

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

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1. Genesis

Accelerating ageing, its importance and necessity of analyzing the data thus obtained, have been already emphasized by Porck¹. 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, will be discussed below.

2. Fundamentals

Fundamentals of the chemical kinetics should be recalled here. If one wants to use Arrhenius equation for the description of temperature dependence of rate constants, then one must be sure that the considered kinetic equation is in agreement with the results of isothermal experiments in the whole range of temperatures studied. When the kinetic equation is simple (an elementary step or rate determining step (*rds*) of a complex reaction are the examples) the application of 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 a temperature range.

Taking into account another fundamental premise – *a reaction mechanism cannot be proven by kinetic data; it can be, however, easily excluded* – 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. 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 equation² have been summarised in Fig. 1.

Model paper samples containing cellulose only, pure and impregnated with aluminium sulphate, have been aged for 2–21 days within the temperature range 40–

100 °C. Every kinetic curve, characterized by temperature (°C) and Al content (‰ by weight) 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 publication² that within the 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.

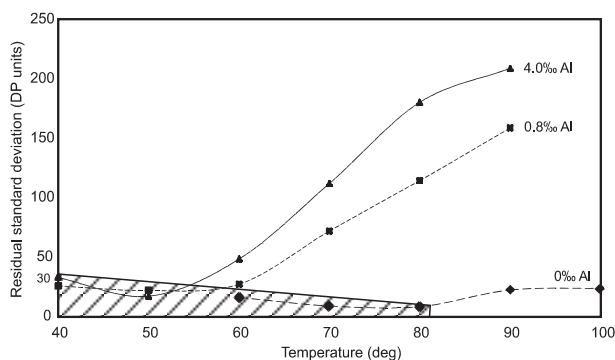


Figure 1: Residual standard deviations (expressed as *DP* values), obtained for paper samples impregnated with various amounts of Al, as a function of temperature. Taken from ref. 2 – however, in the description of the original drawing, time (days) has been indicated erroneously instead of temperature (deg).

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. 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. Therefore 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 outside the borderline. This is why the extrapolation of k_{ox} value to the temperatures below the borderline should be avoided.

4. The concept of Arney and Novak revisited

The ideas outlined just above can be emphasized by taking into account the publication by Arney and Novak³ entitled informatively “Accelerated Ageing of Paper. The Influence of Acidity on the relative Contribution of Oxygen-Dependent and Oxygen-Independent Processes”. Arney concludes that the rate of paper degradation 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.

5. 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. If no rate-determining step can be postulated, then one should suggest a kinetic equation considering two or more elementary steps occurring with similar rates and contributing to the overall reaction rate in a similar way. 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 ore grains by hydrogen. The shape of grains is considered as being approximately spherical. The reduction temperature and the grain radius are variables equally important as the temperature and pH of paper in the process of cellulose degradation. The reaction of oxide reduction on the grain surface and diffusion of water vapour and hydrogen within the porous structure of the grain are partial processes of the overall reduction of ore; similarly acid hydrolysis and oxidation are partial processes of the overall process of cellulose degradation.

Fig. 2 has been redrawn after the already classical drawing published in the monograph of Szekely⁴. 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;
- 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 in solid – e.g. effective diffusivity;

- 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.

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

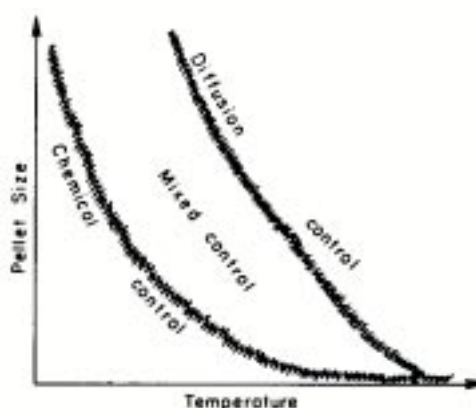


Figure 2: Three zones of reaction control.

describing the overall reduction process in the mixed-control region. Examples of mixed-control equations can be found in the textbooks by Levenspiel^{5,6}.

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 model samples of paper should be studied first.

7. References

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