

VERIFICATION OF THE CALCULATION OF THE CONSTANT-VOLUME  
HEAT CAPACITY DIFFERENCE OF SUBSTANCES IN THE LIQUID  
AND GAS PHASES FROM THE TEMPERATURE DEPENDENCE  
OF HEAT OF VAPORIZATION\*

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The possibilities were verified of the proposed method for calculating the difference between constant-volume heat capacities of liquids and gases in the ideal state from known data on the volumetric behaviour and temperature dependence of heats of vaporization of pure substances.

In our previous work<sup>1</sup>, the methods for calculating the difference between constant-volume heat capacities of liquids and gases were discussed. The known methods were compared with a newly proposed one stemming from the relations describing the interconnection between the temperature derivative of internal energy of vaporization or cohesive energy on the one hand and the difference of heat capacities  $c_v^l - c_v^g$  on the other hand. By an *a priori* analysis of errors of input data, it was found that the upper limit of the expected error of calculation would correspond to the error in the quantity  $c_v^l - c_v^g$  obtained from direct experimental heat capacity data, *i.e.* to a value about 18–20%.

The aim of this work is to prove the preceding theoretical conclusions by treating available literature data which would substantiate assumptions of the method proposed.

Since the needed information on the temperature dependence of both the cohesive energy and internal energy of vaporization is hitherto obtained almost solely from values of heats of vaporization, the verification of the method is therefore demonstrated on the modification employing directly the temperature dependence of heat of vaporization. The relations involving data on internal energy of vaporization or cohesive energy led in our case to identical results.

The equation used has the form

$$c_v^l - c_v^g = \Delta c_v = -d \Delta H_v / dT - P^0 TB'' + R - TV^1 \alpha^2 / \beta - \\ - (V^1 - B - \alpha TV^1 + B'T) (dP/dT). \quad (1)$$

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Symbol  $\Delta H_v$  denotes the heat of vaporization,  $c_v^{g0}$  and  $c_v^l$  the constant-volume heat capacities of the vapour phase in the state of an ideal gas and the liquid phase, respectively,  $T$  the temperature,  $P^0$  the saturated vapour pressure,  $V^l$  the molar volume of the liquid phase,  $R$  the gas constant,  $\alpha$  the coefficient of isobaric expansion,  $\beta$  the coefficient of isothermal compressibility,  $B$  the second virial coefficient and the symbols  $B'$  and  $B''$  denote the first and second temperature derivative of the second virial coefficient. The ordinary derivatives in the equation designate the change of the quantity with temperature along the equilibrium curve.

The verification of the method proposed was carried out so that the values  $\Delta c_v$  calculated in terms of Eq. (1) were compared with those obtained from the literature data on  $c_v^g$  and  $c_v^l$ . The data on volumetric behaviour of liquid and on constant-volume molar heat capacity of the liquid phase required for calculating were found only for these substances: methane<sup>2</sup>, hexane<sup>3</sup>, heptane<sup>2</sup>, benzene<sup>2,4,5</sup>, toluene<sup>4</sup>, chloroform<sup>5,6</sup>, tetrachloromethane<sup>2,4,5,6</sup>, acetone<sup>4,5,7</sup>, methanol<sup>4</sup> and water<sup>2,6</sup>. In the works cited, the values of  $c_v^l$  available experimentally with difficulty were calculated by authors from constant-pressure molar heat capacities  $c_p^l$  measured with accuracy of 0.5–1%. The values of  $c_v^l$  were determined with accuracy of 1–3%.

The quantities  $\alpha$ ,  $\beta$ ,  $V^l$  and  $c_v^l$  have been given mostly at atmospheric pressure (except ref.<sup>2</sup>) whereas the calculations performed refer to the values of pressures corresponding to the saturated vapour pressure. The dependence of the above quantities on pressure is, however, so small that in the given low pressure range, the use of the quantities taken is justified.

The needed data on  $c_v^{g0}$  were determined from the relation  $c_p^{g0} - c_v^{g0} = R$ . Data on the temperature dependence of  $c_p^{g0}$  were obtained from the following sources: methane<sup>8</sup>, hexane<sup>9</sup>, heptane<sup>10</sup>, benzene<sup>11</sup>, toluene<sup>13</sup>, chloroform<sup>8</sup>, tetrachloromethane<sup>8</sup>, acetone<sup>12</sup>, methanol<sup>14</sup> and water<sup>8</sup>. Accuracy of the data is within 0.2 to 0.5%. However, it was necessary to carry out extrapolations in calculations, namely with hexane, benzene, toluene, acetone and methanol about by 60°C towards lower temperatures, with methane even by 160°C.

The values of other quantities wanted for verifying the method proposed were obtained and treated in the following way:

Data on the temperature dependence of heats of vaporization were taken from these sources: methane<sup>15</sup>, hexane<sup>9,17,16</sup>, heptane<sup>16,18</sup>, benzene<sup>11,17,19–22</sup>, toluene<sup>13,17,22</sup>, chloroform<sup>22,23</sup>, tetrachloromethane<sup>22,23,24</sup>, acetone<sup>12</sup>, methanol<sup>19,22,25–27</sup> and water<sup>17,24,25,28,29</sup>.

These data were correlated by the empirical relation

$$\Delta H_v = A_1 e^{-A_2 T_r} (1 - T_r)^{A_3}, \quad (2)$$

where  $A_1$ ,  $A_2$  and  $A_3$  are the constants,  $T_r$  the reduced temperature. For most substances, it was sufficient to use the relation in its two-constant form, *i.e.* to set

$A_2 = A_3$ , and only with methane and methanol it was necessary to correlate the data by Eq. (2) with three different constants. The constants of Eq. (2) are given for the substances in Table I. In the last but one column of the table, the temperature interval is given which the correlation constants are referred to, and in the last one the standard deviation is given. The constants  $A_1$  to  $A_3$  inserted into Eq. (2) yield the values of  $\Delta H_v$  in kJ/mol.

For the derivative of the temperature dependence of heat of vaporization along the saturated vapour pressure curve, the relation holds

$$d \Delta H_v / dT = (-A_1 / T_k) e^{-A_2 T_r} [A_2 (1 - T_r)^{A_3} + A_3 (1 - T_r)^{A_3 - 1}]. \quad (3)$$

The values of the second virial coefficients and their temperature derivatives were calculated for nonpolar substances by the Pitzer-Curl method<sup>30</sup> and for polar substances by the O'Connell-Prausnitz method<sup>31</sup>, the required constants being taken from the literature<sup>32</sup>.

The critical temperature, critical pressure and constants of the Antoine equation were taken from the literature<sup>33</sup> for all the substances.

The results of calculation are summarized in Table II. In the column denoted  $\Delta c_v(\text{calc})$ , the values are given calculated from the temperature derivative of heat of vaporization, in the column denoted  $\Delta c_v(\text{exp})$ , the literature values are given. The third and fourth columns of the table give the literature  $c_v^{\text{go}}$  and  $c_v^1$  values.

The comparison of  $\Delta c_v(\text{calc})$  and  $\Delta c_v(\text{exp})$  can be carried out only qualitatively because the literature values of  $c_v^{\text{go}}$  and  $c_v^1$  are subject to an error. Especially the error

TABLE I  
Constants of correlation relation (2) for heat of vaporization of selected group of substances

Substance	$A_1$	$A_2$	$A_3$	Temperature interval	$\delta$ kJ/mol
Methane	10.1071	-0.220	0.3880	-161 to -81	0.02
Hexane	47.3926	0.2760	0.2760	25-80	0.02
Heptane	53.6646	0.2831	0.2831	25-90	0.02
Benzene	48.9256	0.2870	0.2870	25-104	0.03
Toluene	53.0874	0.2774	0.2774	25-137	0.02
Chloroform	46.5135	0.2902	0.2902	25-70	0.07
Tetrachloromethane	45.8504	0.2656	0.2656	25-85	0.04
Acetone	46.9487	0.2826	0.2826	27-72	0.02
Methanol	43.3064	-0.4564	0.4711	25-110	0.04
Water	55.8322	0.2210	0.2210	5-100	0.02

TABLE II

Comparison of values  $\Delta c_v$  (exp) and  $\Delta c_v$  (calc) for tested substances in J/mol K

Substance	$t, ^\circ\text{C}$	$c_v^{80}$	$c_v^1$	$\Delta c_v$ (exp)	$\Delta c_v$ (calc)	Abs. dev.
Methane	-163.15	22.1	30.6	8.5	13.2	-4.7
	-161.49	22.1	30.5	8.4	13.1	-4.7
	-153.15	22.2	30.5	8.3	12.0	-3.7
	-143.15	22.3	30.4	8.1	11.6	-3.5
	-133.15	22.5	31	9	11.1	-3
	-123.15	22.7	31	8	13.2	-5
	-113.15	22.9	30	7	15.1	-8
Hexane	20	132.1	149.1	17.0	16.1	0.9
	30	136.0	152.9	16.9	16.4	0.5
n-Heptane	20	154.4	176.3	21.9	17.9	4.0
	40	163.4	183.2	19.8	18.6	1.2
	60	172.4	110.6	19.2	19.0	-0.8
	80	181.4	198.0	16.6	19.1	-2.5
	100	190.4	206.9	16.5	20.6	-4.1
Benzene	20	71.7	93.5	21.8	17.1	4.6
	30	75.1	95.2	20.1	17.4	2.7
	40	78.4	97.2	18.8	17.7	1.1
	50	81.6	99.3	17.7	18.0	-0.3
	60	84.8	101.8	17.0	18.3	-1.3
	70	87.9	104.6	16.7	19.7	-3.0
Toluene	25	94.1	115.1	21.0	16.3	4.7
	35	98.1	117.2	19.1	16.7	2.4
	45	102.0	119.2	17.2	17.2	0.0
Chloroform	20	56.8	76.5	19.7	16.5	3.2
	30	57.8	76.7	18.9	16.2	2.7
	40	58.8	76.8	18.0	16.0	2.0
	50	59.7	77.0	17.3	15.9	1.4
Tetrachloromethane	20	74.8	91	16	11.3	5
	30	75.9	91	15	11.6	3
	40	76.9	92	15	11.9	3
	50	77.9	92	14	12.5	2
	60	78.8	93	14	12.7	1
	70	79.7	94	14	13.9	0
Acetone	20	65.4	91.6	26.2	26.6	-0.4
	30	67.1	93.1	26.0	26.3	-0.3
	40	68.9	94.4	25.5	25.8	-0.3
	50	70.6	96.1	25.5	25.3	-0.2

TABLE II  
 (Continued)

Substance	$t, ^\circ\text{C}$	$c_v^{80}$	$c_v^1$	$\Delta c_v(\text{exp})$	$\Delta c_v(\text{calc})$	Abs. dev.
Methanol	35	37.6	71.1	33.5	42.7	-9.2
	45	38.1	73.6	35.5	42.2	-6.7
Water	10	25.9	75.5	49.6	47.5	2.2
	20	26.0	74.9	48.9	47.6	1.3
	30	26.3	73.4	48.1	47.2	-0.1
	60	26.6	71.6	45.0	46.2	-1.2
	80	26.9	69.8	42.9	44.7	-1.8
	100	27.3	67.8	40.5	42.7	-2.2

of  $c_v^1$  values is considerable (up to 3%), which can cause an absolute error as much as 2.7 J/mol K for a mean value of  $c_v^1 = 90$  J/mol K. Therefore it is not justified to consider the quantity  $\Delta c_v(\text{exp})$  as decisive, and to express deviations with regard to it. For the given possible error and a comparatively low value  $\Delta c_v \approx 20$  J/mol K, the deviation in per cent would give distorted results. In spite of these shortcomings, the comparison was carried out in this way to obtain at least an approximate picture of present possibilities of the method checked.

Discussion is exemplified in the last column of Table II in which the absolute deviations  $\Delta c_v(\text{calc}) - \Delta c_v(\text{exp})$  are given. All the quantities in columns 3-7 of Table II are in J/mol K. Let us recall that the upper estimate of error in calculated  $\Delta c_v$ , about 18%, was assessed on the assumption that all the errors added in one direction. This case is statistically of very little probability considering a large number of terms in Eq. (1). This fact follows partly from results of Table II, too. It is evident that for all the substances tested except methane, the mean value of the difference  $\Delta c_v(\text{calc}) - \Delta c_v(\text{exp})$  does not exceed the estimated upper limit of error. Rather higher deviations at lower temperatures are probably brought about by far extrapolation of  $c_p^{80}$  (and with this of reference  $c_v^{80}$ , too) from the region of higher temperatures. The results obtained prove the justification of assumptions of the method proposed.

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