

THE CONCEPT OF MIXED-CONTROL MECHANISMS AND ITS APPLICABILITY TO PAPER DEGRADATION STUDIES

FULL PAPER

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Analysis of kinetic data obtained during accelerated ageing of paper is frequently based on the use of Arrhenius equation for extrapolation of kinetic data. However this kind of analysis can be misleading if two or more concurrent processes occur simultaneously. In the case of paper degradation these are, most frequently, acidic hydrolysis and oxidation of cellulose. In such cases application of a mixed-control concept, for many years used in practical applications of chemical kinetics (especially in metallurgy) can be helpful. The present paper is an attempt of explaining the fundamental terminology and concepts connected with the kinetic equations of mixed-control type.

1. Introduction

Accelerated ageing of paper, its importance and necessity of analyzing the data thus obtained, have been already emphasized by Porck.¹ He pointed out that “the small number of research projects that have tried to verify the predictive value of artificial aging analysis strongly contrasts with the widespread use of this analysis in practice”.

The analysis is based on the use of Arrhenius equation for extrapolation of kinetic data. Hence application of the equation to the description of complex phenomena of cellulose degradation, being the problem typical of Preservation Science,² will be discussed below.

2. Fundamentals

Fundamentals of the chemical kinetics should be recalled here. A researcher must be sure that the considered kinetic equation is in agreement with the results of isothermic experiments in the whole range of temperatures studied if the Arrhenius equation is to be used for the description of temperature dependence of the rate constants. Let us note that the kinetic equation contains one or more rate constants. In the most simple case of an elementary step there is – by definition – a single rate constant. More complex reactions consist of two or more elementary steps. If one of them is the rate determining step (rds - the only step that contributes its rate constant to the overall kinetic equation), then - by virtue of its definition, as proposed by Boudart and Tamaru³ – a complex reaction contains also a single rate constant. In both cases, considered above, the application of

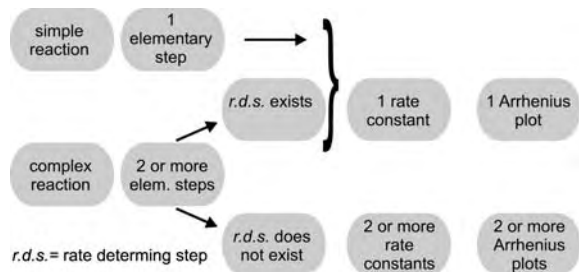
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Arrhenius relation is straightforward. However, in the more general case, when *rds* is absent, kinetic equation is more complicated, and it contains two or more rate constants. This implies the use of two or more Arrhenius plots for the interpolation or extrapolation of kinetic data within the considered temperature range. The following scheme illustratively explains the considerations presented above.



Taking into account another fundamental premise – a reaction mechanism cannot be proven by kinetic data; it can be, however, easily excluded⁴ – let us consider the following example.

3. Hydrolytic and oxidative pathways of mixed-control mechanism of cellulose degradation

The rate of acid hydrolysis is described by the Ekenstam equation.

$$\frac{1}{DP} - \frac{1}{DP_0} = k \cdot t \quad (1)$$

Where DP_0 and DP are polymerization degrees of cellulose at time zero (t_0) and time (t), respectively. Symbol k stands for the reaction rate constant.

If, under certain conditions, this equation does not hold, then acid hydrolysis cannot be the only pathway of cellulose degradation. The results of the kinetic studies dealing with applicability of Ekenstam equation⁵ have been summarized in Fig. 1.

Samples of model P1 paper (containing more than 95% of cellulose from coniferous trees and 0.45% of ash), pure and impregnated with aluminum sulphate, have been aged for 2–21 days within the

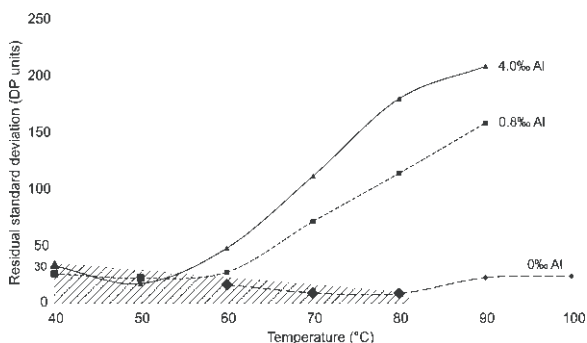


Figure 1: Residual standard deviations (expressed as DP values) originating from the Ekenstam equation, obtained for degradation of paper samples impregnated with various amounts of Al, as a function of temperature. Reproduced from reference 5.

temperature range 40–100 °C and at the relative humidity of $RH = 100\%$. Every kinetic curve, characterized by the temperature (°C) and Al content (weight %, equivalent to the number of milligrams of aluminum per 1 gram of dry paper) has been indicated by a single point in Fig. 1. On the abscissa, the deviation of the curves from Ekenstam equation has been shown. It was indicated in publication⁵ that within shaded area of Fig. 1 a single degradation route (this being acid hydrolysis) dominates, whereas outside the area (i.e. at higher temperature and higher Al content) oxidation of cellulose should also be taken into account. Thus Arrhenius equation can be safely applied to the rate constant of Ekenstam equation inside the shaded area only.

Two degradation routes exist outside the area – acid hydrolysis and oxidation – and, therefore, the Ekenstam equation does not hold. Another, at this time unknown, equation (let's call it a mixed-control equation) will properly describe the kinetic data. The postulated equation will contain two rate constants – k_h and k_{ox} – for acid hydrolysis and oxidation respectively. There will be two Arrhenius plots: $\ln(k_h)$ versus $1/T$ and $\ln(k_{ox})$ versus $1/T$, and, consequently, two activation energies can be calculated. It seems obvious that continuity behaviour should be observed in such a case. Therefore, one can expect that the mixed-control equation, when extended to the low-temperature region (inside the region encircled by the borderline in Fig. 1), will yield Ekenstam equation as the limiting case. Consequently, the Arrhenius plot for k_h should be valid (i.e. no sharp direction changes observed) in the whole range of experimental conditions – outside and inside the Fig. 1 borderline. On the other hand, as assumed, the kinetic data providing k_{ox} values are restricted only to the temperatures T_{ox} outside the borderline. This is why the extrapolation of k_{ox} value to the temperatures below the borderline should be avoided.

Fig. 2 illustrates the considerations given above.

The ideas outlined just above can be emphasized by taking into account the publication by Arney and Novak.⁶ Arney concludes that the rate of paper de-

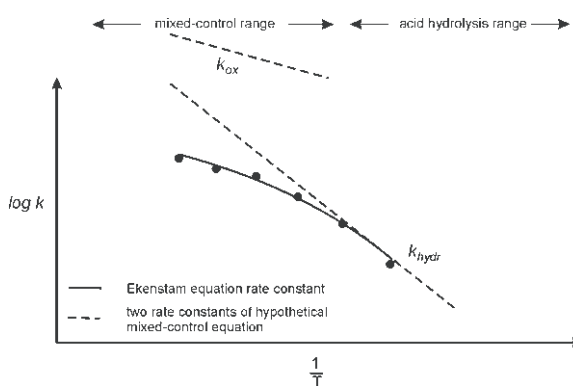


Figure 2: Arrhenius plots for rate constants of a hypothetical mixed-control kinetic equation describing the degradation of paper P1 containing 0.8% Al and for the rate constants obtained for Ekenstam equation.

gradation is a sum of four terms, depending on (i) oxygen pressure, (ii) pH value, (iii) both oxygen pressure and pH, and (iv) neither oxygen nor pH. Hence, there are four rate constants, and, consequently, four Arrhenius plots could be drawn. In fact, a complex mixed-control mechanism is taken into account in the publication in question.

Only the concept of paper⁶ is taken into account here. Its experimental verification is a difficult problem and will not be discussed in the present paper.

4. The case of metallurgy

There is nothing new in the concept of mixed-control mechanisms. The idea can be directly linked to the fundamentals of chemical kinetics. Let us assume that for a two-step or a multi-step chemical reaction a shift in the rate-determining step does exist.⁴ It may happen so that, at low temperatures, step No. 1 is the rate-determining step. Consequently, k_1 is the overall rate constant. At high temperature another step, designated as No. 2, is the rate-determining step, and, hence, k_2 is the overall rate constant. Obviously, a middle-temperature range should exist, where a kinetic equation, considering two or more elementary steps occurring with similar rates and contributing two rate constants to the overall reaction rate, is valid. This idea, initially introduced in solid-state chemistry in mid-twentieth century, has been successfully extended in the research on solid-gas reactions, being of primary importance in metallurgical processes. An extremely simplified example would help the reader to understand the concept in question.

Let us consider the reduction of iron oxide grains, of density d , by hydrogen. The concentration of hydrogen outside a grain is equal to c . One mole of hydrogen is consumed during reduction by b moles of iron oxide. The shape of grains is considered as being approximately spherical. Reduction temperature and grain radius R are the main variables. The reaction of oxide reduction on the gas-solid interface and diffusion of water vapour and hydrogen within the porous structure of the grain

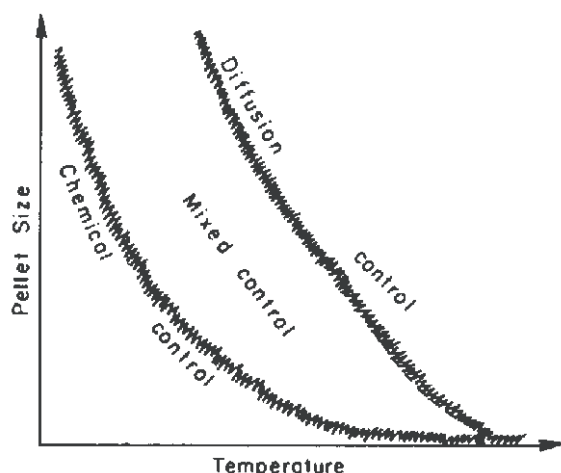


Figure 3: Three zones of reaction control for high-temperature reduction of iron oxide.

are partial processes of the overall reduction of iron oxide.

The Fig. 3 has been drawn after the already classical drawing published in the monograph of Szekely.⁷ Three zones can be observed in this Figure: that of chemical control, diffusion control and mixed control:

In the region of chemical control the chemical reaction is a rate-determining step, and a kinetic equation has one term containing only one parameter: reaction rate constant (k). The kinetic equation, i.e. the relation between the reduction degree x ($x = 0$ for the non-reduced sample, whereas for the completely reduced sample $x = 1$) and time t is given below.

$$t = \left[1 - (1-x)^3 \right] \cdot \frac{Rd}{bkc} \quad , (2)$$

This equation, as well as next two, are taken from the local edition of textbook by Levenspiel.⁸ Other examples can be found in his classical textbook⁹ and in many papers.¹⁰⁻¹²

In the diffusion control region the gas (H_2 , H_2O) diffusion in the pores of solid is a rate-determining step, and the kinetic equation has only one term containing only one parameter characterizing the diffusion phenomena – e.g. effective diffusivity (D_e). In this case the kinetic equation has the following form:

$$t = \left[1 - 3(1-x)^3 + 2(1-x) \right] \cdot \frac{R^2d}{6bD_e c} \quad , (3)$$

in the mixed-control region there is no rate-determining step, and the kinetic equation consists of two terms – called reaction term and diffusion term – containing two parameters: reaction rate constant and effective diffusivity, respectively. This is a more complicated case

$$t = \left[1 - (1-x)^3 \right] \cdot \frac{Rd}{bkc} + \left[1 - 3(1-x)^3 + 2(1-x) \right] \cdot \frac{R^2d}{6bD_e c} \quad , (4)$$

One can easily notice that the kinetic equations valid in the regions of chemical control and diffusion control are boundary cases of the more general equation describing the overall reduction process in the mixed-control region.

5. Similarity between high-temperature oxide reduction and degradation of paper

Despite the obvious chemical differences, a similarity between the postulated kinetic formalisms valid for the high-temperature reduction of iron ore and the expected formalism for degradation of cellulose can be now easily understood. Temperature, time and the grain radius are the main experimental variables in the case of oxide reduction. For degradation of cellulose – these are: temperature, time and pH (as determined in the considered case by the Al-content in the sample of paper). The reduction of oxide crystallites and diffusion phenomena are the partial processes of the overall

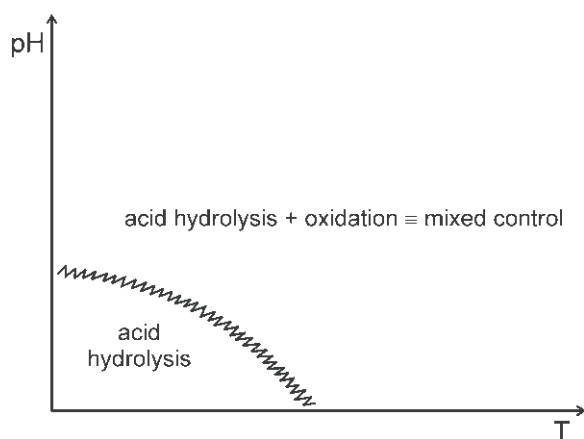


Figure 4: Zones of reaction control for cellulose degradation.

reduction of ores. The same part in the degradation of cellulose is taken by acid hydrolysis and oxidation. The zones of the reaction control for cellulose degradation are shown in Fig. 4 in an attempt to illustrate the same idea as that presented in Fig. 3 for the reduction of iron ore.

Inside the region of acid hydrolysis, the Ekenstam equation is valid.

$$t = \frac{1}{k_h} \left(\frac{1}{DP} - \frac{1}{DP_0} \right) \quad (5)$$

where k_h is the rate constant for acid hydrolysis.

Within the field of mixed control one can expect the validity of kinetic equation of the following type:

$$t = \frac{1}{k_h} \left(\frac{1}{DP} - \frac{1}{DP_0} \right) + \frac{1}{k_{ox}} \cdot f(DP, pH) \quad (6)$$

where $f(DP, pH)$ is an unknown function yet.

One should be aware, however, that the similarity of Figures 3 and 4 is not a complete one. There is no area of domination of oxidative degradation. Obviously, the importance of oxidation is growing as the pH value is raised. A systematic examination of temporal changes of DP as a function of different pH values and partial pressure of oxygen could provide more detailed information about this lacking part of the diagram.

6. Conclusions

The success of extrapolation procedure during the analysis of accelerated ageing experiments depends on getting the proper mixed-control description of degradation phenomena within the high-temperature range. Not enough primary kinetic data, enabling characterization of simultaneous hydrolytic and oxidative degradation of cellulose, can be found in literature. The advance of both

processes should be independently determined by properly planned experiments. It is obvious that degradation of model samples of paper should be studied first. This conclusion is a further enhancement of statements given by Emsley and Stevens.¹³

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