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Uncertainty estimation of the mean specific heat capacity for the major gases contained in biogas

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Abstract: The paper is focused on the uncertainty estimation of the mean isobaric and isochoric specific heat capacity calculation. The differences in the data among the individual sources for the technical calculation are presented in the first part of the paper. These differences are discussed in this paper. Research of scientific work with listed values of measurement uncertainties has been carried out in the second part of the paper. Furthermore, mathematical models were calculated which describe the dependence of the specific heat capacities and temperature. The maximal error models were carried out. Two approaches were used for the calculation of the mean specific heat capacity. The first approach is the calculation with help of integration of the function which describes the dependence of the specific heat capacity and temperature. The second approach is the calculation of a simple arithmetic mean of the specific heat capacity related to the maximal and minimal value of the temperature interval. The conclusion of the work shows that the time-effective second way is applicable in the case of a narrow temperature range. A value of 5.5% (Δ_t = 200 K) was reached for the relative uncertainty. This is a similar value to that in the case of using the first way.

Keywords: enthalpy; energy; mathematical model; error models

Generally, the specific heat capacity is an important physical quantity which is used in thermodynamic calculations. These include the calculation of the change in the gas specific enthalpy, the determination of the adiabatic exponent, etc. Heat capacities are also used to correlate the main thermodynamic properties including the phase equilibrium, to further check the validity of existing equations of state or to even develop new ones (Dordain et al. 1995). The knowledge of the specific heat capacity of various gases is also important for determining the specific heat capacity of their mixture. These include, for example, biogases (Vitázek et al. 2016). The specific heat capacity of a real gas is a function of temperature and pressure. The function describing the dependence of the specific heat capacity is not always monotonous throughout the temperature range. The dependence of the isobaric specific heat capacity of water vapour on the temperature is an example of this. In this case, the dependence is expressed by a polynomial. On the other hand, the dependence of the isobaric specific heat capacity on the pressure is linear (Vestfálová, Šafařík 2016).

Generally, the influence of pressure on the value of the specific heat capacity is considerable. For example, the isobaric specific heat capacity of air at atmospheric pressure is c_p = 1 004.9 J·kg^{-1}·K^{-1}. The value of c_p is 1 256.1 J·kg^{-1}·K^{-1} when the pressure will increase to the value of 30 MPa (Jastržembskij 1954). However, the influence of pressure is decreased when the temperatures of the gas are higher (Jastržembskij 1954; Hála, Reiser 1971). This fact can be observed in the result of the paper by the authors Vestfálová and Šafařík (2016).

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The problem is often solved in the technical computation when the temperature and pressure of a working substance (gas) change during the process. The mean specific heat capacity of the gas is determined for this purpose. The dependence function of the specific heat capacity and temperature is necessary to know to determine the mean specific heat capacity. The information source (data) for the calculations is primarily professional literature or databases. These literature sources state values of the isobaric or isochoric specific heat capacity for the individual temperatures or polynomial ones (including coefficients) expressing the dependence of the value on the temperature or pressure. However, the values of the isobaric and isochoric specific heat capacities vary depending on the choice of literature or papers. These differences may be due to various factors: the original values were measured on different instruments with a different relative error; human error when rewriting from the original paper; rounding errors in unit conversions, etc. Given the above, every technical calculation is burdened with uncertainty. The choice of method of determining the mean specific heat capacity has the influence on the uncertainty value.

The aim of this paper is to determine uncertainty estimation during the calculation of the mean specific heat capacity depending on the method of its calculation.

MATERIAL AND METHODS

The literary source of Groda (1991) was selected to determine the functional dependence of the specific heat capacity and temperature. The advantage of this source is its comprehensive dataset for a wide temperature range.

A total of three types of gases were selected for the purpose of this paper: air, carbon dioxide, methane. These gases are widely used in technical practice. It is also about the gases, which are necessary to determine the thermodynamic and operating values of a biogas (Vitázek et al. 2016).

The dependence of the isobaric and isochoric specific heat capacities were described by several mathematical models: a polynomial of the second degree, the third degree and the fourth degree. The polyfit function (software Octave, version 4.4.0) was used to determine of the polynomial coefficients.

The mean specific heat capacity was calculated by a known mathematical relationship (Equation 1) (Kalčík 1963):

$$\left|c_s\right|_{t_1}^{t_2} = \frac{1}{t_2 - t_1}\int_{t_1}^{t_2} c \times dt \qquad (1)$$

where: c – function of temperature (t).

The combined uncertainty was determined in accordance with the Guide to the Expression of Uncertainty in Measurement (JCGM – the Joint Committee for Guides in Metrology – 2008) using the following relationship (Equation 2):

$$u_c = \sqrt{u_A^2 + u_B^2} \qquad (2)$$

where: u_A – uncertainties of type A; u_B – uncertainties of type B.

The expanded uncertainty is determined by the following relationship (Equation 3):

$$U = k_r \times u_c \qquad (3)$$

where: k_r – coverage factor; u_c – combined uncertainity.

It is assumed that the data comes from a normal distribution. The coverage factor $k_r = 2$ is set. It means that there is a 95% probability that the real value is within the interval $x \pm U$.

RESULTS AND DISCUSSION

It can be assumed that the values stated in professional literature are burdened by error. Among others, it is the error of the measurement and subjective or random errors. Table 1 shows the values of the isobaric and isochoric specific heat capacities at various temperatures from various measurements by the authors of the presented publications. Sources that are available and used in technical practice were selected for the purpose of the mutual comparison. In general, these literary sources are characterised in that the pressure values at which c_v and c_p were determined are not mentioned in most cases. That is probably why various values of c_v and c_p are presented for the same temperature in some cases.

The differences are evident from this table. For example, the c_p values of air range from 1 001 J·kg^{-1}·K^{-1} to 1 006 J·kg^{-1}·K^{-1} at the temperature of 0 °C. This relative difference is about 0.5%. The index of change among the highest and lowest value is about 2% with carbon dioxide. The measurement error in source publications can be one of the possible reasons of

Table 1. The values of the isobaric and isochoric specific heat capacities of the selected gases

Source	Gas	t (°C)	c_p (J·kg^{-1}·K^{-1})	c_v (J·kg^{-1}·K^{-1})	κ
Brož et al. 1980	air	20	1 006.4	–	1.402
	oxygen	20	917.0	–	1.398
	carbon dioxide	20	837.0	–	1.293
	methane	20	2 219.0	–	1.308
Mikulčák et al. 1970	air	15	1 005	–	1.400
	oxygen	15	912	–	1.401
	carbon dioxide	15	833	–	1.304
	methane	15	2 212	–	1.310
Vohlídal et al. 1999	air	20	1 004.5	717.50	–
	oxygen	0	916.6	–	1.400
		20	918.8	–	
	carbon dioxide	25	843.0	654.60	1.288
	methane	25	2 201.0	–	–
Groda 1991	air	0	1 001.0	–	1.400
			1 003.6	716.40	–
	oxygen	0	913.0	–	1.400
			914.8	654.80	–
	carbon dioxide	0	825.0	–	1.310
			814.8	625.90	–
	methane	0	2 177.0	–	1.300
			2 165.4	1 647.10	–
Engineering Toolbox	air	20	1 006.1	717.67	–
		0	1 006.0	717.1	–
Pavelek et al. 2003	air	0	1 005.0	714.00	1.402
	oxygen	0	917.0	657.00	1.400
	carbon dioxide	0	821.0	628.00	1.310
	methane	0	2 173.0	1 675.00	1.300
Kalčík 1963	air	0	1 004.0[a]	716.60[a]	–
	oxygen	0	914.3[a]	654.20[a]	–
	carbon dioxide	0	810.9[a]	622.00[a]	–
Ražnjevič 1969	air	0	1 003.6[b]	716.40[b]	1.400[b]
		20	1 013.0	–	
	oxygen	0	914.8	654.80	1.400
	carbon dioxide	0	814.8	625.90	1.310
	nitrogen	0	1 039.2	742.30	1.400
Chyský 1977	air	0	1 004.0	–	–
		0	1 005.0[b]	–	–
		20	1 013.0[c]	–	–
Cihelka 1969	air	0	1 004.8[a]	–	–
		20	1 009.0[b]	–	–

[a]the values were converted from kcal·kp^{-1}·deg; [b]the value is valid for a pressure of 98 kPa; [c]the source states a deviation value of ± 13 J·kg^{-1}·K^{-1}; κ – adiabatic index

the differences between these values. The measurement errors may come from several sources: an error of the mass flow measurement, a pressure measurement, a temperature measurement, the choice of the heating method. The source of errors can vary in dependence on the choice of measurement

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instruments (Magee 1994; Kubota et al. 1995). Table 2 represents the maximal deviation of the measured quantities according to the selected authors.

The highest deviation was estimated at the value of 2.4% (Kagawa et al. 2012), which is evident from Table 2. It is similar to the value of deviation as in the first case. Table 1 shows the highest value index of change to be 1.7% with carbon dioxide and a temperature of 0 °C.

In the case of the calculation of change for some thermodynamic quantities (such as the change of specific enthalpy) in dependence on the temperature, the determination of the mean specific heat capacity is necessary. As mentioned above, the determination of the change of the specific enthalpy is very important for the thermodynamic analyses of various systems. These are, for example, the analysis of an ideal cycle of a combustion engine (Vitázek et al. 2016b) or an exergy analysis (Adamovský et al. 2004). The calculation of the change of the specific enthalpy including a deviation may have a fundamental influence on the interpretation of the results.

The mean specific heat capacity is calculated by Equation (1), i.e., by integration of the function describing the dependence of the specific heat capacity and temperature multiplied by the reciprocal value of the temperature difference. The determination of the function (mathematical model) is decisive in this calculation. The dependence of the isochoric and isobaric specific heat capacity on a temperature is evident from Tables 1–3.

The accuracy of the mathematical models describing the dependence of the specific heat capacity and the temperature is given by the type of function, which we decided to use. The difference among the measured point and the calculated point can be various in dependence on the type of the function. Is evident that the accuracy of the mathematical model will have an influence on the final uncertainty value. The approximation by the polynomial function of the second, third and fourth degree was carried out for three types of gases: air, carbon dioxide and methane. These gases belong to most widely used ones in technical practice. The polynomial's coefficients were determined by the least squares method. The results are stated in Table 3. The graphical expression of the dependence of the specific heat capacities and temperature is given by Figure 1. The polynomials of the fourth degree achieved the lowest deviation value (MME – maximum model error) between the measured and calculated values according to the assumption (Table 3).

Generally, the model shows greater inaccuracy at the starting point, i.e., for a temperature of 0 °C. The isochoric specific heat capacity deviation is 12.07% in the case of carbon dioxide. However, the deviation is only 3.87% when the starting point will not be included. The differences among the values of the maximal deviation including the starting point and excluding starting point can be compared with help of Table 3. Here again, the higher the degree of the polynomial, the lower the difference between these deviations is (Figure 1A).

Table 4 presents the values of the isochoric and isobaric mean specific heat capacities which are calculated using the a polynomial second, third and fourth degree. The calculation is executed for three, or two various temperature intervals. Furthermore, the values of the mean specific heat capacity calculated with the use of the simple arithmetic mean are stated in this table. It is the way which is preferred because of the speed of the calculation. The inaccuracy, compared to the previous procedure, is its disadvantage. Deviations between the solutions when

Table 2. The values of the maximal deviation of the measured quantities

M.Q.	Substance	Used device	Max. temp.	Max. press.	Max. deviation	Source
			(K)	(MPa)	(%)	
C_v	chlorotrifluoromethane	–	350	35	> 2.0	Magee et al. 2000
C_p	difluoromethane	flow calorimeter	343	0.5	> 1.0	Kubota et al. 1995
C_v	air	–	300	35	± 2.0	Magee 1994
C_p	ammonia vapour	flow calorimeter	423	2.03	> 2.0	Osborne et al. 1924
c_p	difluoromethane	flow calorimeter	353.15	2.4	1.3–2.4	Kagawa et al. 2012
c_p	pentafluoroethane	flow calorimeter	333.15	2.4	1.3–2.3	Kagawa et al. 2011

M.Q. – measurement quantity; C_v – the molar heat capacity at a constant volume; C_p – the molar heat capacity at a constant pressure; c_p – the specific heat capacity at a constant pressure (J·kg^{-1}·K^{-1})

Table 3. The values of the polynomial coefficients representing the dependence of c_p, c_v and temperature

Substance	Quantity	Degree	Polynomial	MME* (%)	MME** (%)
Air	c_p	2	$-4.8311 \cdot 10^{-8} \times t^2 + 2.37056358 \cdot 10^{-4} \times t + 0.98113736264$	2.24	1.27
		3	$4.1453 \cdot 10^{-12} \times t^3 - 6.3856 \cdot 10^{-8} \times t^2 + 2.5230 \cdot 10^{-4} \times t + 0.98625$	1.73	1.11
		4	$2.0283 \cdot 10^{-14} \times t^4 - 9.7272 \cdot 10^{-11} \times t^3 + 9.7108 \cdot 10^{-8} \times t^2 + 1.6682 \cdot 10^{-4} \times t + 0.99505$	0.86	0.68
	c_v	2	$-4.86 \cdot 10^{-8} \times t^2 + 2.37693205 \cdot 10^{-4} \times t + 0.701967094017$	2.01	1.46
		3	$4.3343 \cdot 10^{-12} \times t^3 - 6.4854 \cdot 10^{-8} \times t^2 + 2.5363 \cdot 10^{-4} \times t + 0.69898$	2.43	1.52
		4	$2.0194 \cdot 10^{-14} \times t^4 - 9.6633 \cdot 10^{-11} \times t^3 + 9.5396 \cdot 10^{-8} \times t^2 + 1.6853 \cdot 10^{-4} \times t + 0.70773$	1.21	0.97
Carbon dioxide	c_p	2	$-1.3728 \cdot 10^{-7} \times t^2 + 0.00052677817 \times t + 0.89040103785$	9.28	3.08
		3	$7.6130 \cdot 10^{-11} \times t^3 - 4.22771843 \cdot 10^{-7} \times t^2 + 8.06708935184 \cdot 10^{-4} \times t + 0.837871197002232$	2.83	1.21
		4	$-3.9434 \cdot 10^{-14} \times {}^{4} + 2.7330 \cdot 10^{-10} \times t^3 - 7.3571 \cdot 10^{-7} \times t^2 + 9.7289 \cdot 10^{-4} \times t + 0.82077$	0.73	0.47
	c_v	2	$-1.3725 \cdot 10^{-7} \cdot t^2 + 0.00052674788 \cdot t + 0.70145787546$	12.07	3.87
		3	$7.5947 \cdot 10^{-11} \times t^3 - 4.22049723 \cdot 10^{-7} \times t^2 + 8.06006191257 \cdot 10^{-4} \times t + 0.649054220874911$	3.70	1.49
		4	$-3.9368 \cdot 10^{-14} \times t^4 + 2.7279 \cdot 10^{-10} \times t^3 - 7.3446 \cdot 10^{-7} \times t^2 + 9.7191 \cdot 10^{-4} \times t + 0.63198$	0.97	0.60
Methane	c_p	2	$-1.0515 \cdot 10^{-6} \times t^2 + 4.0252710 \cdot 10^{-3} \times t + 2.0941173077$	3.29	1.79
		3	$-8.2042 \cdot 10^{-10} \times t^3 + 3.0217560 \cdot 10^{-7} \times t^2 + 3.45507757058 \cdot 10^{-3} \times t + 2.13472820512821$	1.42	1.39
		4	$2.0218 \cdot 10^{-12} \times t^4 - 5.2683 \cdot 10^{-9} \times t^3 + 3.3666 \cdot 10^{-6} \times t^2 + 2.7752 \cdot 10^{-3} \times t + 2.1576$	0.36	1.06
	c_v	2	$-1.0513 \cdot 10^{-6} \times t^2 + 4.0250824 \cdot 10^{-3} \times t + 1.5758170330$	4.33	2.20
		3	$-8.2075 \cdot 10^{-10} \times t^3 + 3.0289710 \cdot 10^{-7} \times t^2 + 3.45466400266 \cdot 10^{-3} \times t + 1.61644395604396$	1.86	1.76
		4	$2.0214 \cdot 10^{-12} \times t^4 - 5.2678 \cdot 10^{-9} \times t^3 + 3.3667 \cdot 10^{-6} \times t^2 + 2.7749 \cdot 10^{-3} \times t + 1.6393$	0.47	1.17

*the maximum model error (except for 0 °C); **the maximum model error (including 0 °C); t – temperature (°C); c_p – the specific heat capacity at a constant pressure [$\mathrm{J \cdot kg^{-1} \cdot K^{-1}}$]; c_v – the specific heat capacity at a constant volume [$\mathrm{J \cdot kg^{-1} \cdot K^{-1}}$]

using the polynomial of the fourth degree and the simple arithmetic mean are stated in Table 4. In general, the error increases, the higher the temperature interval is. However, it is not always the rule. This is the case, for example, of air. Here, a slight decrease occurred. The shape of the curve determining the dependence between the specific heat capacity and the temperature has considerable influence. It is evident, that the more the curve will resemble a linear function, the lower the deviation will be (Table 4.).

From the above-mentioned information, it is clear that the stated deviation has influence on the final uncertainty value of the mean specific heat capacity. Furthermore, a conservative approach will be applied and we will accept the simplification of the assumption (i.e., the final uncertainty is only influenced by the model error and maximal measurement error). Under these assumptions, consider the measurement error of 2.4% and an error model 1.21% (in the case polynomial of fourth degree). Then the final uncertainty value was determined as an expanded uncertainty in the case of direct measurement, i.e., the square root of the sum of quadrates of the individual uncertainties/errors (Vdoleček et al. 2001). The spread coefficient was set to $k_r = 2$. In the case the resulting uncertainty, $U = 5.4\%$. The value of the relative deviation is 0.5% for the temperature interval of 200 K in the case of the calculation using the simple arithmetic mean. The relative deviation is 5% for a temperature interval of 900 K, respectively 12%,

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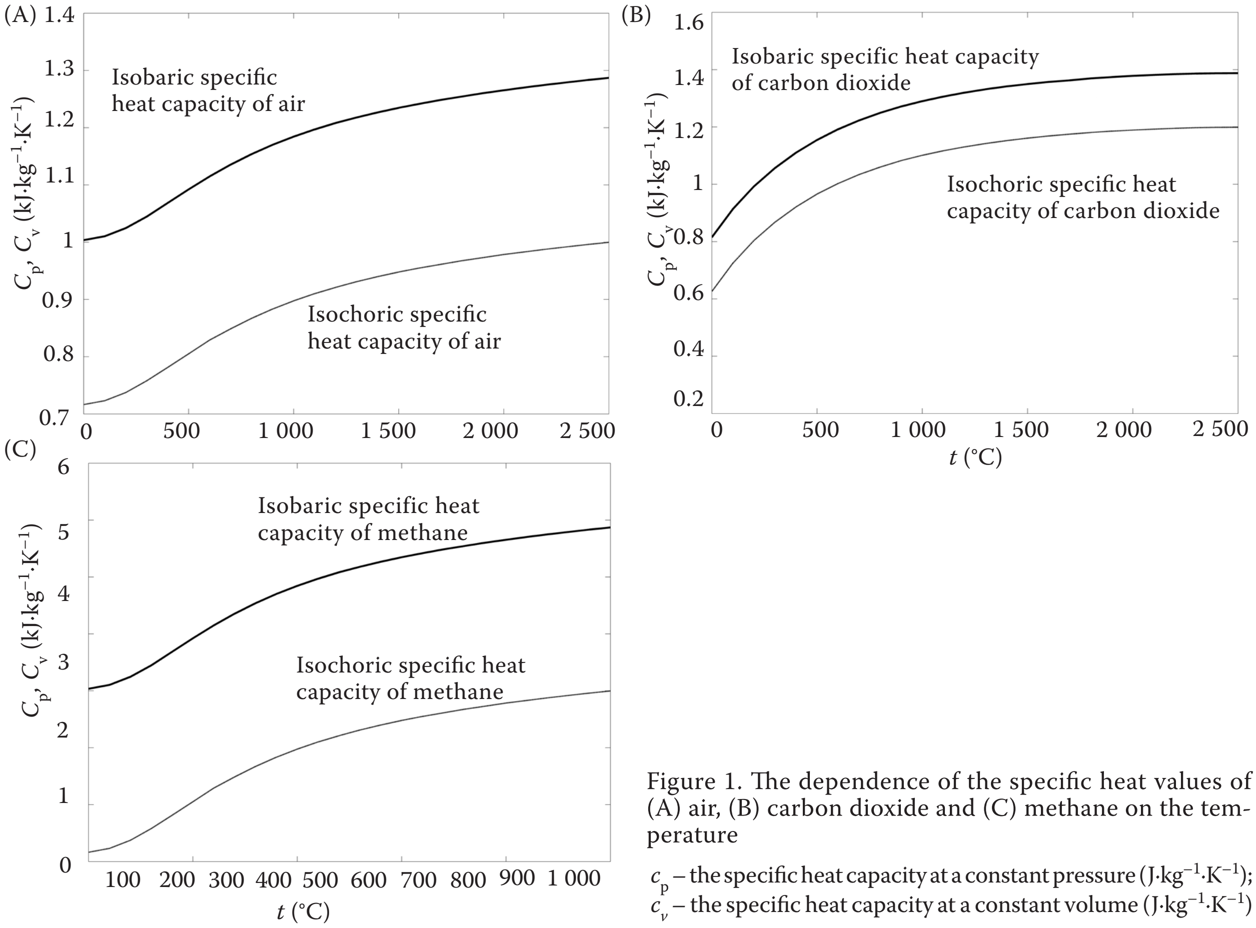

Figure 1. The dependence of the specific heat values of (A) air, (B) carbon dioxide and (C) methane on the temperature

c_p – the specific heat capacity at a constant pressure (J·kg^{-1}·K^{-1}); c_v – the specific heat capacity at a constant volume (J·kg^{-1}·K^{-1})

Table 4. The values of the mean specific heat capacities calculated by the various methods

Substance	Quant.	Temp. range	Mean specify heat capacity (kJ·kg^{-1}·K^{-1})				Deviation*
		(°C)	degree 2	degree 3	degree 4	mean value**	(%)
Air	c_p	100–300	1.02646	1.03398	1.03170	1.02745	0.41
		100–1 000	1.09364	1.10254	1.10022	1.09735	0.26
		100–2 500	1.18448	1.19254	1.19190	1.14865	3.63
	c_v	100–300	0.74740	0.74694	0.74465	0.74045	0.56
		100–1 000	0.81472	0.81568	0.81337	0.81035	0.37
		100–2 500	0.90551	0.90560	0.90497	0.86145	4.81
Carbon dioxide	c_p	100–300	0.98981	0.98165	0.98610	0.98981	0.1
		100–1 000	1.12934	1.14628	1.15079	1.12934	4.26
		100–2 500	1.27732	1.27895	1.28018	1.27732	10.11
	c_v	100–300	0.80086	0.79273	0.79717	0.79630	0.11
		100–1 000	0.94039	0.95729	0.96180	0.91290	5.08
		100–2 500	1.08840	1.09004	1.09129	0.96190	11.86
Methane	c_p	100–300	2.85361	2.83063	2.81074	2.81185	0.04
		100–1 000	3.91896	3.80726	3.91562	3.7549	4.1
	c_v	100–300	2.33528	2.31229	2.29238	2.29350	0.05
		100–1 000	3.40063	3.40062	3.39724	3.23660	4.73

*the ratio between the absolute error and the value "degree 4" multiplied by a hundred; **the arithmetic mean of the specific heat capacity for the maximal and minimal value of the temperature interval; c_p – the specific heat capacity at a constant pressure (J·kg^{-1}·K^{-1}); c_v – the specific heat capacity at a constant volume (J·kg^{-1}·K^{-1})

for a temperature interval of 2 400 K. The resulting uncertainty then is U_{200} = 5.5%, U_{900} = 11.4% and U_{2400} = 24.6%. From the results, it is evident that the uncertainty is considerable in the case where the temperature interval is wide.

In the case calculating thermodynamic quantities (for example, the change in specific enthalpy), it is appropriate to indicate the uncertainty of the calculated value. For example, let us consider calculating the difference of the specific enthalpy of air for the temperatures t_1 = 100 °C and t_2 = 300 °C at constant pressure. Then the resulting value can be written as follows: $i = (205.5 \pm 11.3)\ \text{kJ}\cdot\text{kg}^{-1}$. However, this applies when the mean specific heat capacity is determined by the simple arithmetic mean. Furthermore, this result is valid when no other quantities appear in the equation, which is burdened by the error. For example, the mass of the gas must be determined for the calculation of the enthalpy difference. However, the mass measurement is burdened by an error too. This error must be included into the calculation of the widespread uncertainty also.

CONCLUSION

The calculation of the mean specific heat capacity is burdened by errors which can have several sources. These sources include: the measurement error of the thermodynamic quantity, the model error, the calculation method of the mean specific heat capacity. The resulting uncertainty of the mean specific heat capacity calculation can be estimated in the case of knowledge of these errors. Generally, the higher the polynomial degree, the lower the model error and the value of resulting uncertainty.

The calculation of the mean specific heat capacity when using knowledge of the functional dependence of the specific heat capacity and temperature is time consuming. From this reason, the mean specific heat capacity is often calculated as the arithmetic mean of the specific heat capacities for the maximum and minimum values of the temperature interval. The resulting uncertainty increases as the result of this choice. From the result of this paper, it is evident that the resulting uncertainty determined by using the polynomial of the fourth degree is estimated to be U = 5.4%. The resulting uncertainty is U = 5.5% if the mean specific heat capacity is determined as the simple arithmetic mean for a temperature interval of 200 K. However, the uncertainty estimation quickly increases with an increasing temperature difference. The uncertainty estimation is U = 24.6% when the temperature difference is 2 400 K. The calculation of the mean specific heat capacity when using the arithmetic mean can be recommended for a narrow temperature interval, up to about 200 K.

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