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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Thermogravimetric Method Used To Determine the Saturated Vapor Pressure in a Wide Range of Values

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Abstract—Thermogravimetric method was used to study the evaporation of a number of solvents. The evaporation coefficients in the Langmuir equation were calculated in relation to the conditions of a thermogravimetric experiment (atmospheric pressure, carrier-gas) and nature of a substance under study.

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There exist a large number of various methods for measuring the saturated vapor pressure. They include direct measurements with a gage, use of mass spectrometry for recording the concentration of evaporating particles in the gas phase, evaporation of a sample into a vacuum from a Knudsen cell, application of chromatography, and determination of the boiling point at a lowered pressure.

Recently, papers describing application of thermogravimetry for determining the saturated vapor pressure of organic compounds have been appearing in the scientific literature increasingly frequently [1–3]. Probably, use of thermogravimetry for studying the evaporation was first demonstrated by Gueckel and coworkers [4], who measured the evaporation rates of pesticides under atmospheric pressure by means of isothermal thermogravimetry. The basic principle underlying the experiment is that both evaporation and sublimation are zeroth-order kinetic processes. Consequently, the rate of mass loss by a substance under isothermal conditions as a result of evaporation must be constant, provided that the free surface area of evaporation remains unchanged.

Among methods used for thermal analysis, thermogravimetry has shown good performance as a fast and reliable technique for analyzing the sublimation and evaporation of substances. Although the conventional methods for measuring the vapor pressure are rather accurate, they involve gross expenditure of time. Thermogravimetry has the following main advantages: it uses standard factory equipment, requires comparatively small amounts of a sample, and takes a short time for a measurement.

With the use of programmed temperature and a thermogravimetric analyzer, the loss of mass by a sample is recorded from a constant surface area in a controlled atmosphere. The data obtained can be represented as a TG curve, in which the loss of mass is recorded as a function of temperature or time. The Langmuir equation for free evaporation in a vacuum relates the rate of mass loss to the saturated vapor pressure:

$$-\mathrm{d}m/\mathrm{d}t = P\alpha(M/2\pi RT)^{1/2}, \quad (1)$$

where $-\mathrm{d}m/\mathrm{d}t$ is the rate of mass loss from unit surface area; P, vapor pressure; M, molecular mass of the vapor; R, gas constant; T, absolute temperature; and α, evaporation coefficient (commonly taken to be unity in a vacuum).

Samples are placed in a crucible with parallel walls in such a way that a clearly defined surface area is obtained. Measurements can be made in isothermal or dynamic conditions of linearly increasing temperature in a pure inert atmosphere under atmospheric pressure.

When a material is evaporated in a gas flow under atmospheric pressure, the coefficient α cannot be considered to be unity, as it can be done in a vacuum. Transformation of Eq. (1) gives

$$P = k\nu, \quad (2)$$

where $k = \sqrt{2\pi R/\alpha}$, $\nu = \mathrm{d}m/\mathrm{d}t\sqrt{T/M}$.

The plot of P against ν is a straight line on which fall data for a set of compounds with known vapor pressures, irrespective of their chemical structure, provided that a sample is not associated in a solid, liquid, or gas phase. In other words, k is independent of a sample, being determined by the measuring device, which makes it possible to determine the calibration constant k and thus find the vapor pressure of unknown materials.

Frequently, the role of a reference in thermogravimetric analyses for thermal characterization of sublimating or evaporating substances is played by benzoic acid [2], recommended for use as a calibration material by IUPAC. The acid has gained acceptance as a reference because of its "ideal" properties, i.e., well characterized melting and evaporation points reproducible in thermochemical studies. Further analysis of the temperature dependence of a compound under study can be made using the Clausius–Clapeyron equation for calculating the sublimation or evaporation, or the Antoine equation for analytically expressing the vapor pressures in a given temperature interval.

The Langmuir equation (1) was derived for the case of evaporation into a vacuum on the assumption of equal rates of evaporation and condensation from an open surface. It is commonly believed that this condition is satisfied only at low pressures, when the presence of a back flow of molecules can be neglected [5]. In this case, the evaporation coefficient α is introduced as a correction that accounts for the fact that not each molecule falling onto the surface is deposited there.

To refine the applicability limits of the thermogravimetric method in the case of evaporation of a material in a gas flow under atmospheric pressure (when the coefficient α cannot be considered equal to unity), an experiment was performed with a set of substances having widely varying saturated vapor pressures under the experimental conditions. The following substances were examined: benzoic acid, water, methanol, ethanol, isopropanol, *n*-butanol, *n*-hexane, benzene, toluene, dichloromethane, chloroform, carbon tetrachloride, acetonitrile, and acetone. Benzoic acid ($C_7H_6O_2$, M = 122.1, ≥ 99.5% purity) was purchased from Sigma Chemical Co., St. Louis, USA; twice-distilled water was used; methanol of HPLC purity was obtained from Fisher Scientific; isopropanol of special-purity grade 13-5, TU (Technical Specification) 6-09-07-1718–91; n-butanol of chemically pure grade, TU 2632-044-444931079–98; n-hexane, 99%, HPLC purity, purchased from Lab-Scan Analytical Sciences; toluene of chemically pure grade, TU 2631-002-29483781–2005; dichloromethane, ethanol, chloroform, benzene, and carbon tetrachloride, all of spectral purity grade, purchased from Sigma-Aldrich; acetonitrile of chemically pure for chromatography grade, TU 6-09-4326–76; acetone of special purity grade 9-5, TU 6-09-3513–86.

Values of the coefficient k in Eq. (2) and the corresponding values of the evaporation coefficient α for the substances studied

Substance	$k \times 10^5$, $J^{1/2}\,K^{1/2}\,mol^{1/2}$	$\alpha \times 10^5$
Benzoic acid	1.114	6.488
n-Butanol	1.322	5.467
Water	2.598	2.782
Toluene	1.827	3.956
Isopropanol	1.748	4.135
Ethanol	1.979	3.652
Acetonitrile	1.785	4.049
Carbon tetrachloride	1.729	4.180
Benzene		
Methanol	1.781	4.058
Hexane	1.682	4.297
Chloroform	1.659	4.357
Acetone	1.617	4.470
Dichloromethane	1.512	4.780
n-Butanol	1.152	6.274

EXPERIMENTAL

The thermogravimetric experiment was performed with an MOM Q-1500D derivatograph (Hungary). The device is an integrated installation that can simultaneously record four parameters: temperature of a sample being analyzed (T), variation of the sample mass (TG), rate of variation of the sample mass (DTG), and temperature difference between a sample and the reference crucible (DTA). Platinum crucibles with a cross-section area of $4.064\ 10^{-5}$ m^2 were used. The weighed portion of benzoic acid was approximately 20 mg in each experiment. An empty platinum crucible served as reference. Zero nitrogen of B brand (TU-6-21-39–96) was used as carrier-gas. The carrier-gas was passed through a column packed with a calcined silica gel of KSKG brand [GOST (State Standard) 3956–76 (rev. 3)]. The flow rate of the carrier-gas was measured at the inlet of the derivatograph

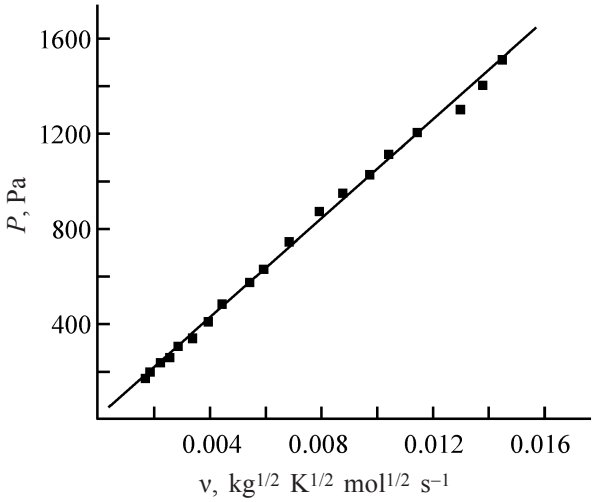

Fig. 1. Determination of the constant k of Eq. (2) with benzoic acid. Nitrogen flow rate 50 ml min^{-1}, heating rate 5 deg min^{-1}; the same for Fig. 2. (*P*) Saturated vapor pressure of benzoic acid and (ν) parameter of a transformed Langmuir equation.

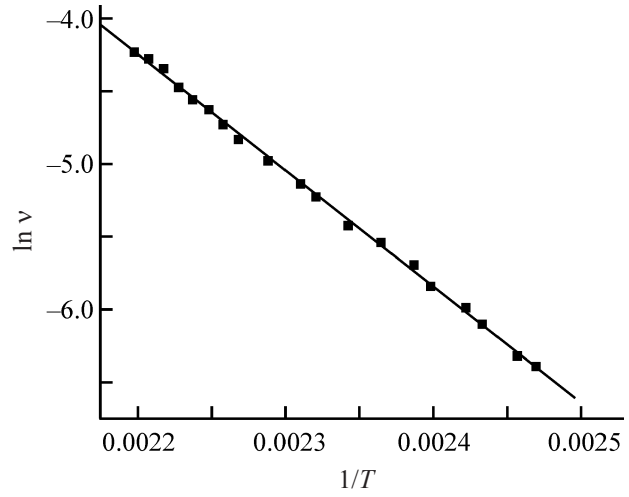

Fig. 2. Calculation of the enthalpy of evaporation for benzoic acid (ν, kg$^{1/2}$ K$^{1/2}$ mol$^{1/2}$ s^{-1}). Parameter of a transformed Langmuir equation and (*T*) temperature.

and maintained constant using a fine-control valve. The calibration constant *k* in Eq. (2) was found using benzoic acid at carrier-gas flow rates of 25, 50, and 100 ml min-12 and heating rates of 2.5, 5, and 10 deg min^{-1}. The heating was done from room temperature to 250°C. The temperature dependence of the vapor pressure *P* (mm Hg) of benzoic acid is expressed, using the Antoine equation, as

$$\log P = A - B/(C + T) \quad (3)$$

where A, B, and C are Antoine constants valid in a certain temperature range for the evaporation process; for benzoic

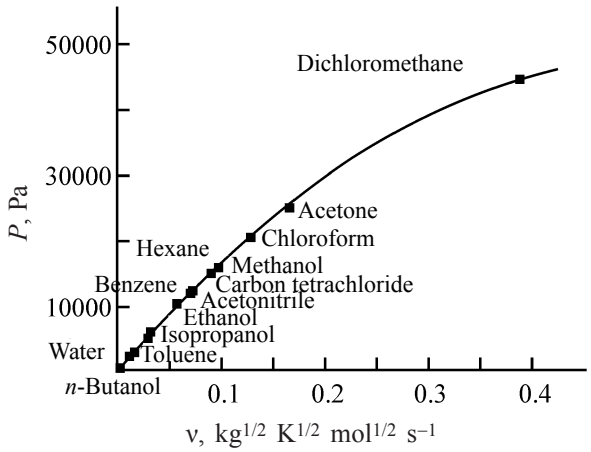

Fig. 3. Thermogravimetric data for the solvents under study, plotted in the coordinates of Eq. (2). (*P*) Saturated vapor pressure and (ν) parameter of a transformed Langmuir equation.

acid, A, B, and C in the temperature range 405–523 K are 7.80991, 2776.12, and –43.978, respectively [2].

Equation (2) was used to construct a linear dependence of *P* on ν, whose slope is *k* (Fig. 1). It was found that the optimal mode of the thermogravimetric experiment is that with a nitrogen flow rate of 50 ml min^{-1} and heating rate of 5 deg min^{-1}. In this case, the coefficient *k* in Eq. (2) is 1.114 105 J$^{1/2}$ K$^{-1/2}$ mol$^{-1/2}$, in good agreement with published values [2, 3]. The slope rate of the dependence of lnν on T was used to calculate, using the Clausius–Clapeyron equation

$$\ln\nu = \text{const} - \Delta H/RT$$

where *R* is the gas constant and *T* is absolute temperature, the enthalpy of benzoic acid evaporation, Δ*H*, whose value is 65.5 ± 0.2 kJ mol^{-1} (Fig. 2), which almost coincides with the recommended published values [2].

The thermogravimetric study of the evap¬oration of the solvents was performed in the isothermal mode, with the experimental temperature varied from 18 to 28°C and maintained constant with an accuracy of ±0.1°. Temperature dependences of the saturated vapor pressure for the set of the solvents studied are known and can be found in reference books [6, 7]. Accordingly, isothermal thermogravimetric data can be used to calculate the constants *k* of Eq. (2) for these solvents. Figure 3 shows thermogravimetric data for the set of the solvents studied, plotted in the coordinates of Eq. (2).

The experimental data plotted in the coordinates of Eq. (2) are described by a second-order polynomial with

a correlation coefficient of 0.998. At the same time, the dependence of P on ν can be approximated in a rather wide range of pressures (up to that of benzene) with a linear function (also with a correlation coefficient of 0.998). Thus, in the conditions of a thermogravimetric experiment with a carrier gas, the proportional relationship between the saturated vapor pressure P and parameter ν is preserved in a very wide range of pressures (to above 10000 Pa in the given case). At higher pressures, the dependence deviates from linear behavior and is described by a second-order polynomial (the maximum pressure exceeds 40000 Pa). The table lists values of the coefficient *k* in Eq. (2) and the corresponding values of the evaporation coefficient α for the compounds studied. It can be seen that, under the conditions of the thermogravimetric experiment with a carrier-gas, the evaporation coefficient α is substantially smaller than unity and has the same order of magnitude for all of the compounds studied, including benzoic acid.

The issue of the evaporation (condensation) coefficient α has long been discussed in the literature. Nesmeyanov, Lozgachev, Ozhegov, and others analyzed the existing concepts of its physical meaning, methods for its estimation, and the effect of the condensation coefficient on the vapor pressure measured by the Langmuir and Knudsen techniques [5, 6]. Nesmeyanov [5] specified the features characterizing the process at $\alpha \neq 1$: (a) inequality of the evaporation (sublimation) rates measured by the Langmuir method and calculated from data on the saturated vapor pressure, (b) dependence of the rate of vapor outflow from the Knudsen chamber on the area of the effusion orifice, (c) difference in the evaporation (sublimation) rates measured by the Langmuir and Knudsen methods, and some others. It should be noted in this context that that the upper applicability limit of the effusion Knudsen method does not exceed a pressure of 10 Pa, and the radius of the effusion orifice, 1 mm. This is so because the conditions of molecular outflow of the vapor from the effusion orifice are satisfied if the mean free path of molecules within the effusion chamber substantially exceeds the diameter of the effusion orifice. When measuring pressures markedly exceeding 10 Pa, various corrections taking into account the departure of the vapor outflow mode from the molecular effusion are commonly introduced.

In [8–10], application of the effusion method to measurements of the saturated vapor pressure of *n*-octanol, dimethyl sulfoxide, and water was described. The authors noted that the vapor pressures calculated for these solvents by the Knudsen equation approach the true saturated vapor pressure as the diameter of the effusion orifice becomes smaller, i.e., the evaporation coefficient α decreases as the effusion orifice becomes larger. The Langmuir and Knudsen techniques are kinetic methods, because they are based on concepts of the molecular-kinetic theory of gases. The difference is in that the Langmuir method is based on evaporation of a substance from a free surface into a vacuum, and the Knudsen method analyzes the effusion (outflow) rate of a gas jet from the effusion chamber. The expression for the vapor pressure Pch in the effusion chamber is similar to the relation in the Langmuir method:

$$P_{ch} = (\Delta m/S_{or}t\beta)(2\pi RT/M)^{1/2}, \quad (4)$$

where Δm is the mass of a substance effused from the chamber; S_{or}, area of the effusion orifice; t, evaporation time; β, coefficient characterizing the resistance of the effusion orifice to the vapor flow (Clausing factor); and M, molecular mass of the substance.

As the effusion orifice becomes larger, the Knudsen method practically transforms into the Langmuir method. There is no fundamental difference between these two techniques, with the limitations being only quantitative. If $\alpha = 1$, the vapor pressures calculated using the Langmuir and Knudsen methods coincide. In the thermogravimetric experiment performed under atmospheric pressure, the mean free path of evaporating molecules will be substantially shorter than that expected for an experiment in high vacuum. Therefore, the very small values of the evaporation coefficient α for all of the substances studied (on the order of 10^{-5}) probably characterize the experimental conditions (atmospheric pressure, evaporation surface area, carrier-gas flow velocity, heating rate). In this case, α depends on the nature of a substance to a lesser extent: the dependence of P on ν deviates from linear behavior only at pressures exceeding 10000 Pa.

CONCLUSIONS

Thermogravimetric method can be successfully used to determined the saturated vapor pressure of substances in a very wide range of pressures (to above 40000 Pa). The very small values of the evaporation coefficient α (on the order of 10-5) are determined to a greater extent by conditions in which the thermogravimetric experiment is performed, and to a lesser extent, by the nature of a substance under study.

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