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KINETIC STUDIES OF REACTIONS CONNECTED WITH GAS EVOLUTION UNDER ISOTHERMAL CONDITIONS IN THE DERIVATOGRAPH

V. M. GORBACHEV, V. E. FEDOROV and V. A. SHESTAKOV

Institute of Inorganic Chemistry, Siberian Department of the Academy of Sciences of the U.S.S.R., Novosibirsk

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A simple method has been proposed to achieve reliable thermostatic control of the oven of the Derivatograph by applying a calibrated stabilized voltage to the heater to compensate heat losses.

A simple method has been proposed for calculating the order of reaction n in the equation $1-(1-\alpha)^{1-n}=(1-n)Kt$, and of the kinetic parameter m in the topochemical equation $\alpha = 1-\exp(-Kt^{m})$, from a single gravimetric kinetic curve (conversion vs. time). The values of n and m calculated by this method for a chosen conversion range have been compared.

The Derivatograph has now attained widespread application in thermal analysis under non-isothermal conditions. Quasi-isothermal measurement [1] is a very interesting development of the instrument. However, the Derivatograph developed by Paulik, Paulik and Erdey can also be successfully utilized to investigate chemical reactions corresponding to the scheme $A_{\text{solid}} \rightarrow B_{\text{solid}} + C_{\text{gas}}$, under isothermal conditions.

When using the Derivatograph for kinetic studies under isothermal conditions, the experimenter must first of all solve two problems that are preconditions for satisfactory results. First, a reliable method must be chosen for the thermostatic control of the oven. It should be noted that, owing to the great inertia of the standard oven of the Derivatograph, the thermoregulator of the instrument does not always allow the maintenance exact of isothermal conditions. This manifests itself in the "serrated" temperature vs. time curve when the oven is switched on by the thermoregulator. It appears more practical to apply a stabilized voltage to the heater of the oven. Previously, the oven must be calibrated by measuring the relationship oven temperature vs. applied voltage under established steady-state conditions. Other thermostating methods can also be utilized of course, provided that they allow sensitive temperature control and maintenance of stable temperature conditions within the required limits.

Secondly, in kinetic investigations it is usual to apply various devices for introduction of the sample into the thermostated part of the reactor, with the objective of reducing to a minimum the period required to heat the sample to the reaction temperature. It is desirable to make use of this technique too when kinetic isotherms are to be taken with the Derivatograph. However, a number of experimental difficulties are encountered, resulting from the design of the instrument. It is therefore necessary to develop a technique for the introduction of the sample into the thermostated oven so as to allow the sample to adopt the required temperature as rapidly as possible. The following procedure proved to be successful: the temperature of the oven (without the sample) is first raised to the given temperature and is maintained for the time required to establish steady-state conditions. Subsequently, the temperature of the oven is further raised for a defined time to a previously-determined value, the oven is lifted, the sample is introduced, the oven is rapidly lowered over the sample and stabilized calibrated voltage is applied to the heater. All operations are so calculated that the "superheated" oven should rapidly heat up the sample to the temperature of the experiment during these manipulations. Conditions experimentally determined prior to the measurements allow good kinetic curves to be obtained for minimum periods of heating up the sample.

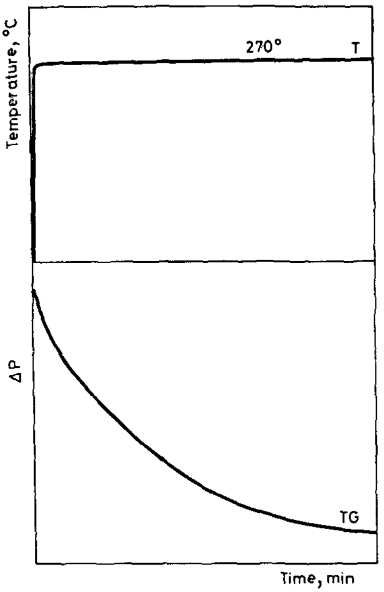

Fig. 1. Typical gravimetric curve taken with the Derivatograph under isothermal conditions (thermal decomposition of platinum tetrachloride)

Numerous experiments have demonstrated the feasibility of this method, particularly when the temperature in question is not very high, and reaction rates are relatively low, since in such cases the period required for heating up the sample is negligible as compared to the period of the experiment. Kinetic curves similar to the one shown in Fig. 1 will be obtained under such conditions.

In the practice of kinetic studies on heterogeneous reactions under isothermal conditions, analysis of the kinetic curves is usually done by means of the generalized topochemical equation [3]

$$\alpha = 1 - \exp(-Kt^{m}) \tag{1}$$

Here α is conversion, K a constant and m a kinetic parameter. Eq. (1) written in the logarithmic form is

$$\ln[-\ln(1-\alpha)] = m \ln t + \ln K \tag{2}$$

In this form, the equation is termed the anamorphous kinetic curve [4] and is applied for kinetic analysis. If $m \geq 1$, the process proceeds in the kinetic range, while at $m < 1$ it proceeds in the diffusion range. It should be noted here that, according to Kazeev [4], if $m \leq 1$, the process takes place without increase of the rate of the transformation. Such kinetic curves can satisfactorily be described by a simple exponential equation:

$$\frac{d\alpha}{dt} = K(1-\alpha)^{n} \tag{3}$$

where n is the order of the reaction. After integration, Eq. (3) has the following form:

$$1 - (1-\alpha)^{1-n} = (1-n)Kt \tag{4}$$

The determination of the order of reaction n directly from a single gravimetric kinetic curve is of great interest. For this purpose, the transcendent equation (4) must be solved for n. However, this equation cannot be solved in its general form. Some authors [5, 6] have tried to find an expedient by expanding in series the factor $(1-\alpha)^{n}$ and neglecting all but the first two terms of the series. However, this simplification of the initial equation does not yield reliable results.

In the following, a simple method will be proposed, which allows calculation of the order of the reaction from a single gravimetric kinetic curve.

Let us write the relationship

$$\frac{1-(1-\alpha_1)^{1-n}}{1-(1-\alpha_2)^{1-n}} = \frac{t_1}{t_2} \tag{5}$$

for two arbitrary conversion values $\alpha_1(t_1)$ and $\alpha_2(t_2)$, for which the equality $(1-\alpha_2)^2 = (1-\alpha_1)$ is valid.

Eq. (5) may be expressed in another form:

$$\frac{1-[(1-\alpha_2)^{1-n}]^2}{1-(1-\alpha_2)^{1-n}} = 1 + (1-\alpha_2)^{1-n} = \frac{t_1}{t_2} \tag{6}$$

After the required simplifications, a simple formula is obtained that allows calculation of the order of reaction for the portion of the kinetic curve lying between $(1-\alpha_1)$ and $(1-\alpha_2)$:

$$n = 1 - \frac{\ln\left(\frac{t_1}{t_2} - 1\right)}{\ln(1-\alpha_2)} \tag{7}$$

For calculations using this formula, it appears favourable to choose standard values, e.g.

$$(1-\alpha_2) = 0.5 \text{ and } 0.71, \text{ and consequently}$$
$$(1-\alpha_1) = 0.25 \text{ and } 0.5.$$

Then $(1-\alpha_2) > (1-\alpha_1)$, but $t_1 > t_2$.

A comparison of the order of reaction n and the kinetic parameter m in Eq. (1), determined in one and the same conversion range between $(1-\alpha_2)$ and $(1-\alpha_1)$, might be of great interest. Let us assume that $\ln(1-\alpha_1) = Kt_1^m$ and $\ln(1-\alpha_2) = Kt_2^m$. Their ratio will yield

$$\frac{\ln(1-\alpha_1)}{\ln(1-\alpha_2)} = \frac{t_1^m}{t_2^m}$$

This expression can readily be transformed into a suitable formula for calculation of the kinetic parameter m within the selected conversion range:

$$m = \frac{\ln\left\{\dfrac{\ln(1-\alpha_1)}{\ln(1-\alpha_2)}\right\}}{\ln\dfrac{t_1}{t_2}} \tag{8}$$

From Eqs (7) and (8), the order of reaction n and the kinetic parameter m were calculated for the conversion range $(1-\alpha_1) = 0.25 \ldots (1-\alpha_2) = 0.5$. The calculated values are listed in Table 1.

Table 1

Values of n and m as a function of the ratio t_1/t_2 at conversions $(1-\alpha_2) = 0.5$ and $(1-\alpha_1)\,K\,0.25$

t_1/t_2	1.5	1.6	1.7	1.8	1.9	2.0	3.0
n	0	0.26	0.48	0.68	0.85	1	2
m	1.7	1.47	1.31	1.18	1.08	1	0.63

It may be seen from the Table that the values of n and m change in opposite directions and become equal at $t_1/t_2 = 2$. The correspondence between n and m in the general case is universal in character.

Finally, the question should be discussed as to whether it is justified to transfer the order of reaction determined from isothermal investigations to non-isothermal kinetics with programmed heating. Our data on the dissociation kinetics of hydrofluorides [2] under both isothermal and non-isothermal conditions indicate that this is inadmissible; formally at least and referring to an actual investigation it must not be done. In the general case, it should be considered that in non-iosothermal kinetics the activation energy of the reaction is related to the order of reaction [7].

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Résumé — On propose une méthode simple et exacte pour effectuer le réglage thermostatique du four du "Derivatograph" en appliquant une tension stabilisée et étalonnée à l'élément chauffant pour compenser les pertes de chaleur.

On propose également une méthode simple pour calculer l'ordre de réaction n dans l'équation

$$l - (1 - \alpha)^{1-n} = (1 - n)Kt$$

ainsi que le paramètre cinétique m dans l'équation topochimique

$$\alpha = 1 - \exp(-Kt^m),$$

à partir d'une seule courbe thermogravimétrique (transformation en fonction du temps). On compare les valeurs n et m calculées par cette méthode dans un domaine de transformation choisi.

Zusammenfassung — Eine einfache Methode zur zuverlässigen thermostatischen Regelung des Ofens des Derivatographen wurde vorgeschlagen, welche auf der Anwendung einer geeichten stabilisierten Spannung bei der Heizvorrichtung zur Kompensierung von Wärmeverlusten beruht.

Eine einfache Methode wurde zur Berechnung der Reaktionsordnung n in der Gleichung $1 - (1 - \alpha)^{1-n} = (1 - n)Kt$ und des kinetischen Parameters m in der topochemischen Gleichung $\alpha = 1 - \exp(-Kt^m)$ aus einer einzigen gravimetrischen kinetischen Kurve (Konversion als Funktion der Zeit). Die nach dieser Methode für eine gewählte Konversion errechneten Werte wurden verglichen.

Резюме — Исследование кинетики химических превращений с выделением газовой фазы на дериватографе в изотермических условиях.

Предложен простой метод надежного термостатирования печи дериватографа путем подачи в нагреватель колиброванного стабилизированного напряжения для компенсации тепловых потерь.

По одной гравиметрической кривой в координатах степень превращения α — время t предложен простой способ расчета порядка реакции n в уравнении $1-(1-\alpha)^{1-n} = (1-n)Kt$ и кинетического параметра m топохимического уравнения $\alpha = 1-\exp(-Kt^m)$. Проведен сопоставление величин n и m внутри выбранного интервала превращения α_1 и α_2.