

Non-Isothermal Reaction Analysis

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NON-ISOTHERMAL REACTION ANALYSIS

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Preface

"Reaction Analysis" is a comparatively rare expression; but it seems that this title optimally characterizes the main subject of this book, which is to analyse chemical systems rather with a view to their possible reactions than to the particles involved. The point at which to start in obtaining optimal information on the kinetic behaviour of a poorly investigated system, including the final aim of characterizing the individual reactions, is the chemist's basic problem. This concept raises the following practical questions. What kind of quantities should be measured in a special case? What is the best way of measurement? Which facts can really be concluded from a kinetic curve? How may the data typical for a reaction be evaluated?

These problems deal with scientific efficiency and involve various natural sciences. Nevertheless, this monograph is in fact not a reference book; based on well-known foundations, it is rather intended to show that a higher yield in reaction-analytical work is often achieved by temperature-programmed measurement of the overall change of an adequate property of the system. Apart from the discussion of the well-known techniques which give such a plot (such as thermogravimetry or differential scanning calorimetry), other modern methods are also considered from a non-isothermal point of view, and mathematical derivations (partly unpublished) are presented which may clarify many relations between signals measured and the basic kinetic laws.

It is clear that the realization of such a project has needed the assistance of many colleagues and experts. First, Prof. G. O. Schenck initiated my strong interest in temperature-dependences, that was the fascinating theme for my doctoral thesis in photochemistry. On the other hand, many impressions which guided my further work originate from some contacts with the former "Max-Planck-Institut für Physikalische Chemie" in Göttingen.

However, the essential impulse for my exposition with the non-isothermal field was given by the numerous difficulties and dangers of preparative work in low-temperature photochemistry which became apparent after Prof. Schenck left Göttingen and came to Mülheim a.d. Ruhr in 1958. At that time, my interest in thermal reactions was stimulated by the contact with organometallic subjects which were

studied in the "Max-Planck-Institut für Kohlenforschung", and, subsequently, in the new "Max-Planck-Institut für Strahlenchemie".

After the arrival of Prof. O. E. Polansky from the "Institut für Theoretische Organische Chemie" in Vienna, my original interest in mathematics was reactivated so that, in the last two years, I could make significant contributions to the theoretical background of the subject.

Any chemist who has been engaged in non-isothermal reaction kinetics will feel that an extension and modification of our kind of analytical thinking is necessary in order to achieve optimal benefits. Thus, a chemist, who mainly deals with this subject within an "isothermally educated" environment, may often appear as a self-willed, queer fellow. Therefore, I have to thank especially those colleagues who in spite of this situation helped me to follow a stony, but promising path.

I am indebted to Dr. H. Klever, Dr. G. Koltzenburg, Dr. H. Hermann, Dr. I. Leitich, Dr. P. Potzinger, Dr. H. Schenkluhn, B. Stalkerieg and Dr. B. Weimann in Mülheim as well as to Prof. Dr. F. Becker (Frankfurt), H. Heimsath (Aachen), Prof. Dr. R. Huisgen (München), Dr. W. Koepe (Jülich), Prof. Dr. R. C. Mackenzie (Craigiebukler, Scotland) and Dr. J. H. Sharp (Sheffield, U.K.) for improving and advising me on my original manuscript. I also acknowledge the numerous suggestions involving the preliminary work given by Dr. S. Arora, Dr. E. Kisch, Dr. E. Koerner von Gustorf, Prof. Dr. O. E. Polansky, Dr. A. Ritter, Prof. Dr. G. O. Schenck, Prof. Dr. D. Schulte-Frohlinde, Dr. S. von Sonntag, Dr. O. B. Wagner and Prof. Dr. G. Wilke.

I would like to express my special thanks to my direct coworkers, B. Stalkerieg, R. Frings, G. Lindner and H. Siepmann, and the efficient technical departments of this institute for the reconstruction of many experiments which justified the concepts I have presented. I am indebted to Dr. P. O'Neill, Dr. S. Arora and H. Gruen for their critical revision of my English, as I am an inexperienced writer in this language, to A. W. Bock for typing the final manuscript, to I. Schneider and B. Stalkerieg for preparing the drawings and to D. Braemert for checking the reference lists. There are many other people, whom I can not mention here, who helped me in the collection of useful material and to whom I owe my thanks.

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American Chemical Society (Figs. 7.8, 16 and 8.31)

Girardet, Essen (Fig. 8.26)

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Finally, I express my deep appreciation to Elisabeth Koch who had to bear with the special moods of a book-writing husband for several years.

Remarks on and criticisms of this text are cordially invited. These will be valuable for planning future revisions and will, no doubt, stimulate further developments.

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Glossary

A Nomenclature

1 General

The considerations and the results in this monograph are based on fundamental reaction kinetics as well as on conditions of thermal analysis. Although notations of both fields will be used (cf. Mackenzie 1970, pp. 5-9; cf. Chapter 5), changes of some recommended terms seemed useful because of the interaction of both fields. Thus, a short summary of preferred important notations which may sometimes differ from other commonly used definitions is presented.

2 Reaction and recorded curve at increasing temperature

A chemical *reaction* [or (chemical) process, (chemical) event] converts a starting product or *educt* into (a) *final product(s)*. Often, *intermediates* (transients) may appear and vanish during the experiment. The *progress* (proceeding, advancement) of the reaction (with time!) or its (temporal) course is accompanied by a change of an appropriate *measuring quantity* which may be observed, detected or followed as a function of time by suitable equipment. Frequently, the derivative form of this quantity is proportional to the *reaction rate* or represents a value of similar character which shows a maximum (or minimum) for an elementary reaction (peak). The notation *signal*, preferentially used for the representation of the reaction, is given by the entire run of the (derivative) *measuring quantity* versus time which for some methods is proportional to the *rate*. The *signal height* is equivalent to the maximum signal height, whilst *maximum* equals peak.

The corresponding temperature is the *peak temperature* (cf. Schultze, 1969, Chapter 5); other discrete temperatures are *starting temperature* (start of the experiment), *initial temperature* (first deviation from the base line), both inflection-point temperatures or half-width temperatures and the *final temperature* (last noticeable deviation at the end of the measurement).

Further notations are explained in the text.

3 Types of reactions

Reactions exhibit chemical character, whereas *processes* may include physical events. First of all, we distinguish *elementary reactions* (processes) and *complex reactions*; the latter are built up from *elementary reactions*. An elementary reaction is either a *first-order reaction* or a *second-order reaction*, or even sometimes a higher-order reaction. Dealing with several *concurrent* (competitive) *reactions*, we have to consider *mixed-order reactions* and *equal-order reactions*. The term "order" does not apply to the majority of "elementary" solid-state steps which do not show time laws of the n order type.

4 Methods of investigation

In principle, the recommendations suggested by the I.C.T.A. committee (see details in Chapter 5) are used. For the two-dimensional methods (Chapter 8.II), the condition of continuously increased temperature is generally signalled by the prefix "thermo", e.g. thermogravimetry, thermoconductometry, etc. However, this notation is not applied to the three-dimensional methods (Chapter 8.III); here, the well-known expressions for the isothermal techniques are used.

B Abbreviations

1 Mathematical and physicochemical quantities

Those symbols which are repeatedly used in the text and in the legends are listed in order of their first appearance.

(a) Chapter 2

ΔH = enthalpy, heat of reaction, reaction energy

n = reaction order, order of reaction

$[A]$ = concentration of species A

t = time

k = (reaction) rate constant

T = absolute temperature

\tilde{n} = number of moles in the system

K_C = equilibrium constant

E = (Arrhenius) activation energy

k_∞ = frequency factor

E_0 = activation energy at zero temperature

R = gas constant = 0.00837 kJ/mole K

E_{th} = theoretical activation energy

K^\ddagger = "equilibrium constant" in the Transition State Theory

- m = temperature exponent
 h = Planck's efficiency quantum
 k = Boltzmann factor
 ΔG^\ddagger = free enthalpy of activation (Gibbs' free energy)
 ΔS^\ddagger = entropy of activation
 ΔH^\ddagger = enthalpy of activation
 \bar{T} = "isokinetic" temperature

(b) Chapter 3

- x = measuring quantity
 y = reactivity ($= dx/dt$)
 λ = reactivity coefficient
 T_s = starting temperature
 $T_0, T_m, \dots E_0$ etc. see Section (h)
 α = heating rate
 t = time if heating had begun at absolute zero temperature
 $\varepsilon = \frac{E}{\alpha R}$ = relative activation energy
 u = specific time $\left(= \frac{\int k dt}{k} \approx \frac{t^2}{\varepsilon} \approx \frac{\varepsilon}{\ln^2 k_\infty} \right)$
 $e = 2.71828 \dots$
 χ = sensitivity limit
 h = half width [K]
 S = shape index
 \bar{x} = conversion variable, fractional conversion
 \bar{M}_1, \bar{M}_2 = Mechanistic index (reaction type index) for first- or second-order reaction (0.0183 or 0.012 kJ/mole·K, respectively)

(c) Chapter 4

- $E_1, E_2 \dots k_{\infty 1} \dots t_1, t_2$ etc. see Chapter 2 and section (h)
 ν = total number of reaction steps
 i = individual number of the reaction step
 π_i = first-order reaction: concentration of reactant second-order reaction: product of two reactant concentrations
 u_i = specific time of step i
 $k_{\infty i}$ = frequency factor of step i
 ψ_i = elementary function of step i
 $S_{1,2}$ = shape index for a first-step or second-order reaction

(d) Chapter 5

- Θ = temperature difference
 y^* = similar to a reactivity

H_f^0 = enthalpy of formation

$D(A-B)$ = bond dissociation energy of compound AB

C_{pp} or C_p = heat capacity of the sample

K = heat transfer coefficient, energetic cell constant

c = kinetic cell constant [min^{-1}]

V = volume of the sample

$\frac{dq}{dt}$ = heat per unit time, heat power

(e) Chapter 6

$\bar{M}_{1,2}$ = reaction type indices M_1 and M_2 for an elementary reaction of first- or second-order, respectively

$Z = Z(t)$ = special time function = $f(t, u)$

t_s = t -value of extrapolated straight line for $Z = 0$

d = fitting constant [= $f(c)$]

$f_h(c)$ = correction factor for the half width with respect to c and analogous abbreviations

(f) Chapter 7

l = true (maximum) signal height

k^* = second-order rate constant [$\text{M}^{-1} \text{min}^{-1}$]

(g) Chapter 8

I_0 = original light intensity

I_{abs} = light intensity absorbed

$\tilde{\chi}$ = natural extinction coefficient

z = variable parameter for measurement

W = weight

$[G]$ = molar concentration of gas in solution

$[G]_s$ = molar supersaturation limit of gas

β = half-value concentration

$\tilde{\alpha}$ = reactivity calibration constant

\mathcal{H} = electric conductivity coefficient

e_0 = unit charge

z_i = ion valence

\tilde{E} = optical extinction

$\tilde{\epsilon}$ = decadic extinction coefficient

(h) Indices

Subscripts

0 corresponds to initial value of the reactivity e.g. T_0 = initial temperature

m corresponds to maximum (or minimum) value of the reactivity

e corresponds to final value of the reactivity

- 1,2 corresponds to the first and second half-values of the reactivity; in other cases: first, second, etc. step of a reaction scheme
- 1-- back reaction attributable to reaction 1
- 3,4 values at the inflection points
- s start (or intersection)
- i value for reaction i
- exp experimental
- calc calculated
- corr corrected
- stand pertaining to standard conditions

Sometimes there may be deviations from these significations for practical reasons

Superscripts

- ← diffusive forward step, e.g. \bar{k} = diffusion rate constant
- diffusive back step
- * excited species
- mean value
- ^ discrete value

(k) *Other mathematical symbols*

- \approx approximate equal to
- \propto proportional to
- approaches
- $|a|$ absolute magnitude of a
- \sqrt{a} square root of a
- Δx difference of two x -values
- $\log x$ decadic logarithm of x ; $\ln x$ natural logarithm of x
- $f(x)$ function of x
- [] dimension
- $\int_a^b y \, dx$ integral of y from $x = a$ to $x = b$
- $x > y$ x is larger than y
- $x \gg y$ x is large compared with y

(l) *Special (verbal) abbreviations in the text*

- (sol) = in solution
- (s) = in solid phase
- (l) = in liquid phase
- (g) = in gas phase
- DTA = differential thermal analysis
- TG = thermogravimetry
- DTG = derivative thermogravimetry
- nmr = nuclear magnetic resonance
- esr = electron spin resonance

uv = ultraviolet
ir = infrared
EGA = evolved gas analysis
DSC = differential scanning calorimetry
M = mole per dm³
v. = versus

Special terminology for reaction mechanisms: cf. Chapters 4.IIIA and 6.IIID, especially Figs 16, 18.

C Units

The international System of Units (SI) is used which was developed from the cgs system (length [cm], weight [kg], time [s], absolute temperature [K], amount of material [mole]). In this system, instead of the kilocalorie [kcal] the kilojoule [kJ] (= 0.239 kcal) has to be used.

With respect to time, the second [s] as well as the minute [min] is applied, since it is common in the thermoanalytical field to use the unit K/min, not K/s, for the heating rate which represents a kinetic quantity. Consequently, in the isothermal sections of the book (Chapter 2) [s] is used, while in the other, more non-isothermal sections [min] was preferred.

D References

The reference lists (at the end of the chapters) cannot be exhaustive; since the correlations of the material presented to other fields are various, a strong restriction was necessary. Papers or books not available before January 1975 in general have not been considered.

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