Heat Capacity of Liquid *n*-Heptane Converted to the International Temperature Scale of 1990

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Heat capacities of liquid *n*-heptane, that is the recommended calorimetric reference material, have been converted to the International Temperature Scale of 1990 (ITS-90) and new reference data have been generated. Raw experimental data measured at the National Bureau of Standards, Washington and at the Bureau of Mines, Bartlesville have been critically selected from a large compilation of liquid heat capacity data. A joint correlation of the converted data has been performed. Sets of reference data are presented for both the saturation and the isobaric heat capacities in the range from 182.6 to 480 K. Parameters of a correlating equation and tables of heat capacities are provided.

Key words: conversion to the ITS-90; heat capacity; *n*-heptane; liquid; reference data.

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1. Introduction

At the fourth conference on low-temperature calorimetry held in 1949 *n*-heptane was recommended as one of three materials suitable for calibration of heat capacity calorimeters (49FOU). The selection of *n*-heptane was based on several rationales. *n*-Heptane is inexpensive and readily available, can be purified by a simple procedure, is thermally and chemically stable up to the critical temperature 540 K, and can be distilled easily into a vessel of a calorimeter. Although the calorimetric conference recommended *n*-heptane as the heat-capacity standard from 10 to 300 K, the results of measurements from the National Bureau of Standards (NBS)[a], Washington D.C. (47OSB/GIN, 54DOU/FUR) indicated that with proper care the substance can be used for this purpose up to 400 K. The recommended heat capacity data of *n*-heptane were published by Ginnings and Furukawa (53GIN/FUR). *n*-Heptane is the only standard substance that is liquid in the interval from 182.6 to 400 K, whereas other standard substances, benzoic acid and alpha-aluminum oxide, are solids over the whole recommended interval of temperatures. The data from the NBS having the stated accuracy 0.1 % are widely used as standard data for the verification of the measurement precision, calibration of calorimeters, and in the differential measurements.

The Bureau of Mines (BM)[b], Bartlesville, Oklahoma, is another laboratory that was involved in a high-precision measurement of the heat capacity of *n*-heptane. They

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[a] Now called the National Institute of Standards and Technology (NIST).

[b] Now called the National Institute for Petroleum and Energy Research (NIPER).

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published both the raw data (61MCC/MES) and the smoothed recommended data (61HUF/GRO).

Since the original measurements in both groups were performed, two changes of the temperature scale have come into effect. The International Temperature Scale of 1948, ITS–48, (49STI) that was valid at the time when the measurements in the two groups were done, was revised firstly to the International Practical Temperature Scale of 1968, IPTS–68, (69MET, 69DOU), and then to the International Temperature Scale of 1990, ITS–90 (90MET, 90MCG). The differences in temperature between any of the older temperature scales and the ITS–90 reach the maximum value 0.045 K in the range from the melting temperature to the critical temperature of *n*-heptane. The introduction of the new temperature scale, the ITS–90, affects reference heat capacities of *n*-heptane; the corresponding changes in the heat capacity are in some cases comparable with the measurement accuracy. Therefore, a detailed analysis of the original experimental data from the NBS and BM was carried out, the heat capacities were converted to the ITS–90, jointly correlated, and a new set of reference heat capacities was generated.

The paper by Růžička *et al*., 91RUZ/ZAB, presents the recommended heat capacities of C_1 to C_{18} *n*-alkanes without taking into account changes in the heat capacity due to the temperature scale change. A detailed analysis revealed that the conversion of the heat capacities of all *n*-alkanes but *n*-heptane is either unnecessary or impossible due to two main reasons: first, the differences in heat capacities due to the conversion to the ITS–90 are substantially lower than the stated measurement accuracy; second, some data that are required for the exact conversion, in particular temperature differences in experiments, are unavailable.

We closely followed procedures of data treatment described by authors in the original papers. However, we used recent data on volume and vapor pressure for the treatment of raw data and modern statistical methods for the correlation of converted data. This might have added an additional contribution to the change due to the conversion to the ITS–90 temperature scale and consequently affected the reference data developed here. To convert specific and molar heat capacities, the current molar mass of *n*-heptane, 100.20404 g·mol^{-1}, was used.

2. Conversion of Calorimetrically Determined Heat Capacities to the ITS–90

The temperature scale change affects a physical-chemical quantity in a manner that depends upon the method of measurement of such quantity. When we measure a physical-chemical quantity at a constant temperature, we simply convert the original temperature of measurement to a new temperature scale and assign the value of a quantity to a new temperature. This procedure is applied for example for the conversion of vapor pressure or density.

The conversion of thermophysical quantities that are determined by the measurement of temperature, such as heat capacity or enthalpy, is slightly more complicated; in addition to the change of temperature to which the quantity is assigned, the quantity itself is changed as well. The latter change is usually more significant which means that neglecting it may lead to an error. Head and Sabbah (87HEA/SAB) used an incomplete procedure when converting the recommended heat capacities of *n*-heptane from the ITS–48 to the IPTS–68 as they converted only temperatures to the new temperature scale and did not consider the change of the heat capacity despite all information required for the conversion is available in original papers.

The heat capacity C measured in an adiabatic or isoperibol calorimeter is calculated as the ratio of the heat ΔQ and the difference in the final and the initial temperature of the experiment $\Delta T = T_2 - T_1$:

$$C = \frac{\Delta Q}{T_2 - T_1} \quad . \tag{1}$$

The calculated heat capacity is assigned to a temperature T that is calculated as an arithmetic mean of the initial and the final temperature:

$$T = \frac{T_1 + T_2}{2} \quad . \tag{2}$$

The procedure for the conversion of thermodynamic quantities from an old to a new temperature scale is described by Douglas (69DOU). Goldberg and Weir (92GOL/WEI) simplified the expression derived by Douglas for the conversion of the heat capacity to the following form:

$$C_{90} - C_{\mathrm{old}} = -(T_{90} - T_{\mathrm{old}})\frac{\mathrm{d}C}{\mathrm{d}T} - C\,\frac{\mathrm{d}(T_{90} - T_{\mathrm{old}})}{\mathrm{d}T} \tag{3}$$

where subscripts 90 and old denote the temperature scale. Values of $(T_{90} - T_{\mathrm{old}})$ and of the derivative $\mathrm{d}(T_{90} - T_{\mathrm{old}})/\mathrm{d}T$ can be either determined by interpolation from tables presented by Goldberg and Weir (92GOL/WEI) or for the conversion from the IPTS–68, can be calculated from analytical equations given by Rushby (91RUS).

Archer (93ARC) showed that if one applies the Eq. (3) to the smoothed data incorrect values of heat capacities are obtained as smoothing of data "wipes out" small fluctuations in temperature due to the difference between the thermodynamic temperature and the current temperature scale. We have neither used the Eq. (3) for the conversion of heat capacities of *n*-heptane nor followed the procedure suggested by Archer. Instead, we have adopted the method described in the next paragraph.

The exact procedure for the conversion of the heat capacity to the current temperature scale follows these steps:

1. T_2 and T_1 are converted to the ITS–90;

2. A new value of C_{90} is calculated from Eq. (1) using the new values of T_2 and T_1 and the original value of ΔQ;
3. A new average value of T_{90} is calculated from Eq. (2); this is the new temperature to which the new C_{90} is assigned.

This procedure requires that experimental values of T_2 and T_1 or of ΔT are known. They are, however, published only in exceptional cases.

3. Conversion of Heat Capacities for Individual Sets of Data

The heat capacity of *n*-heptane which is the recommended calorimetric reference material has been measured very often. Růžička *et al.* (91RUZ/ZAB) list 34 different measurements. We have critically selected 2 sets of raw data for the joint correlation and generation of the reference heat capacities. The measurement procedure, calculation of data, and presentation of results was different in the individual sets of selected data. Therefore, different procedures of conversion of data have been used and are presented below.

3.1. Conversion of Data Measured at the National Bureau of Standards (NBS), Washington D.C. (47OSB/GIN, 54DOU/FUR)

The measurement of the heat capacity of *n*-heptane was carried out at the NBS very carefully over an extended period of time. Four different devices were used for the measurement between 1939 and 1954: three adiabatic calorimeters and the Bunsen isothermal ice calorimeter in the drop arrangement. Table 1 gives some concise characteristics of the four measurements including the references.

We have used the procedures described in the paper by Douglas *et al.* (54DOU/FUR) as a basis for calculating the reference data converted to the ITS–90. In the measurements with adiabatic calorimeters the authors used the low- and high-filling of the calorimetric vessel that eliminates the determination of the heat capacity of the calorimeter. We have converted the two sets of data for two fillings obtained with the low-temperature calorimeter to the ITS–90 using the procedure described in chapter 2 of this work. We have subtracted 0.05 J from the raw data in the low-filling experiments as noted in the footnote in Table 3 of the paper 54DOU/FUR. For both sets the data has been corrected for curvature (25OSB/STI) using the equation:

$$C_{\mathrm{cor}} = C_{\mathrm{exp}} - \frac{(T_2 - T_1)^2}{24} \cdot \left(\frac{\partial^2 C}{\partial T^2}\right) \tag{4}$$

where T_1 and T_2 are the lower and upper temperatures of the measurement of C_{exp}, and T is calculated from Eq. (2).

The specific heat capacity at the saturation, in $\mathrm{J{\cdot}K^{-1}{\cdot}g^{-1}}$, has been calculated from the following equation:

$$C_{\mathrm{sat}} = \frac{(C_{\mathrm{HF}} - C_{\mathrm{LF}})}{(m_{\mathrm{HF}} - m_{\mathrm{LF}})} + T\left[\left(\frac{\partial v}{\partial T}\right)_{\mathrm{sat}} + v \cdot \left(\frac{\partial^2 p}{\partial T^2}\right)_{\mathrm{sat}}\right] \tag{5}$$

where subscripts HF and LF refer to high- and low-filling, respectively, and subscript sat denotes the quantities at the saturation curve. The second term on the right-hand side of Eq. (5) is the correction for the vapor space in the calorimetric vessel (46HOG) that becomes significant at temperatures above 240 K. At this temperature the correction equals 0.01 % of the value of the heat capacity. The specific volume of liquid *n*-heptane, v, and its temperature derivative were calculated from the Martin equation that expresses the dependence of the density with temperature (86SMI/SRI):

$$\rho = \sum_{i=0}^{3} A_i \cdot (1 - T/T_c)^{i/3} \tag{6}$$

The parameters A_i ($A_0 = 0.236000$, $A_1 = 0.314256$, $A_2 = 0.779017$, $A_3 = -1.06427$, $T_c = 540.15$ K) were taken from Cibulka (93CIB). The derivative of the vapor pressure was calculated from the Wagner equation:

$$\ln\frac{p}{p_c} = (A\,\tau + B\,\tau^{1.5} + C\,\tau^{2.5} + D\,\tau^{5})/T_r \tag{7}$$

where $\tau = 1 - T/T_c$ and the parameters A, B, C, D ($A = -7.77404$, $B = 1.8561$, $C = -2.8298$, $D = -3.5070$,

TABLE 1. Measurements of the heat capacity of *n*-heptane at the NBS, Washington D.C.

Year measured	Reference	Temperature interval, K	Impurities mol%	Accuracy %	Type of calorimeter	Reference to calorimeter
1939	47OSB/GIN	278–363	0.07[a]	0.1	adiabat. large vessel	39OSB/STI
1941	47OSB/GIN	283–308	0.07[a]	0.1	adiabat. small vessel	47OSB/GIN
1954	54DOU/FUR	20–370	0.001	0.1[b]	low-temperat. adiabat.	45SCO/MEY
1954	54DOU/FUR	273–523	0.001	0.2–0.5[c]	drop, ice- isotherm.	50GIN/DOU

[a] From 46FOR/GLA

[b] Above 50 K; below 50 K the error increases up to 1 %.

[c] 0.2 % at 370 K, 0.5 % at 520 K.

$T_c = 540.15$ K) were taken from Ambrose and Walton (89AMB/WAL).

Saturation heat capacities C_{sat} have been obtained by the substitution of the corrected smoothed values of C_{HF} and C_{LF} into Eq. (5) in the temperature range from the triple point to 370 K with the step of 10 K. The triple point temperature converted to the ITS–90 is equal to 182.603 K.

Two sets of measurements done at the NBS in 1939 and 1941 (47OSB/GIN) were carried out in adiabatic calorimeters that were specifically developed for measurements at ambient and super-ambient temperatures and were also used for the measurement of the heat of vaporization. A method identical to that described by Douglas *et al.* (54DOU/FUR) was used for the measurement of the heat capacity. The authors 47OSB/GIN used the same initial and final temperatures in the low- and high-filling experiments. Therefore, we have not repeated the entire procedure of the calculation of the heat capacity from the raw data as described for the measurements by 54DOU/FUR. We have converted T_1 and T_2 from the ITS–27 to the ITS–90; the ITS–27 is in the range of the data identical to the ITS–48. Then, we have obtained the corrected values of C_{90} and T_{90} using Eqs. (1) and (2) for both sets of data containing 9 and 5 data points, respectively.

The data measured at the NBS in adiabatic calorimeters were supplemented with data obtained in an isothermal ice calorimeter using the drop arrangement. In the latter calorimeter heat changes of the saturated liquid are measured between the temperature of a sample heated in a furnace and the temperature of the ice calorimeter equal to 273.15 K. The derivative of the heat change gives the saturation heat capacity C_{sat} in the temperature range from 273 to 520 K. The correction of the heat capacity due to the conversion to the ITS–90 is negligibly small compared to the measurement error as the temperature difference in all experiments was 100 K or higher. The authors reported that the measurement error equals to 0.2 % at 370 K and increases up to 0.5 % at 520 K. Therefore, we have converted only the measurement temperatures to the ITS–90.

All four sets of data from the NBS have been correlated simultaneously by cubic splines (90ZAB/RUZ) with four knots located at 182.6, 260, 400, 480 K using the weighted least-squares method. The statistical weights were estimated on the basis of the error of measurement.

Douglas *et al.* (54DOU/FUR) noted that their own data become less reliable at temperatures above 280 K due to the possibility of heat loss by radiation. In the range from 280 to 360 K, they gave in their joint correlation of data the greatest weight to the values of Osborne and Ginnings (47OSB/GIN), and reduced the weight of their own data. At 280 K, they set the weight of their own data to 0.5 and they reduced the weight gradually with the increasing temperature up to 360 K where they set the weight equal to zero. We have adopted the rationale of Douglas *et al.* and we have corrected the statistical weights in our least-squares correlation by multiplying them by the weighing factors used by Douglas *et al.*

The reference saturation molar heat capacities calculated from the parameters of cubic splines are given in Table 2 in the column NBS. The next column in the table lists deviations between the reference heat capacities and the original values given in 54DOU/FUR. Deviations are given for heat capacities calculated at the same numerical value of temperature in the original scale and in the ITS–90.

TABLE 2. Heat capacity of *n*-heptane converted to the ITS–90

T_{90}/K	C_{sat}/J·K^{-1}·mol^{-1}			
	NBS	d^a %	BM	d^a %
182.603	202.77^b	−0.19	202.74^b	−0.13
190	201.81	−0.02	201.92	−0.02
200	201.33	0.01	201.56	0.05
210	201.67	0	201.93	0.07
220	202.73	0	202.97	0.04
230	204.41	0.02	204.58	0.03
240	206.59	0.06	206.69	0.04
250	209.18	0.12	209.23	0.05
260	212.07	0.16	212.12	0.08
270	215.17	0.17	215.28	0.12
280	218.45	0.10	218.64	0.13
290	221.92	0.08	222.13	0.09
298.15	224.88^c	0.06	225.08	0.07
300	225.57	0.05	225.76	0.05
310	229.37	0.04	229.51	0.01
320	233.35	0.04	233.47	0.02
330	237.48	0.04	237.47	0.01
340	241.76	0.04	241.69	0.01
350	246.18	0.04	246.07	0.04
360^d	250.74	0.04	250.63	0.02
370	255.42	0.05	255.37^b	−0.01
380	260.23	0.05		
390	265.15	0.05		
400^e	270.19	0.02		
410	275.3	−0.02		
420	280.6	−0.05		
430	286.1	−0.07		
440	291.8	−0.06		
450	297.9	−0.02		
460	304.2	0.02		
470	310.9	0.04		
480	318.1	0.12		

[a] $d = (C_{90} - C_{old}) \times 100/C_{90}$

[b] Extrapolated; triple point temperature in (54DOU/FUR) is 182.562 K, in (61MCC/MES) is 182.55 K.

[c] Original temperature in (54DOU/FUR) is 298.16 K

[d] Above this temperature only conversion of temperatures was done.

[e] Above this temperature *n*-heptane is not the calorimetric standard.

3.2. Conversion of Data Measured at the Bureau of Mines (BM), Bartlesville (61MCC/MES)

The heat capacity of *n*-heptane was measured at the BM five times in the period from 1947 to 1954 using the low-temperature adiabatic calorimeter with different vessels described by Ruehrwein and Huffman (43RUE/HUF). The heat capacity of the calorimeter was determined by an independent measurement without a liquid sample. The authors stated the precision of measurement to be 0.1 % and the accuracy of measurement to be 0.2 % when measuring a liquid sample. The results at the BM were obtained by using the following constants: molar mass 100.198 g·mol^{-1}, 1 cal = 4.184 *J* (exactly). The ITS–48 temperature scale was used for the calibration of thermometers. The authors 61MCC/MES obtained the selected values of the heat capacity at integral temperatures from the three more recent measurements internally denoted as BM 1951A, BM 1951B, and BM 1954 using the Calorimetric Conference samples of *n*-heptane distributed by the NBS. The concentration of impurities in the three measurements determined by the freezing point depression was 0.004, 0.004, and 0.006 mol. %, respectively. The reported triple point temperature converted to the ITS–90 is 182.59 ± 0.01 K which is in good agreement with the value determined at the NBS, 182.603 K. Due to a higher purity of the sample measured at the NBS, we have accepted their triple point temperature.

McCullough and Messerly (61MCC/MES) reported experimental values of C_{sat}, T, and ΔT. This permitted one to convert the original heat capacities to the ITS–90 following the procedure described in Chapter 2, using Eqs. (1) and (2). The converted heat capacities from all three measurements mentioned above have been correlated simultaneously with a fourth degree polynomial.

The authors 61MCC/MES considered the data from the BM 1951B measurement at temperatures around 300 K less accurate due to a slight distortion in adiabatic conditions. We have assigned the gradually decreasing weight to the data in the same manner as described in the original paper. The weight was set to 0.8 at 255 K, was decreased to 0.1 at 287 K, and was set to 0 at all temperatures above 287 K.

The reference saturation molar heat capacities calculated from the parameters of the polynomial are given in Table 2 in the column denoted BM. The next column in the table lists deviations between the reference heat capacities and the original values given in 61MCC/MES.

4. Reference data

We recommend the heat capacities obtained by the joint correlation of the converted data from the National Bureau of Standards, Washington D.C., and the Bureau of Mines, Bartlesville, as the reference data of *n*-heptane. The original experimental data from the two laboratories contain all information that is necessary for the conversion to the current temperature scale. The joint correlation by the weighted least-squares method was carried out using cubic splines with four knots located at 182.6, 260, 400, 480 K. Some other selections of knots have been examined, in particular positioning the third knot at 370 K, where the accuracy of the NBS data changes. However, none of the other selections of knots yielded an improved fit of the data. The statistical weights were calculated from the error of measurement which was assigned as follows: NBS data from 182.6 to 370 K 0.1 %, NBS data above 370 K 0.3 %, BM data 0.2 %.

Reference data are presented as parameters of a correlating equation in Table 3 and in tabular form in Table 4. We preferred to tabulate the parameters of cubic polynomials rather than the results of the spline correlation as in the latter case the spline routine is required to generate the reference data. The tabulated adjustable parameters, A_j, relate to the equation expressing the dimensionless quantity, C/R, as a function of the scaled temperature, $T/100$:

$$\frac{C}{R} = \sum_{j=0}^{3} A_j \left(\frac{T}{100}\right)^j \tag{8}$$

where $R = 8.31451$ J·K^{-1}·mol^{-1}. A rating called level of uncertainty that expresses the expected overall uncertainty of the recommended data and reflects both the uncertainty in the experimental value and possible error due

TABLE 3. Parameters of cubic polynomials (see Eq. (8))

Temperature range K	A_0	A_1	A_2	A_3	Level of uncertainty[a]
			C_{sat}		
182.6–260.0	6.09258E+1[b]	−4.50536E+1	1.75504E+1	−2.10051	I
260.0–400.0	2.62792E+1	−5.07669	2.17466	−1.29263E−1	I[c]
400.0–480.0	−4.11778E+1	4.55161E+1	−1.04735E+1	9.24753E−1	II
			C_p		
182.6–260.0	6.11411E+1	−4.53403E+1	1.76764E+1	−2.11880	I
260.0–400.0	2.54134E+1	−4.11613	1.82098	−8.60461E−2	I[c]
400.0–480.0	−8.76637E+1	8.06917E+1	−1.93810E+1	1.68078	II

[a] Level of uncertainty expresses the expected overall uncertainty of the recommended data. It has the following meaning: I uncertainty below 0.1 %, II uncertainty below 0.3 %.

[b] Parameter values given in the E notation. The first part of the number denotes the fractional part which is followed by the exponent to the base 10 (e.g. 6.051177E+1 means 6.051177·10^1).

[c] The level of uncertainty changes to II above 370 K.

TABLE 4. Reference saturation heat capacities C_{sat} and isobaric heat capacities C_p of *n*-heptane converted to the ITS–90

T_{90}/K	C_{sat}/J·K^{-1}·mol^{-1}	C_p/J·K^{-1}·mol^{-1}	δ_r/%[a]
182.603	202.77	202.77	0.1
190	201.82	201.82	0.1
200	201.35	201.34	0.1
210	201.68	201.69	0.1
220	202.75	202.75	0.1
230	204.43	204.43	0.1
240	206.62	206.62	0.1
250	209.20	209.20	0.1
260	212.09	212.09	0.1
270	215.19	215.19	0.1
280	218.47	218.47	0.1
290	221.93	221.93	0.1
298.15	224.89	224.89	0.1
300	225.58	225.58	0.1
310	229.38	229.39	0.1
320	233.36	233.38	0.1
330	237.49	237.53	0.1
340	241.76	241.85	0.1
350	246.18	246.32	0.1
360	250.73	250.94	0.1
370	255.41	255.71	0.1
380	260.22	260.62	0.3
390	265.14	265.68	0.3
400[b]	270.17	270.87	0.3
410	275.3	276.2	0.3
420	280.6	281.8	0.3
430	286.1	287.6	0.3
440	291.8	293.8	0.3
450	297.9	300.5	0.3
460	304.2	307.8	0.3
470	310.9	315.7	0.3
480	318.1	324.3	0.3

[a] Overall uncertainty of the data.

[b] Above this temperature *n*-heptane is not the calorimetric reference material.

to the fitting procedure was assigned to each set of cubic polynomial parameters. The meaning of the level of uncertainty is as follows: I uncertainty below 0.1 %, II uncertainty below 0.3 %. Table of discrete values was generated using polynomial representation of reference data. The uncertainties assigned to parameters in Table 3 apply to the discrete data from Table 4 in corresponding temperature intervals.

Tables 3 and 4 give the isobaric heat capacities in addition to the saturation heat capacities obtained from the original data. The isobaric heat capacities have been generated from the reference saturation heat capacities using the thermodynamic relationship that relates both quantities:

$$C_{sat}-C_p=-T\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{dp}{dT}\right)_{sat} \tag{9}$$

The term $(\partial V/\partial T)_p$ was approximated by $(\partial V/\partial T)_{sat}$ and calculated from the temperature correlation of saturation density using Eq. (6) and parameters taken from Cibulka (93CIB). The derivative $(dp/dT)_{sat}$ was calculated from the Wagner Eq. (7) using parameters given by Ambrose and Walton (89AMB/WAL).

The deviation plot, Fig. 1, illustrates how the NBS and BM data deviate from the reference data developed here. The plot shows that the NBS data deviate by less than 0.02 %. Deviations between the BM and the reference data are higher but still below the stated accuracy of the BM data. The deviation plot also illustrates that cubic splines fit the converted data adequately.

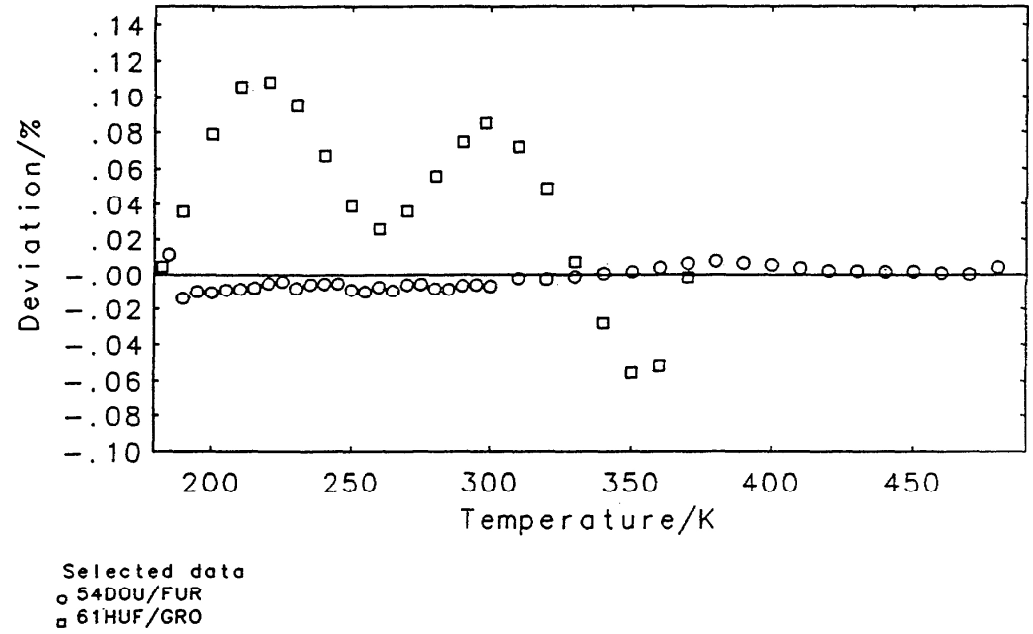

FIG. 1. Deviation Plot

5. Conclusions

Exact conversion of calorimetrically measured heat capacities of *n*-heptane to the current temperature scale has been carried out using the raw data that include the differences in temperature over which the heat capacity measurements were made. All information that is necessary for the conversion of liquid heat capacities is available for data measured at the National Bureau of Standards and the Bureau of Mines. A joint correlation of the data from these two laboratories converted to the current temperature scale, the ITS–90, provides reference heat capacities. Reference data are presented as parameters of a correlating equation and also in tabular form. The tables give the isobaric heat capacities in addition to the saturation heat capacities obtained from the original data.

Differences in heat capacities due to the conversion to the ITS–90 are roughly of the same magnitude as the measurement error of the NBS and the BM data. The largest deviations between the converted and the original data appear in the temperature range from 260 to 280 K. Large deviations in this range agree well with slightly larger values of the derivative $d(T_{90}-T_{48})/dT$ than at other temperatures (see Table 4 in 92GOL/WEI). Our reference heat capacities generated from the data measured at the NBS, exhibit deviations from the smoothed data of Douglas *et al.* (54DOU/FUR) which are somewhat larger than deviations from the smoothed data of McCullough and Messerly (61MCC/MES) over the same temperature interval. We believe that this may be due to different auxiliary data used for the treatment of the original raw data and due to a different correlating equation used for smoothing the converted data from low- and high-filling experiments.

6. Acknowledgement

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7. References

25OSB/STI Osborne N. S., Stimson H. F., Sligh T. S., Cragoe C. S., BS Sci. Pap. **20**, 65 (1925).

39OSB/STI Osborne N. S., Stimson H. F., Ginnings D. C., J. Res. Natl. Bur. Std. (U. S.) **23**, 197 (1939).

43RUE/HUF Ruehrwein R. A., Huffman H. M., J. Am. Chem. Soc. **65**, 1620 (1943).

45SCO/MEY Scott R. B., Meyers C. H., Rands R. D., Brickwedde F. G., Bekkedahl N., J. Res. Natl. Bur. Std. (U. S.) **35**, 39 (1945).

46FOR/GLA Forziati A. F., Glasgow A. R., Jr., Willingham C. B., Rossini F. D., J. Res. Natl. Bur. Std. (U. S.) **36**, 129 (1946).

46HOG Hoge H. J., J. Res. Natl. Bur. Std. (U. S.) **36**, 111 (1946).

47OSB/GIN Osborne N. S., Ginnings D. C., J. Res. Natl. Bur. Std. (U. S.) **39**, 453 (1947).

49FOU Fourth Conference on Low-Temperature Calorimetry, Chem. Eng. News **27**, 2772 (1949).

49STI Stimson H. F., J. Res. Natl. Bur. Std. (U. S.) **42**, 209 (1949).

50GIN/DOU Ginnings D. C., Douglas T. B., Ball A. F., J. Res. Natl. Bur. Std. (U. S.) **45**, 23 (1950).

53GIN/FUR Ginnings D. C., Furukawa G. T., J. Am. Chem. Soc. **75**, 522 (1953).

54DOU/FUR Douglas T. B., Furukawa G. T., McCoskey R. E., Ball A. F., J. Res. Natl. Bur. Std. (U. S.) **53**, 139 (1954).

61HUF/GRO Huffman H. M., Gross M. E., Scott D. W., McCullough J. P., J. Phys. Chem. **65**, 495 (1961).

61MCC/MES McCullough J. P., Messerly J. F., U. S. Bur. Mines Bull. **596**, 1 (1961).

69DOU Douglas T. B., J. Res. Natl. Bur. Std. (U. S.) **73A**, 451 (1969).

69MET Metrologia **5**, 35 (1969).

84COM Commission on Atomic Weights and Isotopic Abundances, Pure Appl. Chem. **56**, 653 (1984).

86SMI/SRI Smith B. D., Srivastava R., "Thermodynamic Data for Pure Compounds, Physical Science Data 25, Part B: Halogenated Hydrocarbons and Alcohols." Elsevier, Amsterdam 1986.

87HEA/SAB Head A. J., Sabbah R., in: Marsh K. N. (Ed.) "Recommended Reference Materials for the Realization of Physicochemical Properties", p. 247, Blackwell Sci. Publ., Oxford 1987.

89AMB/WAL Ambrose D., Walton J. Pure Appl. Chem. **61**, 1395 (1989).

90MCG McGlashan M. L., J. Chem. Thermodyn. **22**, 653 (1990).

90MET Metrologia **27**, 3 (1990); ibid **27**, 107 (1990).

90ZAB/RUZ Zábranský M., Růžička V., Jr., Majer V., J. Phys. Chem. Ref. Data **19**, 719 (1990).

91RUS Rusby R. L., J. Chem. Thermodyn. **23**, 1153 (1991).

91RUZ/ZAB Růžička V., Jr., Zábranský M., Majer V., J. Phys. Chem. Ref. Data **20**, 405 (1991).

92GOL/WEI Goldberg R. N., Weir R. D., Pure Appl. Chem., **64**, 1545 (1992).

93ARC Archer D. G., J. Phys. Chem. Ref. Data, **22**, 1441 (1993).

93CIB Cibulka I., Fluid Phase Equilib., **89**, 1 (1993).