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**HEAT CAPACITIES OF 4-METHYL-2-PENTANONE,  
2,6-DIMETHYL-4-HEPTANONE, 1-HEXANOL, 1-HEPTANOL, AND  
1-OCTANOL IN THE TEMPERATURE RANGE 298—318 K**

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Molar heat capacities of 4-methyl-2-pentanone and 2,6-dimethyl-4-heptanone in the liquid state have been measured at a constant pressure over the temperature range 298·15 to 318·15 K. In order that the appropriateness of selection of literature data for correlation of the heat capacity as a function of temperature may be verified, results for three 1-alkanols (1-hexanol, 1-heptanol, and 1-octanol) have been measured over the same temperature range.

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Both 4-methyl-2-pentanone (isobutylmethylketone, IMK) and 2,6-dimethyl-4-heptanone (diisobutylketone, DIK) serve as convenient solvents because of their relatively high boiling temperature (IMK : 117°C, DIK : 168°C). Moreover, IMK is used as an extraction solvent in the production of acrylates and as a starting material in making Antioxidant 13. The literature only offers a single value of heat capacity for IMK.<sup>1</sup>

Heat capacities of 1-hexanol, 1-heptanol and 1-octanol have been measured as functions of temperature quite frequently. There have been eleven studies<sup>2-12</sup> on 1-hexanol covering the temperature range 229 to 424 K, four measurements<sup>3,5,13,14</sup> on 1-heptanol over the range 240 to 453 K, and five measurements<sup>3,5,14-16</sup> on 1-octanol over the range 246 to 468 K. In a collective treatment of C<sub>1</sub> to C<sub>10</sub> 1-alkanols for the 3rd IUPAC Workshop<sup>17</sup>, however, a considerable inconsistency between the published data was revealed. It was very difficult to select data suitable for correlation of the heat capacity as a function of temperature over a wide temperature range, and despite the careful approach and strategy adopted in sifting the data, it was not possible to avoid subjective element in the selection<sup>18,19</sup>. In order to verify the appropriateness of the data selection, heat capacities of the above 1-alkanols have been measured over the temperature range 298·15 to 318·15 K and compared with values obtained from correlated data.

## EXPERIMENTAL

*Calorimeter and measurement.* All measurements were carried out on a mixing calorimeter of our own design<sup>20</sup>. The use of the calorimeter to measure the heat capacity of liquids, and the procedure of measurement have been described earlier<sup>21</sup>. Heat capacities were measured over the temperature range 298.15 to 318.15 K in steps of 5 K. The values given in Table I are averages of from 3 to 7 measurements of  $C_p$  at the indicated temperature. The correction for pressure change and evaporation on increasing the temperature was small enough (less than 0.01%) to be neglected. The reproducibility of measurements was within 0.3%. With the analysis of the input and output data taken into account, the error of measurement was estimated to be less than 0.5%.

*Chemicals.* Samples of the two ketones were prepared at the Department of Organic Technology, Prague Institute of Chemical Technology. The purity as determined by gas chromatography was 99.97 mass % for IMK and 99.99 mass % for DIK. All the alcohols were purified by methods described earlier<sup>20,22,23</sup>; the same references give comparison of some of the measured physical constants with literature data. The water content as determined by Fischer's method was 0.047 mass % for 1-hexanol, 0.007 mass % for 1-heptanol, and 0.039 mass % for 1-octanol.

## RESULTS AND DISCUSSION

The measured molar heat capacities at constant pressure,  $C_p$ , for all the compounds at various temperatures are listed in Table I. The only published result for 4-methyl-2-pentanone, reported by Fuchs<sup>1</sup>, is by 1.8% higher than our measurement. The difference may be due to lower accuracy of the simple calorimeter used by Fuchs (a Dewar flask with a heating element and a thermometer), or to sample contamination. In view of the narrow temperature range of measurements, the data were correlated assuming as sufficient the linear form of the polynomial used to represent the heat capacity as a function of temperature

$$C_p = \sum_{j=0}^m A_j (T/100)^j, \quad (1)$$

where  $m = 1$ . This expression differs from the commonly used form by involving the term  $(T/100)$  instead of  $T$ . The introduction of this term proved necessary<sup>17</sup> since it ensures a greater numerical stability of the least-squares fit for  $m \geq 4$ . A further advantage is that the calculated constants  $A_j$  show no great order-of-magnitude differences, unlike the results obtained from the relationship involving  $T$ . The calculated constants of Eq. (1) and the temperature ranges of their validity are listed in Table II.

The measurements of  $C_p$  for 1-alkanols as a function of temperature are represented graphically in Figs 1 to 3, along with the available literature data. Some of the published values were measured as saturation heat capacities,  $C_{\text{sat}}$ , and their conversion to isobaric heat capacities,  $C_p$ , was made using the relationship

$$C_p = C_{\text{sat}} + T(\partial V/\partial T)_p (\partial p/\partial T)_{\text{sat}}, \quad (2)$$

where the pressure change with temperature along the saturation curve,  $(\partial p/\partial T)_{sat}$ , was calculated from Antoine's equation, and the term  $(\partial V/\partial T)_p$  was approximated by the volume change with temperature for saturated liquid calculated from Rackett's equation<sup>24</sup>.

It was difficult to select mutually consistent data from the eleven studies available for 1-hexanol. On the basis of criteria for data assessment<sup>18,19</sup>, sets of Kelley<sup>2</sup> (the

TABLE I  
Measured values of the molar heat capacity  $C_p$  ( $J K^{-1} mol^{-1}$ ) as a function of temperature  $T$  (K)

$T$	$C_p$				
	IMK	DIK	1-hexanol	1-heptanol	1-octanol
298.15	211.9 <sup>a</sup>	297.3	242.5	270.8	304.0
303.15	213.3	300.1	247.2	276.3	308.8
308.15	214.5	302.1	251.3	280.9	314.6
313.15	215.0	304.1	255.9	286.1	319.7
318.15	217.1	306.3	260.9	291.5	325.2

<sup>a</sup>  $(215.18 \pm 1.1) J K^{-1} mol^{-1}$  at 298.15 K by Fuchs<sup>1</sup>.

TABLE II  
Constants of Eq. (1) for the molar heat capacity  $C_p$  ( $J K^{-1} mol^{-1}$ ) as a function of temperature  $T$  (K) over the temperature range  $(T_1 - T_2)$  (K)

Parameter	IMK	DIK	1-Hexanol	1-Heptanol	1-Octanol
$(T_1 - T_2)$	298—318	298—318	229—424	240—425	298—452
$A_0$	133.803	166.274	1 015.2820	1 489.3586	13 571.612
$A_1$	26.207	44.038	-867.75317	-1 288.5044	-14 874.605
$A_2$	—	—	290.67312	420.51155	6 114.1615
$A_3$	—	—	-29.087144	-42.024811	-1 093.0335
$A_4$	—	—	—	—	72.128859
$\sigma^a$	0.001	0.002	0.054	0.026	0.010
$\sigma_r^b$	0.05	0.09	2.43	1.06	0.34

<sup>a</sup> Standard deviation  $\sigma = [(\sum d_i^2)/(n - m - 1)]^{1/2}$ , where  $d_i$  is the difference between the measured ( $C_p^{exp}$ ) and calculated ( $C_p^{cal}$ ) values of heat capacity for individual points,  $n$  is the total number of points, and  $m$  is the degree of polynomial (1); <sup>b</sup> standard percentage deviation  $\sigma_r = [(\sum d_i/C_p^{exp})^2/(n - m - 1)]^{1/2} \cdot 100$ ; data from the following references were used to calculate constants  $A_j$ : 1-hexanol<sup>2,3,5,7-11</sup>, 1-heptanol<sup>3,5,13</sup>, 1-octanol<sup>5</sup>, and our measurements.

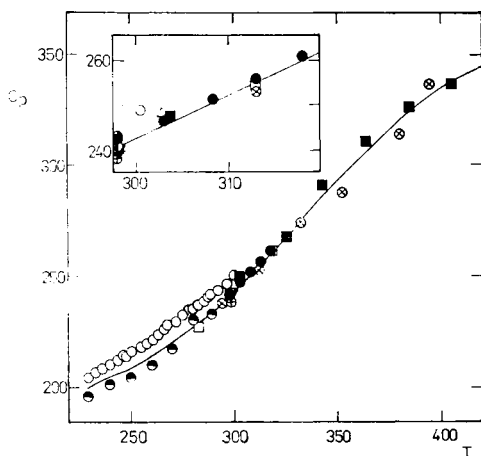


FIG. 1

Dependence of heat capacity  $C_p$  ( $\text{J K}^{-1} \cdot \text{mol}^{-1}$ ) on temperature  $T$  (K) for 1-hexanol. Curve calculated from Eq. (1).  $\odot$  Kelley<sup>2</sup>,  $\bullet$  Hutchinson<sup>3</sup>,  $\Delta$  Kalinowska<sup>4</sup>,  $\blacksquare$  Grigor'ev<sup>5</sup>,  $\otimes$  Arutyunyan<sup>6</sup>,  $\ominus$  Benson<sup>7</sup>,  $\ominus$  Bravo<sup>8</sup>,  $\circ$  Kalinowska<sup>9</sup>,  $\square$  Costas<sup>10</sup>,  $\nabla$  Tanaka<sup>11</sup>,  $\oplus$  Ortega<sup>12</sup>,  $\bullet$  our measurements

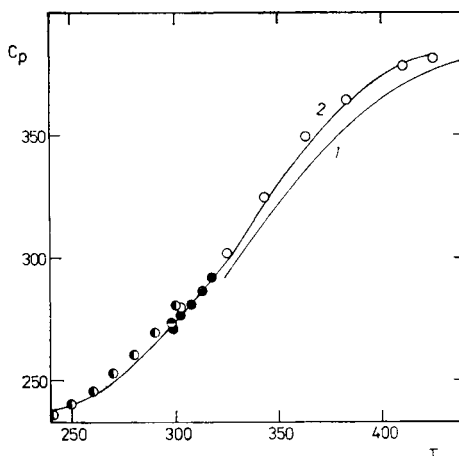
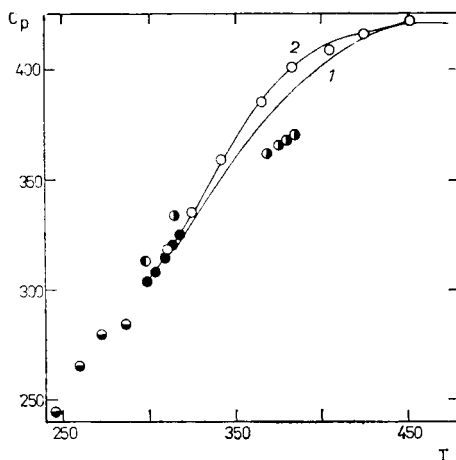


FIG. 2

Dependence of heat capacity  $C_p$  ( $\text{J K}^{-1} \cdot \text{mol}^{-1}$ ) on temperature  $T$  (K) for 1-heptanol. 1 Vasil'ev<sup>14</sup>, 2 calculated from Eq. (1).  $\bullet$  Parks<sup>13</sup>,  $\ominus$  Hutchinson<sup>3</sup>,  $\circ$  Grigor'ev<sup>5</sup>,  $\bullet$  our measurements

FIG. 3

Dependence of heat capacity  $C_p$  ( $\text{J K}^{-1} \cdot \text{mol}^{-1}$ ) on temperature  $T$  (K) for 1-octanol. 1 Vasil'ev<sup>14</sup>, 2 calculated from Eq. (1).  $\bullet$  von Reis<sup>15</sup>,  $\ominus$  Cline<sup>16</sup>,  $\ominus$  Hutchinson<sup>3</sup>,  $\circ$  Grigor'ev<sup>5</sup>,  $\bullet$  our measurements



temperature range 229.6–290 K), Grigor'ev, Yanin and Rastorguev<sup>5</sup> (303.7–424.3 K), Kalinowska and Woycicki<sup>9</sup> (229.1–300.6 K), Costas and Patterson<sup>10</sup> (283.1–313.1 K), and individual values for 298.15 K from further studies<sup>3,7,8,11</sup> were included in the correlation. The other published results<sup>4,6,12</sup> show little consistency with the above data, and therefore were rejected. Of measurements at higher temperatures, those of Grigor'ev et al.<sup>5</sup> were preferred over the data of Arutyunyan<sup>6</sup>, because of the higher accuracy stated (0.3–1% as compared with 1.5%) and good experience with data of the former authors for other alcohols. From comparison with  $C_p$ - $T$  curves for the neighbouring  $C_5$  and  $C_7$  alcohols, the curve represented in Fig. 1 appears to be the most probable. The data of Kalinowska and Woycicki<sup>9</sup> are numerous (a total of 35 points), but by 2 to 5% higher than the other measurements, so that their data set was assigned a lower weight in the correlation. In this way, parameters of Eq. (1) listed in Table II were obtained and used to calculate the curve drawn in Fig. 1. The data are highly scattered, resulting in a very large standard percentage deviation,  $\sigma_r = 2.53\%$ . Our results are in good agreement with the correlated data, with  $\sigma_r = 0.48\%$ , a value corresponding to the estimated error of measurement.

The available results for 1-heptanol and 1-octanol are less numerous, making the data selection easier. The constants of Eq. (1) for 1-heptanol (Table II, Fig. 2) were calculated on the basis of all known discrete data<sup>3,5,13</sup> and our measurements, the only rejected results being those of Vasil'ev et al.<sup>14</sup>, covering the temperature range 323–453 K.

For 1-octanol (Fig. 3), we rejected the very old, average values of von Reis<sup>15</sup>, a single value for 298.15 K of Hutchinson and Bailey<sup>3</sup>, low-temperature measurements (246–286 K) by Cline and Andrews<sup>16</sup>, and the quadratic equation of Vasil'ev et al.<sup>14</sup> (313–463 K). Thus the correlation only included the measurements of Grigor'ev et al.<sup>5</sup> and our data, because the other sets were grossly inconsistent.

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