) in the calculation of thermodynamic properties of dissociated steam with changes in the composition of the components of the mixture due to the temperature of hydrogen combustion was insignificant (less than 0.00015%).

3. Estimated equations for the caloric parameters of dissociated steam

The equation for calculating the enthalpy of the chemically reacting mixture formed by the dissociation of steam is part of the theoretical expression of the thermal effect of the reaction, starting from the triple point.

\[
H_{CM} = \sum_{i}^{5} Q_i^0(x_i - Q_{H_{2}O}^0(1 - x_{H_{2}O})) + \sum_{i}^{7} x_i H_i(T) + H_{H_{2}O}(T)x_{H_{2}O}, \text{ kJ/kmol},
\]  

Figure 2. The mole fractions of the radical \( \text{HO}_2 \) (a) and molecules \( \text{H}_2\text{O}_2 \) (b) in the mixture that are dependent on the pressure and temperature

1 – 1 MPa, 2 – 10 MPa, 3 – 20 MPa, 4 – 40 MPa, 5 – 100 MPa

\[
\text{Mole fractions } \text{HO}_2
\]

\[
\text{Mole fractions } \text{H}_2\text{O}_2
\]

\[
\text{Temperature, K}
\]
where \[ \sum_{i=1}^{3} Q_i^0(0) x_i \] is the sum of the products of the standard heat of formation \( OH, O, H, HO_2, H_2O_2 \) per mole fraction of the components of the resulting mixture \( x_i \); \( Q_{H,O}^0(0) \) and \( x_{H,O} \) – heat of formation and mole fraction of \( H_2O; \sum_1^6 H_i(T) x_i \) – the sum of the products of enthalpies per mole fraction of the components of the mixture \( H_2, O_2, OH, H, \) and \( O \) at a temperature \( T \).

Numerical values for the standard heat of formation of reaction products were taken as 298.15 K according to previous data \([7, 8]\).

The entropy of one mole of a mixture at a reference temperature from a triple point was determined by the sum of the products of the entropy of the components per their corresponding mole fraction

\[
S_{CM} = \sum_{i=1}^{6} S_i(T) x_i - \Phi \sum_{i=1}^{6} x_i \ln x - S_{H,O}(273.16), \text{ kJ/(kmol·K)}
\]  

(4)

When counting from \( S_{CM} = \sum_{i=1}^{6} S_i(T) x_i - S_{H,O}(273.16) \), where \( S_{H,O}(273.16) \) kJ/(kmol·K) – is the entropy of water at a temperature of 273.16 K \([8]\).

The isobar specific heat of one mole of dissociated steam was determined from the equation:

\[
C_{PCM} = \sum_{i=1}^{6} C_{P_i} x_i, \text{ kJ/(kmol·K)}
\]

where \( C_{P_i} \) – is the heat capacity of 1 kmol of the component of the mixture.

The volume of 1 mole of the mixture was calculated by the equation:

\[
V = \sum_i V_i x_i, \text{ m}^3/\text{kmol}
\]

where \( V_i \) – is the volume of 1 kmole of the component of the mixture.

All of the formulas given refer to molar quantities. The specific values presented in the tables (referred to as 1 kg) are determined by dividing the molar values by the apparent molecular weight of the mixture as a function of:

\[
M_{CM} = \sum_{i=1}^{6} M_i x
\]

where \( M_i \) – is the molecular mass of the \( i \)-th component of the mixture.

The effect of chemical reactions on the properties of dissociated steam is used to calculate the isobaric specific heat of \( C_p \) kJ/(kg·K).

In addition to the sum of the enthalpy derivatives of the components, the calculated expression for the heat capacity of the dissociated steam also includes the sum of the derivative parts of the mixture components and the quadratic dependence on the molecular mass of the mixture \([3]\).

\[
C_p = \frac{1}{M_{CM}} \left[ \sum_i \left( \frac{\partial H}{\partial T} \right)_p x_i + \sum_i H_i \left( \frac{\partial x_i}{\partial T} \right)_p \right] \frac{H_{CM}}{M_{CM}^2} \sum_i M_i \left( \frac{\partial x_i}{\partial T} \right)_p
\]  

(5)

In accordance with expression (5), due to a change in the composition of the components during the chemical reaction, the heat capacity of the dissociated steam differs significantly from the heat capacity of the undissociated steam.

The thermodynamic properties of the dissociated water steam formed during reactions (1) are represented by detailed tables in the reference book published by N.B. Vargaftika on the thermophysical properties of gases and liquids \([4]\) at a reference temperature of 0 K. All thermodynamic properties, except for the caloric parameters, do not depend on the reference temperature. Using the standard heat of formation at a temperature of 298.15 \([7]\), the authors compiled tables of caloric parameters starting from 0°C \([6]\).
On the basis of these tables [4–6], the authors developed a system of equations for calculating the properties of dissociated water steam over a pressure range of 0.01–10 MPa and a temperature range of 1250–2300 K [9]. The properties of H$_2$O as a component of the mixture are calculated from previously published equations [10].

In the current study, the authors have developed a system of equations to determine the properties of dissociated water steam over a pressure range of 0.1–10 MPa and a temperature range of 2200–3600 K using previously reported tables [4–6].

To develop these equations, an analysis was conducted of the tabulated functions [4–6] that determine the dependence of the caloric parameters and heat capacity on the thermal parameters of the dissociated steam. Using the method of numerical differentiation for the given tabular functions, calculations of the first and second derivatives of these functions with respect to temperature were performed. It was established that the second derivative of the functions under consideration could change the sign (+/-) or substantially change the value over a certain range of pressures and temperatures. This indicated a significant change in the curvature of the function over these intervals. This functional dependence of the parameters on changes in temperature and pressure was in accordance with equations (1)–(5) and was explained by a change not only in the thermophysical properties, but also by the inconsistency of these changes with the changes in the composition of the mixture. Over the range of pressures and temperatures under consideration, the fraction of undissociated water steam in the mixture varied from 17.06% at a pressure of 0.1 MPa to 99.42% at a pressure of 10 MPa [4]. To reduce the deviation in the properties of dissociated steam calculated from the tabulated equations, the region of investigated parameters was divided into subregions.

The use of one equation for calculating the properties of dissociated steam across the temperature and pressure ranges under consideration with a large degree of dissociation leads to significant deviations from the values presented in the previously reported tables [4, 6].

To calculate the thermodynamic parameters of the dissociated steam, a system of equations was constructed based on the Gibbs energy equation.

In the equations being developed, changes in the properties of the steam during dissociation due to the decay of its molecules and the formation of new substances were taken into account by corrections to the equations. With a decrease in pressure and an increase in temperature, the effect of corrections on the properties of the dissociated steam increased and the deviations of the dissociated steam from the undissociated steam also increased.

In the equations being developed, changes in the properties of the steam during dissociation were determined by corrections to the equations for undissociated steam separately from the calculations of Gibbs energy, entropy, enthalpy, heat capacity, and specific volume.

To estimate the uncertainty of the properties for dissociated steam, a previous study [4] used the generalized error of the calculated properties of gases outside of the experimental studies presented in [11]. In the calculated range of parameters with a confidence level of 95%, we assumed the following uncertainty intervals: for enthalpy ± 3 kJ/kg, entropy ± 0.02 kJ/(kg·K), isobaric heat capacity ± 0.01 kJ/(kg·K), and specific volume ± 0.2%. The standard uncertainty of the input quantities used to develop the system of equations was determined by assuming the coefficient for the normal distribution to be 1.96 [12]. In accordance with the adopted coefficient, the standard uncertainties of the input tabular values were: enthalpy – $u(h)$ = 1.5 kJ/kg, entropy – $u(s)$ = 0.01 kJ/(kg·K), isobaric heat capacity – $u(c_p)$ = 0.005 kJ/(kg·K), and specific volume – 0.1%. The standard uncertainty of the output values calculated from the compiled equations was found using the deviations as the differences in the values presented in the reference tables [4] and was calculated using the equations. The standard uncertainty values of the output variables with a confidence level of 95% were: enthalpy – 0.08%, entropy – 0.05%, isobaric heat capacity – 0.13%, and specific volume – 0.07%.

4. Conclusions

1. Existing tables of the thermodynamic properties of dissociated water steam are based on the six components of the mixture involved in the elementary chemical reactions (excluding HO$_2$ radicals and
hydrogen peroxide $\text{H}_2\text{O}_2$). The calculations showed that at pressures over 100 MPa and temperatures exceeding the temperature of burning hydrogen, it is necessary to consider all of the components in the chemical reactions.

Excluding components $\text{HO}_2$ and $\text{H}_2\text{O}_2$ at a pressure of 100 MPa and a maximum temperature of hydrogen combustion, the calculation of the composition of the mixture of dissociated steam showed additional inaccuracy of 0.09%. At higher temperatures of water steam (e.g. 5500 K), this level of inaccuracy increased to 0.2%.

For calculating the properties of dissociated steam for industrial use at pressures of less than 100 MPa, a temperature equal to or less than the temperature of burning hydrogen was sufficient to consider a mixture of six components.

2. On the basis of the equation for Gibbs energy with corrections for the dissociation of steam using differential equations of thermodynamics, equations were compiled to calculate the enthalpy, entropy, heat capacity, and specific volume with or without regard to the specific volume. The calculation of the composition of the mixture of dissociated steam was carried out taking into account the dynamic changes in the composition of a chemically reacting mixture.

Acknowledgments

The work was funded by the Russian Scientific Foundation (grant no. 15-19-10027).

References

[1] Zel'dovich Ya B, Barenblatt G I, Lavrovich V B and Makhviladze G M 1980 Mathematical theory of combustion and explosion (Moscow: Nauka) p 478 [in Russian]

[2] Korolchenko A Ya 2007 Processes of combustion and explosion (Moscow: Poznauka) p 266 [in Russian]

[3] Kessel'man P M, Blank Yu I, Mogilevskii V I 1968 Thermodynamic properties of thermally dissociated water steam at temperatures of 1600–6000 K and pressures of 0.1–1000 bar High Temp. 6(4) 658–64

[4] Vargaftik N B 1972 Tables on the Thermophysical Properties of Liquids and Gases: In Normal and Dissociated States (Moscow: Nauka, 1972; Washington: Hemisphere, 1975) p 758

[5] Aminov R Z, Gudym A A 2014 Calculating the caloric properties of dissociated steam at high temperatures Thermal Engineering 61(11) 822–8 doi:10.1134/S004060151409002X

[6] Aminov R Z, Gudym A A 2016 Lookup tables properties dissociated water steam from the reference temperature of 0°C Proc. of Akademenergo 4 67–76 [in Russian]

[7] Gurvich L V, Veit'z I V, Medvedev V A et al. 1978 Thermodynamic properties of individual substances: Handbook. Methods for calculating thermodynamic properties (Moscow: Nauka) Vol. 1, Part 1 p 496 [in Russian]

[8] Gurvich L V, Veit'z I V, Medvedev V A et al. 1978 Thermodynamic properties of individual substances: Handbook (Moscow: Nauka) Vol. 1, Part 2 p 328 [in Russian]

[9] Aminov R Z, Gudym A A 2017 Equations for Calculating the Properties of Dissociated Steam Thermal Engineering 64(8) 597–603 doi:0.1134/S004060151708002X

[10] Alexandrov A A 1998 System of equations IAPWS-IF-97 to calculate the thermodynamic properties of water and steam in industrial calculations. Part 1. Basic equations Thermal Engineering 46 782–790

[11] Zubarev V N, Kozlov A D, Kuznetsov V M, Sergeeva L V, Spiridonov G A 1989 Thermophysical properties of technically important gases at high temperatures and pressures: Handbook (Moscow: Energoizdat) p 232 [in Russian]

[12] ISO/IEC Guide 98-3:2008 Uncertainty of measurement. Part 3. Guide to the expression of uncertainty in measurement (GUM:1995)