

DETERMINATION OF HEATS OF VAPORIZATION
AND SOME OTHER THERMODYNAMIC QUANTITIES
FOR THREE FLUORINATED HALOGEN ETHANES*

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Some thermodynamic properties were investigated for three fluorinated halogen ethanes: 1-bromo-2-chloro-1,1,2-trifluoroethane, 1,2-dibromotetrafluoroethane and 1,2-dibromo-1-chlorotrifluoroethane. The temperature dependence of heats of vaporization, saturated vapour pressures, densities and refractive indices was measured at two temperatures. On the basis of the experimental quantities obtained, the standard heats of vaporization and the cohesive and internal energies of vaporization in their dependence on temperature were determined.

This work reassumes our previous paper of this series¹ where we have dealt with the determination of some thermodynamic properties of a group of four fluorinated halogen derivatives of ethane and propane (abbreviated designation Mixhal 1–4). In this work we have focused our attention to further three fluorinated halogen ethanes which contain the functional group —CF₂Br. It is 1-bromo-2-chloro-1,1,2-trifluoroethane (Mixhal 5), 1,2-dibromotetrafluoroethane (Mixhal 6) and 1,2-dibromo-1-chlorotrifluoroethane (Mixhal 7). Only few reliable experimental values of physico-chemical constants and thermodynamic quantities are given in the literature for these substances. Therefore we have measured, similarly to our foregoing work, the temperature dependence of heats of vaporization and saturated vapour pressures, densities and refractive indices at two temperatures and, on the basis of the experimental values, evaluated the standard heats of vaporization and internal and cohesive energies of vaporization. During the experimental determinations and data processing, the same methods as in our work¹ have been used and therefore we shall mention them quite briefly in the next text.

* Part XXII in the series Enthalpy Data of Liquids; Part XXI: This Journal 46, 535 (1981).

EXPERIMENTAL

Preparation and Purity of Substances

Mixhal 5, supplied by Léčiva, Měcholupy, ČSSR and *Mixhal 6* by K & K Labs, U.S.A. were commercial products. The substances have been distilled on a twenty-plate distillation column before measurement. It has been found by a chromatographic analysis that the admixture content has not exceeded 0.4%.

Mixhal 7. Chlorotrifluoroethylene has been brought into a solution of bromine in 1,1,2-trichlorotrifluoroethane till the decolourization of reaction mixture. After washing and drying the reaction mixture has been rectified. The purity of sample of 99.8% has been determined by chromatographic analysis.

To prevent the contamination with water all three substances have been maintained in the presence of molecular sieves of the A3 type.

Measurement

Heats of vaporization have been measured in an isothermal vaporization calorimeter² in the temperature range of 25 to 85°C (until the saturated vapour pressure exceeds 200 kPa) with a step of 15°C. The error of measurement has been estimated on the basis of analysis of accuracy of input quantities and single corrections; it should not exceed 0.3%.

Densities and refractive indices have been measured at 20 and 30°C. To measure densities the Ostwald-Springer pycnometers have been used, the refractive indices n_D have been determined by using the Pulfrich refractometer.

The measurements of saturated vapour pressures have been carried out on a standard apparatus³ (the temperature measured with an accuracy of $\pm 0.01^\circ\text{C}$, the pressure ± 30 Pa).

TABLE I
Measured Values of Heats of Vaporization (kJ/mol) and Results of Correlation

°C	Mixhal 5	Mixhal 6	Mixhal 7
25	29.99	28.38	35.01
40	29.00	27.47	34.17
55	28.14	26.53	33.45
70	27.23	—	32.55
85	—	—	31.57
K	42.30	41.29	47.25
α	0.3809	0.4030	0.3982
T_k	499.8	492.4	563.3
δ	0.069	0.008	0.045
ΔH_{vNBP}	28.32	27.03	31.11

RESULTS

The results of measurements of heats of vaporization ΔH_v have been correlated using the Thiesen relation

$$\Delta H_v = K(1 - T/T_c)^a, \quad (1)$$

TABLE II
Densities ρ (g cm^{-3}) and Refractive Indices n_D at 20 and 30°C

Mixhal	ρ^{20}	ρ^{30}	n_D^{20}	n_D^{30}
5	1.8458	1.8707	1.3720	1.3668
6	2.1842	2.1501	1.3708	1.3647
7	2.2492	2.2212	1.4286	1.4234

TABLE III
Measured Values of Saturated Vapour Pressures

P^0 , kPa	Temperature, °C/Deviation in pressure, Pa		
	Mixhal 5	Mixhal 6	Mixhal 7
9.210			28.09/0
10.426			30.76/—8
11.876			33.66/—7
13.159			36.02/18
15.372			39.62/22
18.252			43.67/—9
21.892			48.13/—26
25.265			51.78/—17
30.864			57.02/—33
37.544		20.25/27	62.38/9
45.356	30.45/—34	24.95/—28	67.71/—39
56.449	36.09/5	30.65/—32	74.14/—4
69.488	41.66/38	36.30/4	80.55/51
86.053	47.64/72	42.35/—16	87.39/5
98.179	51.67/—124	46.67/15	91.76/—42
<i>A</i>	6.191654	6.173540	6.042680
<i>B</i>	1.190.295	1.196.828	1.274.632
<i>C</i>	232.0	240.0	222.9
δ , kPa	0.107	0.037	0.028
t_{NBP} , °C	52.36	47.16	92.84

where K and α are constants, T_c is the critical temperature. The experimental values and results of correlation are given in Table I, where δ denotes the standard correlation deviation and $\Delta H_{v,NBP}$ the heat of vaporization at normal boiling point. The measured values of densities and refractive indices are summarized in Table II. The measured values of saturated vapour pressures P^0 in dependence on temperature $t(^{\circ}\text{C})$ have been correlated on using the Antoine equation

$$\log P^0 = A - B/(t + C). \quad (2)$$

In Table III the measured values of temperatures and the deviations of saturated vapour pressures calculated from Eq. (2) from the experimental values are given for pressures P^0 at which the measurements have been carried out. Then the constants of the Antoine equation, the standard deviations of the correlation and the temperature of normal boiling point t_{NBP} calculated from Eq. (2) follow.

TABLE IV

Temperature Dependence of Standard Heat of Vaporization, Internal Energy of Vaporization and Cohesive Energy in kJ/mol

	K'	β	δ	X_{25}^a	X_{NBP}^a
Mixhal 5					
ΔG_v^0	43.002	0.2360	0.012	30.15	28.76
ΔU_v	45.545	0.3350	0.011	27.51	25.73
ΔU_c	43.608	0.3020	0.017	27.68	26.06
Mixhal 6					
ΔH_v^0	41.997	0.2490	0.009	28.65	27.49
ΔU_v	44.655	0.3530	0.009	25.97	24.49
ΔU_c	42.529	0.3160	0.012	26.17	24.84
Mixhal 7					
ΔH_v^0	48.488	0.2519	0.020	35.09	31.61
ΔU_v	50.615	0.3439	0.021	32.54	28.22
ΔU_c	49.053	0.3180	0.018	32.61	28.58

^a X denotes calculated values of ΔH_v^0 , ΔU_v , ΔU_c .

The standard heats of vaporization ΔH_v^0 , internal energy of vaporization ΔU_v and cohesive energy ΔU_c have been calculated from the values of heats of vaporization by using the data on saturated vapour pressures and densities. The relation of these quantities to heat of vaporization is given by the equations

$$\Delta H_v^0 = \Delta H_v + \Delta H^*, \quad (3)$$

$$\Delta U_v = \Delta H_v - P^0(V^g - V^l),$$

$$\Delta U_c = \Delta H_v + \Delta H^* - RT + P^0V^l,$$

where ΔH^* denotes the difference of the enthalpy of ideal gas and of saturated vapour, P^0 , V^g , V^l , R and T stand for the saturated vapour pressure, molar volume of the gaseous and liquid phases, the gas constant and the temperature in K , respectively. On using the volume-explicit virial expansion truncated after the second term, we get

$$\Delta H^* = \frac{RT}{V^g} \left(T \frac{dB}{dT} - B \right). \quad (4)$$

The second virial coefficients necessary for evaluating the volume of the vapour phase V^g and the term ΔH^* have been estimated according to Tsonopoulos^{4,5}, the volume of the liquid phase has been estimated from the modified Rackett equation⁶ (the adjustable parameter z_{RA} has been estimated from an experimental value at 30°C). The calculations have been carried out in the temperature ranges identical with those in the heats of vaporization measurement. The data have been correlated by the empirical two-constant relation¹

$$X = K'[(1 - T_r) \exp(-T_r)]^\beta, \quad (5)$$

where X denotes the correlated quantity (ΔH_v^0 , ΔU_v , ΔU_c), K' , β are correlation constants and T_r is the reduced temperature. The results are summarized in Table IV. For all the substances, the constants of Eq. (5) for calculating the quantities ΔH_v^0 , ΔU_v , ΔU_c , their respective values at 25°C and at normal boiling point and the standard deviations of correlations δ are given.

A strong effect of fluorine diminishing heats of vaporization as well as further derived quantities follows from the comparison of the measured and calculated values of vaporization quantities determined in this and in the foregoing work¹. For isomers, a mild decrease occurs with increasing asymmetry resulting from the occupation of carbon atoms with halogens (compare Mixhal 1 and Mixhal 2 or Mixhal 3 and Mixhal 5). A deeper analysis of the correlation of vaporization properties with the structure of substances studied will be carried out in next papers.

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