The extended Eyring kinetic equation and the compensation effect in catalysis

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Abstract

The compensation effect observed in the kinetics of all branches of catalysis, which by its nature is a multi-step phenomenon, can only be understood by using the extended Eyring rate constant equation, $k_{exp} = kT/h \cdot \prod K \cdot K^{\neq}$, where $\prod K$ includes every equilibrated individual step preceding the activation step. © 1998 Elsevier Science B.V.

The compensation effect is very well known in all areas of catalysis [1] and is expressed as a linear relationship between the logarithm of the preexponential factor A and the activation energy E as derived from the Arrhenius plots for a given group of reactions. It is usually observed for the same catalyst and a homologous series of reactants, or for the same reaction and a family of closely related catalysts [2]. However, compensation is not confined to kinetics as it is also observed in many other physico–chemical areas, e.g. the thermodynamics of solutions [3,4].

Fundamentally the effect in general has its origins in the Gibbs–Helmholtz Eq. (1),

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

because ΔG can remain constant at constant temperature for families of solvents, reactants, or catalysts, etc., while ΔH, and thus ΔS may vary widely. This is readily understood from statistical thermodynamics and the nature of the molecular partition function, q. Here G and S are expressed by Eqs. (2) and (3) respectively [5].

$$G = -NkT \ln(q/N) \tag{2}$$

$$S = H/T + Nk \ln(q/N) \tag{3}$$

The free energy is governed solely by the value of q while entropy depends on the amount of energy required to maintain a certain temperature as well as on its distribution (q). Almost invariably the values of q for vibration are unity so ΔG_{vib} is constant within a given family, as above, being equal to the zero point energy difference between reactants and products for each step; but ΔH_{vib} and ΔS_{vib} can vary widely and thus interdependently. This is at the core of an understanding of compensation because the corresponding values of ΔH and

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ΔS, as well as ΔG, for rotational and translational modes tend to remain constant.

The Eyring rate theory, Eq. (4), which was developed to explain the Arrhenius rate equation is also grounded in reversible equilibrium thermodynamics so it must also be the cornerstone of any understanding of compensation in kinetics.

$$k_{\exp} = kT/h \cdot K^{\neq} \qquad (4)$$

A major development therefore was the realization [6,7] that Eq. (4) can be extended for multistep processes, such as catalysis, by incorporating an additional equilibrium constant for every step preceding the activation step which is represented by $K^{\neq}$. This is summarized in Eq. (5) where $\prod K$ is the multiple of all such equilibrium constants including the Langmuir adsorption coefficients.

$$k_{\exp} = kT/h \cdot \prod K \cdot K^{\neq} \qquad (5)$$

Each K is raised to the power to which it occurs in the overall rate equation. When the latter is based on Langmuir adsorption theory, as for heterogeneous catalysis, it is readily appreciated that $\prod K$ may also be a quotient since Langmuir coefficients often appear in the denominator as well as in the numerator of the corresponding derived rate equation. Thus for a binuclear reaction where adsorption of A and B is competitive the general rate equation is given by Eq. (6) ($r = $ rate).

$$r = \frac{k_1 K_A P_A \cdot K_B P_B}{\left(1 + K_A P_A + K_B P_B\right)^2} \qquad (6)$$

The commonly noted limiting forms of such an equation are, $r = k_1 K_A P_A \cdot K_B P_B$, $r = k_1 K_A P_A / K_B P_B$, and $r = k_1 K_B P_B / K_A P_A$, depending on the strengths of adsorption and pressures of A and B. The latter two limits are realized when $K_A P_A \gg 1.0$ and $K_B P_B \gg 1.0$, with $K_A P_A \ll K_B P_B$, and then $K_A P_A \gg K_B P_B$.

Eq. (5) can be expanded to give Eqs. (7) and (8).

$$\ln(k_{\exp}) = \ln(kT/h) - \sum \Delta G^0 / RT$$
$$- \Delta G^{\neq} / RT \qquad (7)$$
$$\sum \Delta G^0 + \Delta G^{\neq} = \sum \Delta H^0 + \Delta H^{\neq}$$
$$- T\left(\sum \Delta S^0 + \Delta S^{\neq}\right) \qquad (8)$$

When there is isokinetic behaviour, i.e., the experimentally determined value of the rate constant, $k_{\exp}$, is constant at a certain temperature for the whole family, $\sum \Delta G^0 + \Delta G^{\neq}$ is constant or zero. The value of $E \cong \sum \Delta H^0 + \Delta H^{\neq}$, and the $\ln A$ factor is given approximately by $\ln(kT/h) + (\sum \Delta S^0 + \Delta S^{\neq})/R$. Quite clearly compensation is noted because Eq. (9) is then valid (the content = 0).

$$\Delta\left(\sum \Delta H^0 + \Delta H^{\neq}\right) = T\Delta\left(\sum \Delta S^0 + \Delta S^{\neq}\right) \qquad (9)$$

Theoretical considerations show that $\Delta H^{\neq}$ cannot vary very much within a given family because when adsorption or complexation is stronger for the ground state it is also almost equally stronger for the corresponding transition state complex [2]. Wide variations in the value of E and in $\ln A$ therefore reside in the magnitudes of $\sum \Delta H^0$ and $\sum \Delta S^0/R$ respectively.

The extended Eyring Eq. (5) and the ensuing equations are therefore as rigorous theoretically as the original Eq. (4) and cannot be regarded merely as speculation. Equally important in understanding compensation is the realization from statistical thermodynamics that $\sum \Delta G^0 + \Delta G^{\neq}$ may remain constant for a given family as described above.

In a recent paper Bond et al. [8] have drawn attention to the fact that compensation may also be found for the same reaction and the same catalyst provided that the kinetics change when the pressures of the reactants change, as shown by Eq. (6) and its limiting forms. A classical example is the hydrocracking of simple paraf-

fins on Ru catalysts [7]. The limiting rate equations applicable were expressed as in Eq. (10).

$$r = k_1 K_c P_C / K_{H_2}^n P_{H_2}^n, \quad \text{and}$$
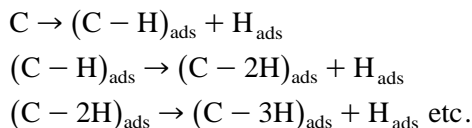$$r = k_1 K_{H_2}^n P_{H_2}^n / K_c P_C \quad (10)$$

where P_C and P_{H_2} are the pressures of paraffin and hydrogen respectively; K_c is the collective Langmuir dissociative adsorption constant for the paraffin and K_{H_2} that for dissociative adsorption of H_2. The limiting values of E at high and low pressures of H_2 respectively are then given as in Eq. (11).

$$E \cong \Delta H^{\neq} + \Delta H_C^0 - n_H \Delta H_H^0$$
$$E \cong \Delta H^{\neq} - \Delta H_C^0 + n_H \Delta H_H^0 \quad (11)$$

The magnitude of E was found to be determined mainly by the very large positive value of ΔH_C^0.

While this analysis is fine, as far as it goes, it is unfortunately rather confusing since the initial chemisorption of the paraffin must be exothermic, not endothermic. However, if K_C which in reality is a multiple of constants is extended as $K_{ads} \cdot \prod K_d$, one for each of the following series of steps, the situation becomes a lot clearer (C is the free paraffin).

$$C \rightarrow (C - H)_{ads} + H_{ads}$$
$$(C - H)_{ads} \rightarrow (C - 2H)_{ads} + H_{ads}$$
$$(C - 2H)_{ads} \rightarrow (C - 3H)_{ads} + H_{ads} \text{ etc.}$$

Now K_{ads} is for this first step while $\prod K_d$ is for the series of consecutive surface dehydrogenation steps until $(C-xH)_{ads}$ is reached, the critical species responsible for the cracking step.

This more detailed analysis reveals that the limiting values of E are determined by Eq. (12).

$$E \cong \Delta H^{\neq} + \Delta H_{ads}^0 + \sum \Delta H_d^0 - n_H \Delta H_H^0$$

$$E \cong \Delta H^{\neq} - \Delta H_{ads}^0 - \sum \Delta H_d^0 + n_H \Delta H_H^0 \quad (12)$$

Compensation is possible even within each of these limits because the strengths of chemisorption will vary with surface coverage as the pressures of the reactants change from one run to another. This is especially true of drastic reactions such as hydrocracking where the metal surface may become almost fully carbided. The initial chemisorption is now exothermic with ΔH_{ads} negative as theory demands, but the ensuing series of surface dehydrogenation steps is endothermic with $\sum \Delta H_d$ large and positive, and it is this quantity which is mainly responsible in determining the range of E values. The importance of using the fully extended Eyring equation is well illustrated by this excellent example. It can also be applied in like fashion with the same advantage to an understanding of the kinetics of hydrogenolysis of neopentane on a family of Pd catalysts [9] where a very wide range of E values and a very good compensation plot are recorded.

In conclusion the paradox which has held up the understanding of compensation for so long is that a multiple and/or quotient of equilibrium constants must be used in the Eyring equation for catalysis and not simply one such equilibrium constant, $K^{\neq}$. This is beautifully illustrated by one example [10] from gas phase kinetics where the rate of chlorine atom catalyzed decomposition of N_2O is given by Eq. (13).

$$r = k_{exp} \cdot P_{Cl_2}^{1/2} \cdot P_{N_2O} \quad (13)$$

The corresponding Eyring equation is Eq. (14)

$$k_{exp} = kT/h \cdot K^{1/2} \cdot K^{\neq} \quad (14)$$

Here K is the equilibrium constant for dissociation of Cl_2 and $K^{\neq}$ is for activation to the transition state of the N_2OCl intermediate formed by collision of a Cl atom with a N_2O molecule [7]. This example also serves to illustrate that inclusion of equilibrium constants is not confined to Langmuir adsorption coefficients and similar complexation constants in setting up extended Eyring equations for kinetics in catalysis.

The isokinetic temperature [1] which is an integral feature of the best examples of the compensation effect, is the point of intersection of any particular family of Arrhenius plots such that there is one value of k_{exp} at one unique

temperature for that family. At this point, and only at this point, is $\sum \Delta G^0 + \Delta G^{\neq} = 0$. At all other points, as required by the overall equilibrium between free reactants and transition state, $\sum \Delta G + \Delta^* G^{\neq} = 0$ ($\Delta^* G^{\neq}$ includes the free energy associated with the critical transition state vibration whose molecular partition function is $q = kT/h\nu$, whereas, $\Delta G^{\neq}$ excludes this contribution). When $\sum \Delta G^0 + \Delta G^{\neq} = 0$ the standard state conditions of one atmosphere pressure applies, and, $\prod K \cdot K^{\neq} = 1.0$, so at this unique point, $k_{exp} = kT_{iso}/h$. It is noteworthy that T_{iso} is characteristic of the family (catalysts or reactants) and that k_{exp} at this temperature is a characteristic frequency.

This understanding of the isokinetic temperature, T_{iso}, reinforces the validity of applying Eyring transition state theory and equilibrium thermodynamic concepts to kinetics in catalysis [11].

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