

DETERMINATION OF HEATS OF VAPORIZATION
AND SOME OTHER THERMODYNAMIC QUANTITIES
FOR SEVERAL FLUORINATED HALOGEN DERIVATIVES
OF ETHANE AND PROPANE*

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Some physico-chemical properties were determined for 1,1,1-trichlorotrifluoroethane, 1,1,2-trichlorotrifluoroethane, 1-bromo-1-chloro-2,2,2-trifluoroethane and 1,2-dichlorohexafluoropropane. For all the substances, their heats of vaporization in dependence on temperature were measured and their densities and refractive indices at two temperatures were determined. For 1,1,1-trichlorotrifluoroethane and 1,2-dichlorohexafluoropropane the saturated vapour pressures were measured, too. The temperature dependences of standard heats of vaporization, vaporization internal energies and cohesive energies were determined on the basis of the experimental data.

Recently mixed halogen derivatives of hydrocarbons have been the centre of interest owing to the possibility of their practical exploitation in a number of fields. So far, however, it is known too little about physico-chemical properties of these substances. Therefore the aim of this work has been to provide new experimental data and calculate on their basis some further characteristic thermodynamic quantities. Our attention has been paid to three derivatives of ethane, *viz.* 1,1,1-trichlorotrifluoroethane (Mixhal 1), 1,1,2-trichlorotrifluoroethane (Mixhal 2), 1-bromo-1-chloro-2,2,2-trifluoroethane (Mixhal 3) and to one derivative of propane, *viz.* 1,2-dichlorohexafluoropropane (Mixhal 4). For the given substances, the temperature dependence of their heats of vaporization has been determined and their densities and refractive indices have been measured at two temperatures. In case of Mixhal 1 and Mixhal 4, their saturated vapour pressures have been measured, too, whereas for the other two substances, reliable values have been known from the literature. On the basis of the obtained experimental data, the heats of vaporization referred to the state of ideal gas, vaporization internal and cohesive energies have been then computed in dependence on temperature.

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EXPERIMENTAL

Preparation and Purity of Substances

Mixhal 1. A mixture of 1,1,2-trifluorotrichloroethane and anhydrous aluminium chloride, rubbed and weighed in a dry atmosphere, has been stirred intensively for 4.5 hours at 48–50°C. After cooling, the reaction mixture has been decomposed by a diluted hydrochloric acid, the organic layer has been separated, dried and then rectified, a fraction at 46°C being taken. A purity of 99.5% has been found by chromatographic analysis.

The other substances have been commercial products: *Mixhal 2* produced by Spolek pro chemickou a hutní výrobu, Ústí nad Labem, Czechoslovakia; *Mixhal 3*, Léčiva, Měcholupy, Czechoslovakia; *Mixhal 4*, Aldrich Chemical Co., Inc., U.S.A. All three substances have been redistilled on a twenty-plate packed column before measurement. The purity of substances has been checked by gas chromatography, the impurity content being 0.1–0.3%.

Measurement

Heats of vaporization ΔH_v have been determined using the adiabatic-isothermal calorimeters which have been described previously^{1,2}. The simultaneous use of two different calorimeters has made it possible to check the consistency of results and to diminish the probability of occurrence of systematic errors. The heats of vaporization have been measured for the given substances from the temperature of 25°C to the temperatures close above their normal boiling points. The error of measurement has been estimated, on the basis of the analysis of inaccuracies of input quantities and reproducibility of results, at $\pm 0.3\%$. In comparison with our foregoing works, the error of these measurements is rather higher. With regard to the generally very low values of heats of vaporization, the measured heat effects are rather low. The uncertainty in some input quantities (correction for heat leakage and that for the vapour space of vessel, etc.), whose magnitude does not depend on the total amount of heat absorbed during evaporation, results in the corresponding increase of the per cent error of heats of vaporization.

Densities and refractive indices have been measured at the temperatures of 20 and 30°C. For the density measurements, the Springer–Ostwald pycnometers have been used and the refractive indices have been determined using the Pulfrich refractometer.

Saturated vapour pressures in dependence on temperature for *Mixhal 2* have been measured in a wide temperature range by Benning and McHarness³ and for *Mixhal 3* by Bottomley and Seiflow⁴. Therefore the measurements have been carried out just for *Mixhal 1* (the saturated vapour pressures reported by Hiraoka and Hildebrand⁵ show a great correlation deviation⁶) and for *Mixhal 4* (no literature data are available). For measuring we have used a standard apparatus described previously⁷; the temperature has been measured with an accuracy of $\pm 0.01^\circ\text{C}$, the pressure in the apparatus has been maintained to ± 30 Pa.

RESULTS

The values of heats of vaporization determined in both types of calorimeters have been correlated simultaneously by means of the Thiesen relation

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

where K and α are correlation constants and T_c denotes the critical temperature. For Mixhal 2, the critical properties have been found in tables of Timmermans⁸, for the others the estimation according to Lydersen⁹ has been carried out. The results are summarized in Table I. Besides the given experimental values and constants of correlation relation (1), we have considered useful to give also further often desirable values, viz. the value of heat of vaporization at the temperature of 25°C ($\Delta H_{v,25}$) and the value at normal boiling point $\Delta H_{v,NBP}$. Besides we give the critical temperature T_c used, the standard deviation δ , the temperature range Δt of validity of correlation constants together with the temperature of normal boiling point t_{NBP} .

The measured values of densities and refractive indices are given in Table II.

The results of measurements of the temperature dependence of saturated vapour pressures are given for both substances in Table III in the form of the Antoine equation constants

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

for P^0 in kPa and t in °C. Further we give the mean correlation deviation $\bar{\delta}$, the number of experimental points n and the temperature interval Δt .

The standard heat of vaporization ΔH_v^0 is given by the difference of enthalpy of ideal saturated lignidat vapour H^g and saturated liquid H^l at the same temperature:

$$\Delta H_v^0 = H^g(T, P = 0) - H^l(T, P^0).$$

The vaporization internal energy ΔU_v represents the difference between the internal energy of saturated vapour U^g and liquid U^l at the same temperature:

$$\Delta U_v = U^g(T, P^0) - U^l(T, P^0).$$

The cohesive energy ΔU_c is the difference between internal energy of ideal gas and saturated liquid at the same temperature:

$$\Delta U_c = U^g(T, P = 0) - U^l(T, P^0).$$

In the definition relations, T denotes the temperature, P the pressure and P^0 the pressure of saturated vapour. The quantities mentioned above are connected by the simple relationships:

$$\begin{aligned} \Delta H_v^0 &= \Delta H_v + \Delta H^*, \\ \Delta H_v &= \Delta H_v - P^0(V^g - V^l), \\ \Delta U_c &= \Delta H_v + \Delta H^* - RT + P^0V^l, \end{aligned} \quad (3)$$

where ΔH^* denotes the difference between the enthalpy of ideal gas and that of saturated vapour, V^g and V^l the molar volume of the vapour and liquid phase, respectively, and R the gas constant. When expressing the P - V - T behaviour in terms of the pres-

TABLE I

Heats of Vaporization of Fluorinated Halogen Derivatives of Ethane and Propane (kJ mol^{-1})

$t, ^\circ\text{C}$	Mixhal 2	Mixhal 2	Mixhal 3	Mixhal 4
25	28.10	26.43	29.64	26.93
28	27.89 ^a	28.20 ^a	29.42 ^a	
39.65	27.20 ^a			
40	27.23	27.46	28.69	25.85
50			29.03 ^a	
55	26.30	26.59	27.81	
70			26.81	
K	40.073	40.849	42.267	41.130
α	0.3703	0.3843	0.3879	0.3835
T_c, K	482.9	487.2	496.3	446.0
$\delta, \text{kJ/mol}$	0.030	0.049	0.045	—
$\Delta t, ^\circ\text{C}$	25—55	25—55	25—70	25—40
$\Delta H_{v25}, \text{kJ/mol}$	28.08	28.39	29.60	26.93
$t_{\text{NBP}}, ^\circ\text{C}$	46.04 ^b	47.46 ^c	50.07 ^c	34.08 ^b
$\Delta H_{v\text{NBP}}, \text{kJ/mol}$	26.85	27.04	28.09	26.28

^a Experimental values determined using calorimeter type¹, non-designated values, calorimeter type²; ^b determined from our measurements of saturated vapour pressures; ^c taken over from ref.⁵.

TABLE II

Densities ρ (g cm^{-3}) and Refractive Indices n_D at 20 and 30 $^\circ\text{C}$

Mixhal	ρ^{20}	ρ^{30}	n_D^{20}	n_D^{30}
1	1.5752	1.5551	1.3605	1.3553
2	1.5731	1.5535	1.3594	1.3538
3	1.8677	1.8446	1.3696	1.3647
4	1.5825	1.5585	1.3032	1.2980

sure-explicit virial expansion truncated after the second virial coefficient B , we get

$$\Delta H^* = (RT/V^B)(TdB/dT - B). \quad (4)$$

TABLE III

Constants of the Antoine Equation for Pressure P^0 (kPa) and t ($^{\circ}\text{C}$)

Mixhal	A	B	C	$\bar{\delta}$, Pa	n	Δt , $^{\circ}\text{C}$
1	6.517049	1385.150	261.0	22	6	24—46
4	5.599338	841.1832	200.0	19	4	23—34

TABLE IV

Temperature Dependence of Standard Heat of Vaporization, Vaporization Internal Energy and Cohesive Energy in kJ mol^{-1}

Mixhal	K'	β	δ	X_{25}^a	X_{NBP}^a
1					
ΔH_v^0	40.560	0.2270	0.011	28.35	27.31
ΔU_v	43.150	0.3290	0.009	25.67	24.33
ΔU_c	41.637	0.3009	0.042	25.87	24.67
2					
ΔH_v^0	41.523	0.2380	0.008	28.65	27.50
ΔU_v	44.147	0.3400	0.010	25.99	24.52
ΔU_c	41.979	0.3030	0.013	26.17	24.85
3					
ΔH_v^0	43.076	0.2420	0.011	29.82	28.51
ΔU_v	45.630	0.3410	0.010	27.18	25.52
ΔU_c	43.603	0.3070	0.011	27.35	25.84
4					
ΔH_v^0	41.785	0.2400	0.011	27.30	26.76
ΔU_v	45.032	0.3420	0.009	24.56	23.87
ΔU_c	42.432	0.3020	0.021	24.83	24.21

^a X denotes ΔH_v^0 , ΔU_v , ΔU_c .

The computations have been carried out in the entire temperature range of measurements. The second virial coefficients have been estimated according to Tsonopoulos^{10,11}. They have been used for calculating the values of molar volumes V^{R} in system of Eqs (3)–(4) and for calculating the coefficients in Eq. (4). Molar volume of the liquid phase V^{L} as a function of temperature has been estimated on using the Rackett equation^{12,13}. The adjustable parameter z_{RA} has been calculated from the value of density at 30°C.

The calculated values have been correlated by means of the two-constant empirical relation

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

which has complied better for the given quantities than Eq. (1). X is ΔH_v^0 , ΔU_v , ΔU_c and K' , β are adjustable constants and T_r is reduced temperature. The results of calculations are summarized in Table IV. For all the substances, the obtained correlation constants K' and β are given for three investigated thermodynamic functions along with the standard deviation δ . Further we give the corresponding values of X at 25°C and at normal boiling point.

At temperatures around normal boiling point, the error in ΔH_v^0 , ΔU_c (ΔU_v , resp.) is 0.2–0.3 higher (0.1, resp.) in comparison with that in ΔH_v . With decreasing temperature, the effect of this error diminishes with respect to the decreasing value of P^0 .

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