CALCULATION OF THE DIFFERENCE BETWEEN MOLAR HEAT CAPACITY OF LIQUID AND IDEAL GAS FROM THE TEMPERATURE DEPENDENCE OF HEAT OF VAPORIZATION*

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Received April 17th, 1978

A method was developed for calculating the difference Δc_P between molar heat capacity of liquid c_P^l and of ideal gas c_P^{go} from the temperature dependence of heat of vaporization. By an *a priori* analysis the maximum error of the calculation procedure was determined. The exploitation of the method was demonstrated on a group of 20 saturated hydrocarbons. Besides these Δc_P values, the data on c_P^l and c_P^{go} were calculated in the regions where no experimental data are available, by combining Δc_P with the experimental values of molar heat capacities.

The difference between the molar heat capacity of liquid c_P^l and the molar heat capacity of ideal gas c_P^{go} is a thermodynamic quantity (denoted henceforth as Δc_P) important for the thermodynamic description of vapour–liquid phase equilibrium. This quantity is useful when calculating the enthalpy balances of some engineering processes, it can be used further for mutual conversions between the molar heat capacity of liquid and that of ideal gas. The quantity Δc_P has a close relation to the temperature derivative of heat of vaporization. In chemical-engineering relations for estimating c_P^l on the basis of the knowledge of c_P^{go}, however, the value Δc_P is usually calculated from the second-order derivative of saturated vapour pressures with respect to temperature[1]. Such a procedure is numerically badly stable and the calculation is usually subject to a considerable error. The calculation of Δc_P directly by using the temperature dependence of heat of vaporization, however, has not been applied yet above all for considerable lack of accurate experimental data on heat of vaporization which would enable to determine the derivative of heat of vaporization with respect to temperature with sufficient accuracy. In our laboratory we have been dealing for several years with the accurate measurements of heats of vaporization in their dependence on temperature. Therefore we decided to develop a method allowing to exploit these data for the determination of Δc_P. The aim of this paper is to test the chosen method, to judge its accuracy, reliability and to delimit the region in which its reasonable application is possible. The calculations of Δc_P were demonstrated on a group of saturated hydrocarbons (16 aliphatic and 4 cyclic) C5 – C8.

* Part XIII in the series Enthalpy Data of Liquids; Part XIII: This Journal *44*, 637 (1979).

Hydrocarbons are very suitable for the first test of the method proposed because accurate data on heat of vaporization are available for them, it is possible to express comparatively easily the P–V–T behaviour of these substances and for some of them also experimental values c_P^{go} and c_P^l may be found in the literature which can be employed for the comparison of Δc_P calculated from heats of vaporization with the values determined from experimental molar heat capacities.

THEORETICAL

The change of heat of vaporization with temperature along the line of saturation (pressure and temperature are bound by the Clapeyron equation and designated by subscript σ) can be expressed by the following way

$$(\partial \Delta H_v/\partial T)_\sigma = (\partial H^g/\partial T)_P + (\partial H^g/\partial P)_T (\partial P/\partial T)_\sigma + \\ - (\partial H^l/\partial T)_P - (\partial H^l/\partial P)_T (\partial P/\partial T)_\sigma \,, \qquad (1)$$

and by rearranging we obtain the relation

$$(\partial \Delta H_v/\partial T)_\sigma = c_P^g - c_P^l + \Delta H_v/T[1 - T((\partial V^g/\partial T)_P + \\ - (\partial V^l/\partial T)_P)/(V^g - V^l)] \,. \qquad (2)$$

Considering that it holds

$$c_P^g - c_P^{go} = -T\int_0^P (\partial^2 V^g/\partial T^2)_P \, dP \,, \qquad (3)$$

it is possible by combining Eqs (2) and (3) to attain the expression giving the difference of molar heat capacity of liquid and ideal gas in the form

$$c_P^l - c_P^{go} = -(\partial \Delta H_v/\partial T)_\sigma + \Delta H_v/T(1 - T((\partial V^g/\partial T)_P + \\ -(\partial V^l/\partial T)_P)/(V^g - V^l)) - T\int_0^P (\partial^2 V^g/\partial T^2)_P \, dP \,. \qquad (4)$$

The accuracy of the first member on the right-hand side of Eq. (4) usually above all conditions the success of calculation and for simplicity it will be denoted further as DH_v. The values of next two terms increase with increasing non-ideality of the vapour phase and in further text they will be denoted as correction terms D_1 and D_2. Then holds

$$\Delta c_P = -DH_v + D_1 + D_2 \,. \qquad (5)$$

To express the first member DH_v the data on temperature dependence of heat of vaporization were used which were published in the foregoing part of our series[2]. The given data set was obtained on the basis of critical analysis of literature values and of the results obtained recently in our laboratory. The data were selected which were considered to be the most accurate. In some cases the data of several authors were combined to attain wider temperature range and to diminish the probability of occurrence of systematic errors. The data were correlated by the Thiesen relation

$$\Delta H_v = K(1 - T_r)^\alpha . \qquad (6)$$

In Table I, the values of constants of the Thiesen correlation relation K(kJ/mol) and α are given for the substances investigated together with the temperature ranges within which they hold. We assume that it is possible to determine heat of vaporization with an accuracy of 0·2% in terms of the given constants in the respective temperature ranges.

It is evident from Eq. (4) that for determining the correction terms D_1 and D_2 it is necessary to estimate as well the P–V–T behaviour of the liquid and above all of the vapour phase. Considering that temperatures within the range of 0 to 100°C and pressures altogether lower than 150 kPa are concerned in this work, the virial expansion truncated after the second virial coefficient was used to express the P–V–T behaviour of the vapour phase. Attention was paid to the choice of suitable relation for the second virial coefficient which would make it possible to express with sufficient accuracy above all the first- and second-order derivative of volume with respect to temperature. The fact that the results can be influenced to a considerable extent by the use of virial expansion explicit in pressure or volume has been discussed before[3]. It was found by an analysis carried out by us that in the given case it is most advantageous to make use of the pressure-explicit form of virial equation where the value of second virial coefficient is determined according to Pitzer and Curl[4]. This estimation relation is especially advantageous for our case because when evaluating constants of this equation, experimental data on pressure dependence of c_p^g of some hydrocarbons had been used, too.

To express molar volume of the liquid phase the Rackett equation[5] was used

$$V^1 = (RT_c/P_c)\, z_c^{[1+(1-T_r)^{0.28571}]} , \qquad (7)$$

$$(\partial V^1/\partial T)_P = -0{\cdot}28571 V^1 \ln (V^1)\,(1 - T_r)^{0.28571}/(T_c - T) . \qquad (8)$$

The terms in Eq. (5) can be then expressed as follows:

$$DH_v = -\alpha\, \Delta H_v/(T_c - T) , \qquad (9)$$

TABLE I

Constants of Correlation Relations $\Delta H_v = K(1 - T_r)^{\alpha}$ and $\Delta c_P = K_0 + K_1 T + K_2 T^2 + K_3 T^3$

Substance	K	α	K_0	$K_1 \cdot 10^3$	$K_2 \cdot 10^6$	$K_3 \cdot 10^9$	Temperature range, °C
Pentane	38·58	0·375	−191·371	2 394·46	−8 106·82	9 346·67	25—80
2-Methylbutane	36·36	0·365	−161·151	2 118·123	−7 372·67	8 738·77	6—28
Hexane	43·97	0·375	−131·434	1 671·70	−5 214·58	5 594·54	25—80
2-Methylpentane	42·04	0·373	−138·278	1 765·63	−5 648·46	6 197·56	25—60
3-Methylpentane	42·03	0·367	−140·176	1 754·19	−5 555·27	6 025·57	25—80
2,2-Dimethylbutane	39·07	0·366	−127·048	1 673·65	−5 511·39	6 207·37	23—50
2,3-Dimethylbutane	39·85	0·346	−117·242	1 514·28	−4 838·74	5 288·75	23—60
Heptane	50·11	0·393	− 70·6846	1 049·27	−2 983·95	3 008·83	25—90
2-Methylhexane	48·42	0·398	− 76·5763	1 127·09	−3 298·10	3 403·13	25—80
3-Methylhexane	47·99	0·386	− 66·5903	1 004·76	−2 887·71	2 931·31	25—80
2,3-Dimethylpentane	46·28	0·372	− 64·9402	969·247	−2 805·15	2 856·78	25—80
2,2,3-Trimethylbutane	43·72	0·377	− 95·6909	1 263·72	−3 795·12	3 938·88	40—80
Octane	56·24	0·411	− 5·8167	436·766	− 953·328	822·620	25—80
2-Methylheptane	54·30	0·413	− 23·9006	613·649	−1 536·91	1 447·49	25—80
4-Methylheptane	54·29	0·414	− 23·1073	605·683	−1 513·49	1 421·24	25—80
2,2,4-Trimethylpentane	47·33	0·375	− 67·3557	984·072	−2 817·22	2 836·97	25—80
Cyclopentane	39·21	0·364	− 82·1108	1 163·08	−3 685·78	4 016·51	25—50
Methylcyclopentane	43·12	0·378	− 72·5517	1 050·00	−3 157·52	3 296·64	25—72
Cyclohexane	44·10	0·383	− 60·4179	901·149	−2 622·59	2 657·74	25—80
Methylcyclohexane	46·90	0·384	− 30·2960	606·497	−1 626·04	1 560·90	25—80

[a] Values of constants are given for ΔH_v in kJ mol^{-1} and Δc_P in J mol^{-1} K^{-1}.

$$D_1 = \Delta H_v/T\{1 - T[R/P + dB/dT - (\partial V^1/\partial T)_P]/(RT/P + B - V^1)\}, \quad (10)$$

$$D_2 = -TP(d^2B/dT^2). \quad (11)$$

Possibilities of the method proposed were first justified on the basis of an *a priori* estimate of possible error in calculated values of Δc_P. For such an estimation it is necessary to know at least approximately the magnitude and error of the three members occurring on the right-hand side of Eq. (*5*). The terms DH_v, D_1 and D_2 and the final values of Δc_P for normal hydrocarbons in their dependence on temperature are given in Table II for illustration. It clearly follows from the table that the importance of estimated terms D_1 and D_2 increases with rising temperature so increasing also the inaccuracy in Δc_P. Heats of vaporization are known for most substances in the range not exceeding very much the temperature of normal boiling

TABLE II

Members of Eq. (*5*) in Dependence on Temperature for Normal Hydrocarbons (J mol^{-1} K^{-1})

Temperature °C	DH_v	D_1	D_2	$c_P^1 - c_P^{go}$
		Pentane		
10	−54·9	− 8·5	2·4	48·8
40	−61·2	−14·9	4·1	50·5
70	−70·0	−22·9	6·4	53·5
		Hexane		
10	−54·1	− 4·7	1·4	50·8
40	−59·2	− 9·3	2·6	52·5
70	−65·8	−15·9	4·3	54·2
		Heptane		
10	−57·2	− 2·5	0·7	55·5
40	−61·7	− 5·6	1·6	57·7
70	−67·2	−10·6	2·9	59·6
		Octane		
10	−61·0	− 1·2	0·4	60·1
40	−65·1	− 3·3	0·9	62·7
70	−70·1	− 6·9	1·9	65·0

point. To estimate the maximum error it is therefore possible to start from the magnitude of values of input properties in the vicinity of normal boiling point. For the maximum error of Δc_P then holds

$$\delta\,\Delta c_P = \delta\,DH_v + \delta D_1 + \delta D_2\,. \tag{12}$$

The error in ΔH_v was estimated at 0·2% and therefore we can assume that the relative error $\delta_r\,DH_v$ in the derivative of heat of vaporization will be about 0·5%; for an average value $DH_v = 66$ J mol^{-1} K^{-1} the absolute error will be then about $\delta\,DH_v = 0{\cdot}33$ J mol^{-1} K^{-1}. When estimating the error of the member D_1 we can consider as typical the following values of input properties (in parentheses the estimated inaccuracy in per cent is always given): $B = -1\,300$ cm^3 mol^{-1} (10%), $dB/dT = 10$ cm^3 . . mol^{-1} K^{-1} (15–20%), $V^1 = 150$ cm^3 mol^{-1} (3%), $(\delta V^1/\partial T)_P = 0{\cdot}2$ cm^3 mol^{-1} . . K^{-1} (6%), $T = 340$ K. Under these circumstances the relative error $\delta_r D_1$ is then about 14% and for an average value of $D_1 = 16$ J mol^{-1} K^{-1} the upper limit of error is $\delta D_1 = 2{\cdot}2$ J mol^{-1} K^{-1}. By comparing the values of the member D_2 calculated according to Eq. (*11*) with the experimental data on $c_P^g - c_P^{go}$ given by Waddington and coworkers for some of substances investigated it followed that the error $\delta_r D_2$ did not exceed 20%; for a typical value of D_2 in the vicinity of the temperature of normal boiling point equal to 4 J mol^{-1} K^{-1} it is to be expected that $\delta D_2 = 0{\cdot}8$ J mol^{-1} K^{-1}.

By adding the individual absolute errors of members of Eq. (*12*) we get $\delta\,\Delta c_P = 3{\cdot}3$ J mol^{-1} K^{-1}. Assuming that Δc_P is on the average 54 J mol^{-1} K^{-1} it is then an error approximately 6%. In this connection it is necessary to emphasize that the error determined by this *a priori* analysis is the upper limit of the error which may occur just under the assumption that all inaccuracies of input quantities will sum up in one direction. With regard to a considerable number of input data it is, however, very little statistically probable. In reality practically always a compensation of some inaccuracies occurs and the results are generally subject to a lower error. The error also decreases substantially with decreasing temperature owing to the decreasing significance of the terms D_1 and D_2. In the region about the pressure of saturated vapour equal to 50 kPa, the maximum limit of the error determined by the above-mentioned way is already $\delta\,\Delta c_P = 1{\cdot}9$ J mol^{-1} K^{-1}, $\delta_r\,\Delta c_P = 3{\cdot}5$%. When the value of Δc_P is employed for calculating $c_P^{go}(c_P^1)$ on the basis of knowledge of experimental values $c_P^1(c_P^{go})$ the inaccuracy in the value Δc_P can cause a maximum error in $c_P^{go}(c_P^1)$ 2% (1·5%). We assume that for temperatures about normal boiling point the values $c_P^{go} = 160$ J mol^{-1} K^{-1} and $c_P^1 = 210$ J mol^{-1} K^{-1} are typical of the set of substances investigated.

RESULTS

The results of calculating the difference between molar heat capacity of liquid and ideal gas Δc_P are summarized in Table I in the form of constants of the correlation polynomial $\Delta c_P = K_0 + K_1 T + K_2 T^2 + K_3 T^3$ (J mol^{-1} K^{-1}). The values Δc_P calculated from the temperature dependence of heat of vaporization are compared in Table III with the values determined from the experimental molar heat capacities c_P^1 and c_P^{go}. The comparison was carried out for those substances for which a temperature range exists where the heats of vaporization and experimental values of c_P^1 and c_P^{go} are known simultaneously or their slight extrapolation is sufficient. In the second and third column, the absolute average deviations $\bar{\delta}\,\Delta c_P$ and the relative average deviations $\bar{\delta}_r\,\Delta c_P$ of calculated values of Δc_P from experimental ones are given together with the temperature ranges where the comparison was carried out.

By combining the values Δc_P determined from the temperature dependence of heat of vaporization with the experimental values of c_P^{go} and c_P^1 and on using the relations $c_P^1 = c_{P,Exp}^{go} + \Delta c_P$ and $c_P^{go} = c_{P,Exp}^1 - \Delta c_P$, the data on c_P^1 and c_P^{go} were obtained which reach to the temperature regions where no experimental data are known. The results are summarized in Table IV for all the set of substances investigated in the form of constants of the correlation polynomial $c_P = K_0' + K_1' T + K_2' T^2$. If the values of constants of the expansion for c_P^1 are not given for some substances it means that no sufficiently accurate values of c_P^{go} were found in the literature allowing the con-

TABLE III

Deviations of Values Δc_P Calculated from Temperature Dependence of Heat of Vaporization from Values Determined from Experimental Data on c_P^1 and c_P^{go}

Substance	$\bar{\delta}\,\Delta c_P$ J mol^{-1} K^{-1}	$\bar{\delta}_r\,\Delta c_P$ %	Temp. range of comparison, °C
Pentane	0·5	0·9	5— 25
2-Methylbutane	1·0	2·6	30— 40
Hexane	0·5	0·9	40— 80
2-Methylpentane	0·7	1·3	35— 45
3-Methylpentane	0·2	0·4	40— 50
2,2-Dimethylbutane	1·5	3·2	40— 50
2,3-Dimethylbutane	3·3	6·7	35— 55
Heptane	2·8	4·8	70—100
2,2,3-Trimethylbutane	1·1	2·3	40— 60
Cyclopentane	0·9	2·1	35— 45
Methylcyclopentane	0·2	0·5	40— 50
Cyclohexane	1·3	2·8	85— 95

TABLE IV

Constants of Correlation Polynomial for Calculated Values of c_p^l a c_p^{go} (J mol^{-1} K^{-1})

Substance	Value	K_0'	$K_1' \cdot 10^3$	$K_2' \cdot 10^6$	Temp range, °C	Ref.
Pentane	c_P^l	47·3947	408·571		25— 55	6
	c_P^{go}	162·276	— 646·132	1 688·35	5— 55	7
2-Methylbutane	c_P^l	43·0877	410		30— 40	8
	c_P^{go}	35·636	276·935		—5— 40	9
Hexane	c_P^l	58·6759	453·219		40— 90	10
	c_P^{go}	139·189	— 281·748	1 000	5— 85	7
2-Methylpentane	c_P^l	55·1935	462·667		35— 75	11
	c_P^{go}	45·5708	328·333		10— 45	12
3-Methylpentane	c_P^l	51·04	462·969		40— 85	11
	c_P^{go}	45·1912	325·413		5— 50	12
2,2-Dimethylbutane	c_P^l	44·2829	480·001		40— 60	10
	c_P^{go}	— 29·8659	846·9	— 904·748	10— 50	12
2,3-Dimethylbutane	c_P^l	44·4538	467·857		40— 70	11
	c_P^{go}	94·5522	— 9·08899	591·193	10— 55	12
Heptane	c_P^l	63·9054	526·787		65—100	13
	c_P^{go}	155·865	— 211·449	847·824	5—100	7
2-Methylhexane	c_P^{go}	154·341	— 287·067	1 099·63	5— 45	14
3-Methylhexane	c_P^{go}	342·879	—1 639·63	3 493·59	5— 45	15
2,3-Dimethylpentane	c_P^{go}	237·202	— 882·838	2 166·63	5— 40	15
2,2,3-Trimethylbutane	c_P^l	52·2595	535·667		40— 80	13
	c_P^{go}	47·3591	395·667		25— 65	14
Octane	c_P^{go}	183·487	— 217·566	812·725	5—100	7
2-Methylheptane	c_P^{go}	82·9531	361·711		5— 60	16
4-Methylpentane	c_P^{go}	113·586	99·0779	532·024	5— 60	16
2,2,4-Trimethylpentane	c_P^{go}	—153·785	1 878·02	—2 451·6	5— 60	16
Cyclopentane	c_P^l	6·08292	402·725		35— 60	17
	c_P^{go}	— 0·462498	280·133		15— 45	18
Methylcyclopentane	c_P^l	21·7152	453·992		40— 85	17
	c_P^{go}	77·8392	— 90·8065	683·198	10— 50	18
Cyclohexane	c_P^l	51·8587	364·881		80—100	19
	c_P^{go}	63·2925	— 10·8584	571·929	5—100	20—22
Methylcyclohexane	c_P^{go}	116·882	— 230·786	1 005·9	5— 55	23

version mentioned. In other columns, the temperature ranges are given in which the constants hold and references from which the experimental values of $c^{go}_{P,Exp}(c^{l}_{P,Exp})$ for calculation of $c^{l}_{P}(c^{go}_{P})$ were taken over.

DISCUSSION

When judging the applicability and accuracy of the method developed it is necessary to take into account the present state of our knowledge of experimental molar heat capacities of liquids and gases. The up-to-date adiabatic calorimetry is able to provide values of molar heat capacities of liquids within the range from very low temperatures up to a temperature 20 – 30°C below normal boiling point with an accuracy better than to 0·5%, the best laboratories report even the error lower than 0·2%. In the vicinity of the temperature of normal boiling point, however, the scattering of values given for the same substance by different authors is usually considerable (often 1 – 2%). The experiments are commonly, in the region of higher saturated vapour pressures, subject to systematic errors usually due to evaporation effects. The values of molar heat capacities of ideal gas are most often determined by calculating from spectra; however, these data do not often correspond to the real values of c^{go}_{P} because even for not too complicated molecules it is not possible to determine and resolve all fundamental vibrations and to establish the values of energy barriers which influence the value of gas molar heat capacity especially in the region of lower temperatures. The direct calorimetric determination of c^{go}_{P} by extrapolating molar heat capacities measured at several pressures to the value of zero pressure is experimentally rather troublesome. Some authors attain the accuracy of as much as 0·2% by elaborating this method; however, small number of systems in not too wide temperature ranges has been measured in this way for the present and generally the values of c^{go}_{P} determined from spectral data are preferred. It follows unambiguously from the Touloukian and Makita critical compilation[7], summarizing all the data on molar heat capacities of 55 industrially and theoretically important substances, that at high temperatures the agreement among the authors reporting c^{go}_{P} of organic substances is usually good but at temperatures around normal boiling point the scattering is always 3 – 4% and with decreasing temperature it has yet increasing trend.

It follows from the above-mentioned facts that the values Δc_P determined from experimental values of molar heat capacities can be liable to a considerable uncertainty (several per cent) which can strongly exceed the sum of errors in molar heat capacity of liquid and gas given by authors. Under these conditions it is then possible to consider the values of Δc_P calculated from the temperature dependence of heat of vaporization, as very good. This confirms also the altogether satisfactory agreement of experimental and calculated values of Δc_P.

If the values Δc_P are calculated from heats of vaporization by the way indicated they can be easily used for conversions between molar heat capacity of ideal gas and liquid. It enables an advantageous estimate in the regions where one of the quantities mentioned is experimentally accessible with difficulty while the second is known with sufficient accuracy. The concrete calculations and the presented survey of the contemporary knowledge of experimental c_P data indicate under which circumstances is advantageous to exploit such a type of conversions. The combination of Δc_P with an experimental value of c_P^l is suitable for estimating c_P^{go} at temperatures far below the temperature of normal boiling point because the values of molar heat capacity of liquid are known here with sufficient accuracy, while it is not possible to obtain here reliable data on c_P^{go}. On the other hand the calculation of c_P^l on the basis of combination of Δc_P with experimental value of c_P^{go} can be used at temperatures around normal boiling point where the determination of molar heat capacity of liquids is complicated and of little reliability.

LIST OF SYMBOLS

B	second virial coefficient
c_P	molar heat capacity at constant pressure
Δc_P	difference between molar heat capacity of liquid and ideal gas
D_1, D_2	corrrection terms defined by Eqs (*10*) and (*11*)
DH_v	deivative of heat of vaporization with respect to temperature
H	molar enthalpy
ΔH_v	heat of vaporization
K	adjustable constant of Thiesen relation
$K_0 - K_3$	adjustable constants of polynomial for expressing Δc_P
$K_0' - K_2'$	adjustable constants of polynomial for expressing c_P
P	pressure
R	gas constant
T	temperature (K)
V	molar volume
z	compressibility factor
α	adjustable constant of Thiesen relation
δ	absolute deviation
$\bar{\delta}$	average absolute deviation
δ_r	relative deviation
$\bar{\delta}_r$	average relative deviation

Indices

c	critical property
g	vapour property
go	ideal-gas property
l	liquid property
r	reduced quantity
σ	change along saturation line

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Translated by J. Linek.