DIFFERENTIAL THERMOGRAVIMETRY FOR DISTINGUISHING BETWEEN EVAPORATION AND DECOMPOSITION IN THERMO-GRAVIMETRIC ANALYSIS

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In the evaluation of thermogravimetric data obtained in the analysis of liquid products, and particularly in that of petroleum products, it is of practical importance whether the observed change in weight is due to evaporation or decomposition. The use of a derivatograph [1] for the measurements has the advantage of plotting more sensitively than by other methods, thus e.g. by graphical method, also the derivative of the TG curve with respect to time (DTG curve). Therefore, the knowledge of the DTG curve permits the direct application of the rate function of the change in weight to the study of phenomena occurring during thermogravimetric analysis.

The derivatograph used for the measurements is suitable also for the recording of the differential thermal analysis curve (DTA). In view of the fact that there is only an indirect correlation between the DTA curve and the rate functions, the DTA curves were not evaluated in this work.

Temperature being measured in the samples, the adjustment of a linear temperature-time function was not necessary, since this would be of advantage only in the integration of the used differential equation.

Investigation of evaporation

Assuming the vapour of the evaporationg liquid to be an ideal gas at the pressure p_g, the number of moles of the vapour, condensing in unit time on unit surface can be expressed by the following relationship:

$$\frac{dn}{d\tau} = \frac{p_g}{\sqrt{2 \pi MRT}} .$$ (1)

Due to the independence of the two processes, the rate of evaporation must be the same [2].

For measurements with a derivatograph, expediently the weight will be used instead of the number of moles per unit surface in the formula of the evap-

oration rate.

$$\frac{dx}{d\tau} = \frac{MF}{\sqrt{2\pi MRT}} \cdot p_g \tag{2}$$

where: τ = time, sec

x = quantity of the substance evaporated up to the time τ, mg

$\dfrac{dx}{d\tau}$ = rate of evaporation, mg/sec
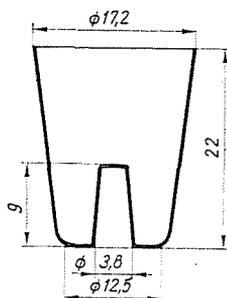
Fig. 1

M = molecular weight of the tested substance
F = surface of evaporation, cm^2
R = universal gas constant, cal/$^\circ$
T = absolute temperature, $^\circ$K
p = vapour pressure, torr

The shape and the dimensions of the largest crucible available for the tests is shown in Fig. 1.

It follows from the shape of the crucible that the surface area of evaporation changes during the measurements. This change is further complicated by the heat dilatation of the liquid and the crucible.

Additional difficulties arise from the fact that for the application of Equ. (2) condensation should be eliminated, because else the apparent evaporation surface F' ought to be considered instead of the true surface F, which, however, is strongly dependent on test conditions.

For the evaluation of the applicability of the relationship (2), measurements were undertaken with water as well-known modell substance. Fig. 2 shows that measurement, where care has been taken that the stub, protruding into the crucible and serving for the measurement of the temperature of the sample (and the recording of the DTA curve), shall be covered with water even after the termination of the measurement.

Measuring results are summarized in Table 1.

Table 1

Evaporation rate of water for the experiment
shown in Fig. 2

Temperature °C	Pg theoretical [3] torr	$\dfrac{dx}{d\tau}$ mg/sec	F' calculated surface cm^2
30	31.824	0.0088	0.022
40	55.342	0.0262	0.039
50	92.51	0.0525	0.047
60	149.38	0.0875	0.049
70	233.7	0.1224	0.045
80	355.1	0.1924	0.047
90	525.76	0.2798	0.047
94	625	0.3148	0.045
98.5	735	0.3760	0.046

As can be seen from the last column of Table 1, the apparent surface of evaporation F' can be considered as fairly constant. At low vapour pressures, this constant character of the apparent surface ceases.

It was found that due to recondensation only a fraction of the true evaporation surface behaves according to Equ. (2). F' is only the fraction

$$F' = F/C \tag{3}$$

of the true surface of evaporation, however, C is constant, that is to say, independent of temperature.

To verify condensation, experiments were carried out, in which suction was applied in the immediate vicinity of the evaporation zone in the upper part of the crucible. Dimensions of the crucible of the derivatograph necessitated for the realization of suction a change in experimental conditions. Data of two comparable measurements are contained in Table 2. In these measurements, where the smaller crucible, costumary with the apparatus, was used, the water weighed in did not cover the stub protruding into the crucible. (The crucible was proportionally smaller than that shown in Fig. 1.)

Data in Table 2 prove that, due to the reduction of condensation, the apparent surface of evaporation increases when suction is applied. The comparison of Tables 1 and 2 shows that, under the given experimental conditions and within the error arising from the heat dilatation of the liquid and the shape of the crucible, the apparent surface of evaporation becomes constant in the vapour pressure range higher than 50 to 80 torr.

Table 2

Apparent surface area of the evaporating water

Temperature, °C	F' cm² without suction	Temperature °C	F' cm² with suction
20.5	0.004		
28.0	0.009	30.0	0.015
40.0	0.018	40.0	0.019
50.0	0.019	50.0	0.022
58.0	0.017	60.0	0.021
70.0	0.017	70.0	0.021
80.0	0.018	80.0	0.022
88.0	0.018	90.0	0.021
93.0	0.019	94.7	0.021

The reproducibility of the measured values is very good, which is demonstrated by the fact that the average surface F' calculated from data without suction in Table 2 for the temperature range from 50 to 93 °C is 0.0180 cm², while the average surface calculated from parallel results is 0.0176 cm².

The relationship (2) contains the square root of temperature, permitting to disregard in a small temperature intervall the dependence on temperature. In evaporation, $dx/d\tau$ is always a positive number, and hence, Equ. (2) can be written in the form:

$$\frac{dx}{d\tau} = c \cdot p_g \quad \text{and} \quad \lg \frac{dx}{d\tau} = \lg p_g + \lg c \tag{4}$$

where:

$$c = \frac{MF'}{\sqrt{2\pi MRT}} \ .$$

Using the well known empirical formula

$$\lg p_g = -\frac{A}{T} + B \tag{5}$$

and neglecting the temperature dependence of the heat of evaporation λ, the equation can be written in the form:

$$\lg p_g = -\frac{\lambda}{4 \cdot 576 \, T} + B \tag{6}$$

where B is an integration constant.

The combination of equations (4) and (6) gives the following expression:

$$\lg \frac{dx}{d\tau} = - \frac{\lambda}{4 \cdot 576\, T} + \lg c + B = - \frac{\lambda}{4 \cdot 576\, T} + \lg C'. \qquad (7)$$

Thus, a direct relationship exists between the rate of evaporation and the vapour pressure. This rate, which can be calculated from the DTG curve, is suitable for the determination of the average heat of evaporation. This calcula-

Weight of sample: 2861 mg
Inert substance: 1300 mg Al_2O_3
Sensitivity: TG : 2000
DTG: 1/3
DTA: 1/100
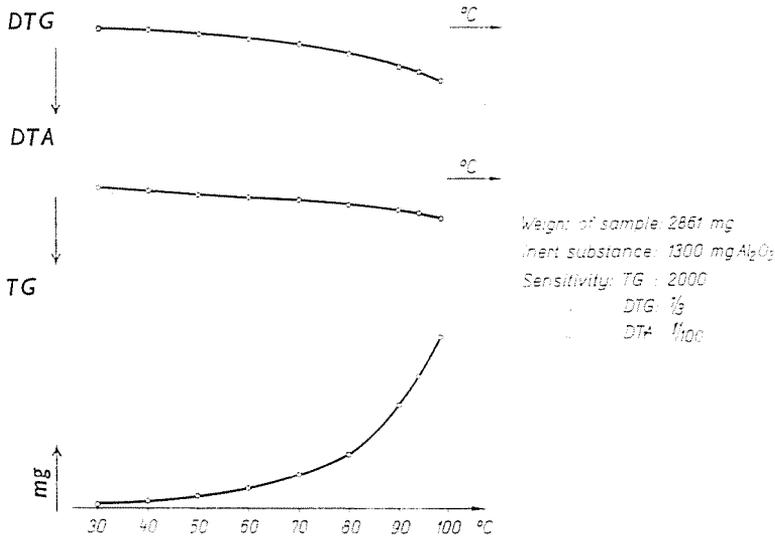
Fig. 2

tion does not necessitate the knowledge of the true *(F)* or of the apparent *(F')* surface of evaporation, or even that of the molecular weight.

Denoting the $\left(\dfrac{dx}{d\tau}\right)_i$ values appertaining to the temperature T_i by K_i, the average heat of evaporation can be calculated with the following formula:

$$\lambda = 4 \cdot 576 \cdot \frac{T_1 \cdot T_2}{T_2 - T_1} \left(\lg K_2 - \lg K_1\right). \qquad (8)$$

Average values of λ, between 50 and 90 °C calculated from measurements under varying the dimensions of the crucible, the quantity of the substance, the suction and the sensitivity, were found to be 9.8; 9.7; 9.6; and 10.2 kcal/mole, respectively, while calculations from the equation

$$\lg \frac{p_1}{p_2} = \frac{\lambda}{4 \cdot 576} \cdot \frac{T_1 - T_2}{T_1 \cdot T_2} \qquad (9)$$

gave 10.1 kcal/mole.

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The deviation between the value 9.8 kcal/mole, calculated from experimental data, and the value 10.1 kcal/mole, calculated from Equ. (9), projected on the distance of the DTG curve from the base line resulted 1 mm, This error can be readily corrected by the proper recording of the DTG base curve (the base line from which the distance of the DTG curve is measured), however, a further study of the temperature dependence of the DTG base curve is required.

Eliminating the error of the $dx/d\tau$ determination, and in knowledge of conjugate vapour pressure-temperature values, the temperature dependence
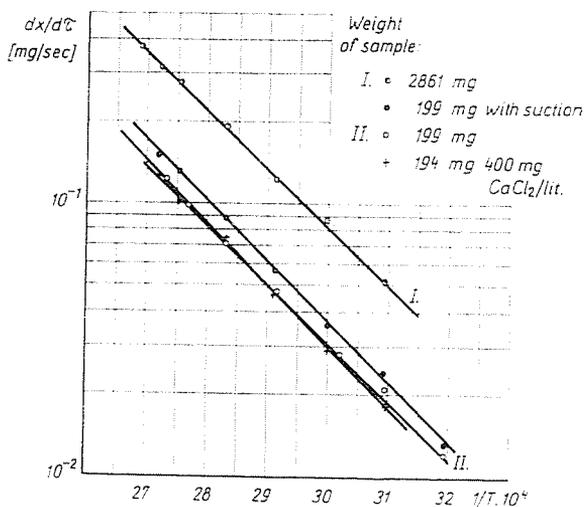
Fig. 3

of vapour pressure, the heat of evaporation and the apparent surface of evaporation can be calculated from the diagram recorded with the derivatograph.

The relationship (7) plotted as a $\lg dx/d\tau$ and $\dfrac{1}{T}$ diagram gives, notwithstanding the shape of the crucible and other mentioned sources of error, a remarkably good straight line for that section, where the apparent surface of evaporation F' is constant. The salt content of water seems to influence the slope of the straight line. The measured data are shown in Fig. 3.

Fig. 4 shows in connection with Fig. 3 the temperature-time relationships for the straight lines denoted by I and II. It can be seen from Fig. 3 that in case of a single component system (in the given case: water) the slope of the straight line is not modified by the quantity of the weighed in substance, and — as becomes clear from Fig. 4 — results are not sensitive to the shape of the temperature-time function.

Fig. 5 shows the DTG curves, plotted as lg $dx/d\tau$ versus $1/T$ diagrams, of a few selected lubricating oils of extreme character. The curves VIa and VIb in Fig. 5 were recorded with the same oil but at different rates of heating and for different weights of sample, and their comparison with the results shown in Fig. 3 (plotted for water) serves to prove that for mixtures the slope of the straight line is dependent on experimental conditions.
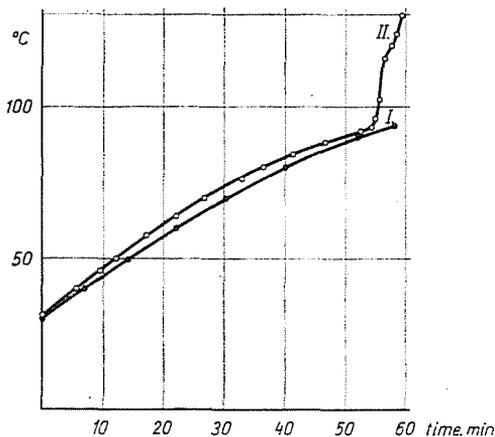
Fig. 4
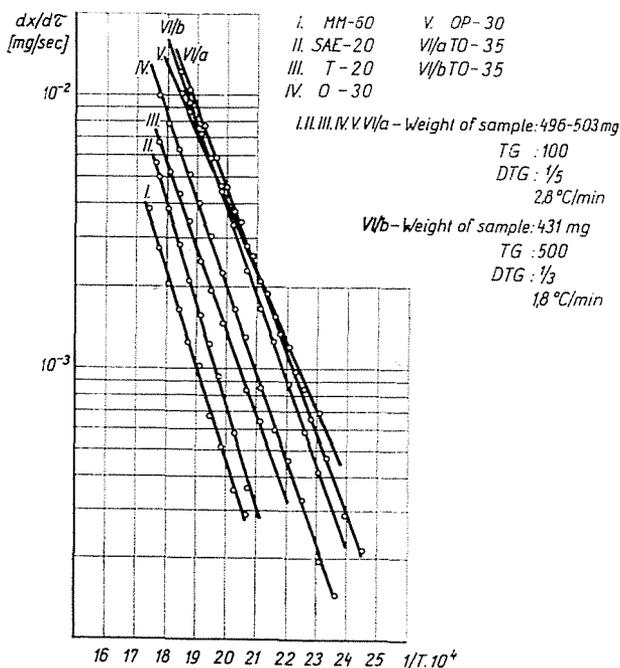
Fig. 5

Distinguishing between evaporation and decomposition

A succession of authors, as shown by the review of COATS and REDFERN [6], started from the equation which has been used first by van KREVELEN et al. [4] and subsequently by FREEMAN and CARROLL [5] in the kinetic evaluation of thermogravimetric analysis data in the presence of decomposition:

$$\frac{dx}{d\tau} = -k\,(a-x)^\nu \tag{10}$$
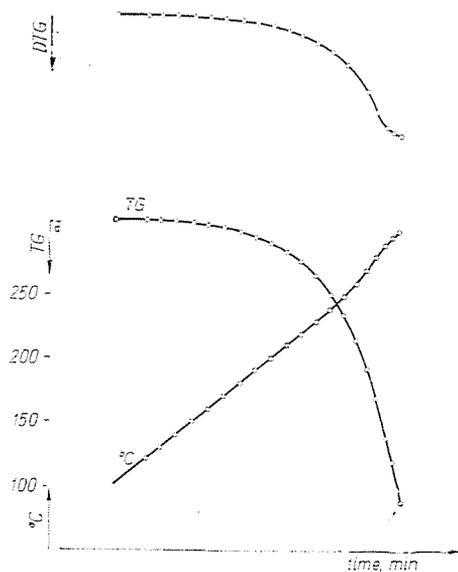
Fig. 6

where:

τ = time, sec

x = quantity of substance lost up to the time τ, mg

$\dfrac{dx}{d\tau}$ = rate of the change in weight, mg/sec

a = total change in weight occurring until the termination of the reaction

ν = order of the reaction

$k = A\,e^{-\frac{E}{RT}}$, the rate constant of Arrhenius.

Though COATS and REDFERN [6] think it improbable that this simple differential equation, to which in the last analysis, all the deductions known up to the present can be traced back, is valid for every decomposition reaction, in want of a better relationship, this will form the starting point. (In many cases, this equation was used with good results.)

It becomes evident from the contemplation of Equ. (10) that, with the exception of an order of reaction of zero, the lg dx/dt versus $1/T$ plot must give in case of decomposition a curve.

Pertinent measuring and evaluation are shown in Figs 6 and 7. Fig. 6 is the derivatogram of the lubricating oil TO—35, selected as modell substance, while Fig. 7 is the lg dx/dt versus $1/T$ plot of the DTG curve in Fig. 6.
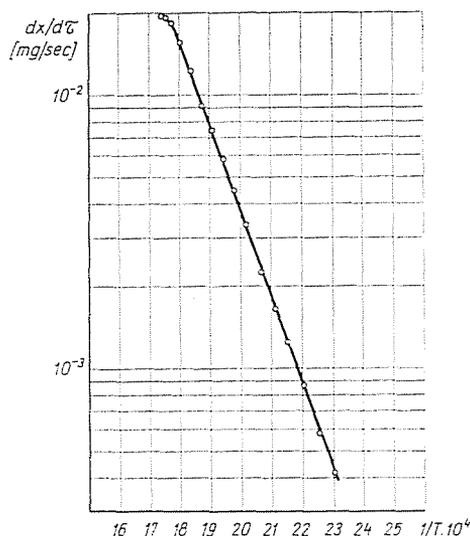
Fig. 7

It can be established from Fig. 7 that up to 285 °C the loss in weight is caused by evaporation (being proportional to the surface), while at temperatures above 285 °C by decomposition (being proportional to the mass). Calculated from the TG curve, up to 285 °C the lubricating oil suffers a loss of 46.0 per cent.

Without going into a further analysis of the experimental results obtained with the modell substance, it can be established that evaporation and decomposition can be easily distinguished on the dx/dt versus $1/T$ diagram plotted for thermogravimetric data. Evaporation is characterized by a straight line, decomposition by a curve. The curve section of the diagram can be linearized with the aid of Equ. (10).

Summary

In the thermogravimetric analysis of liquids, the derivate of the TG curve with respect to time (the DTG curve) is directly correlated with the differential equations of the rate of change in weight.

Following from the differential equations of evaporation and decomposition, these two processes can be clearly distinguished on the lg $dx/d\tau$ versus $1/T$ diagram, since the period of evaporation is represented by a straight line, and that of decomposition (with the exception of reactions of zero order) by a curve.

With the aid of the DTG curve, which in the case of derivatography is the derivative of the TG curve with respect to time, the apparent evaporation surface (F') and the heat of evaporation of the liquid can be calculated on the basis of the equation

$$\frac{dx}{d\tau} = -\frac{MF'}{\sqrt{2\pi\,MRT}} \cdot p_g,$$

and in knowledge of a conjugated temperature — vapour pressure value the temperature dependence of the vapour pressure.

For the evaluation of the section of decomposition the costumary equation

$$\frac{dx}{d\tau} = -k\,(a - x)^\nu$$

can be used.

Acknowledgement

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