ENTHALPY DATA OF LIQUIDS. II.*

THE DEPENDENCE OF HEATS OF VAPORIZATION OF METHANOL, PROPANOL, BUTANOL, CYCLOHEXANE, CYCLOHEXENE, AND BENZENE ON TEMPERATURE

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The dependence of heats of vaporization of six organic liquids on temperature was measured. The measured data were correlated by means of a two-constant equation. The results were mutually in good agreement.

In previous paper[1], the construction of calorimeter for measuring heats of vaporization of pure liquids was described in detail. This calorimeter was developed with the aim to enable the direct measurement not only at the temperatures about 25°C, or at normal boiling point, as it has been usual so far with most apparatuses but also over the whole region bounded by these two points and in this way to obtain more detailed experimental data on heat of vaporization and its dependence on temperature. The apparatus was tested by measuring heats of vaporization of methanol, cyclohexane, benzene, and water at 25°C and at n.b.p. The measurements exhibited good agreement with the data which can be found for these substances in the literature and so they gave the possibility to try the calorimeter for measuring between these two points, too.

The knowledge of the dependence of heat of vaporization on temperature is required in practice very often. Experimental data are available, however, only very rarely and therefore the only source of data has been, up to now, mostly either the calculation from the dependence of saturated vapour pressures on temperature, the semi-empirical one- or two-constant equations for the dependence of heat of vaporization on temperature[2], or less accurate estimations based on the theorem of corresponding states. With the aim to fill up this blank, the results of measuring the dependence of heat of vaporization on temperature are described in this work for the first six organic liquids which were chosen on the one hand because of their practical importance, and on the other hand because they were studied in our laboratory especially with respect to their phase vapour–liquid behaviour[3-7]. Since the substances chosen belong to different groups of organic compounds, the experimental

TABLE I

Physico-Chemical Constants of Substances Measured (this work/literature)

Value	Methanol	Propanol	Butanol
n.b.p.	64·56	97·2	118·0
°C	64·51—64·65	97·15—97·20	117·7—118·0
d_4^{25}	0·7866	$0·80347^a$	0·8057
	0·78657—0·78668	$0·8035^a$	0·80567—0·80570
n_D^{25}	$1·3286^a$	$1·3840^b$	1·3973
	$1·3286^a$	$1·3840^b$	1·3970—1·3974
% H_2O	<0·0025	<0·005	<0·003

^{a} 20°C, ^{b} 23·6°C.

measurement can also contribute to the qualitative extension of our knowledge of force interaction the manifestation of which is just the value of heat of vaporization.

EXPERIMENTAL AND RESULTS

Methanol, an analytical grade reagent, was refluxed with the Grignard reagent for 5 hours and then distilled on a sixty-plate bubble-cup column. Propanol, butanol, cyclohexane, and benzene, all of the analytical reagent purity, were dried with metallic sodium and as well distilled on a sixty-plate bubble-cup column. Cyclohexene was prepared by dehydrating a distilled cyclo-hexanol by concentrated H_2SO_4. The distilled-out crude cyclohexene was freed of peroxides by five-fold shaking with $FeSO_4$ solution and then rectified at a reflux ratio of 1 : 2. To the product, calcium hydride in 20-fold excess of the water content as determined according to K. Fisher was added and the product was rectified again on a sixty-plate bubble-cup column in the N_2 stream and collected into ampoules over the molecular sieve of the Nalsit A 4 type. It was shown by mass spectrometry that all substances contained less than 0·01% impurities with the exception of cyclohexene where impurities amounted to less than 0·4%. The physico-chemical constants of single substances are presented, together with comparable data from the literature, in Table I.

The calorimeter with closed system whose detailed description together with the procedure are given in the foregoing paper[1] was used for measuring.

The calculation of heat of vaporization was made in all cases by means of the relation

$$h_v = (h'_v) \, k/m \,, \tag{1}$$

where $h'_v = W - q_1$, h_v is the heat of vaporization of pure substance, m the weight of liquid evaporated, W the total amount of heat supplied into the evaporating vessel during vaporiza-tion, q_1 the correction for the heat losses and k the correction for an increase of the vapour space of evaporating vessel on evaporating liquid from calorimeter which is given by the relation

TABLE I
(continued)

Benzene	Cyclohexane	Cyclohexene
80·10	80·7	83·01
80·07—80·106	80·75	82·8—83·2
0·87368	0·7739	—
0·87366—0·87368	0·77383—0·77389	—
1·4979	1·4236	$1·4467^a$
1·4979—1·4981	1·42354—1·42358	$1·4467^a$
<0·007	<0·003	<0·004

TABLE II

Measured Values of Heats of Vaporization (cal g^{-1}) as a Function of Temperature and Results of Correlating Calculations

°C	Measured values			Literature		Δh_v, %^{a}
	h_v'	k	h_v	h_v	ref.	
Methanol, $A = 11·4038$, $\alpha = 0·3$						
25	279·41	0·99978	279·35	278·1	11	−0·089
				281·2	12	
40	274·06	0·99942	273·90	273·2	13^b	0·110
50	269·95	0·99910	269·71	269·1	13	0·106
60	265·61	0·99865	265·25			0·060
64·7	263·58	0·99843	263·17	262·5	13	0·067
70	260·44	0·99802	259·92	259·9	13^b	−0·254
Propanol, $A = 14·2461$, $\alpha = 0·36$						
40	184·48	0·99975	184·43			−0·114
50	181·99	0·99962	181·92			0·264
60	178·54	0·99948	178·45			0·065
70	175·11	0·99910	174·95	174·8	14	−0·101
				175·38	15	−0·101
80	171·78	0·99867	171·55	171·08	14	−0·151
				171·78	15	
90	168·83	0·99785	168·47			0·050

TABLE II

(Continued)

°C	Measured values			Literature		Δh_v, %[a]
	h_v'	k	h_v	h_v	ref.	
Butanol, $A = 15\cdot3640$, $\alpha = 0\cdot46$						
60	159·54	0·99973	159·50	—	—	0·201
70	156·77	0·99955	156·70	—	—	0·298
80	153·41	0·99928	153·30	—	—	0·060
90	149·73	0·99891	149·57	—	—	−0·353
Benzene, $A = 9\cdot78055$, $\alpha = 0\cdot40$						
25	103·53	0·99954	103·48	103·6	19	0·112
40	101·47	0·9991	100·98	100·7 (41·6°C)	20	0·077
				100·9	13[b]	
55	98·66	0·9984	98·50			0·007
60	97·60	0·9982	97·42	97·4 (60·9°C)	20	−0·231
				97·6	13[b]	
70	96·24	0·9975	96·00	95·9	13[b]	0·086
80·1	94·47	0·99661	94·15	94·1	20	0·019
				94·35 (80·2°C)	18	
				94·1 (80·0°C)	13	
Cyclohexane, $A = 9\cdot97084$, $\alpha = 0\cdot39$						
40	91·65	0·99896	91·55	—	—	−0·147
50	90·69	0·99851	90·55	—	—	0·413
60	88·62	0·99792	88·44	—	—	−0·210
70	87·18	0·99716	86·93	86·32 (71·11°C)	16	−0·119
80·7	85·68	0·99615	85·35	85·43 (80·8°C)	17	0·086
				85·62	18	
				84·47 (82·2°C)	16	
Cyclohexene, $A = 9\cdot5338$, $\alpha = 0\cdot37$						
40	95·18	0·99911	95·10	—	—	−0·087
50	93·87	0·99872	93·75	—	—	0·018
60	92·36	0·99820	92·20	—	—	−0·046
70	90·87	0·99753	90·65	—	—	−0·069
80	89·50	0·99669	89·20	—	—	0·072

[a] $\Delta h_v = 100(h_v^{exp} - h_v^{calc})/h_v^{exp}$.   [b] Extrapolated.

$k = d^g/(d^g + d^1) = v^g/(v^g + v^1)$, where d^g and d^1 are densities of vapour and liquid and v^g, v^1 the corresponding molar volumes at the temperature of experiment. The values of liquid molar

volumes were taken over the literature, the molar volume of vapours was determined from the virial equation of state $Pv = RT[1 + (B/v)]$. The needed values of second virial coefficients were taken from the Dymond and Smith paper[8], the dependence of saturated vapour pressures on temperature was considered in the form of the Antoine equation whose constants were given previously[3-10].

The measured data are summarized in the first part of Table II. In the second column, the data are presented as they were measured, the third one expresses the correction for the increase of the vapour space and in the next ones there are the final values of heats of vaporization in cal g^{-1} together with the data from the literature.

The experimentally found values were correlated by means of an equation of the type $h_v = a(1 - T_r)^\alpha$ which was for the given purpose expressed in the dimensionless form

$$Q \equiv h_v/RT = A(1 - T_r)^\alpha/T_r. \qquad (2)$$

In this equation, h_v denotes molar heat of vaporization, T_r reduced temperature, A and α are constants.

The results of correlating calculations carried out by minimizing the difference of measured and calculated values of Q are presented in the second part of Table II. It is evident from the results that mutual agreement is satisfactory.

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