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COMMENTS ON THE INTERPRETATION OF TEMPERATURE DEPENDENCE OF PROCESSES IN POLYMERS

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Abstract

The interpretation of the results of thermal measurements followed over decades the Arrhenius law. In recent years an apparently different interpretation (Eyring's equation) has been emerging in the literature on polymers. As the main reason for this, a direct connection to material properties has been claimed.

The paper shows some weak points in the Eyring theory and in its application as well. Firstly, the parameters of the two equations are mathematically convertible to each other. Thus Eyring's conceptual quantities (entropy and enthalpy of activation) give no new physical information. Secondly, the Eyring theory postulates an equilibrium for the activated state. In the case of processes, however, in which change is an inherent characteristic, this assumption seems to be unjustified.

Keywords: activated state, ageing compensation effect, Arrhenius law, Eyring equation, polymers, temperature dependence

Introduction

Many of the processes in polymers are studied as a function of temperature. The interpretation of the results followed – over decades – the well known

$$\log k = \log A - \frac{E}{2.303RT} \tag{1}$$

Arrhenius law, where k is the rate constant of the chemical reaction, A is the pre-exponential term, E is the energy of activation, T is the temperature, R is the gas constant. Although Eq. (1) has its origin in chemical reaction kinetics, it could be applied in the study of physical processes as well. (For example, the temperature dependence of the conduction current has often been presented through the Arrhenius plot: $\log I$ *vs.* $1/T$.)

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In recent years a seemingly different interpretation has been emerging in the literature on polymeric dielectrics. It has been proposed [1, 2] to replace the Arrhenius Eq. (1) by another one (2), associated with Eyring's theory [3] of absolute reaction rates, or briefly [2] 'rate theory':

$$\log\frac{k}{T} = \log\frac{k}{h} + \frac{\Delta S^{\neq}}{2.303R} - \frac{\Delta H^{\neq}}{2.303RT} \tag{2}$$

Here k and h are the Boltzmann and the Planck constant, $\Delta S^{\neq}$ and $\Delta H^{\neq}$ are the activation entropy and activation enthalpy, respectively. (It is evident from Eq. (2) that while the Eyring plot will differ from the Arrhenius plot in its ordinate, the $1/T$ abscissa will remain the same. For example, in the case of dielectric relaxation [2]: $\log\omega/T$ *vs.* $1/T$).

As the main reason for this change from the Arrhenius to the Eyring equation a direct connection with material properties has been claimed.

The aim of this paper is to show some weak points in the Eyring theory and in its application as well.

The meaning of the concepts $\Delta S^{\neq}$ and $\Delta H^{\neq}$

We show below that the replacement of the Arrhenius parameters A and E by Eyring's $\Delta S^{\neq}$ and $\Delta H^{\neq}$ renders no new information. This is easy to see by considering the

$$\Delta H^{\neq} = E - RT \quad \text{or} \tag{3}$$

$$E = \Delta H^{\neq} + RT \tag{4}$$

and

$$\Delta S^{\neq} = R\log A + R\log\frac{ekT}{h} \qquad \text{or} \tag{5}$$

$$A = \frac{ekT}{h}\,e^{\Delta S^{\neq}/R} \tag{6}$$

relations between [3] the characteristic quantities of the two approaches. We can conclude that the functional relations (3–4) and (5–6) between the Eyring quantities on the one hand, and the Arrhenius parameters on the other, consist of universal material constant and the (average) temperature T of the process as well. In other words, it is shown by the relationships (3–4) and (5–6) that the quantities $\Delta H^{\neq}$ and E or $\Delta S^{\neq}$ and A are mathematically convertible to each other, thus they do not carry different information. The seemingly different mathematical interpretations reflect in fact the same physical significance by using slightly different quantities.

The question of the equilibrium postulated concerning the activated state

(To show the weakness of the 'rate theory' in this respect, we have to return to its original concepts belonging to reaction kinetics.) The fundamental postulate of the theory of absolute reaction rates [3] is the assumption of thermodynamic equilibrium between $X^{\neq}$, the activated complex and its constituent starting molecules in the transition state of the

$$A+B \leftrightarrow X^{\neq} \rightarrow C+D \tag{7}$$

process. The irreversible decomposition of the activated complex – to a greater or lesser extent, depending on its rate – disturbs the equilibrium. Therefore the assumption [3, 4] of the equilibrium value of $[X^{\neq}]$ also means that the supplying of the concentration of $X^{\neq}$ goes much faster (more precisely, two or several orders of magnitude faster) than the rate at which it will be consumed by the unidirectional 'decomposition' reaction. The rates of the three elementary reactions cannot be commensurable, or more precisely, the

$$X^{\neq} \rightarrow C+D \tag{8}$$

reaction must proceed only with a negligibly low rate. (This was also recognized by Eyring himself: 'This is one of the fundamental postulates of the theory developed here; it is supposed that the reaction does not appreciably disturb the equilibrium concentration of activated complexes.'[3/185] If, on the other hand, the rates of the three reactions are commensurable, equilibrium states or equilibrium concentrations cannot develop.

Formulated from another angle: in the case of commensurable rates, the concentration of the activated complex is not an equilibrium concentration, but a commensurable one at most. However, the theory of absolute reaction rates still uses, instead of the real value, the formula of equilibrium concentration of activated complex to deduce the corresponding kinetic equations. These relations, derived in this manner, have the appearance of exact formulae, although they are approximate equations at best on the basis of the above consideration. The elimination of this contradiction, which has been built in 'unnoticed' in the theory is not possible within the frame of the theory.

It could be the subject of further discussion and investigation that to what extent this inherent contradiction makes the theory of absolute reaction rates inaccurate. It is certainly evident that the accuracy of these relations improves if the decomposition rate of the activated complex decreases, and in the extreme case – at zero decomposition rate – the formulae become exact.

There is another feature of the activated complex which differs from the starting components and end-products of the reaction. These – in the state of chemical equilibrium – belong to the minima of the corresponding chemical potential functions. However, the activated complex – in function of the reaction coordinate – belongs to the maximum of the corresponding potential function, which in fact means an unstable (hence par excellence non-equilibrium) state.

And if the assumption of equilibrium is unjustified [5, 6], enthalpy and entropy as 'activation' concepts are questionable, because the attribute 'activation' deprives the expressions enthalpy and entropy of their original meaning which is associated with the concept of equilibrium.

Connection of the question with ageing processes

In can be seen from the above that there is not reason to criticize [7] the Ageing Compensation Effect (ACE) earlier predicted [8], then – concerning insulation ageing – introduced [9], because it was presented originally [9] using the Arrhenius model and not Eyring's. It does not affect the validity of ACE correlation (between related life lines) whether it is presented through either the Arrhenius or the Eyring plot [10–12]. The latter differs from the Arrhenius plot only in an insignificant and disputable correction. The occasional deviations – in the case of usual experimental errors – are not significant numerically. The part of the criticism [7] which claims physical significance only for Eyring's representation does not hold either, because the very ACE cited [6] as an example of physical significance proved to be [13, 14] an apparent ACE, without physical sense. Thus, even Eyring's interpretation is unable to protect its user from the occasional occurrence of a misleading apparent ACE.

With respect to the characteristics of the real and apparent ACE [15, 16] and to their distinction, we refer to several methods [5, 17–19].

Conclusion

We have shown that the parameters of the two equations (Arrhenius and Eyring) are mathematically convertible to each other by the use of universal material constants and the average temperature of the process. Thus the conceptual quantities 'entropy of activation' and 'enthalpy of activation' in the Eyring equation – stemming from the unjustified assumption of equilibrium for the activated state of reactions – give no more or no newer physical information that the Arrhenius parameters (A and E). Despite the 'direct connection' to material properties claimed for the Eyring interpretation, it was shown earlier that it will not prevent the occasional occurrence of a misleading (apparent) phenomenon.

Abbreviations

DMMA = Dielectric Materials, Measurements and Applications
IEE = Institution of Electrical Engineers (UK)
IEEE = Institution of Electrical and Electronic Engineers (USA)
ICSD = International Conference on Conduction and Breakdown in Solid Dielectrics

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References

1 J.-P. Crine, J. Macromol. Sci.-Phys., B 23 (1984) 201.
2 J.-P. Crine, IEEE Trans. Elec. Insul., 22 (1987) 69.
3 S. Glasstone, K. J. Laidler and H. Eyring 'The Theory of Rate Processes', McGraw-Hill, London 1941.
4 S. Vysocki and R. A. Fouracre, IEEE Conf. Elec. Insul. Diel. Phenom., Annual Report: 1992, p. 160–165.
5 F. Tüdős, 1969, IUPAC Intern. Symp. Macromol. Chem., Proceedings: 'Kinetics and Mechanism of Polyreactions', Vol. 6., Publ. Hung. Acad. Budapest, 1971, p. 485–506.
6 M. Simonyi and F. Tüdős 'Advances in Physical Organic Chemistry', ed. by Gold. V. Vol. 9, Academic Press, London-New York p. 127–183.
7 J.-P. Crine, IEEE Trans. Elec. Insul., 26 (1991) 811.
8 P. K. Dávid, 4th Intern. Symp. 'Enviroeffect', Liblice, Proc: Vol. 1, Czechosl. Acad. Sci., Prague. 1975, p. 28–30.
9 P. K. Dávid, IEEE Trans. Elec. Insul., 22 (1987) 229.
10 G. C. Montanari, P. K. David, IEEE Trans. Elec. Insul., 23 (1988) 1057.
11 P. K. Dávid, IEE Conf. Publ., 289 (1988) 151.
12 P. K. Dávid and G. C. Montanari, Europ. Trans. Elec. Power Engng., 2 (1992) 187.
13 P. K. Dávid, IEEE Trans. Elec. Insul., 28 (1993) 889.
14 P. K. Dávid and G. C. Montanari, IEE Conf. Publ., 363 (1992) 378.
15 F. Tüdős and P. Dávid, 5th IEEE 'ICSD '95' Conf. Leicester, Proc: 95CH3476-9, 1995, p. 190–193.
16 F. Tüdős and P. K. Dávid, Polymer Degr. Stab., (1995) (to be published).
17 O. Exner, Collection Czechoslovak Chem. Comm., 29 (1964) 1094.
18 O. Exner, Collection Czechoslovak Chem. Comm., 37 (1972) 1425.
19 O. Exner, Collection Czechoslovak Chem. Comm., 38 (1973) 781.