RELATION OF THE TEMPERATURE DERIVATIVE OF HEAT OF VAPORIZATION TO THE DIFFERENCE OF HEAT CAPACITIES ALONG THE SATURATED VAPOUR PRESSURE CURVE*

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A method of calculating the heat capacity difference of liquid and its vapour along saturated vapour pressure curve is discussed. The qualitative course of this difference in dependence on temperature obtained from the data on the temperature dependence of heat of vaporization of pure substances is judged.

Heats of vaporization of substances in dependence on temperature are measured for the purposes of theoretical modelling of solutions and chemical-engineering practice. Accurate data on the temperature dependence of heat of vaporization can be employed among others also for calculating other thermodynamic quantities. In accordance with this, studies on calculating the heat capacity difference of liquids and gases under constant pressure and volume[1,2] have been carried out previously. A continuation of this project is the calculation of the molar heat capacity difference of liquids and gases along the saturated vapour pressure curve, Δc_σ.

The quantity Δc_σ, which is not accessible experimentally, has a considerable importance. Above all it is the quantity that characterizes the given type of the vapour–liquid phase equilibrium of pure substances. From the Δc_σ values it is possible to determine the molar heat capacity of vapour along the saturated curve, c_σ^g, which cannot be determined experimentally; it is possible to calculate the values of the term $(\partial S^g/\partial T)_\sigma$ characterizing the saturated vapour phase. The known values Δc_σ are further exploited in the experimental determination of values of molar heat capacity of liquid along the saturated vapour pressure curve, c_σ^l, by the method of "two-phase system"[3]. A further use is offered on using the interrelations between c_σ, c_p and c_v of coexisting phases[4] above all for estimating the state-behaviour terms.

The aim of this work was to verify the proposed method for calculating Δc_σ and c_σ^g starting from the known data on the temperature dependence of heat of vapori-

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zation and to compare it with other potential methods of calculation. Further, to carry out the qualitative judgement of the dependence of Δc_σ on temperature.

THEORETICAL AND DISCUSSION

The derivation of the sought interrelation between the temperature dependence of heat of vaporization ΔH_v and Δc_σ can be carried out as follows:

$$(\partial \Delta H_v/\partial T)_\sigma = [\partial(T\Delta S_v/\partial T)]_\sigma = [T(\partial \Delta S_v/\partial T) + \Delta S_v]_\sigma = \Delta c_\sigma + \Delta S_v, \quad (1)$$

where $\Delta S_v = \Delta H_v/T$ is the entropy of vaporization and the relation

$$T(\partial \Delta S_v/\partial T)_\sigma = T(\partial S^g/\partial T)_\sigma - T(\partial S^1/\partial T)_\sigma = c_\sigma^g - c_\sigma^1 = \Delta c_\sigma. \quad (2)$$

Relation (2) is simultaneously the definition relation for c_σ^g and c_σ^1. The molar heat capacity difference Δc_σ is then given by the relation

$$\Delta c_\sigma = (\partial \Delta H_v/\partial T)_\sigma - \Delta H_v/T. \quad (3)$$

To calculate Δc_σ from Eq. (3) it is necessary to choose a suitable correlation relation for expressing the temperature dependence of ΔH_v and its temperature derivative. Such a relation is here the Thiesen relation.

$$\Delta H_v = k(1 - T_r)^C, \quad (4)$$

where k and C are constants and T_r the reduced temperature. After substituting it into Eq. (3) and rearranging we get finally the relation in the form

$$\Delta c_\sigma = -(k/T_c)(1 - T_r)^{C-1}(C - 1 + 1/T_r), \quad (5)$$

which has been used for calculating Δc_σ in this work.

The direct calculation of c_σ^g from Δc_σ is not, in a general case, possible because rather very few data only are known on c_σ^1. Therefore we use the approximation which starts from the interrelation between c_σ^1 and c_p^1

$$c_\sigma^1 = c_p^1 - T(\partial V^1/\partial T)_P(\partial P/\partial T)_\sigma \quad (6)$$

then employing the fairly extensive information on c_p^1 values[5]. Further we know that for the prevailing part of substances (expecially hydrocarbons[6]), the state-behaviour terms in Eq. (4), take, up to reduced temperatures equal 0·8, so small values

that it is possible to neglect them and to assume with sufficient accuracy that it holds $c_\sigma^l = c_p^l$. Then we use the following relation for calculating c_σ^g:

$$c_\sigma^g = \Delta c_\sigma + c_p^l . \tag{7}$$

Calculation

The proposed method of calculating Δc_σ and c_σ^g is demonstrated for a group of industrially important hydrocarbons. Their temperature dependences of ΔH_v have been determined experimentally and published[7]. The given values of correlation constants and of used values of reduced temperatures in the Thiesen relation have been taken over and employed in this work. The calculated values of Δc_σ and c_σ^g for the chosen group of hydrocarbons are given in Table I. In the first column of the table, the names of substances and the symbols of calculated quantities Δc_σ and c_σ^g along with the literature values of c_p^l (ref.[5,6]) are given. In the next columns, the values of studied quantities for the chosen temperatures are presented.

Since the quantity c_σ^g cannot be determined experimentally it is also impossible to compare the calculated values of Δc_σ with the values calculated from the experimental data on c_σ^l and c_σ^g and to verify in this way the possibilities of the method proposed. Its use can be characterized just by an *a priori* analysis of errors in quantities entering the calculation and by determining the upper limit of errors in calculated values of Δc_σ. To this purpose, Eqs (3) and (7) will be considered.

In the cited work dealing with ΔH_v of chosen hydrocarbons, the accuracy of the measured and correlated values of heats of vaporization is given to be $0.1 - 0.2\%$. On the basis of experience from our previous studies[1,2], it can be assumed that the error due to the determination of the term $(\partial \Delta H_v/\partial T)_\sigma$ does not exceed 0.5%. Considering that the values of heats of vaporization have, in the vicinity of normal boiling point, the value about 30 kJ mol^{-1} and the term of the first derivative $(\partial \Delta H_v/\partial T)_\sigma$ about $70 \text{ J K}^{-1} \text{ mol}^{-1}$, the first term in Eq. (3) introduces an absolute error of $0.35 \text{ J K}^{-1} \text{ mol}^{-1}$ and the second term up to $0.2 \text{ J K}^{-1} \text{ mol}^{-1}$ into the calculation. The quantity Δc_σ acquires the values about $150 \text{ J K}^{-1} \text{ mol}^{-1}$; then the relative error in Δc_σ does not exceed 0.4%.

The absolute error in determining c_σ^g is given by the error with which the data on c_σ^l are determined and by the error introduced by neglecting the state-behaviour terms in Eq. (6). It can be assumed that this error does not exceed the value of $1 \text{ J K}^{-1} \text{ mol}^{-1}$ (ref.[1,2]) in the temperature range in which the calculations in this work have been carried out. Since the values of molar heat capacity along the saturated vapour pressure curve are within the range of -25 to $+110 \text{ K J}^{-1} \text{ mol}^{-1}$ the relative error would not yield useful information.

From the other possible ways of calculating Δc_σ only one method comes into con-

sideration. It starts from the assumption that we know the experimental c_p^l (or c_σ^l) values and calculate the c_σ^g values; estimation methods for Δc_σ are not known. The problem of calculation is connected only with the problems of calculating c_σ^g.

For calculating the c_σ^g values, it is possible to use practically only one method. It starts from the known values of heat capacity of vapour c_p^g and from the state behaviour of the vapour phase along the saturated vapour pressure curve. The method which stems from the calculation of the term $(\partial S^g/\partial T)_\sigma$ and from the equation of state of real gas is not applicable[7,8]. For the method recommended we use an analogous relation to Eq. (6):

$$c_\sigma^g = c_p^g - T(\partial V^g/\partial T)_P (\partial P/\partial T)_\sigma. \tag{8}$$

The error connected with the determination of values of the derivative terms in Eq. (8) has been extensively discussed in papers[1,2]. It has been proved that the error connected with determining the term $(\partial V^g/\partial T)_P$ amounts to about 5% and the term $(\partial P/\partial T)_\sigma$ about 1%. Then the relative error of the second expression in Eq. (8) will be 6%. Since c_p^g acquires, in the range of temperatures discussed by us, the values of approximately 180 J K^{-1} mol^{-1}, the absolute error in c_σ^g will be about 11 J K^{-1} mol^{-1}. It is an error which is one order higher than that connected with determining c_σ^g from calorimetric data.

On the basis of the performed discussion it is possible to say that the method of calculating Δc_σ and c_σ^g starting from the data on the temperature dependence of heat of vaporization and from the calorimetric data on c_p^l can be recommended.

Course of Temperature Dependence of Δc_σ

When calculating the quantity Δc_σ for a few substances for which the data on temperature dependence of ΔH_v are known up to the vicinity of the critical point[9-11], we have always found a local maximum on the curve $\Delta c_\sigma = \Delta c_\sigma(T)$. A question arises whether the existence of local maximum of the quantity Δc_σ is a general property of Δc_σ or whether its occurrence is brought about by the type and properties of the correlation relation for ΔH_v. The answer to this question can be found by the following consideration: We shall assume that the dependence of heat of vaporization ΔH_v on reduced temperature T_r is continuous and continously differentiable to all orders and satisfies the following conditions:

1) d $\Delta H_v/dT_r < 0$ for all T_r, i.e. heat of vaporization is a decreasing function of temperature. 2) $d^2 \Delta H_v/dT_r^2 < 0$ for all T_r, i.e. heat of vaporization is a concave function of temperature. 3) $\lim_{T_r \to 1}$ d $\Delta H_v/dT_r = -\infty$. 4) $d^3 \Delta H_v/dT_r^3 < 0$ for all T_r, i.e. the second derivative of heat of vaporization with respect to temperature is a decreasing function of temperature.

TABLE I

Summary of calculated values of heat capacities of some important hydrocarbons

Substance	Quantity $J\,K^{-1}\,mol^{-1}$	Temperature, °C							
		10	20	30	40	50	60	70	80
Pentane	$-\Delta C_\sigma$	151·3	148·0	145·2	142·8	141·0	139·6	138·8	138·0
	C_P^l	163·5	167·3						
	C_σ^g	12·2	19·3						
2-Methylbutane	$-\Delta C_\sigma$	143·5	140·5	138·1	136·0				
	C_P^l	159·9	163·2	166·5	170·0				
	C_σ^g	16·4	22·7	28·4	34·0				
Hexane	$-\Delta C_\sigma$	168·5	164·3	160·5	157·2	154·3	151·8	149·7	148·1
	C_P^l	190·5	193·9	197·6	201·5	205·6	210·0	214·5	219·3
	C_σ^g	22·0	29·6	37·1	44·3	51·3	58·2	64·8	71·2
2-Methyl-pentane	$-\Delta C_\sigma$	158·0	154·0	151·5	148·9	146·7			
	C_P^l	191·8	195·6	199·4					
	C_σ^g	33·7	41·0	47·9					
3-Methyl-pentane	$-\Delta C_\sigma$	161·2	157·2	153·7	150·5	147·8	145·5	143·5	142·0
	C_P^l	185·3	188·9	192·7	196·5	200·4			
	C_σ^g	24·1	31·7	39·0	46·0	52·6			
2,2-Dimethyl-butane	$-\Delta C_\sigma$	151·2	147·6	144·5	141·8	139·5			
	C_P^l	183·3	187·0	190·5	193·9	197·1			
	C_σ^g	32·1	39·4	46·0	52·1	57·6			
2,3-Dimethyl-butane	$-\Delta C_\sigma$	149·3	146·0	143·0	140·5				
	C_P^l	186·8	190·6	194·6	198·6				
	C_σ^g	37·4	44·6	51·5	58·1				
Heptane	$-\Delta C_\sigma$	189·4	184·3	179·7	175·5	171·5	168·4	165·2	162·9
	C_P^l	219·5	223·0	226·6	230·4	234·4	238·5	242·8	247·2
	C_σ^g	30·1	38·7	46·9	54·9	62·6	70·1	77·3	84·3
2-Methyl-hexane	$-\Delta C_\sigma$	183·7	178·9	174·5	170·6	167·1	164·0	161·2	158·9
	C_P^l	216·6	220·8	225·2	229·7				
	C_σ^g	32·9	41·9	50·7	59·1				
3-Methyl-hexane	$-\Delta C_\sigma$	181·7	176·9	172·5	168·5	165·0	161·9	159·1	156·7
	C_P^l	211·6	216·1	221·2	226·9				
	C_σ^g	29·9	39·2	48·7	58·4				

TABLE I

(Continued)

Substance	Quantity $J\,K^{-1}\,mol^{-1}$	Temperature, °C							
		10	20	30	40	50	60	70	80
2,3-Dimethyl-	$-\Delta C_\sigma$	175·0	170·3	166·1	162·2	158·8	155·8	153·1	150·8
pentane	C_P^l	210·4	214·7	219·4	224·4				
	C_σ^g	35·4	44·4	53·3	62·2				
2,2,3-Trimethyl-	$-\Delta C_\sigma$			157·4	153·8	150·7	147·9	145·4	143·3
butane	C_P^l			215·7	220·1	224·5	228·9		
	C_σ^g			58·3	66·3	73·8	81·0		
Octane	$-\Delta C_\sigma$	210·6	204·7	199·3	194·4	189·9	185·8	182·1	178·9
	C_P^l	248·2	251·5	255·1	258·8	262·6	266·5	270·6	274·8
	C_σ^g	37·6	46·8	55·8	64·4	72·7	80·7	88·5	95·9
2-Methyl-	$-\Delta C_\sigma$	203·9	198·7	193·1	188·4	184·2	180·3	176·9	173·8
heptane	C_P^l	244·9	249·3	253·8	258·2	262·6	267·0		
	C_σ^g	41·0	50·6	60·7	69·8	78·4	86·7		
4-Methyl-	$-\Delta C_\sigma$	203·8	198·1	193·0	188·3	184·0	180·1	176·7	173·6
heptane	C_P^l	243·6	248·5	253·5	258·6	263·7	268·9		
	C_σ^g	39·8	50·4	60·5	70·3	79·7	88·8		

The quantity Δc_σ is a function of reduced temperature, i.e. we can write

$$\Delta c_\sigma = Y(T_r)\,. \qquad (9)$$

Then Eq. (3) can be rewritten into the form

$$Y(T_r) = \frac{1}{T_c}\left[f'(T_r) - \frac{f(T_r)}{T_r} \right], \qquad (10)$$

where $f(T_r) = \Delta H_v(T_r)$, $f'(T_r) = \Delta H'_v(T_r) = d\,\Delta H_v/dT_r$ and T_c is the critical temperature. Since heat is a decreasing function of temperature, i.e. $f' < 0$ for all T_r, then it is evident from Eq. (10) that Δc_σ is in the entire definition range negative and for $T \to T_c$ it holds $\Delta c_\sigma \to -\infty$. For the first derivative of the function $Y(T_r)$ it is

$$Y'(T_r) = \frac{1}{T_c}\left[f''(T_r) - \frac{f'(T_r)}{T_c} + \frac{f(T_r)}{T_c^2} \right] = \frac{f''(T_r)}{T_c} - \frac{Y(T_r)}{T_r}\,. \qquad (11)$$

For low values of reduced temperature, heat of vaporization can be expressed with very good approximation as a linear function of temperature, i.e. $f''(T_r) \approx 0$. Thus it follows from Eq. (11)

$$Y' \, (\text{low } T_r) > 0 \, . \tag{12}$$

Further it follows from Eq. (11)

$$\lim_{T_r \to 1} Y'(T_r) = \frac{1}{T_c} \lim_{T_r \to 1} \left(f''(T_r) - f'(T_r) \right) \, . \tag{13}$$

Let us assume for a moment that in the vicinity of the critical point it holds $f''(T_r) < < f'(T_r)$. Then it follows from Eq. (13)

$$Y'(T_r \approx 1) < 0 \tag{14}$$

and consequently $\left(\text{Eq. } (12)\right)$ there exists a reduced temperature T_r^+ for which

$$Y'(T_r^+) = 0 \, . \tag{15}$$

TABLE II
Dependence of the maximum value of Δc_σ and its position on the values of parameters of the Thiesen relation (J K^{-1} mol^{-1})

Substance	T_r^+, max	Δc_{σ}, max	k/T_c
Pentane	0·7509	−138·4	82·16
2-Methylbutane	0·7505	−133·0	78·98
Hexane	0·7509	−146·0	86·66
2-Methylpentane	0·7509	−142·4	84·51
3-Methylpentane	0·7506	−140·3	83·33
2,2-Dimethylbutane	0·7506	−134·6	79·94
2,3-Dimethylbutane	0·7501	−134·1	79·71
Heptane	0·7519	−156·3	92·76
2-Methylhexane	0·7522	−153·8	91·31
3-Methylhexane	0·7515	−151·1	89·67
2,3-Dimethylpentane	0·7508	−145·1	86·14
2,2,3-Trimethylbutane	0·7510	−138·7	82·32
Octane	0·7532	−166·5	98·88
2-Methylheptane	0·7533	−163·4	97·04
4-Methylheptane	0·7534	−162·9	96·73

When deriving the validity of the given assumption, we employ the l'Hospital rule and the validity of relations $f(1) = 0$, $\lim_{T_r \to 1} f'(T_r) = -\infty$. Obviously it holds

$$0 = \lim_{T_r \to 1} \frac{f(T_r)}{f'(T_r)} = \lim_{T_r \to 1} \frac{f'(T_r)}{f''(T_r)} , \qquad (16)$$

and accordingly $|f'(T_r)| < |f''(T_r)|$ in a certain vicinity of the critical point. Since it holds $f'(T_r) < 0$ and $f''(T_r) < 0$ for all T_r it is possible to write $f'(T_r) < f''(T_r)$ in a certain vicinity of the critical point, which proves the validity of the assumption. Type of the extreme is determined from the property of the second derivative of the function $Y(T_r)$:

$$Y''(T_r) = \frac{1}{T_c}\left[f'''(T_r) - \frac{f''(T_r)}{T_r} + \frac{2f'(T_r)}{T_r^2} - \frac{2f(T_r)}{T_r^3}\right] =$$

$$= \frac{f'''(T_r)}{T_c} - \frac{Y'(T_r)}{T_r} + \frac{Y(T_r)}{T_r^2} . \qquad (17)$$

We know that the function Y has an extreme $(Y' = 0)$. Then the right-hand side of Eq. (17) is lower than zero, which proves that the extreme is a local maximum. Since the function $f(T_r)$ is continuous and continuously differentiable to all orders, the same holds for the function $Y(T_r)$. Owing to these conditions the local maximum is just one.

In the next step the coordinates of the local maximum of Δc_σ on the temperature axis and the value $\Delta c_{\sigma,\max}$ have been sought for prospective generalization of the temperature dependence of Δc_σ. For the case when the temperature dependence of ΔH_v is described by the Thiesen relation, we get by calculating from Eqs (10) and (11) for the studied set of hydrocarbons the results which are summarized in Table II. The first column of the table gives the values of reduced temperature $T_{r,\max}^+$ for $\Delta c_{\sigma,\max}$; $\Delta c_{\sigma,\max}$ is the maximum value of Δc_σ. Whereas in using the Thiesen relation, the value of coordinate $T_{r,\max}^+$ is dependent only on the value of the exponent C (Eq. (4)), the value of $\Delta c_{\sigma,\max}$ depends also on the magnitude of the term k/T_c which is as well given in Table II.

The calculated values of $T_{r,\max}^+$ for the given set of substances mislead to the presumption that their mean value could characterize the local extreme. Unfortunately the results of calculation on using other correlation relations show that $T_{r,\max}^+$ for the given set of substances and for the chosen type of correlation relations lies within the range of $T_r = 0.7 - 0.8$. It is evidently due to the different flexibility of relations, which appears especially when calculating the term of the second derivative $f''(T_r)$ in Eq. (11). Since in this work the data have been correlated by the Thiesen relation, which is recommended in the literature, the results for this relation only are given in Table II so that the calculations should be conformal.

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