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Abstract

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SATURATED VAPOR PRESSURE OF TETRACHLOROALKANES AT LOW TEMPERATURES

Until now, the literature has contained no data on the saturated vapor pressure at low temperatures of a number of tetrachloroalkanes (TCA), which are obtained in the telomerization reaction of carbon tetrachloride and ethylene. V. M. Olevskii measured the saturated vapor pressures of TCA with the number of carbon atoms in the molecule 3, 5, 7, and 9 (from C_3 to C_9) in the range from 2 to 760 mm Hg.

In the present work we give data on the measurement of the saturated vapor pressure of TCA from C_9 to C_{17} in the region of lower pressures (from $1 \cdot 10^{-4}$ to $5 \cdot 10^{-2}$ mm Hg), which are necessary for calculating the processes of molecular and high-vacuum distillation of TCA mixtures. From among the most widespread methods for measuring the saturated vapor pressure of high-boiling liquids and some solids (dynamic, effusion, Langmuir methods, etc.), we selected one variant of the static method, namely a direct method of determining vapor pressure directly in units of force acting per unit area. This method was first applied by Hickman (1), and later by other investigators (2,3), for measuring the saturated vapor pressure of phthalic and sebacic acid esters, various plasticizers, fats, oils for filling diffusion pumps, etc. The advantage of this method is that it is free of errors associated with the need to know the accommodation coefficients during evaporation in high vacuum, and with assumptions concerning the structure and degree of association of the molecules of the substance under investigation, which are characteristic of all other methods of measuring vapor pressure.

The principle of the method is based on the fact that, in an apparatus for measuring vapor pressure (a tensimeter), the vapors of the liquid under test leave the evaporator through a nozzle and deflect, through a certain angle, a light disk covering the nozzle and suspended vertically on thin wires.

The deflection of the disk from its initial (“zero”) position is compensated by an equal inclination of the tensimeter.

The main part of the apparatus*—the tensimeter (Fig. 1)—is made of molybde-

Fig. 1. Tensimeter for measuring vapor pressure

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num glass. At the bottom of the tensimeter there is an evaporator 1, with a nozzle 2 having an internal diameter of 30 mm and carefully ground edges. A molybdenum rod 5 mm in diameter (4) is sealed into the ground stopper 3 of the tensimeter; onto the end of this rod is fitted the suspension holder 5. A light duralumin disk 6, 0.1-0.3 mm thick, is suspended from the holder on two thin molybdenum wires, annealed in vacuum, 35 μ in diameter. The upper part of the tensimeter serves as a condenser for the vapors. The condensate collects in the annular trough of the condenser and, through a thin tube 7 with a capillary constriction, flows back into the evaporator.

* The apparatus for measuring vapor pressure was made according to drawings of the All-Union Scientific Research Vacuum Institute.

tube. By means of the ground-joint side arm 8 the tensimeter is connected to the vacuum system.

The tensimeter is fastened in the coupling of a rotating head of special design, by means of which smooth rotation of the tensimeter in two mutually perpendicular directions is accomplished. During measurement of the vapor pressure the tensimeter is immersed in an oil thermostat, in which the temperature is maintained to an accuracy of $±0.2°C.Throughanobservationwindowinthewallofthethermostat,usingalong−
focushorizontalmicroscope,thepositionofthediskinthetensimeterisobserved.Thevacuuminthesystemisprod
461−Mfore−vacuumpumpandanSDN−1glassoiltwo−stagepump.Toincreasetheaccuracyofmeasuringthear
^{2}), direct measurement of the angle of rotation of the tensimeter on a circular scale with a vernier was used, which introduced significant errors into the determination of the magnitude of the angle of rotation of the instrument.

Fig. 1. Tensimeter for measuring vapor pressure

The determination of the vapor pressure of liquids was carried out in a vacuum corresponding to an absolute pressure of residual gases in the system not exceeding $1 \cdot 10^{-4}$ mm Hg. The amount of test liquid poured into the evaporator of the tensimeter was 6-7 cm^3.

During measurement, by rotating the tensimeter such a position of the disk was reached at which the vapor pressure in the evaporator was balanced by the effective weight of the disk. The position of the light "spot" from the beam reflected by the mirror was then marked on the scale. The magnitude of the vapor pressure was calculated by the following formula

$$P = 0.735 \frac{m}{S} \sin \left(\frac{1}{2} \operatorname{arc\,tg} \frac{n_1 - n_0}{z} \right),$$

Fig. 2. Dependence of the vapor pressure of tetrachloroalkanes on temperature

Figure 2: Fig. 2. Dependence of the vapor pressure of tetrachloroalkanes on temperature

where P is the vapor pressure, mm Hg; m is the weight of the disk, g; S is the cross-sectional area of the nozzle, cm^2; n_0 is the reading on the scale at room temperature (zero position), mm; n_1 is the reading on the scale at the temperature under investigation, mm; 0.735 is the conversion factor for going from g/cm^2 to mm Hg; Z is the distance from the mirror to the scale, mm.

Fig. 2. Dependence of the vapor pressure of tetrachloroalkanes on temperature

As the values of n_0 and n_1, the mean values of several readings at one and the same temperature were taken.

The instrument had previously been tested by measuring the vapor pressure of substances whose values were known from the literature. As a

standard substances were di-2-ethylhexyl sebacate and dibutyl phthalate. The measurement results showed very close agreement between the data obtained and the literature data ([1,3]).

The vapor pressures of five tetrachloroalkanes with numbers of carbon atoms 9, 11, 13, 15, 17 ($C_9, C_{11}, C_{13}, C_{15}, C_{17}$) were determined on the apparatus. Pure tetrachloroalkanes were obtained by molecular and high-vacuum distillation of a mixture of TCA from the Kaluga Combine of Synthetic Fragrances.* Initially the TCA mixture at a pressure of 0.1–0.05 mm was distilled in a simple single-stage still (flask) into fractions differing in boiling temperature by 10–15°C. Fractions containing the lower TCA (with a number of carbon atoms less than 11) were then separated into individual components in a packed column with an efficiency of 6 theoretical plates at a pressure in the still of ~ 1 mm Hg abs. Fractions containing the higher TCA (with 11 and more carbon atoms) were separated into individual components in glass multistage molecular columns of the ladder type ([4,5]). As a result of repeated distillations, sufficiently pure TCA were obtained, the physicochemical constants of which are given in Table 1.

Fig. 3. Dependence of the hidden heats of vaporization of tetrachloroalkanes on the number of carbon atoms

Table 1

TCA	Experimental data n_D^{20}	Experimental data d_4^{20}	Experimental data: viscosity at 20°C, centistokes	Experimental data: mol. wt.	Literature data n_D^{20}	Literature data d_4^{20}	Literature data: viscosity at 20°C, centistokes	Literature data: mol. wt., calc.
C_9	1.4820	1.1942	7.57	268.0	1.4821 (6)	1.1856 (6)	7.45 (6)	266
C_{11}	1.4813	1.1479	10.95	290.4	1.4827 (6)	1.1476 (6)	11.5 (6)	294
C_{13}	1.4807	1.1150	15.6	323.7	1.4801 (7)	1.1166 (7)	14.61 (7)	322
C_{15}	1.4802	1.083	21.4	349.0	1.4795 (7)	1.0935 (7)	19.65 (7)	350
C_{17}	–	–	26.5	–	1.4795 (7)	1.0773 (7)	21.89 (7)	378

Chromatographic analysis of the samples of TCA obtained, carried out at the State Institute of the Nitrogen Industry, showed the presence of a certain quantity of impurities, the peaks of which on the chromatogram were located between the peak of the TCA under study and the peak of the neighboring TCA with a smaller number of carbon atoms. Removal of these impurities by repeated molecular distillation proved impossible. Therefore it must be assumed that the vapor elasticity of these impurities is very close to the vapor elasticity of the component under study and should not substantially affect the measurement results.

The results of determining the saturated vapor pressure of TCA are presented in Fig. 2 in coordinates $\lg P$–$1000/T$, where T is the absolute temperature. The straight lines drawn through the experimental points can be expressed by an equation of the general form:

$$\lg P = -\frac{A}{T} + B.$$

In view of the fact that the temperature intervals in which the TCA vapor pressure was measured were small (50–60°C), within these the temperature, the latent heat of vaporization of individual TCA can be taken as constant and it can be assumed that $A = \frac{L}{2.303R}$, where L is the latent heat of vaporization, and R is the universal gas constant, equal to 1.986 cal/deg.

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* V. I. Baranova and N. P. Abramova took part in obtaining the pure TCA.

The heats of vaporization of TCA calculated in this way are given in Table 2. Fig. 3 presents the dependence of the latent heats of vaporization of TCA on the number of carbon atoms in the molecule of the corresponding TCA. From Fig. 3 it is evident that a linear dependence is observed quite well between these quantities.

Table 2

TCA	A	B	Latent heat of vaporization, cal/mol
C_9	4650	12.48	21200
C_{11}	4830	12.22	22100
C_{13}	5088	12.25	23280
C_{15}	5405	12.43	24730
C_{17}	5640	12.55	25600

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Note: Figure translations are in progress. See original paper for figures.