Letter

Isokinetic temperature and the compensation effect in catalysis

John J. Rooney [*]

School of Chemistry, Queen's University, Belfast BT9 5AG, UK

Abstract

The extended Eyring rate constant equation, $k_{exp} = kT/h \cdot \Pi K \cdot K^{\neq}$, reduces to the very simple expression, $k_{exp} = ykT_{iso}/h$, at the isokinetic temperature. © 1998 Elsevier Science B.V. All rights reserved.

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Isokinetic temperature and the compensation effect in catalysis [1] are found when a family of Arrhenius rate equation plots intersect at a common point. At this point the rates of reaction are the same with a linear relationship between the logarithm of the pre-exponential factor, $\ln A$, and the experimental activation energy, E. Usually an upper T_{iso} is observed, but there are also rare examples of lower isokinetic temperatures, and the phenomenon is found in all branches of catalysis, homogenous as well as heterogeneous.

$$\ln k_{exp} = \ln A - E/RT \tag{1}$$

$$\ln A = bE + c \tag{2}$$

Combination of these two equations gives Eq. (3), with $\ln Z = c$, and $T_{iso} = 1/bR$.

$$\ln k_{exp} = \ln Z + E/R(1/T_{iso} - 1/T) \tag{3}$$

At the isokinetic point, $\ln k_{exp} = \ln Z$.

Eq. (1) can be accounted for theoretically by the Eyring equation (Eq. (4)), which may be expanded for catalysis as Eq. (5).

$$k_{exp} = kT/h \cdot K^{\neq} \tag{4}$$

$$k_{exp} = kT/h \cdot \Pi K \cdot K^{\neq} \tag{5}$$

The latter equation [2–5] takes care of the fact that catalysis is a multi-step phenomenon so ΠK is a multiple and/or quotient of equilibrium constants for the steps prior to the activated complex forming step.

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[*] Corresponding author.

Eq. (4) can be expanded as Eqs. (6) and (7), where $\Delta H^{\neq} = E - nRT$

$$\ln k_{\exp} = \ln(kT/h) + \Delta S^{\neq}/R - \Delta H^{\neq}/RT \tag{6}$$

$$\ln k_{\exp} = n + \ln(kT/h) + \Delta S^{\neq} - E/RT \tag{7}$$

Likewise Eq. (5) yields Eq. (8)

$$\ln k_{\exp} = n + \ln(kT/h) + (\Sigma\Delta S^{\mathrm{o}} + \Delta S^{\neq})/R - E/RT \tag{8}$$

The isokinetic point is reached when T_{iso} $(\Sigma\Delta S^{\mathrm{o}} + \Delta S^{\neq})$ reaches the same value as E. The major entropy variable in governing the value of ln A then cancels out the activation energy variable, leaving a very simple expression, Eq. (9), for the value of $k_{\exp}$ at T_{iso} ($y = e^{n}$, a constant).

$$k_{\exp} = y \cdot kT_{\mathrm{iso}}/h \tag{9}$$

T_{iso} is therefore a characteristic temperature, comparable to ceiling temperature in polymerization, or to melting point, boiling point, etc., for phase equilibria.

Compensation in kinetics of catalysis is therefore an example of general compensation in thermodynamics according to Eq. (10), where ΔH varies in a linear fashion with ΔS, while ΔG remains zero or has a small constant value.

$$\Delta G = \Delta H - T\Delta S \tag{10}$$

This understanding of Eq. (10) is clear from statistical thermodynamics when Eq. (10) may be written as Eq. (11).

$$\Delta S = \Delta H/T + R \ln(\text{partition function ratio}) \tag{11}$$

An examination of vibrational partition functions shows that the third term in Eq. (11), equal to $-\Delta G/T$, may remain constant or zero, while ΔS and $\Delta H/T$ may vary widely and interdependently. The value of $\Pi K \cdot K^{\neq}$ at T_{iso} in Eq. (5) is therefore unity or a small constant, y. Since the rate constant, $k_{\exp}$, can be regarded as a frequency, $c\omega$ Eq. (9) can be written as Eq. (12), where $y = 1/\chi$.

$$T_{\mathrm{iso}} = \chi \cdot Nhc\omega/R \tag{12}$$

Eq. (12) was developed by Larsson [6] to account for T_{iso}. He maintains that the frequency, $c\omega$, is a fundamental parameter in catalysis arising from resonance of a catalyst frequency with the critical transition state frequency of the substrate. However, the approach here, based on the Eyring rate equation, shows instead that it is T_{iso} and reversible (equilibrium) thermodynamics which determines this frequency, which is really a rate constant.

The Eyring equation, Eq. (4), written as,

$$k_{\exp} = (kT/h\nu)\nu \cdot K^{\neq}$$

where $kT/h\nu$ is the molecular vibrational partition function for the transition state reaction coordinate, shows that ν cancels out. This frequency, ν, which is a genuine vibrational frequency should not be confused therefore with $c\omega$, a frequency equal to the rate constant. Because T_{iso} arises from thermodynamic equilibrium and is characteristic of closely related systems, of necessity theoretically it must be regarded as a characteristic vibrational temperature with an associated characteristic frequency.

References

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