An explanation of isokinetic temperature in heterogeneous catalysis

John J. Rooney

School of Chemistry, The Queen's University of Belfast, Belfast BT9 5AG, N. Ireland

Received 14 November 1997; accepted 20 November 1997

The extended Eyring rate constant equation for catalysis reduces to the very simple form, $k_{\rm exp} = y \cdot kT_{\rm iso}/h$, at the isokinetic temperature.

Keywords: extended Eyring rate constant equation, catalysis, isokinetic temperature

A general, purely physical, theory [1] currently advocated for heterogeneous catalysis is that in the transition state the vibrational frequency of one of the normal modes of the substrate resonates with a vibrational frequency of the solid surface. The widespread observations of isokinetic temperature and the compensation effect [2] for closely related families, substrates or catalysts etc. are then cited [1,3] as evidence for this idea, and equations developed to show that the isokinetic temperature, $T_{\rm iso}$, is given by the following, where x is a small number and all the other symbols have their usual significance:

$$T_{\rm iso} = \frac{Nhc\omega}{R} \cdot x\,.$$

However, recently we have argued [4,5] that isokinetic temperature and the compensation effect are explained by the extended Eyring kinetic rate equation:

$$k_{\rm exp} = y \cdot kT/h \cdot \prod K \cdot K^{\pm}\,.$$

$\prod K$ is a multiple or quotient of the individual equilibrium constants for all the sequence of steps, chemisorption or complexation, etc., preceding the activation step; $k_{\rm exp}$ is the experimental rate constant and y is the transmission coefficient. Isokinetic temperature is then defined as the temperature at which $\prod K \cdot K^{\pm} = 1.0$. Now the corresponding standard free energy summation $\sum \Delta G^{\circ} + \Delta G^{\pm} = 0$, and $\sum \Delta H^{\circ} + \Delta H^{\pm} = T(\sum \Delta S^{\circ} + \Delta S^{\pm})$. This is in complete accord with the understanding that the equation $\Delta G(=0) = \Delta H - T\Delta S$ is the basis of all such compensation effects in thermodynamics [6,7].

In like fashion equilibrium (reversible) thermodynamics are also the cornerstone of an understanding of the Arrhenius and Eyring rate equations in kinetics.

$T_{\rm iso}$ is therefore the temperature at which the Eyring equation reduces to the following equation:

$$k_{\rm exp} = y \cdot \frac{kT_{\rm iso}}{h}\,.$$

Since $k_{\rm exp}$ can be defined as a frequency ($k_{\rm exp} = c\omega$) the first equation is identical to the last ($x = 1/y$). There is therefore no need to have recourse to special resonance effects in order to explain isokinetic temperature and compensation behaviour, as found in all branches of catalysis. Instead the application of the limited form of the extended Eyring equation is further validated by the physical theory derived by Larrson [1,3].

Even if $\prod K \cdot K^{\pm}$ is a constant with a value other than one at $T_{\rm iso}$, the latter is still given by the same expression where y is a constant.

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