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Note

Temperature coefficient of reaction

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Recently, in discussing the kinetic data of Johnson et al.[1] for the isomerization of cyclopropane to propene, Ruthven[2] suggested that the problem of variation of the frequency factor with the activation energy might be due to the method of data correlation used. Ruthven[2] was able to calculate a temperature of reaction for the isomerization, using the data reported by Johnson et al., from the relationship $\Delta \log A/\Delta E = 1/RT \ln 10$. This appears not to be a coincidence, as was suggested by Johnson et al.[3], but a manifestation of the "kinetic compensation effect"[4] well known in heterogeneous catalysis[5–8], and present but not generally recognized in other thermal reactions including decompositions[9–14].

This author[15] has pointed out that the kinetic compensation effect arises from a deficiency in the Arrhenius equation; the form of the equation assuring that the data can be fit to the equation by expressing the rate constant k simply as a function of the fraction of reactant (α) and/or the change of α with time or temperature, then adjusting $f(\alpha, \mathrm{d}\alpha/\mathrm{d}t$ or $\mathrm{d}\alpha/\mathrm{d}T)$ until a plot of its logarithm vs. $1/T$ yields a straight line, without verifying the validity of the form. The quantity needed to complete the equation is ascribed to $\log A$ without considering the physical significance of that quantity. Thermal decompositions of complexes and reactions of the type $ACO_3 + BO_2 \rightarrow ABO_3 + CO_2$ were found to take place at temperatures related to the calculated kinetic parameters, that is, $T = \Delta E/(\Delta \log A \cdot R \ln 10)$.

In a later report[16], the general behavior was found also in reports on degradation of char-forming plastics[12] and styrenated polyester[13], as well as more commonplace inorganic decompositions[7,8]. The conclusion was reached that the Arrhenius equation could not be applied generally to heterogeneous decompositions, and that the reactions involved (except calcium carbonate[13] and possibly zinc carbonate[7,8] had a principal step which established the lower limit of reaction temperature while secondary parameters established the rate dependence upon temperature (the calculated activation energy). The data of Zsakó et al.[17,18] show the "compensation effect" in thermal decompositions of several complexes. The latter authors[18] relate the kinetic compensation parameters to the Co–amine bond strength and the properties of the anion in the external sphere.

For thermal decompositions it is fairly well understood that a calculated activation energy is very closely related to the conditions under which the experiment is conducted. Gallagher and Johnson[19], for example, showed that a considerable range of apparent activation energies could be obtained by varying the sample size and the heating rate. Nikolaev et al.[20] have shown that varying the flow rate of nitrogen (carrying the decomposition products to the detector) changed the apparent activation energy for the decomposition of Mg (EDTA) by 6 kcal mole^{-1}. This caused — in the Arrhenius equation — a change in A of 6000. Classical interpretation would have us believe that a seven-fold increase in the flow of an inert gas caused a 6000-fold increase in the opportunity for the Mg(EDTA) to decompose.

The inevitable conclusion is that the quantity called the activation energy in heterogeneous reaction kinetics has no firm relationship to the well-established activation energy from classical homogeneous kinetics. It is also apparent that it is not constant even for some homogeneous reactions[1] and hence the rate equation from which it is obtained is not accurately descriptive of the process. The false image of a classical activation energy could be avoided by calculating — and referring to — a temperature coefficient of reaction, instead of calling it an activation energy[21,22]. This would be more accurate and less misleading than the borrowed term and would allow a two- or three-term expansion when necessary to describe the actual data.

This temperature-coefficient description would be particularly useful whether the anticipated end use of the data is process design or mechanism studies. If, by some chance, an exponential dependence of the Arrhenius type was descriptive, it would be recognizable from the relative values of the coefficients in the expansion. In the more general case, some physical significance may be deduced for the terms. Most important, however, investigation would not be stifled by the connotations of this extant relating of names.

Temperature coefficient of reaction should be the preferred label until the reaction rate is shown by experiment to be independent of sample weight and geometry and of heating rate. Only then is there any assurance that an intrinsic property of the chemical process itself is being studied.

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