HEATS OF VAPORIZATION OF SIMPLE NON-SPHERICAL MOLECULE COMPOUNDS

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Saturated vapour pressures of carbon disulphide, dichloromethane, trichloromethane, tetrachloromethane, tetrachloroethylene, tribromomethane, methyl iodide, methanol and acetone have been measured in the pressure range of 20—760 Torr. The measured data have been correlated by the Antoine equation. From the constants of the equation for the mentioned substances, heats of vaporization at their normal boiling points were calculated and used to verify the ΔH^V estimations on the basis of the hard convex body equation of state.

Recently[1,2] it was shown that the hard sphere equation of state combined with the first-order perturbation treatment yields a good estimation of the heats of vaporization for the substances formed by monatomic molecules or by small highly symmetrical polyatomic ones. The prediction of the theory becomes worse in case of the non-spherical molecule substances. However, a considerable improvement of the agreement of the theoretical and experimental values of the heats of vaporization of n-alkanes and perfluoro-n-alkanes was attained by using the hard convex body equation of state instead of the hard sphere one. When using the hard convex body system as a reference one, the determination of characteristic functionals (of volume, surface area and the mean curvature integral) of the proposed models of molecules considered becomes evident to be the main problem. The study of representative models (of hard convex bodies) for the simple substances chosen is a subject of this work.

THEORETICAL

The equation for calculating the heat of vaporization was derived on the basis of the idea of the isothermal thermodynamic cycle[3] in which 1 mol of a liquid is evaporated from the liquid volume V_1 to equilibrium vapour (of volume V_g), the vapour is expanded from the pressure P_i to a zero one, the molecules of vapour at $P \to 0$ are "discharged" to hard convex bodies, the hard convex body system is then compressed to volume V_1 (and pressure P^0) and finally the convex bodies are "charged" to the initial potential. From the entropy balance along the cycle, the relation follows

$$\frac{\Delta H^V}{RT} = \ln\frac{RT}{P_i V_1} - \left(\frac{\partial B}{\partial T}\right)\frac{P_i}{R} + \int_{V_1}^{\infty}\left(\frac{P^0}{T} - \frac{R}{V}\right)dV - (S_1 - S^0), \qquad (1)$$

where ΔH^{V} is the heat of vaporization, P_i the saturated vapour pressure, P^0 the pressure of the hard body system, V_1 the volume of liquid, $(S_1 - S^0)$ the entropy change associated with the "charging" of hard bodies in the liquid phase (it is assumed to be of negligible magnitude in comparison with the other terms), B is the second virial coefficient and R the gas constant. For the pressure of the hard convex body system, which was accepted as a reference system, Gibbons[4] derived, within the framework of the scaled-particle theory, the approximative equation

$$P^0 V / RT = [1 + y(\gamma - 2) + y^2(\gamma^2/3 - \gamma + 1)]/(1 - y)^3 , \qquad (2)$$

where

$$y = N V_{\mathrm{C}} / V \qquad (3)$$

and

$$\gamma = R_{\mathrm{C}} S_{\mathrm{C}} / V_{\mathrm{C}} . \qquad (4)$$

In Eqs (2)–(4), N denotes Avogadro's number and V_{C}, S_{C} and R_{C} are the functionals of the parallel convex body[5,6]. The characteristic functionals of the parallel convex body which consist of a convex core (A) and a shell with a constant distance ξ, are given by the following relations

$$V_{\mathrm{C}} = V_{\mathrm{A}} + S_{\mathrm{A}}\xi + 4\pi R_{\mathrm{A}}\xi^2 + 4\pi\xi^3/3 , \qquad (5)$$

$$S_{\mathrm{C}} = S_{\mathrm{A}} + 8\pi R_{\mathrm{A}}\xi + 4\pi\xi^2 , \qquad (6)$$

TABLE I

Characteristic Functionals, Volume (V_{A}), Surface Area (S_{A}) and $(1/4\pi)$-Multiple of the Mean Curvature Integral (R_{A}), for Some Simple Convex Models of Molecules

h Denotes the altitude of cylinder or the length of rod, c the circumference and f the surface area of plate, r the radius of sphere or cylinder (in case of tetrahedron, the minimum radius of circumscribed sphere), a the length of side of equilateral triangle, v the altitude of pyramid and φ_1, φ_2 the complements of angles included by faces.

Figure	R_{A}, Å	S_{A}, Å^2	V_{A}, Å^3
Point	0·0	0·0	0·0
Rod	$h/4$	0·0	0·0
Thin plate	$c/8$	$2f$	0·0
Cylinder	$(h + \pi r)/4$	$2\pi r(r + h)$	$\pi h r^2$
Sphere	r	$4\pi r^2$	$4\pi r^3/3$
Regular tetrahedron	$\sqrt{(6)} \arccos(-1/3)(r/2\pi)$	$8\sqrt{(3)}r^2/3$	$8\sqrt{(3)}r^3/27$
Regular triangular pyramid	$3\{[a\varphi_1 + \sqrt{[v^2 + (a^2/3)]}\,\varphi_2]\}/8$	$\{(a^2\sqrt{(3)}/2 + 3a\sqrt{[(v^2 + a^2)/12)]}\}/2$	$a^2 v/4\sqrt{3}$

$$R_C = R_A + \xi. \hspace{3cm} (7)$$

The volume (V_A), surface area (S_A) and $(1/4\pi)$-multiple of the mean curvature integral (R_A) of the core depend on the size and geometrical shape of the model of the given molecule. For some simple geometrical (convex) models, the corresponding relations are listed in Table I. In this work, the substances were studied the molecules of which can be approximated by cores in the form of a rod (methyl iodide, methanol and carbon disulphide), in the form of a thin plate (acetone, dichloromethane and tetrachloroethylene) and in the form of a regular triangular pyramid or a regular tetrahedron (chloroform, bromoform and tetrachloromethane).

EXPERIMENTAL

Preparation of pure substances. Chemicals of reagent grade purity were used for preparation of the pure substances used for the determination of saturated vapour pressures. The substances were purified by chemical methods, using the procedures recommended in Perrin's monograph[7].

TABLE II

Physical Constants of Pure Substances Used

Substance	n_D^{20} found lit.	d_4^{20} found lit.	Norm. b.p., °C found lit.
CS_2	$1\cdot6318^a$ $1\cdot63190^{a,9}$	$1\cdot26326$ $1\cdot2632^9$	$46\cdot22$ $46\cdot20-46\cdot29^9$
CH_2Cl_2	$1\cdot4241$ $1\cdot42416^8$	$1\cdot32567$ $1\cdot3255^9$	$39\cdot77$ $39\cdot75^8$
$CHCl_3$	$1\cdot4459$ $1\cdot44593^8$	$1\cdot47956^b$ $1\cdot47955^{b,11}$	$61\cdot20$ $61\cdot20^9$
CCl_4	$1\cdot4602$ $1\cdot46020^9$	$1\cdot59410$ $1\cdot5941^9$	$76\cdot69$ $76\cdot65-76\cdot76^9$
C_2Cl_4	$1\cdot5056$ $1\cdot5056^{12}$	$1\cdot62265$ $1\cdot62272^8$	$121\cdot08$ $121\cdot00-121\cdot20^9$
$CHBr_3$	$1\cdot5988$ $1\cdot5988^7$	$2\cdot89165$ $2\cdot8905^9$	$149\cdot13$ $149\cdot18^9$
CH_3I	$1\cdot5308$ $1\cdot5308^8$	$2\cdot27893$ $2\cdot2790^8$	$42\cdot44$ $42\cdot43^8$
CH_3OH	$1\cdot3286$ $1\cdot3287^9$	$0\cdot79128$ $0\cdot7913^9$	$64\cdot52$ $64\cdot50-64\cdot75^9$
$(CH_3)_2CO$	$1\cdot3587$ $1\cdot3588^8$	$0\cdot79005$ $0\cdot78999^{10}$	$56\cdot10$ $56\cdot10^9$

$^a n_D^{15}$, $^b d_4^{25}$.

TABLE III

Saturated Vapour Pressures of Pure Substances

t, °C	P, Torr	t, °C	P, Torr	t, °C	P, Torr	t, °C	P, Torr

Carbon disulphide

t, °C	P, Torr	t, °C	P, Torr	t, °C	P, Torr	t, °C	P, Torr
−17·776	52·26	1·223	134·42	17·168	266·22	31·522	459·75
−12·358	69·80	5·076	159·87	21·087	311·05	38·041	578·49
− 7·204	90·35	9·448	193·37	25·831	372·81	45·142	733·96
− 3·286	109·13	12·981	224·44	—	—	—	—

Dichloromethane

−9·050	90·35	2·228	159·87	13·289	266·22	26·393	459·75
−5·450	109·13	6·230	193·37	16·893	311·05	32·337	578·49
−1·322	134·42	9·457	224·44	21·199	372·81	38·409	723·69

Trichloromethane

−10·356	33·93	11·927	109·13	28·118	224·44	46·583	459·75
− 2·610	52·26	16·417	134·42	32·289	266·22	53·070	578·49
2·882	69·80	20·248	159·87	36·223	311·05	60·319	738·15
8·010	90·35	24·598	193·37	40·913	372·73	—	—

Tetrachloromethane

−10·367	18·40	19·826	90·35	37·508	193·37	54·951	372·81
0·302	33·93	23·992	109·13	41·278	224·44	61·002	459·75
8·532	52·26	28·760	134·42	45·728	266·22	67·971	578·49
14·363	69·80	32·860	159·87	49·914	311·05	75·535	733·75

Tetrachloroethylene

37·088	33·93	63·270	109·13	82·292	224·44	103·930	459·75
46·239	52·26	68·545	134·42	87·183	266·22	111·548	578·49
52·671	69·80	73·064	159·87	91·791	311·05	119·650	730·09
58·697	90·35	78·165	193·37	97·291	372·81	—	—

Tribromomethane

47·209	18·40	82·821	90·35	103·595	193·37	123·929	372·81
59·767	33·93	87·709	109·13	108·003	224·44	130·982	459·75
69·518	52·26	93·356	134·42	113·216	266·22	139·055	578·49
76·389	69·80	98·173	159·87	118·078	311·05	—	—

TABLE III
(Continued)

t, °C	P, Torr	t, °C	P, Torr	t, °C	P, Torr	t, °C	P, Torr
			Methyl iodide				
− 13·819	69·80	2·954	159·87	14·567	266·22	28·342	459·75
− 8·883	90·35	7·146	193·37	18·341	311·05	34·600	578·49
− 5·101	109·13	10·542	224·44	22·879	372·81	41·427	734·17
− 0·788	134·42	—	—	—	—	—	—
			Methanol				
1·719	33·93	22·068	109·13	36·388	224·44	52·262	459·75
8·919	52·26	26·081	134·42	40·005	266·22	57·741	578·49
13·905	69·80	29·483	159·87	43·407	311·05	63·377	726·40
18·552	90·35	33·306	193·37	47·441	372·81	—	—
			Acetone				
− 12·949	33·93	8·666	109·13	24·330	224·44	42·094	459·75
− 5·424	52·26	13·019	134·42	28·351	266·22	48·344	578·49
− 0·103	69·80	16·731	159·87	32·138	311·05	55·285	739·35
4·882	90·35	20·939	193·37	36·649	372·81	—	—

Finally, all substances were rectified on a sixty-plate bubble-cup column, in case of light-sensitive substances on excluding the day-light access. The characteristic physico-chemical constants of the substances used are summarized in Table II.

Measuring equipment. Saturated vapour pressures of the liquids were measured using the Swieto-slawski standard ebulliometer. The ebulliometer was connected to a reservoir of vacuum apparatus maintaining a pressure in the system with an accuracy of ±0·05 Torr. The main part of the equipment[13], which is a modification of the apparatus described by Willingham and coworkers[14], is a thermostated closed U-tube, with sealed tungsten constants, in which mercury closes the electric circuit of the valve between the reference and auxiliary vacuum reservoirs. Temperature was measured by a calibrated platinum resistance thermometer connected to Mueller's bridge (Leeds and Northrup) with an accuracy of ±0·001°C. The pressures that correspond to the individual contacts of the U-manometer were determined indirectly from the boiling points of re-distilled water (by means of the tables of water vapour pressures[15]).

Experimental data. Experimental data on the dependence of saturated vapour pressures (Torr) on temperature (°C) for carbon disulphide, dichloromethane, trichloromethane, tetrachloro-methane, tetrachloroethylene, tribromomethane, methyl iodide, methanol and acetone in the pressure range of 20—760 Torr are given in Table III. The data measured were correlated by the

Antoine equation; the constants A, B, C of this equation for the given pure substances were computed by the weighted least square method and are given together with standard deviations of the measurements in Table IV. In the last column of the table, the normal boiling points as determined on the basis of the Antoine equation constants, are presented. The liquid densities and the second virial coefficients used for the calculations were taken from the literature[8,9,17].

RESULTS AND DISCUSSION

When calculating the theoretical values of heats of vaporization, the characteristic functionals of the hard bodies corresponding to the molecules of substances studied were determined first. The bodies are represented schematically in Fig. 1. Molecules of the mentioned compounds were approximated by parallel convex bodies with cores given by the respective molecule structure, bond lengths and corresponding angles[18]: The carbon disulphide, methyl iodide and methanol molecules were approximated by convex bodies with cores in the form of the rod joining the S—C—S, C—I, or C—O atom centres. For dichloromethane and acetone, a thin plate in the form of the triangle joining the atom centres Cl—C or C—C—O, resp., and for tetrachloroethylene, a thin rectangle plate determined by the Cl-atom centres were chosen. The core of tetrachloromethane was approximated by a regular tetrahedron with Cl-atoms in its corners, whereas the cores of chloroform and bromoform, by triangular pyramids with the Cl- or Br-Atoms, resp., in corners of their equilateral triangle and with apex formed by the carbon of CH-group.
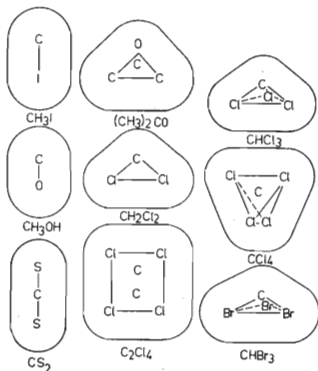

FIG. 1

Cores and Parallel Convex Bodies of Molecules Studied

The parameters ξ (thickness) of the parallel convex bodies to the considered cores were determined in the following way: For methyl iodide, methanol and acetone, the value $\xi = \xi(C-H) = 1\cdot8$ Å was used which was taken over from the previous paper[2] (as for acetone, the apex of the triangle was lowered, *i.e.* placed on the connecting C—O line allowing for a shorter effective radius $\xi(O)$ as compared with $\xi(C-H)$).

TABLE IV

Constants of the Antoine Equation and Normal Boiling Point

Substance	A	B	C	S^a Torr	N.b.p. K
CS_2	6·91204	1 153·50	239·93	0·10	319·37
CH_2Cl_2	7·06159	1 126·53	229·69	0·09	312·92
$CHCl_3$	6·95363	1 170·42	226·17	0·10	334·35
CCl_4	6·86624	1 202·90	225·14	0·06	349·84
C_2Cl_4	6·97680	1 386·90	217·52	0·11	394·22
$CHBr_3$	7·08421	1 544·81	218·38	0·11	422·28
CH_3I	6·98051	1 142·67	236·28	0·10	315·59
CH_3OH	8·12674	1 608·39	242·08	0·10	337·66
$(CH_3)_2CO$	7·11714	1 210·60	229·66	0·17	329·25

[a] Standard deviation.

TABLE V

Characteristic Functionals of Cores and Distances of Parallel Convex Bodies Approximating the Pure Substance Molecules

Substance	R_A, Å	S_A, Å^2	V_A, Å^3	ξ, Å
CS_2	0·776	0·000	0·000	1·55
CH_2Cl_2	0·846	3·669	0·000	1·55
$CHCl_3$	1·109	8·674	0·959	1·55
CCl_4	1·315	14·405	2·827	1·55
C_2Cl_4	1·526	18·563	0·000	1·55
$CHBr_3$	1·206	10·018	1·091	1·65
CH_3I	0·535	0·000	0·000	1·80
CH_3OH	0·357	0·000	0·000	1·80
$(CH_3)_2CO$	0·798	3·621	0·000	1·80

For all chlorinated hydrocarbons, the value $\xi(\text{Cl}) = 1.55$ Å was used calculated on the basis of the rod model of molecule and of the heat of vaporization of chlorine. In a similar way also the distance $\xi(\text{Br}) = 1.65$ Å was found. These parameters were used for calculating the characteristic functionals of the higher-substituted halogen derivatives, *i.e.* dichloromethane, trichloromethane, tetrachloromethane, tetrachloroethylene and tribromomethane. The heights of the geometrical figures were corrected for the difference of the values $\xi(\text{Cl})$ and $\xi(\text{C—H})$ or $\xi(\text{Br})$ and $\xi(\text{C—H})$, respectively. For the thickness $\xi(\text{S})$ in carbon disulphide, the value ξ 1.55 Å (which follows from the consideration of the similarity of electron shells of sulphur and chlorine) was used for the lack of suitable data. The used values of characteristic functionals R_A, S_A, and V_A of cores and of the parameters ξ of the parallel convex bodies for the mentioned compounds are summarized in Table V.

Theoretical values of the heats of vaporization (at normal boiling points) of the compounds studied were calculated from Eq. (*1*) after substituting from the relations (*2*)—(*4*). These values are compared in Table VI with the experimental data. For illustration of the significance of the shape factor of representative system, the values of heats of vaporization that follow from Eq. (*1*) after substituting the hard sphere equation of state are presented in Table VI, too. From the comparison it follows the significance of the use of the hard convex body system as a reference one. Whereas the standard deviation of the theoretical heats of vaporization calculated on the basis of the equation of state of hard spheres with a diameter determined from the parameters of the Lennard–Jones $12-6$ potential (taken over from[19]) amounts to 22.1%, the standard deviation in case of the use of the hard convex body equation of state, taking into account the structure of molecules of the substances studied, is only

TABLE VI
Comparison of Theoretical and Experimental Values of Heats of Vaporization (cal/mol) at Normal Boiling Point

Substance	γ	ΔH^v_{exp}	$\Delta H^v_{h.s.}$	Δ, %	$\Delta H^v_{h.c.b.}$	Δ, %
CS_2	3.602	6 561	5 946	— 9.4	6 001	—8.5
CH_2Cl_2	3.419	6 731	6 522	— 3.1	6 304	—6.3
$CHCl_3$	3.438	6 991	8 044	15.1	6 990	0.0
CCl_4	3.413	7 111	8 768	23.3	7 454	4.8
C_2Cl_4	3.679	8 254	—	—	9 024	9.3
$CHBr_3$	3.465	9 042	—	—	9 433	4.3
CH_3I	3.280	6 520	—	—	6 332	—2.9
CH_2O	3.148	8 520	5 620	—34.0	8 963	5.2
$(CH_3)_2CO$	3.295	6 961	5 528	—20.6	7 470	7.3

6·4% (this value is comparable with a deviation of 5·9% found for a perfluoro-n-alkane series). This improvement of the heats of vaporization estimation gives evidence in favour of the choice of the system of hard convex bodies as a reference system and of the suitability of the used convex models of molecules.

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