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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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Evaporation Coefficients of Liquid C_2H_5OH, BCl_3, BF_3, CH_4

(Presented by Academician N. M. Zhavoronkov, October 27, 1962)

As is known, the rate of evaporation in vacuum τ_v is described by the equation

$$\tau_v = a\frac{P_n}{\sqrt{2\pi mkT}}\,\frac{\text{molecules}}{\text{cm}^2\cdot\text{sec}}, \tag{1}$$

where P_n is the saturated vapor pressure at the temperature of the liquid surface T, m is the molecular mass, and k is Boltzmann' s constant. The coefficient a, whose occurrence is associated with effects taking place at the phase boundary, is called the evaporation coefficient. It can be determined experimentally by measuring τ_v and calculating from formula (1).

However, for substances with saturated vapor pressures of the order of 0.1 mm Hg and higher, an experiment for measuring a by carrying out the evaporation process in vacuum is difficult because of the rapid cooling of the surface. In these cases the experiment is carried out at a finite vapor pressure over the condensed phase. For slow evaporation (evaporation rate $\tau \ll \tau_v$), the process is described by the Hertz-Knudsen formula

$$\tau = \chi a\frac{P_n - P}{\sqrt{2\pi mkT}}\,\frac{\text{molecules}}{\text{cm}^2\cdot\text{sec}}, \tag{2}$$

where P is the vapor pressure, and χ is a coefficient associated with kinetic effects in the gas phase ([1]). For $a \ll 1$, $\chi \to 1$.

Fig. 1

In the present work, measurements have been made of the evaporation coefficients of several substances (BF_3, BCl_3, CH_4) that are of interest as materials

used in the distillation method for obtaining isotopes of boron and carbon. To calibrate the apparatus, the value of a for ethyl alcohol was also measured.

Experimental Part

The evaporation coefficient was determined by a method based on measuring the increase in pressure during evaporation in a closed volume ([2,3]).

A diagram of the apparatus is shown in Fig. 1. The substance under investigation is placed in a glass evaporation vessel (1) and in a counterpressure chamber (2). The levels of the thermostating liquid in the transparent Dewar vessel (4) and of the liquid under investigation in the evaporation vessel are kept the same, which eliminates the possibility of condensation of the vapor of the substance under investigation on the vessel walls. To ensure constancy of the surface temperature in the

During the experiment a screw stirrer (3) was switched on, which produced intensive mixing of the liquid. This ensured good heat exchange between the evaporation surface and the bulk, which made it possible to fix the temperature with an accuracy of up to 10^{-3} deg.

In addition, owing to the stirring, continuous renewal of the evaporation surface occurred, which prevented the possibility of formation of a surface-active film of impurities hindering evaporation.

The experiment was carried out as follows. The apparatus was evacuated by a diffusion pump to $P \approx 10^{-5}$ mm Hg and was "washed" with the gas under study 2-3 times. Then the substance under study was condensed in chambers 1 and 2. After equilibrium had been established ($P_{\text{n}} - P = 0$), the vapor pressure in the evaporating vessel was rapidly lowered by expansion of bellows 5. The subsequent increase in pressure due to evaporation of the liquid in vessel 1 was measured by a specially made differential manometer 6 (4), which made it possible to record the pressure with a microammeter or an ENO-1 oscillograph. The accuracy of reading $P_{\text{n}} - P$ was $5 \cdot 10^{-2}$ mm Hg. The manometer scale was linear, i.e.

$$P_{\text{n}} - P = b(J_{\text{n}} - J).$$

Here $J_{\text{n}} - J$ is the difference in the manometer readings corresponding to the difference between the equilibrium and the measured pressure.

The described instrument also makes it possible to measure condensation coefficients. In this case, at the beginning of the experiment it is necessary to create in vessel 1 a pressure greater than the equilibrium pressure.

Fig. 2

The substances studied, C_2H_5OH, BCl_3, BF_3, and CH_4, were subjected to thorough purification on distillation columns. Their purity was checked by chemical

Fig. 2

Figure 2: Fig. 2

and mass-spectrometric methods, and also by vapor pressure.

Within the accuracy of the analyses (0.1-0.2%), impurities in BF_3, BCl_3, and CH_4 were absent. The impurity content in ethyl alcohol did not exceed 0.3%.

The measurement results were calculated by formula (2):

$$\log(P_n - P) = -\frac{aS}{2.3V}(kT/2\pi m)^{1/2}t + C \tag{3}$$

(P is the pressure at time t, S is the area of the evaporation surface, V is the vapor volume), which makes it possible to calculate a from the slope of the straight line defining the dependence of $\log(P_n - P)$ on t. The time for establishment of the equilibrium pressure in the case of C_2H_5OH is about 2 sec. The uncontrolled time (pumping out of vapor) of the evaporation process was $\sim$ 0.2-0.3 sec. The time for establishment of the equilibrium pressure after pumping out for BCl_3, BF_3, and CH_4 is of the order of 10^2 sec.

The measurement data in the variables $\log(J_n - J)$ and t were plotted on a graph, as shown in Fig. 2. It is seen from Fig. 2 that $\log(J_n - J)$, and hence also $\log(P_n - P)$, varies linearly with time. In calculating a it was assumed that the evaporation surface was equal to half the surface of the torus ($S = 1.5$ cm^2), which approximately corresponded to measurements of the meniscus made during rotation of the stirrer.

Table 1 gives the values obtained by us for the evaporation coefficients of C_2H_5OH, BCl_3, BF_3, and CH_4, and the condensation coefficients of BCl_3, BF_3. In that

the same table gives values of a for ethyl alcohol known from the literature. The evaporation coefficient of C_2H_5OH, within the limits of error, agrees with the value obtained in work ([2]). It should be noted that our results may contain an unaccounted systematic error of the order of 20-30%, associated with a possibly inaccurate estimate of the surface area of the rotating liquid.

Table 1

Substance	Surface temperature, °K	Evaporation coefficient	Condensation coefficient	Authors
C_2H_5OH	273	$2 \cdot 10^{-2}$	–	Baranaev ([5])
C_2H_5OH	288	$2.4 \cdot 10^{-2}$	–	Buka ([3])

Substance	Surface temperature, °K	Evaporation coefficient	Condensation coefficient	Authors
C_2H_5OH	273	$(3.6\pm0.3)\cdot10^{-2}$	–	Bogdandy et al. ([2])
C_2H_5OH	273	$(4.0\pm1.2)\cdot10^{-2}$	–	Our measurements
BCl_3	273	$(6.1\pm1.2)\cdot10^{-4}$	$(4.0\pm1.2)\cdot10^{-4}$	Same
BF_3	170	$(4.8\pm0.5)\cdot10^{-4}$	$(4.4\pm1.0)\cdot10^{-4}$	Same
CH_4	113.5	$(3.3\pm1.0)\cdot10^{-4}$	–	Same

Of interest is the practical coincidence of the condensation and evaporation rates for BF_3 and BCl_3. As far as we know, the condensation coefficient of liquids has not previously been measured. To clarify the reasons for such small values of the evaporation (condensation) coefficients of the substances considered, further theoretical as well as experimental investigations are desirable.

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