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DETERMINATION OF THE HEAT OF EVAPORATION OF PURE SUBSTANCES AND OF AQUEOUS SOLUTIONS OF INORGANIC SALTS WITH THE DERIVATOGRAPH

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The potentials of thermogravimetry for the determination of the heat of evaporation were studied not only for pure substances, but also for aqueous solutions of inorganic salts. The model substances used were water, 1,4-dioxane, naphtalene, ethanol and aqueous solutions of ammonium nitrate with various concentrations. The differences between the experimental and literature data do not exceed 5% rel.

The facility, rapidity and reliabilty of the proposed method are certainly of interest in the calculations for technological and equipment design of new chemical plants and for physicochemical studies of aqueous salt systems.

The performance of thermal analysis with the derivatograph opens up wide prospects for the complex study of various processes, owing to its facility, rapidity and satisfactory reliability. Adonyi [1] reported on the theoretical foundations and experimental data of the thermogravimetric determination of the heat of evaporation of pure substances. Such data are of importance for calculations in the technological and equipment design of new chemical plants, particularly for composite fertilizers. In this connection, the present work was dedicated to study the applicability of the derivatograph for heat of evaporation determinations of inorganic salts in aqueous solution. A comparison to the experimental and literature data showed a maximum difference of only 5% rel.

Experimental

We studied the evaporation of a number of pure substances and aqueous solutions of ammonium nitrate with varying concentrations (Table 1).

The samples were heated from ambient temperature to the end of the process in a conical platinum crucible (No. 1). The first sample weighed fully filled up the crucible; its mass, depending on the nature of the substance, varied between 0.17 and 0.60 g. For each substance, a heating rate was selected ensuring optimum reproducibility of the thermogravimetric curves and facility of subsequent data processing. The rates varied between 1.5 to 4.0 °/min.

As may be seen from Figs 1 and 2, the evaporation of pure substances proceeds as an energetically homogeneous process, whereas in the case of the aqueous

Table 1

Comparison of the results of the experimental determination of ΔH with data from the literature

Substance	Mass of sample, g	ΔH, kcal · mol^{-1}		Difference, % rel.
		literat.	exper.	
Distilled water	0.40	9.72	9.5	2.3
Ethanol (96%)	0.40	9.22	9.2	0.2
1,4-Dioxane	0.45	7.59	4	2.6
Naphtalene	0.17	10.4	10.3	1.0
NH_4NO_3 solution, 10%	0.50	10.16	10.0	1.6
30%	0.60	9.95	9.9	0.5
40%	0.60	10.13	9.9	2.4
50%	0.60	9.83	9.5	3.5
60%	0.60	10.05	9.6	4.7
65%	0.60	10.02	9.9	1.2

ammonium nitrate solutions, the shape of the DTG curves reveals a noticeable deformation close to the boiling point. This is caused by the considerable suppression of the active evaporation surface, owing to the increased concentration (that is, density) of the solution, above all in the surface layer.

If the evaporation process in a thin layer bordering the interface of the phases is considered, one may assume, as a good approach, that the process is at equilibrium, corresponding for a certain time interval to the condition $T =$ const at constant pressure equal to the atmospheric pressure. It has been established earlier [1, 2] that the equation

$$\frac{dx}{d\tau} = \frac{M \cdot F}{\sqrt{2M\,RT}} \cdot P_g \tag{1}$$

may be used for processing the thermogravimetric data. By substitution into the Clausius – Clapeyron equation, one obtains

$$\lg \frac{dx}{d\tau} = -\frac{\Delta H}{2.303\,RT} + \text{const}. \tag{2}$$

where $\frac{dx}{d\tau}$ = evaporation rate, M = molecular mass, R = universal gas constant, F = evaporation surface, T = absolute temperature, P_g = vapour pressure, ΔH = molar heat of evaporation.

As a result of the repeated condensation of the vapour, only a part of the geometric area of the interface participates in the evaporation [1, 2], a so-called virtual evaporation surface is substituted into Eq. (1). When the order of the reaction is zero, the rate of mass loss is equal to the evaporation rate, so that the latter can directly be estimated from the DTG curves. The slope of the function

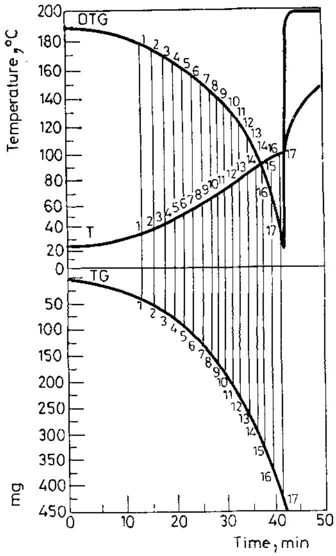

Fig. 1. Thermoanalytical curves of 1,4-dioxane evaporation

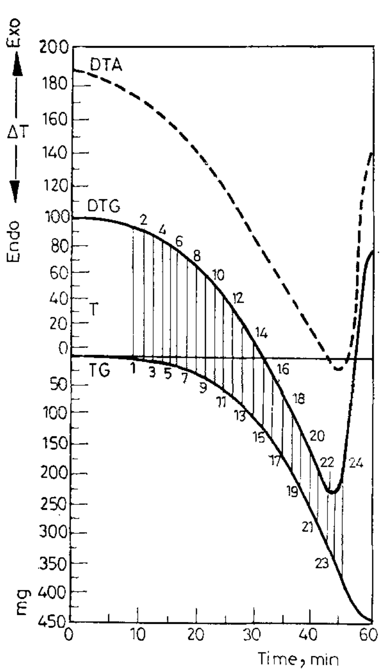

Fig. 2. Thermoanalytical curves of water evaporation from a 30 % aqueous ammonium nitrate solution

$\left(\lg\frac{\mathrm{d}x}{\mathrm{d}\tau}\ vs.\ -\frac{1}{T}\right)$ is equal to $\frac{\Delta H}{2.303R}$. This may be used for the graphical determination of the average value of the heat of evaporation of the substance in question.

The thermal curves were marked with straight parallel lines at distances of 4°. Their point of intersection with the TG curve demonstrates the value of the mass loss, and the deviation of the DTG curve from the zero line the value of the evaporation rate at the given temperature.

The factor for converting the value of the deviation of the DTG curve from the zero line into the dimension mg/s for the evaporation rate was obtained by numerical deviation of the corresponding TG curve. The chosen distance of 4° in marking the thermal curves was converted into minutes by accounting the heating rate. The conversion factor was calculated from seven to eight points at different parts of the TG curve, and subsequently the average value was taken.

To demonstrate the reproducibility of the thermogravimetric curves, the TG and DTG curves of parallel experiments with a 30% aqueous ammonium nitrate solution are presented in Fig. 3. The figure clearly illustrates the suitability of utilizing averaged values for the calculation of heats of evaporation. The average values of $\frac{\mathrm{d}x}{\mathrm{d}\tau}$ were obtained from 4–6 parallel experiments.

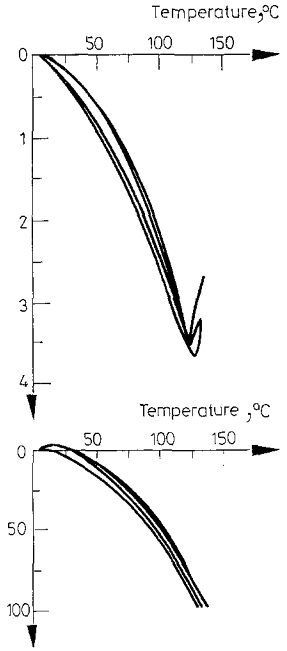

Fig. 3. Comparison of thermogravimetric data from parallel experiments for a 30% aqueous ammonium nitrate solution

Earlier it was demonstrated that Eqs (1) and (2) may only be used for zero-order reactions. We calculated the order of reaction for the experimental materials by the method of Horowitz and Metzger [3]. As was to be expected, one could reckon in all the cases with zero order.

The value of the average heat of evaporation for aqueous solutions of ammonium nitrate was determined by Eq. (2), neglecting the slight pressure of NH_4NO_3 vapour [4]. Thus we assumed that the vapour phase is a pure substance.

The temperature interval in which we carried out the calculation of ΔH was determined from the thermoanalytical curves: within this interval, the temperature curve (T) must be linear and no noticeable break shall appear in the DTG curve. The value of the virtual surface area within the chosen interval must be constant. This was established by special calculations by Eq. (1). The relationship $\left(\lg \frac{dx}{d\tau}\ vs.\ -\frac{1}{T}\right)$ was calculated for each case by the least squares method. As shown in Table 1, the maximum difference between literature data and experimental data for ΔH did not exceed 5% rel.

The results of heat of evaporation calculations were utilized to determine the temperature dependence of the pressure of saturated vapour by means of the approached Clausius–Clapeyron equation.

The results of the experimentally obtained temperature dependence of saturated water vapour and aqueous ammonium nitrate solutions, resp., were processed using the comparative method of physicochemical properties [5–6]. The equation for the calculation of water vapour pressure above salt solutions, on the basis of the similarity of the temperature dependence of the physicochemical properties of the solvent and the solution is known as the Kireev–Othmer equation. It may be written in the following form:

$$\lg P = K_p \lg P_0 + K_p \lg B_p . \qquad (3)$$

Here P and P_0, resp., are water vapour pressures above the solution and the pure solvent at equal temperatures; K_p is the multiplication factor in the similarity transformation, equal to the ratio of the molar heat of evaporation of the substance in solution L and that of the pure solvent L_0, i.e. $K_p = \frac{L}{L_0}$; B_p is the pressure increment. Hence, in the coordinate system $\lg P - \lg P_0$ the experimental data relative to the pressures of saturated vapours above the pure solvent and those to the solvent can be approached by straight lines. Figure 4 demonstrates this on the example of our studied system.

The values of K_p and B_p were calculated by the least squares method. Figure 5 shows the dependence of the multiplication factor K_p and of the pressure increment B_p on concentration, in aqueous ammonium nitrate systems, and also the phase diagram of the $H_2O-NH_4NO_3$ system [7].

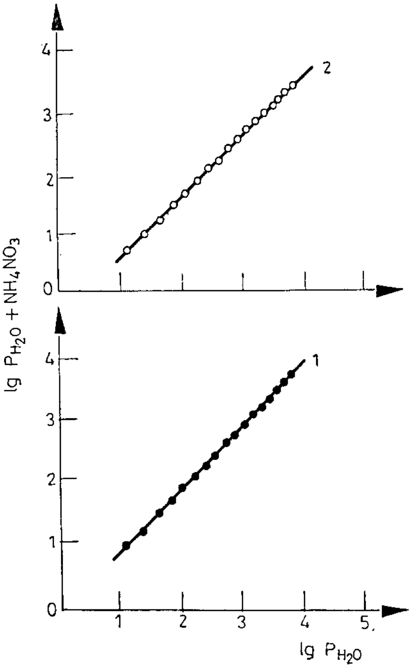

Fig. 4. lg P *vs.* lg P_0 for 30% and 60% ammonium nitrate solutions

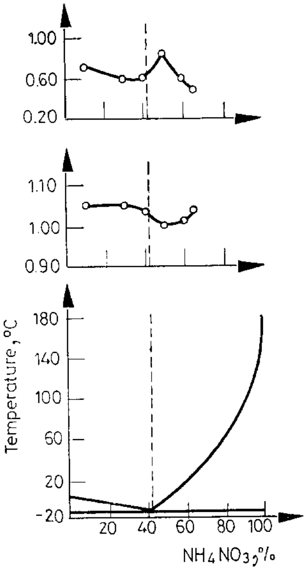

Fig. 5. Dependence of K_p and B_p on the concentration of aqueous ammonium nitrate solutions and phase diagram of the $H_2O-NH_4NO_3$ system

Analogous results [7] obtained by comparative calculations of the viscosity of analogous systems, including the system studied by us, may be regarded as a proof for the truth of the results obtained by the suggested method [8] and for its satisfactory accuracy.

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RÉSUMÉ — On étudie les possibilités d'application de la thermogravimétrie pour la détermination des chaleurs d'évaporation non seulement pour des substances pures, mais aussi pour des solutions aqueuses de sels inorganiques. Les substances-modèles utilisées sont l'eau, le 1,4-dioxane, la naphtaline, l'alcool éthylique et des solutions aqueuses de nitrate d'ammonium de concentrations diverses. Les différences entre les données d'expérience et celle de la littérature n'ont pas dépassé 5 p.c. rel.

La facilité, la rapidité et la fiabilité de la méthode proposée présentent un intérêt certain pour les projets technologiques et la conception de dispositifs pour de nouvelles usines chimiques ainsi que pour les études physicochimiques des systèmes de sels aqueux.

ZUSAMMENFASSUNG — Die Einsatzmöglichkeit der Thermogravimetrie zur Bestimmung der Verdampfungswärme wurde nicht nur an reinen Substanzen, sondern auch an wäßrigen Lösungen anorganischer Salze untersucht. Die verwendeten Modellsubstanzen waren Wasser, 1,4-Dioxan, Naphthalin, Äthanol und wäßrige Lösungen verschiedener Konzentrationen von Ammoniumnitrat. Die Unterschiede zwischen den Versuchsergebnissen und den Literaturangaben überschreiten nicht die 5 rel. %.

Die Leichtigkeit, Schnelligkeit und Zuverlässigkeit der vorgeschlagenen Methode sind bei der technologischen und apparativen Berechnung neuer chemischer Betriebe und für physikalisch-chemische Studien wäßriger Salzsysteme von Interesse.

Резюме — Изучена возможность применения термогравиметрического метода для определения теплот парообразования не только чистых веществ, но и водных растворов неорганических солей на дериватографе. В качестве модельных веществ использовали воду, 1,4-диоксан, нафталин, этиловый спирт и водные растворы нитрата аммония различной концентрации. Расхождение между экспериментальными и литературными значениями ΔH не превышает 5% отн.

Доступность, быстрота и надежность предлагаемого метода представляют несомненный интерес для технологических и аппаратурных расчетов новых химических производств, физико-химического исследования водных солевых систем.