DETERMINATION OF HEATS OF VAPORIZATION
AND SOME OTHER THERMODYNAMIC PROPERTIES
FOR FOUR SUBSTITUTED HYDROCARBONS*

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The temperature dependence of heats of vaporization and some other derived thermodynamic properties were determined for four substituted hydrocarbons, *viz.* 2,2,4-trimethylpentane, 1-octene, ethylbenzene and n-butylbenzene. The temperature dependence of heats of vaporization was measured and, on the basis of these data, the values of standard heats of vaporization, internal and cohesive energies, entropies of vaporization and the difference of heat capacities of liquid and vapour at constant pressure and along the saturated vapour pressure curve were computed.

This work is further contribution to the study of phase equilibrium of the vapour––liquid type of pure substances and reassumes our previous papers dealing with the properties of saturated hydrocarbons[1,2] and alkylcycloparaffins[3]. The aim of the work is to complete or give more precision to the existing knowledge of thermodynamic quantities describing the vapour–liquid phase transition. The subject of the study are above all those groups of hydrocarbons which are the centre of present interest not only of theoretical works but play a significant role in practical applications above all in petrochemistry.

EXPERIMENTAL

Preparation and purity of substances. The substances 2,2,4-trimethylpentane and 1-octene were commercial products of A.R. purity. They were rectified on a rotating hundred-plate column with stainless steel packing. In such a way prepared fractions were stored above molecular sieves for water of the Nalsit A4 type. Ethylbenzene and n-butylbenzene were obtained pure as chromatographic standards. They were also stored above the molecular sieves. Purity of the substances was checked by analysis on a mass spectrograph and the presence of other substances was not found.

Measurement. The temperature dependence of heats of vaporization was measured using the isothermal vaporization calorimeter which has been described in detail previously[4]. The measurement was carried out in the temperature range 25—95°C with a step of 10—15°C. The lower

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temperature limit of measurement was given for individual substances by the value of saturated vapour pressure at which it was still possible to perform the evaporation process in the given calorimetric equipment. The error of measurement was estimated on the basis of the accuracy analysis of input data and of respective corrections; it was lower than 0.2%.

RESULTS

The measured values of heats of vaporization ΔH_v were correlated by the relation proposed in our laboratory[5]

$$\Delta H_v = K(1 - T_r)^\alpha \, e^{-\beta T_r} , \qquad (1)$$

where K, α, β are correlation constants and T_r is reduced temperature.

In the given temperature range (70°C) it is possible to make use of its simpler form, where $\alpha = \beta$ and relation (1) turns into the two-constant one.

To obtain a comprehensive view and objective results in the data treatment, the values of heats of vaporization obtained in this work were completed by the literature data of the authors: Majer[1] — 2,2,4-trimethylpentane at 25, 40, 60 and 80°C (denoted by index a in Table I), Sunner[6] — 1-octene at 25°C (index b), Scott[7] — ethylbenzene at 20.9°C (index c), Osborne[8] — ethylbenzene at 25°C (index d) and Mathews[9] — ethylbenzene at 135.17°C (index e). Compilation of the data along with the results of simultaneous correlations are given in Table I. K and α are values of the correlation constants in Eq. (1), T_c critical temperature in K, T_{NBP} normal boiling point and δ the standard deviation in kJ/mol. Besides, the values of two heats of vaporization most often sought in the literature are given, viz. ΔH_{vNBP} — heat of vaporization at normal boiling point and ΔH_{v25} — heat of vaporization at 25°C. Both the values were obtained by calculating in terms of Eq. (1) using correlation constants obtained for the given temperature ranges. The needed values of physical quantities were obtained from the literature: T_c (ref.[10,11]), P_c (ref.[10,11]), T_{NBP} (ref.[10,12]). The data undesignated in Table I are the values measured in this work. The data denoted by indexes b, e were not considered in the correlation because they exhibited an error higher than 0.2% in the initial correlation. For instance, the data point for 1-octene at 25°C -0.67% and that for ethylbenzene at 135.17°C -2.08%.

The measured values of heats of vaporization combined with the data on saturated vapour pressures, densities of the liquid phase and P–V–T behaviour of the gas phase were used to calculate standard heats of vaporization ΔH_v^0, internal energies of vaporization ΔU_v, cohesive energies ΔU_c and entropies of vaporization ΔS_v. Their relation to the heat of vaporization is given by the equations

$$\Delta H_v^0 = \Delta H_v + \Delta H^+ , \qquad (2)$$

$$\Delta U_v = \Delta H_v - P^0(V^g - V^1), \tag{3}$$

$$\Delta U_c = \Delta H_v + \Delta H^+ - RT + P^0 V^1, \tag{4}$$

$$\Delta S_v = \Delta H_v/T, \tag{5}$$

where ΔH^+ denotes the difference between the enthalpy of ideal gas and that of saturated vapour; P^0, V^g, V^1, R and T denote the saturated vapour pressure, molar volumes of the gas (g) and the liquid (l) phase, the gas constant and temperature in K, respectively.

TABLE I

Compiled values of heats of vaporization (kJ/mol) and results of correlation

°C	2,2,4-Trimethyl-pentane	1-Octene	Ethylbenzene	n-Butyl-benzene
20·9			42·48[c]	
25	35·14[a]	40·27[b]	42·25[d]	
25	35·15			
40	34·40	39·52		
40	34·34[a]			
55	33·44	38·62	40·47	
60	33·16[a]			
70	32·55	37·62	39·45	47·95
80	31·95[a]			
85	31·69	36·57	38·55	46·79
95	31·05	35·80		46·02
137·17			36·02[e]	
K	50·3315	58·6010	59·5224	73·6328
α	0·2674	0·2893	0·2999	0·3425
T_c	543·89	566·60	617·10	660·50
δ	0·017	0·053	0·0372	0·002
T_{NBP}	372·39	394·43	409·34	456·42
ΔH_{vNBP}	30·78	33·95	35·20	38·87
ΔH_{v25}	35·15	40·55	42·25	51·36

[a] Lit. data by Majer[1]; [b] lit. data by Sunner[6], were not used in correlation; [c] lit. data by Scott[7]; [d] lit. data by Osborne[8]; [e] lit. data Mathews[9], were not used in correlation.

To describe the P–V–T behaviour of the gas phase we used the pressure form of the virial equation of state truncated after the second virial coefficient B. Then it is possible to write

$$\Delta H^+ = P\left[T(\mathrm{d}B/\mathrm{d}T) - B\right]. \tag{6}$$

The values of second virial coefficients and their derivatives with respect to temperature were calculated by using the relation proposed by Pitzer and Curl[13]. The data

TABLE II

Temperature dependence of standard heats of vaporization, internal energies of vaporization, cohesive energies in kJ/mol and entropies of vaporization in J/mol K as expressed by Eq. (7)

Quantity	K'	β	δ^a
2,2,4-Trimethylpentane 20—95°C			
ΔH_V^0	48·3700	0·2368	0·039
ΔU_v	50·3868	0·3224	0·010
ΔU_c	48·8444	0·2984	0·038
ΔS_v	311·957	0·7279	0·646
1-Octene 40—95°C			
ΔH_V^0	56·8168	0·2657	0·023
ΔU_v	58·9609	0·3447	0·004
ΔU_c	57·5285	0·3249	0·021
ΔS_v	367·190	0·7857	0·588
Ethylbenzene 20—85°C			
ΔH_V^0	58·6467	0·2868	0·020
ΔU_v	60·1169	0·3614	0·002
ΔU_c	59·4081	0·3509	0·016
ΔS_v	390·537	0·8900	0·658
n-Butylbenzene 70—95°C			
ΔH_V^0	72·8078	0·3329	0·003
ΔU_v	74·6619	0·4024	0·000
ΔU_c	74·0022	0·3948	0·003
ΔS_v	443·468	0·9226	0·131

^{a} Standard deviations are given in kJ/mol, for ΔS_v in J/mol K.

on volumes of the liquid phase for n-butylbenzene and 1-octene were estimated by means of the Rackett equation[14], for 2,2,4-trimethylpentane and ethylbenzene, its modification proposed by Spencer and Danner[15] was used. The factor z_c of the Rackett equation was determined from the known value of density at one temperature (1-octene[16], n-butylbenzene[17]) and the parameter V_{RA} in the Spencer–Danner equation for 2,2,4-trimethylpentane and ethylbenzene from the source[18]. The data on saturated vapour pressures were obtained by calculating from the Antoine equation. The values of constants were taken from the literature[12,19].

The calculations were carried out in the temperature ranges identical with the temperatures of measured heats of vaporization. The data were correlated by the two-constant relation (Eq. (1))

$$X = K'[(1 - T_r) \exp(-T_r)]^\beta, \tag{7}$$

where X denotes the correlated quantity (ΔH_v^0, ΔU_v, ΔU_c, ΔS_v), K' is the correlation constant of Eq. (7). The results are summarized in Table II. The constants of Eq. (7) for all the substances and quantities studied, the values of standard deviations δ in kJ/mol and the temperature ranges for which the given data hold are given there.

Further we made use of the known data on the temperature dependence of heats of vaporization for calculating other characteristic quantities, i.e. the difference of heat capacities of the liquid and vapour phase along the saturated vapour pres-

TABLE III

Expression of the temperature dependence of heat capacity difference Δc_σ and Δc_p in J/mol K by using Eq. (11)

Substance	Heat capacity difference	A	B	$-C \cdot 10^3$	δ^a	Temperature interval, °C
2,2,4-Tri-methylpentane	Δc_σ	−486·781	1·59478	1·8238	0·033	20—95
	Δc_p	41·4478	0·08639	1·61917	0·043	
1-Octene	Δc_σ	−544·171	1·71480	1·88190	0·018	40—95
	Δc_p	41·5324	0·13683	2·18829	0·013	
Ethylbenzene	Δc_σ	−552·857	1·72665	1·84368	0·065	20—85
	Δc_p	37·7354	0·13487	2·09134	0·003	
n-Butyl-benzene	Δc_σ	−631·243	1·83020	1·80996	0·006	70—95
	Δc_p	53·0985	0·12656	1·80737	0·001	

^{a} Standard deviation in J/mol K.

sure curve Δc_σ and at constant pressure Δc_p. The difference Δc_σ is defined as $\Delta c_\sigma = c_\sigma^g - c_\sigma^1$ and $\Delta c_p = c_p^1 - c_p^{g0}$, where c_p^{g0} is the heat capacity of a gas in the state of ideal gas. These quantities are connected with heat of vaporization and its temperature derivative by the following relations

$$\Delta c_\sigma = (\partial \Delta H_v/\partial T)_\sigma - \Delta H_v/T \tag{8}$$

and

$$\Delta c_p = -(\partial \Delta H_v/\partial T)_\sigma + (\Delta H_v/T)\left[1 - T\{(\partial V^g/\partial T)_P - (\partial V^1/\partial T)_P\}/\right.$$
$$\left./(V^g - V^1)\right] - T \int_0^P (\partial^2 V^g/\partial T^2)_P \, dP \,. \tag{9}$$

In the range of low pressures it is possible to describe the P–V–T behaviour of the gas phase by the volume explicit form of the virial equation of state truncated after the second term. For this range Eq. (9) holds in the form

$$\Delta c_p = (\partial \Delta H_v/\partial T)_\sigma + (\Delta H_v/T)\left[1 - T\{R/P^0 + dB/dT - (\partial V^1/\partial T)_P\}/\right.$$
$$\left.(RT/P^0 + B - V^1)\right] - TP^0(d^2B/dT^2) \,. \tag{10}$$

The calculated values of the difference of heat capacities were correlated by the second-order polynomial

$$\Delta c_X = A + BT + CT^2 \,, \tag{11}$$

where the symbol Δc_X denotes Δc_σ or Δc_p, respectively; A, B, C are the correlation constants. The results of correlations are summarized in Table III. The table is arranged so that after the name of each substance there are the correlation constants of Eq. (11) for Δc_σ in the first line and the constants of the same relation for Δc_p in the second line. For both the quantities the data follow on standard deviations and on the temperature range to which the given values refer.

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