

## HEATS OF VAPORIZATION OF ALKYL ESTERS OF FORMIC ACID\*

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Temperature dependence of heats of vaporization of methyl, ethyl, propyl, and butyl ester of formic acid were measured. The calorimeter employed was adjusted in an attempt to improve its mechanical and regulation properties. The experimental temperature dependence of separate esters were correlated with good results by a two-constant equation.

Experimental values of heats of vaporization of pure substances have recently ranked among required physico-chemical properties. As long as they are measured in a wider range of temperatures, their significance and applicability increases proportionally. With intention to extend the existing set of experimental data on heats of vaporization, their values for alkyl esters of formic acid were measured. Measurements along the homological series had been chosen with the aim to obtain — besides the data themselves — also a possibility of their further processing, either for extension of the knowledge and estimation of heats of vaporization of less known compounds or for verification of correlation and consistence relations for derived quantities in the thermodynamics of solutions.

## EXPERIMENTAL

*Preparation and purity of substances.* Methyl, propyl and butyl formates were prepared by esterification of formic acid with the corresponding alcohol in the presence of  $H_2SO_4$ . After salting-out with  $K_2CO_3$ , the product was separated from the aqueous layer, dried with anhydrous  $CaCl_2$  and finally distilled on a 1.5 m-long column packed with stainless helices. Middle fractions, the physico-chemical constants of which agreed with values from the literature, were used for the measurements. Ethyl formate, A.R. grade, was also dried with anhydrous  $CaCl_2$  and distilled on the same column. Results of a comparison of measured and literature values of the physico-chemical constants are given in Table I.

*Apparatus.* For the measurements, the calorimeter was used the detailed description of which may be found in one of our earlier works<sup>1</sup>, but in which, however, some alterations of its mechanical parts and regulation circuits were made in an attempt to simplify the manipulation and increase reproducibility with the consequent reduction of the number of parallel experiments. Firstly, the calorimeter head was altered slightly. Its scheme is obvious from Fig. 1. Vacuum

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valve 3 was provided with teflon cone 6. After its setting into the leftmost position, the calorimeter can be evacuated and filled in the same manner as earlier. By closing the calorimeter, any contact between vapours of the evaporating substance and the packing material of the filling part is avoided. Besides that, the vacuum line need not be provided with a vacuum valve immediately at the orifice of the calorimeter head. This removed high demands on the quality of the material of the plug in the filling part and improved the tightness of the calorimeter head, which is necessary for successful measurements.

This arrangement enables to remove also other unfavourable effects which existed in the original calorimeter in the case of an accidental penetration of air into the vapour space. The presence of a small amount of an inert (air) in the calorimeter not only partially depreciates the measured values, but before all it leads to an irregular evaporation or even checking of the experiment if the inert penetrates into the condensation vessel. The possibility of penetration of a small amount of air into the calorimeter during an incautious extraction of the filling pipette has been also considered in the proposed arrangement; this air is extruded by the vapour which forms immediately after the sampling. Thus it passes together with the vapour into the front part of the vacuum line wherefrom it is exhausted subsequently. The calorimeter is then finally closed with the vacuum valve. The filling lasts approximately 10 s.

Our further efforts were aimed at reduction of the vapour space. A large vapour space does not secure the condition of a steady-state run of the calorimeter. Its manifests itself during flowing of the vapours through the glass line connecting the calorimeter head with the evaporation vessel. Therefore were the dimensions of the evaporation vessel reduced to  $20 \times 40$  mm and those of the evaporation glass line from 8 to 5 mm I.D. Its magnitude was limited by the condition

TABLE I

Physico-Chemical Constants of Pure Substances.

Propyl and butyl formate were mass spectrograph pure substances.

Formate	Property	This work	Literature <sup>2,3</sup>
Methyl	$t_{nbv}, ^\circ\text{C}$	31.5	31.5—31.8
	$n_D^{20}$	1.3433	1.34332
	$d_4^{20}$	0.9742	0.97421
Ethyl	$t_{nbv}, ^\circ\text{C}$	54.2	54.15—54.20
	$n_D^{20}$	1.3598	1.35994
	$d_4^{20}$	0.9226	0.9226
Propyl	$t_{nbv}, ^\circ\text{C}$	80.9	80.85—80.90
	$n_D^{20}$	1.3669	1.37693
Butyl	$t_{nbv}, ^\circ\text{C}$	106.6	106.6
	$n_D^{20}$	1.3890	1.38903

imposing that at an input of 0.75–1.0 W and time of 20 min, approximately 1.5 g of substance would be evaporated without any effect on the amount of the volume work due to the vapours. A further reduction of the vessel dimensions contradicts this condition. For an easier heat transfer into the centre of the liquid, the vessel was made of silver and provided with partitions.

The principle of the measuring and regulation circuit had not been changed. However, some changes were performed, which are depicted in the block scheme on Fig. 2. In contrast to the

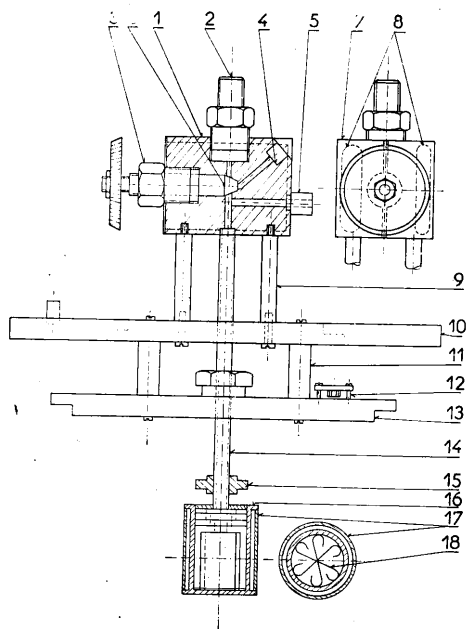


FIG. 1

Evaporation Vessel and the Filling Line

1 Calorimeter head, 2 filling line, 3 vacuum valve, 4 orifice for evacuation, 5 screwing for the condensation vessel, 6 teflon cone, 7 shield for the heating and thermometer, 8 casing of the heating, 9 supporting column of the head, 10 detachable thermostat lid, 11 supporting columns of the thermostat lid, 12 terminals of electric wiring, 13 lid of the isothermal jacket, 14 glass evaporation pipe, 15 teflon terminal of electric wiring, 16 evaporation vessel, 17 nickel plated antireflection jacket, 18 silver partitions.

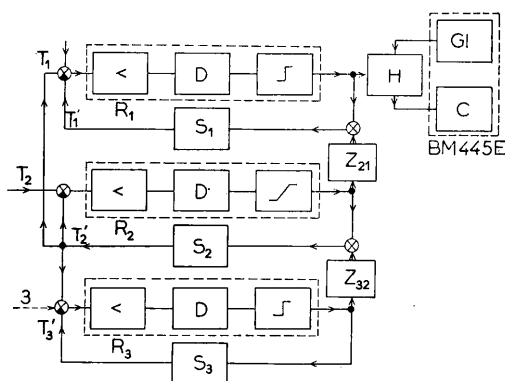


FIG. 2

Block Scheme of the Measuring and Regulation Circuit

$T_1$  Setting of the temperature of the evaporation vessel,  $T_1'$  temperature of the evaporation vessel,  $T_2$  setting of the temperature of the isothermal jacket,  $T_2'$  actual temperature of the isothermal jacket,  $T_3$  controlling property,  $T_3'$  reduced property (temperature of the external jacket),  $R_1$  controller of the temperature of the evaporation vessel,  $R_2$  controller of the temperature of the adiabatic jacket,  $R_3$  controller of the temperature of the external jacket,  $S_1$  controlled system (evaporation vessel),  $S_2$  controlled system (isothermal jacket),  $S_3$  controlled system (external jacket),  $D$  synchronous detector,  $H$  gate,  $Gl$  1 kHz pulse generator,  $C$  counter.

original calorimeter, the regulation circuit of the isothermal jacket (system  $S_2$ ) was selected as the basic regulation circuit. Temperature of this jacket is the reference temperature for the temperature regulation of both the evaporation vessel ( $S_1$ ) and the external thermostat ( $S_3$ ). This change removed the total shift in the temperatures of the adiabatic wall and evaporation vessel during evaporation. The regulation system was maintaining a minimal temperature difference between the evaporation vessel and the adiabatic wall during evaporation, however, a shift in the preliminarily selected temperature of the system by up to  $0.1^\circ\text{C}$  was observed. This was due to the fact that the basic regulation circuit was that of the evaporation vessel the temperature of which oscillates during evaporation. Even though this temperature difference is of no greater significance for the accuracy of the measurements, it would be desirable to remove it. The second favourable effect consisted in removing the necessity of often visual controls of the prescribed temperature of the isothermal jacket, which resulted in simplification of the calorimeter control during the experiment. A further simplification of the operation was achieved by coupling the third regulation circuit to the second one (the temperature of the external thermostat is now controlled automatically by the temperature of the isothermal jacket — the temperature difference may be set to approximately  $3^\circ\text{C}$ ). This removed the necessity of its calibration and control.

TABLE II  
Heats of Vaporization of Esters of Formic Acid

Formate	$t, ^\circ\text{C}$	$H_v^{\text{exp}}$ $\text{cal g}^{-1}$	$H_v^{\text{corr}}$ $\text{cal g}^{-1}$	$H_v^{\text{corr}} - H_v^{\text{calc}}$ $\text{cal g}^{-1}$	
Methyl	20.10	114.30	114.11	0.03	
	31.75	118.28	111.00	-0.08	
A 169.68 B 0.431	40.30	109.23	108.86	0.05	
Ethyl	30.85	102.06	101.92	0.05	
	40.30	99.80	99.61	-0.09	
A 154.71 B 0.459	54.55	96.66	96.32	0.04	
Propyl	52.70	97.10	96.96	0.09	
	57.50	96.07	95.91	-0.03	
	A 144.19	70.50	93.46	93.22	-0.11
	B 0.427	77.75	92.10	91.80	-0.02
		81.50	91.30	90.96	-0.07
		90.25	89.70	89.26	-0.14
Butyl	72.65	90.82	90.63	-0.05	
	81.50	89.44	89.19	0.09	
A 135.99 B 0.426	90.25	87.76	87.44	-0.04	

*Operation.* Firstly, the calorimeter was heated up to the working temperature. After inserting the filling pipette into the calorimeter head, the flange nut was tightened by a closure securing its vacuum tightness. The calorimeter head was then preheated  $2^{\circ}\text{C}$  above the working temperature and the calorimeter itself evacuated. Subsequently, the condensation vessel was closed and the sample in the amount of approximately 5 ml was sucked into the evaporation vessel from the filling pipette. This was followed by pulling out the filling pipette with the capillary from the calorimeter and closing the vacuum valve. The condensed substance (approximately 0.5 ml) in the front part of the vacuum line was drawn away and dried with water pump. After achieving the steady — state of the temperature run, which lasted usually 1 h, the evaporation began by opening the valve in the condensation vessel. When 1–2 g of the measured substance evaporated, the valve was closed again. Simultaneously, the evaporation time and total time of heating were measured on a BM 445E counter. The input of the heating (current and voltage) was determined immediately after the experiment. The amount of the condensate was determined by weighing.

## RESULTS

The heat of vaporization  $H_v$  ( $\text{cal g}^{-1}$ ) of pure substance was calculated from the relation

$$H_v = (1/m)(W - q_1 - q_2), \quad (1)$$

where  $m$  is weight of the evaporated liquid in g,  $W$  is the total heat in cal delivered into the evaporation vessel during the evaporation and  $q_1$  is the correction due to the calorimeter run. The magnitude of the calorimeter run was measured always before the evaporation; experimentally it was verified that it evidently does not change during the evaporation so that it may be replaced by a constant. Term  $q_2$  is an enthalpic correction due to increase in the vapour space of the evaporation vessel after evaporating  $m$  grams of the liquid at temperature  $T$

$$q_2 = (W - q_1) h(m_g/m), \quad (2)$$

$$h = \frac{d_g}{d_g + d_l} = \frac{PM/zd_lRT}{(PM/zd_lRT) + 1}, \quad (3)$$

where  $d_l$  and  $d_g$  are densities of the liquid and vapour at temperature  $T$ ,  $P$  vapour pressure of the pure substance at temperature  $T$ ,  $M$  its molecular weight,  $z$  compressibility factor at  $T$  and  $P$  and  $R$  the gas constant.

Results of the measurements are collected in Table II. Its fourth column contains experimental values corrected to the increase in the vapour volume. Differences between the corrected experimental values and those calculated from the equation

$$H_v = A(1 - T_r)^B \quad (4)$$

are in the fifth column;  $T_r$  denotes the reduced absolute temperature,  $A$  and  $B$  are constants whose values are in the first column of this table under the name of ester.

Any comparison of the measured values is extremely difficult. Direct experimental data are known only for ethyl formate; they were published by Brown<sup>4</sup> and Marshall and Ramsay<sup>5</sup>, however, they are incompatible. A calculation of heats of vaporization of methyl and ethyl formates at the normal boiling temperature from temperature dependences of their vapour pressures was made by Polák<sup>6</sup>. Deviations between his results (113.22 for methyl or 97.46 cal g<sup>-1</sup> for ethyl formate) and our data are considerable (2 or 1.2%, resp.). With respect to the well-known fact that the molecules of esters dimerize easily and that a more precise description of the state behaviour is not available, the experimental values of the heat of vaporization may be considered as more reliable.

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