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Ideal-Gas Thermodynamic Properties for Natural-Gas Applications

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Calculating caloric properties from a thermal equation of state requires information such as isobaric heat capacities in the ideal-gas state as a function of temperature. In this work, values for the parameters of the c_p^0 correlation proposed by Aly and Lee were newly determined for 21 pure gases which are compounds of natural gas mixtures. The values of the parameters were adjusted to selected c_p^0 data calculated from spectroscopic data for temperatures ranging from 10 to 1000 K. The data sources used are discussed and compared with literature data deduced from theoretic models and caloric measurements. The parameters presented will be applied in a current GERG project for evaluating equations of state (e.g., the AGA 8 equation) for their suitability for calculating caloric properties.

KEY WORDS: caloric properties; equation of state; ideal gas; isobaric heat capacity; natural gas; speed of sound.

1. INTRODUCTION

High-accuracy thermodynamic property calculation methods are needed for a wide variety of applications in the gas industry. Areas of applications are (i) flow metering using critical nozzles, orifice meters, or ultrasonic flowmeters, (ii) process simulation such as gas-storage simulation, evaluation of compressor performance tests, or design of interstage coolers, and (iii) energy-flow measurements, which might be simplified by measuring speed of sound instead of gross calorific value.

For these applications, an improved fundamental equation of state is needed. Therefore, a GERG working group (Groupe Européen de Recherches Gazières) was set up to focus on this problem. The objective of

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the GERG project is to recommend a fundamental equation using a molar composition analysis which can accurately and reliably calculate speed-of-sound data and isobaric enthalpy changes of natural gas. The target uncertainty is less than 0.1% for speed of sound and 1 to 2% for isobaric enthalpy changes. The maximum pressure is 30 MPa and the temperature range is 250 to 350 K.

The work program consists of an experimental part and a theoretical part and is contracted to several groups. Speed-of-sound measurements are part of the experimental work and are being performed on three gases in four laboratories. The test gases used are methane, a binary mixture of methane (mole fraction of 0.85) and ethane (0.15), and a multicomponent natural gas. The contractors for the experimental work are Imperial College of Science, Technology and Medicine, London, UK, University College London, UK, Gaz de France, Paris, France, and Murdoch University, Murdoch, Australia. The GERG round-robin test on speed-of-sound data is supplemented by measurements of isobaric enthalpy changes for the three test gases at Karlsruhe University, Germany. The theoretical work of the project involves searching literature, setting up a data bank, collecting existing experimental data on speed of sound and isobaric enthalpy changes, comparing the round robin-data collected during testing, and testing of selected equations of state. Ruhr-University of Bochum, Germany, will be responsible for the theoretical work.

Ideal-gas isobaric heat capacity values need to be selected before testing the equations in question. During the subsequent phase of the GERG project, heat capacity values selected in this work work will be used in an assessment of equations of state using data on speed of sound and enthalpy changes.

2. FUNCTIONS FOR IDEAL-GAS ISOBARIC HEAT CAPACITIES

For the selection of the ideal-gas isobaric heat capacity values, the summarizing works of Laughton and Humphreys [1] and Savidge and Shen [2] were critically examined and compared with the original data published. To describe isobaric heat capacities in the ideal-gas state, the expanded approach of Aly and Lee [3] as proposed by Savidge and Shen [2] was adopted in this work.

$$\frac{c_p^0(T)}{R} = B + C\left\{\frac{D/T}{\sinh(D/T)}\right\}^2 + E\left\{\frac{F/T}{\cosh(F/T)}\right\}^2 + G\left\{\frac{H/T}{\sinh(H/T)}\right\}^2 + I\left\{\frac{J/T}{\cosh(J/T)}\right\}^2 \tag{1}$$

Table I. Numerical Values of the Parameters of Eq. (1) for Isobaric Heat Capacities in the Ideal-Gas State c_p^0/R for Pure Gases ($R = 8.31451\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$)

Gas	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*	*J*
Methane	4.00088	0.76315	820.659	0.00460	178.410	8.74432	1062.82	−4.46921	1090.53
N_2	3.50031	0.13732	662.738	−0.14660	−680.562	0.90066	1740.06		
CO_2	3.50002	2.04452	919.306	−1.06044	−865.070	2.03366	483.553	0.01393	341.109
Ethane	4.00263	4.33939	559.314	1.23722	223.284	13.1974	1031.38	−6.01989	1071.29
Propane	4.02939	6.60569	479.856	3.19700	200.893	19.1921	955.312	−8.37267	1027.29
n-Butane	4.33944	9.44893	468.270	6.89406	183.636	24.4618	1914.10	14.7824	903.185
Isobutane	4.06714	8.97575	438.270	5.25156	198.018	25.1423	1905.02	16.1388	893.765
n-Pentane	4	8.95043	178.670	21.8360	840.538	33.4032	1774.25		
Isopentane	4	11.7618	292.503	20.1101	910.237	33.1688	1919.37		
n-Hexane	4	11.6977	182.326	26.8142	859.207	38.6164	1826.59		
n-Heptane	4	13.7266	169.789	30.4707	836.195	43.5561	1760.46		
n-Octane	4	15.6865	158.922	33.8029	815.064	48.1731	1693.07		
n-Nonane	4	18.0241	156.854	38.1235	814.882	53.3415	1693.79		
n-Decane	4	21.0069	164.947	43.4931	836.264	58.3657	1750.24		
n-H_2	2.47906	0.95806	228.734	0.45444	326.843	1.56039	1651.71	−1.3756	1671.69
O_2	3.50146	1.07558	2235.71	1.01334	1116.69				
CO	3.50055	1.02865	1550.45	0.00493	704.525				
H_2O	4.00392	0.01059	268.795	0.98763	1141.41	3.06904	2507.37		
H_2S	4	3.11942	1833.63	1.00243	847.181				
Helium	2.5								
Argon	2.5								

Table II. Source of c_p^0 Data for Pure Gases Used in Correlating the Parameters of Eq. (1)

Gas	Source	Uncertainty (%)	Number of data	T range (K)	rms (%)[a]	Δc_p^0 max (%)[b]
Methane	McDowell [5]	0.03	34	60–1000	0.003	0.006
N_2	Hilsenrath [6]	0.02	11	50–1000	0.003	0.005
CO_2	Chao [7]	0.02	100	10–1000	0.001	0.003
Ethane	Chao [8]	0.1–0.3	14	50–1000	0.010	0.026
Propane	Chao [8]	0.3–0.5	14	50–1000	0.010	0.025
n-Butane	Chen [9]	0.5–1	17	50–1000	0.006	0.016
Isobutane	Chen [9]	0.1–0.2	18	50–1000	0.010	0.025
n-Pentane	TRC [10]	0.5–1	11	200–1000	0.037	0.095
Isopentane	TRC [10]	0.5–1	11	200–1000	0.026	0.053
n-Hexane	TRC [10]	0.5–1	10	200–1000	0.016	0.033
n-Heptane	TRC [10]	0.5–1	10	200–1000	0.005	0.011
n-Octane	TRC [10]	0.5–1	10	200–1000	0.003	0.006
n-Nonane	TRC [10]	0.5–1	10	200–1000	0.022	0.046
n-Decane	TRC [10]	0.5–1	10	200–1000	0.021	0.042
n-H_2	Schäfer [11]	0.05–0.1	16	100–1000	0.007	0.014
O_2	Baehr [12]	0.02	91	100–1000	0.003	0.006
CO	Baehr [12]	0.02	96	50–1000	0.003	0.007
H_2O	Woolley [13/14]	0.02–0.05	35	100–1000	0.004	0.009
H_2S	JANAF [15]	0.1–0.5	11	100–1000	0.012	0.019

[a] rms: root mean square error. $\text{rms} = 100 \sqrt{(1/n) \sum_{i=1}^{n} ((c_{\text{p exp}, i}^0 - c_{\text{p, cal}, i}^0)/c_{\text{p calc}, i}^0)^2}$.
[b] $\Delta c_{\text{p max}}^0$: maximum deviation. $\Delta c_{\text{p max}}^0 = 100 \max|(c_{\text{p exp } t, i}^0 - c_{\text{p calc}, i}^0)/c_{\text{p calc}, i}^0|$.

The parameters of the expanded Eq. (1) (see Table I) were determined for all pure gases needed for the AGA 8-DC 92 equation of state [4] in the maximum temperature range from 10 to 1000 K. For nitrogen, the parameters published by Savidge and Shen [2] were adopted. For noble gases, it is sufficient to use the first term only, since translation and rotation energies are already fully excited over the relevant temperature range. For 18 substances the parameters of Eq. (1) were correlated from selected literature data by minimizing the root mean square error (rms). The results are presented in Table II. The table lists the data sources [5–15], the estimated uncertainty of the original literature data, the number of selected data, the temperature range, the root mean square, and the maximum error.

The literature data selected have all been calculated from spectroscopic data. For simple molecules (e.g., nitrogen, oxygen) these data are often of greater accuracy than experimental c_p^0 values which are deduced from caloric measurements. For the hydrocarbon compounds butane to decane vibrational anharmonicities, centrifugal effects, and internal

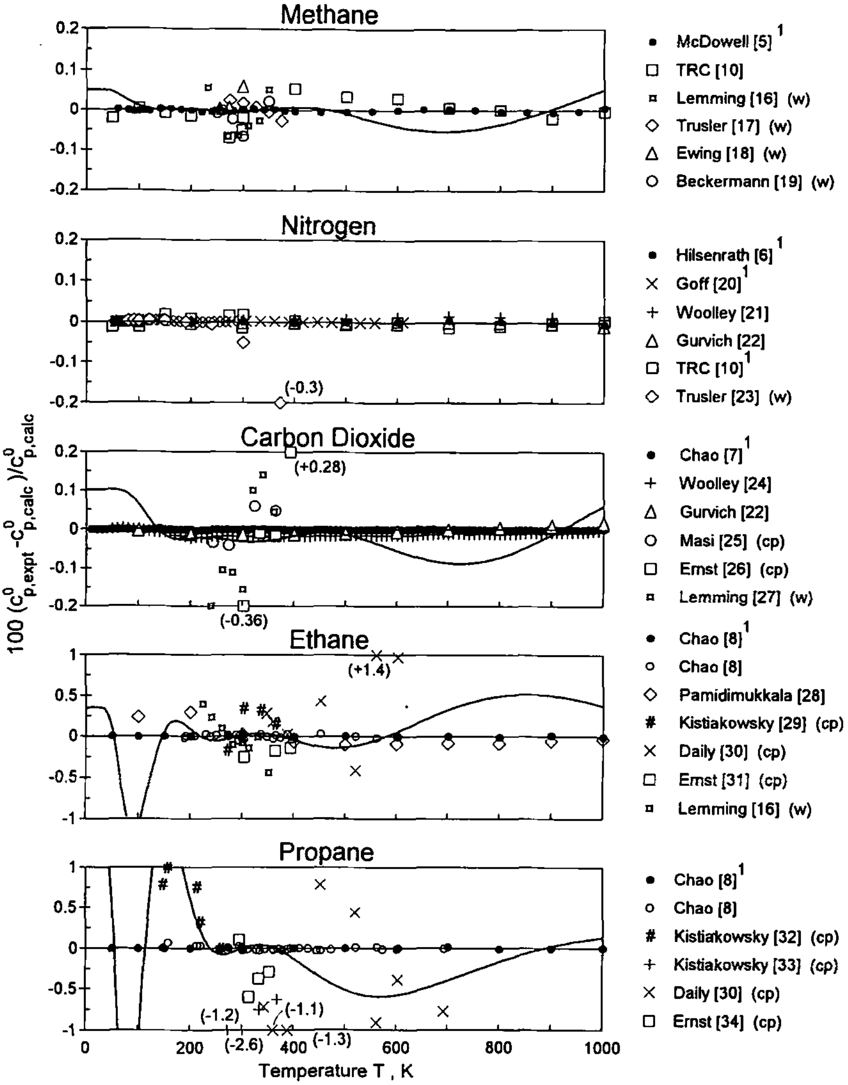

Fig. 1. Percentage deviation of reported ideal-gas isobaric heat capacity values from calculated values [Eq. (1)] for methane, nitroen, carbon dioxide, ethane, and propane, (——) equation of Savidge and Shen [2]. (cp) Experimental isobaric heat capacity values; (w) experimental values from speed-of-sound data.[1] Data used in correlating the parameters of Eq. (1).

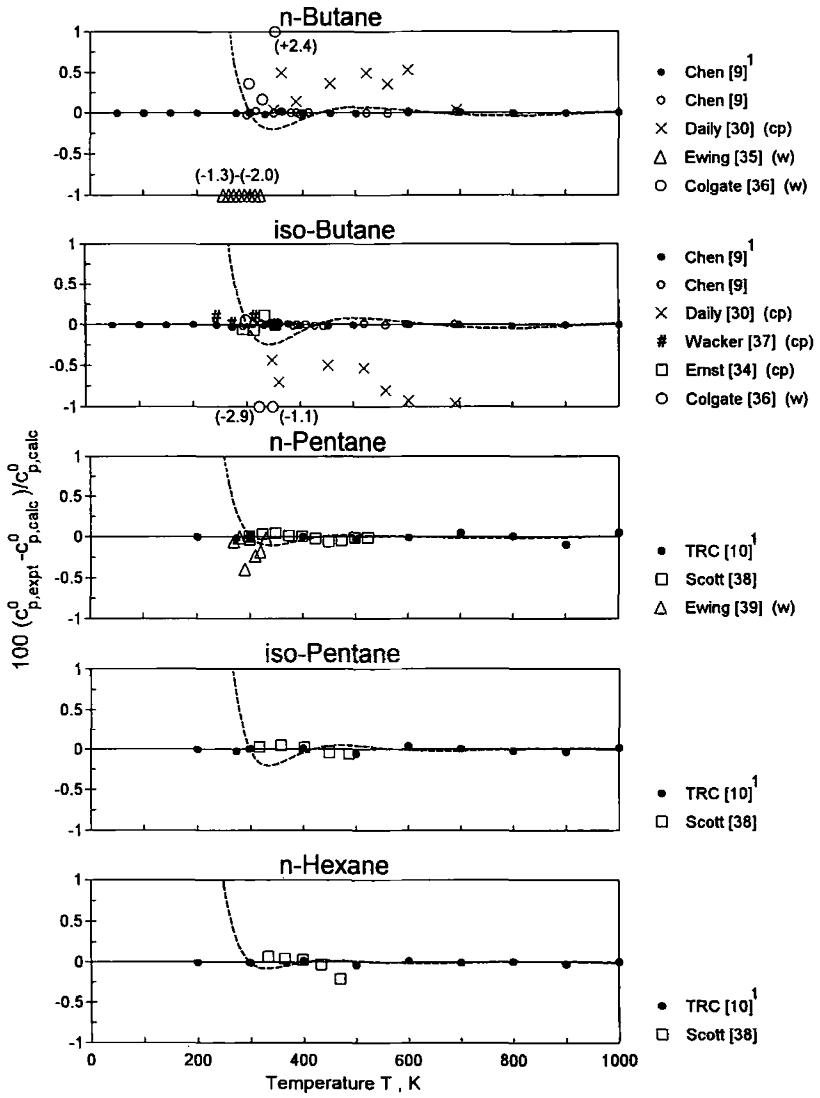

Fig. 2. Percentage deviation of reported ideal-gas isobaric heat capacity values from calculated values [Eq. (1)] for the hydrocarbon compounds butane to decane. (-----) Equation of Aly and Lee [3]. (cp) Experimental isobaric heat capacity values; (w) experimental values from speed-of-sound data.[1] Data used in correlating the parameters of Eq. (1).

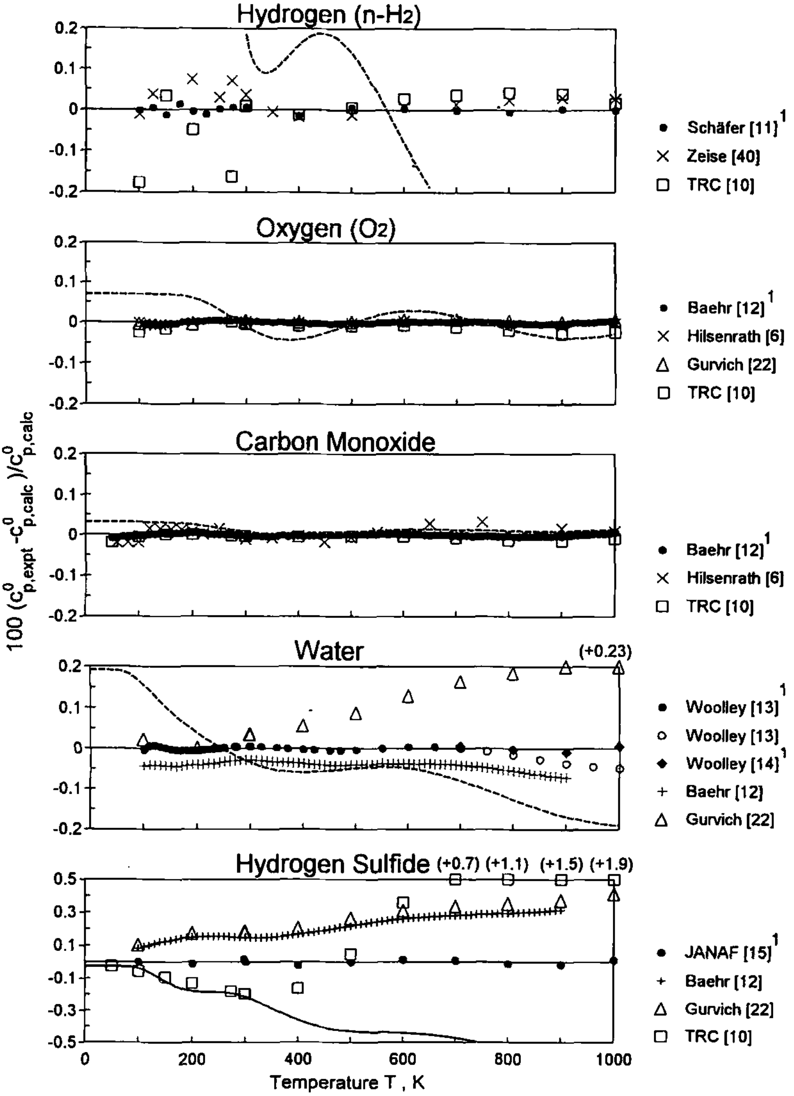

Fig. 3. Percentage deviation of reported ideal-gas isobaric heat capacity values from calculated values [Eq. (1)] for the anorganic compounds hydrogen, oxygen, carbon monoxide, water, and hydrogen sulfide. (-----) Equation of Aly and Lee [3]; (——) equation of Savidge and Shen [2].[1] Data used in correlating the parameters of Eq. (1).

rotations contribute significantly to isobaric heat capacities. These contributions to calculated values are usually adjusted to experimental values.

Due to this calculation procedure, the data are usually free from random errors and therefore the authors refrain from uncertainty statements. The uncertainties given in this work are estimated by comparison with other theoretical models and available experimental literature data. The values given represent an upper limit.

The selected number of parameters in Eq. (1) depends, e.g., on the uncertainty of the original literature data, the number of data available, and the temperature range to be adjusted. A maximum number of nine parameters in Eq. (1) was used mostly for the key pure components. For the hydrocarbon components pentane to decane, few data are available but still it was necessary to use seven parameters to follow the curved slope of $c_p^0(T)$. For simple molecules (e.g., oxygen, carbon monoxide) it was sufficient to adjust five parameters only.

The agreement (maximum deviation) of the values calculated from Eq. (1) with the data used in the correlation work is better than ±0.05% (except for *n*-pentane) and in many cases is even better than ±0.01% (e.g., methane, nitrogen, carbon dioxide). A more detailed comparison of literature data from different authors with calculated values [Eq. (1)] are given in Figs. 1 to 3. For this comparison isobaric heat capacities from spectroscopic data, experimental values, and values deduced from speed of sound data have been selected. Calculated values from the equation of Aly and Lee [3] or Savidge and Shen [2] are also presented.

2.1. Comparison for Methane, Nitrogen, Carbon Dioxide, Ethane, and Propane

For methane, the data of McDowell and Kruse [5] used in correlating the parameters of Eq. (1) are assumed to be the most accurate data. Their agreement with the data published in TRC [10] is within ±0.07% (Fig. 1). The data from Lemming [16], Trusler and Zarari [17], Ewing and Goodwin [18], and Beckermann [19], which are deduced from speed-of-sound measurements, do not deviate by more than ±0.06%. The data from Trusler and Zarari [17] even agree within ±0.025%.

For nitrogen, the parameters of Eq. (1) determined by Savidge and Shen [2] were adopted in this work. Their agreement with other data calculated from spectroscopic data is within ±0.015% (Fig. 1). The data from Trusler [23], deduced from speed-of-sound measurements, show an excellent agreement for temperatures between 80 and 240 K (±0.005%). At 300 K the deviation is −0.05%, and at 370 K −0.3%.

For carbon dioxide, the data from Chao [7] have been used. Agreement with the data calculated by Woolley [24] and Gurvich [22] is within the estimated uncertainty of ±0.02%. Experimental data from flow-calorimeter measurements agree within ±0.06% (Masi and Petkof [25]) and ±0.35% (Ernst et al. [26]). c_p^0 data determined from speed-of-sound measurements (Lemming [27]) scatter around ±0.1 to ±0.2%.

For ethane and propane the tabulated data of Chao et al. [8] were again adopted for correlating the parameters of Eq. (1). Some further data given in Chao's work for comparison reasons were not used for the correlation procedure but are presented in Fig. 1 to test Eq. (1) at intermediate temperatures [the maximum deviation of these data from Eq. (1) is ±0.05% due to the scatter of Chao's data]. The agreement of other experimental data with Chao's data is in general about ±0.5% for ethane and about ±1% for propane.

Results calculated from Eq. (1) and the parameters of Savidge and Shen [2] are also shown in Fig. (1). These parameters were correlated in the temperature range from 150 to 450 K. Within this temperature range the values calculated from Eq. (1) using their parameters agree in most cases with the original literature data within the estimated uncertainty. For higher temperatures, from 450 to 1000 K, the calculated values deviate at most 0.05% for methane, 0.1% for carbon dioxide, and 0.5% for ethane and propane from the literature data.

2.2. Comparison for the Hydrocarbon Compounds Butane to Decane

The data from Chen et al. [9] for *n*-butane show great inconsistency with the data from Ewing et al. [35] and Colgate et al. [36], which were determined from speed-of-sound measurements (see Fig. 2). Whereas the data from Ewing et al. [35] systematically show a negative deviation between −1.3 and −2%, the data from Colgate et al. [36] show a positive deviation of up to +2.4%. The relatively good agreement ($\leqslant \pm 0.5\%$) of Chen's data with the experimental data from Daily and Felsing [30] is expected, since the data from Daily and Felsing were used in Chen's calculation to adjust an empirical correction. To predict the true values for c_p^0 for *n*-butane, additional measurements would be necessary.

For isobutane more good-quality experimental data are available than for *n*-butane. The values from Wacker et al. [37] and Ernst and Büsser [34], which agree within ±0.1%, were used inter alia for the determination of Chen's [9] data.

For the hydrocarbon compounds pentane to decane, the parameters for Eq. (1) were adjusted to data published by TRC [10]. The TRC data were computed following Scott's [38] calculation procedure (group-contribution theory). In cases where experimental c_p^0 values were available, the calculation has been adjusted. Therefore (i) Scott's assumptions and (ii) the experimental data used to adjust contribute to the uncertainty of the computed data. The excellent agreement for *n*-pentane, isopentane, and *n*-hexane between calculated values from Scott and those from TRC (Fig. 2) most probably results from the same experimental data being used to adjust in both works.

The equation of Aly and Lee [3] was correlated for the most important pure components in natural gas in the temperature range from 300 to 1500 K (see Figs. 2 and 3). The temperature range from 250 to 350 K important for the gas industry is thus only partly covered. At 250 K, for example, the deviation of the equation of Aly and Lee [3] from the newly correlated equation of this work mostly exceeds 1%.

2.3. Comparison for Inorganic Compounds (Hydrogen, Oxygen, Carbon Monoxide, Water, Hydrogen Sulfide)

For hydrogen, oxygen and carbon monoxide the different data sets calculated from spectroscopic data in general show good agreement (see Fig. 3). The data of Schäfer and Auer [11] were selected for hydrogen and those of Baehr et al. [12] for oxygen and carbon monoxide.

For water, the data of Woolley [14] show significant differences against data from older works of Woolley [13] only for temperatures above 650 K. Due to the higher data density, therefore, the data of Woolley [13] were used for the 100 to 650 K range and the data of Woolley [14] for the 650 to 1000 K range.

For hydrogen sulfide, the data of JANAF [15] were used. The deviations from other data sets are less than ±0.2% for the 100 to 400 K range (see Fig. 3). For higher temperatures, the data from TRC [10] deviate by up to ±1.9% at 1000 K.

3. CONCLUSIONS

The GERG project presented consists of a round-robin test on speed-of-sound measurements in methane, a binary mixture, and a natural gas and of an examination of existing equations of state for their suitability for calculating caloric data.

In a first step in this work, equations for ideal-gas isobaric heat capacities were examined and newly determined by fitting the parameters of Eq. (1) to selected literature data. These parameters will be used in an assessment of equations of state.

As a preliminary test, the c_p^0 correlation of this work was used to predict caloric properties from the AGA 8 equation [41]. A comparison with experimental pvT, speed-of-sound, and enthalpy data indicated that the target uncertainty of 0.1% for predicting speed-of-sound values and of 1–2% for predicting enthalpy change values can be met only over a restricted range. A more substantiated statement will be possible only after completion of the GERG round-robin test and the current measurements of enthalpy changes on three gages.

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