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Kinetics of alkane reactions on metal catalysts: activation energies and the compensation effect

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Abstract

Compensation phenomena in heterogeneous catalysis take the form of a linear correlation between activation energy E and pre-exponential factor $\ln A$; its occurrence may, however, be due to the use of 'apparent' rather than 'true' Arrhenius parameters. It is shown by model calculations using the Langmuir–Hinshelwood bimolecular rate equation, and experimentally using Pt-catalysed hydrogenolysis of C_3H_8 and of n-C_4H_{10}, that E_{app} increases with P_H, as expected. These values of E_{app} show compensation. Apparent Arrhenius parameters for many different Pt and Pd catalysts and for various reactions lie close to a common compensation line. Alkane activation requires dehydrogenative chemisorption, which is endothermic; this causes E_{app} to exceed E_{true}, and accounts for the dependence of E_{app} on alkane chain length, and the very high values sometimes observed. Compensation occurs as a result of using constant reactant pressures, which give inconstant surface concentrations. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Compensation phenomena; Activation energy; Alkane hydrogenolysis; Metal-catalysed

1. Introduction

The concern of this paper is with metal-catalysed reactions of alkanes with H_2, chiefly hydrogenolysis, under conditions such that neither bifunctional nor heat- nor mass-transfer effects interfere. Laboratory studies, although often complicated by deactivation due to carbon deposition, have provided a wealth of kinetic information, from which certain general conclusions emerge. (i) Rates and turnover frequencies usually obey an Arrhenius relation, at least over a limited temperature range. (ii) Even precisely measured activation energies often show significant sample-to-sample variation. (iii) Their numerical values vary widely (80–400 kJ mol^{-1}), but rational *explanation* of the numbers is commonly lacking. (iv) Compensation phenomena, i.e. linear correlations between activation energy E and $\ln A$ (A=pre-exponential factor) are often seen. This paper's objective is to outline a theoretical framework for these observations.

Activation energies are normally measured using constant reactant pressures. Classical treatments of kinetics of catalysed reactions, described in numerous textbooks, show that in general rates so measured increase with temperature less quickly than they might, because of the progressive desorption of adsorbed reactants. Activation energies determined in this way are properly called 'apparent'; those based on rate constants or on rates where surface coverages are unlikely to change significantly in the temperature used may be labelled 'true'. This distinction is sometimes a source of confusion in the literature. It follows from this that the experimental E will in principle be a function of reactant pressures; this is a fact seldom

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recognised, and the measured E is often seen by implication as some kind of fundamental constant. The functional relation between E_{app} and reactant pressures was first derived by Temkin in 1935 [1]; using the Power Rate Law formalism and the Clausius–Clapeyron equation he obtained the following equation:

$$E_{\mathrm{app}} = E_{\mathrm{t}} + \sum n_{\mathrm{i}} \Delta H_{\mathrm{i}}, \tag{1}$$

where n is an 'order of reaction'. Thus for example for a bimolecular reaction A+B where coverage by other reactants is low, $n_{\mathrm{A}}=n_{\mathrm{B}}=1$ and so

$$E_{\mathrm{app}} = E_{\mathrm{t}} + \Delta H_{\mathrm{A}} + \Delta H_{\mathrm{B}}. \tag{2}$$

When $\theta_{\mathrm{A}} \gg \theta_{\mathrm{B}}$, because P_{A} and/or b_{A} is large in comparison with P_{B} and/or b_{B}, $n_{\mathrm{A}}=-1$ and n_{B}=l, so that

$$E_{\mathrm{app}} = E_{\mathrm{t}} - \Delta H_{\mathrm{A}} + \Delta H_{\mathrm{B}}. \tag{3}$$

The quantities θ_{i}, b_{i} and P_{i} are defined by the Langmuir adsorption equation:

$$\theta_{\mathrm{i}} = b_{\mathrm{i}} P_{\mathrm{i}} / (1 + b_{\mathrm{i}} P_{\mathrm{i}}), \tag{4}$$

b_{i} is an adsorption coefficient, i.e. the equilibrium constant for the adsorption–desorption process.

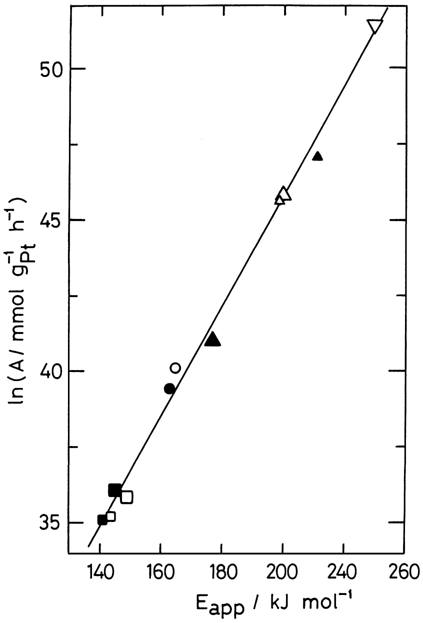

Fig. 1. Compensation plot for the hydrogenolysis of C_2–C_4 alkanes on 0.3% Pt/Al_2O_3 (CK303; EUROPT-3: open points) and 0.6% Pt/Al_2O_3 (CK306: filled points), P_{H}:P_{A}=10: (▽) C_2H_6: (△) C_3H_8; (□) n-C_4H_{10}; (○) i-C_4H_{10}: large points, [2]; small points, [3].

2. The compensation phenomenon

Compensation in the present context is represented by a linear relation between E and $\ln A$, viz.

$$\ln A = mE + c. \tag{5}$$

Correlations of this kind have been frequently reported *either* when the same reaction is studied on a series of different catalysts *or* when different reactions are followed on the same catalyst. An example of the latter type is shown in Fig. 1 [2,3]. Strict adherence to this equation implies the existence of a single temperature T_{i} (the isokinetic temperature) at which rates for all members of the group are the same. Arguments about the exact precision of the intersection verge on the theological [4]; what is important is that there are real and substantial variations in E in the data set being considered. False compensation effects may arise simply from experimental error, so examples where the variance of E is small should be viewed with suspicion [5].

It happens not infrequently, when the data set covers members of widely different activity, that the Arrhenius parameters fall on two or more lines of roughly parallel slope, each corresponding to a different level of activity: the well-known example of ethane hydrogenolysis is shown in Fig. 2 [6]. Most metals fall on the central line, but Pd and Pt, having very low activity, show points about a lower line, while the very active Ru and Os lie above it. Each group of points may have its characteristic mechanism and fraction of active surface; we shall return to this question later.

The literature [8] reveals a number of explanations of compensation phenomena, many of which focus on a sympathetic interaction between enthalpy and entropy of activation. Recently, however, it has been seen that changes in E may be caused by differences in *adsorption enthalpies* [9,10]: we therefore propose the working hypothesis that *compensation often occurs because of the use of apparent rather than true kinetic parameters.*

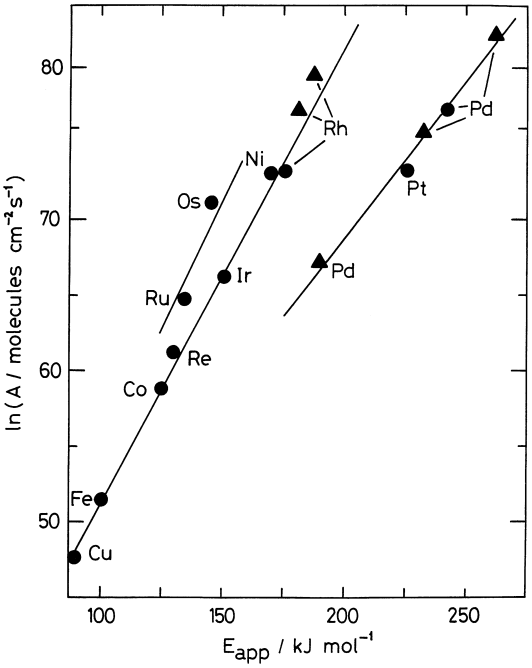

Fig. 2. Compensation plot for the hydrogenolysis of C_2H_6 on various SiO_2-supported metals, P_H:P_A=6.7 [6,7].

3. Model calculations and experimental observations

We have taken the standard Langmuir–Hinshelwood bimolecular rate expression:

$$r = kb_AP_Ab_BP_B/(l + b_AP_A + b_BP_B)^2 \quad (6)$$

and have selected values for the true Arrhenius parameters and for the enthalpies and entropies of adsorption of A and B: we then calculated rate as a function of P_A, P_B being held constant, at four temperatures [10]. The results are in Fig. 3: the rate maximum, where θ_A equals θ_B, moves to higher values of P_A, and the rate above the maximum is less inhibited by A, as temperature is increased. By inspection it is clear that E_{app} will increase with P_A, as predicted qualitatively by the Temkin relation (Eq. (1)); Fig. 4 shows that this is so. Calculated rates at each value of P_A obey the Arrhenius equation quite precisely, but the lines do not intersect at exactly the same point; indeed, they cannot, because if they did there would have to be a temperature at which the rate was totally independent of P_A. Nevertheless, except at the highest values of P_A, the derived Arrhenius parameters show a convincing compensation effect (Fig. 5). At least under conditions where rate does not alter greatly with P_A, but (by reason of its value) $-\Delta H_A$ greatly moderates the value of E_t, the change in the slope of the Arrhenius line, i.e. E_{app}, has to cause a corresponding change in the intercept, viz. ln A_{app}. The occurrence of compensation is then inevitable.

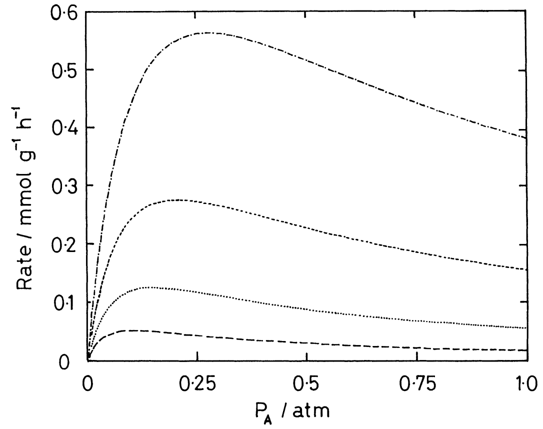

Fig. 3. Rates as a function of pressure of reactant A at 373, 393, 413 and 433 K calculated by the Langmuir–Hinshelwood bimolecular rate expression; pressure of B=0.0714 atm [10].

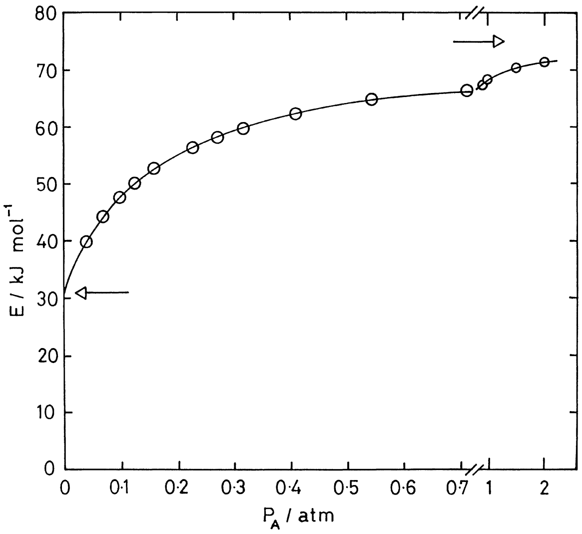

Fig. 4. Dependence of E_{app} on pressure of A derived from the rates shown in Fig. 3: arrows show theoretical upper and lower limits [10].

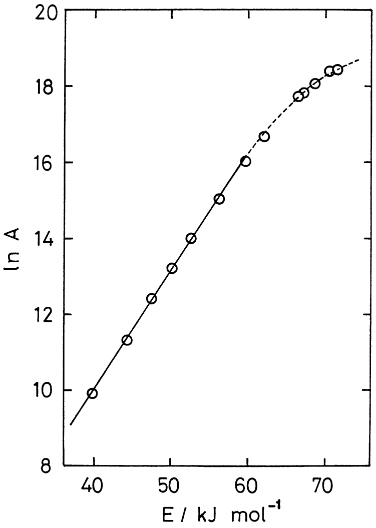

Fig. 5. Compensation plot shown by values of E_{app} in Fig. 4 and the corresponding values of $\ln A_{app}$ [10].

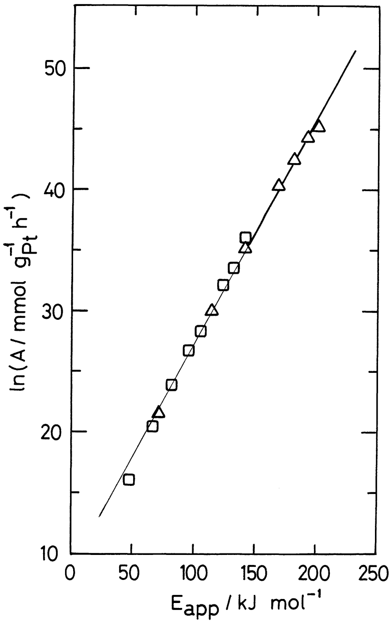

Fig. 6. Compensation plot for selected values of E_{app} and ln A_{app} as a function of H_2 pressure for the hydrogenolysis of C_3H_8 and of n-C_4H_{10} on 0.3% Pt/A_2O_3 (EUROPT-3) [11]: the symbols are as in Fig. 1.

Bond and Cunningham [11] have conducted a detailed study of the hydrogenolysis of C_3H_8 and of n-C_4H_{10} on EUROPT-3 (0.3% Pt/Al_2O_3): this is a typical petroleum reforming catalyst, supplied by AKZO. The dependence of rate on H_2 pressure (P_H) at various temperatures leads to plots of E_{app} vs. P_H similar to that in Fig. 4, without any assumption concerning kinetics or mechanism. The derived values of E_{App} and $\ln A_{app}$ for the two alkanes show compensation (Fig. 6), and it is reassuring that the same line applies to both molecules and that it is virtually the same line as that used in Fig. 1 where the nature of the alkane is the primary variable (Note, however, that reactant pressures may not be exactly the same for all alkanes.). We reach the important conclusion that *compensation between* E_{app} *and* $\ln A_{app}$ *may arise either by changing the pressure of a reactant* (*viz.* P_H) *or by altering the alkane*: this latter will clearly change the adsorption coefficient b_A (A=alkane), and so it is immaterial whether we change a pressure P_i or an adsorption coefficient b_i, because the two always appear in conjunction (see Eqs. (4) and (6)). It is their product b_iP_i and the corresponding coverage θ_i which matter.

The concurrence of the compensation lines derived in these different ways suggests that the procedure has some predictive value. Thus further work *with this catalyst* using different alkanes or different reactant pressures should produce Arrhenius parameters lying on or close to the line shown in Fig. 6. While it does not necessarily follow that all Pt catalysts will behave identically to EUROPT-3, it is of interest to see what variation is shown by different types of Pt catalyst. We are helped in this exercise by extensive compilations of kinetic data made by Somorjai [12,13]; his data for C_2H_6 hydrogenolysis [13] are shown in Fig. 7. This includes Sinfelt's results [6] for Pt (and Pd) and some further points have been added [7]. Not surprisingly, there is a considerable scatter due chiefly to uncertainties in estimating the numbers of 'active sites' and to the use of different reactant pressures, etc. Some parameter values are clearly in error. Corresponding data for higher alkanes [12] cluster about a line corresponding to slightly greater reactivity. However, the best line through the points in Fig. 7 (the bold line) corresponds closely to that for the reactions of C_2–C_6 alkanes on EUROPT-1 (6.3% Pt/SiO_2) [14]: the broken line is taken from Figs. 1 and 6. Although it is possible to deduce minor trends (e.g. greater activity of zeolite-supported Pt) and identify major errors, all in all the results for Pt (and Pd) show remarkable

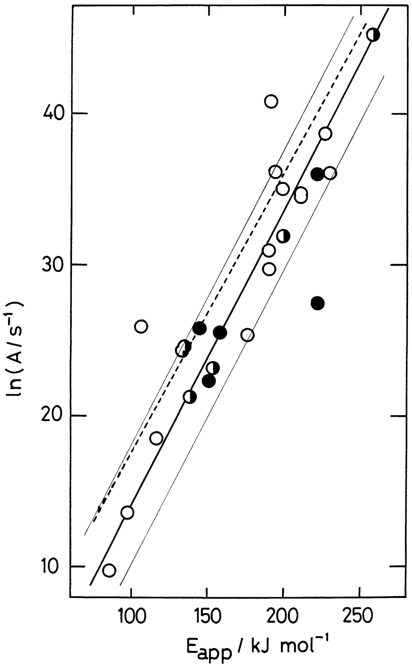

Fig. 7. Compensation plot for the hydrogenolysis of C_2H_6 on various Pt catalysts performed at various reactant pressures [13]: (○) supported Pt; (○) zeolite-supported Pt; (●) unsupported Pt (powder, film, single crystal): the broken line is taken from Fig. 1.

consistency and provide a means of epitomising the behaviour of these metals in alkane reactions.

4. Mechanism and mathematical modelling

To pursue the analysis further it is necessary to speculate on the mechanism, and to indulge in mathematical modelling. A widely (but not universally) assumed mechanism for activating an alkane for chemisorption and subsequent C–C bond-breaking requires the molecule to *lose* one or more H atoms on dissociatively adsorbing, with the formation of the same number of C–metal bonds. The dehydrogenated species then reacts with an H atom (or H_2 molecule or another vacant site) to form fragments which then rapidly desorb as product alkanes, or remain for further fragmentation [15,16]. We have applied one of the derived rate expressions coded ES5B [17] (it assumes an H atom in the rate-determining C–C breaking step) to our results [11] for C_3H_8 and n-C_4H_{10} on Pt catalysts (also to Ru [18] and Rh [19] catalysts), obtaining generally satisfactory fits. Full accounts having already been published, it is unnecessary to do more than summarise the conclusions. Values of E_t are about 70–80 kJ mol^{-1} for Pt and about 55 kJ mol^{-1} for Ru: ΔH_A values are about 80–90 kJ mol^{-1} for both metals.

This mechanism and its subsequent quantitative expression help to provide plausible answers to troublesome questions. (i) The variability of E_{app}, either from sample to sample or from one preparation or form to another (see e.g. Fig. 7), may be ascribed to differences in the adsorption enthalpy of the alkane or the H_2, due in turn to factors such as surface cleanliness, particle size or metal–support interactions, etc. We have recently shown [20] for example that b_H estimated from the kinetics of n-C_4H_{10} hydrogenolysis decreases in the sequence

$$\mathrm{Pt/KL\ zeolite} > \mathrm{Pt/SiO_2} > \mathrm{Pt/Al_2O_3}.$$

(ii) The generally high values of E_{app} for alkane hydrogenolysis (higher than E_t derived by the ES5B equation) are a consequence of the *endothermic* nature of the alkane activation; the concentration of the reactive form therefore *increases* with temperature, unlike the classical situation described above, and therefore E_{app} exceeds E_t. The general tendency for E_{app} to decrease with increasing chain length [14] reflects the more favourable thermochemistry of the dehydrogenation, and the very high values often found for neopentane hydrogenolysis (200–400 kJ mol^{-1}) [5] denote the difficulty of removing more than one H atom from this molecule.

5. The use of 'orders of reaction'

The dependence of rate on reactant pressures is often represented by a simple Power Rate Law, in which the exponent of the pressure needed to give proportionality to rate is 'the order of reaction'. A logarithmic function can sometimes describe the results quite accurately, especially when (as with C_2H_6 hydrogenolysis) the rate maximum occurs at very low pressures. Clearly, however, such a function is not adequate for the entire pressure range, but accepting it for what it is worth we ought to be able to use the Temkin relation (Eq. (1)) by plotting E_{app} vs. n_i to give values for E_t and ΔH_i. Martin [21] has

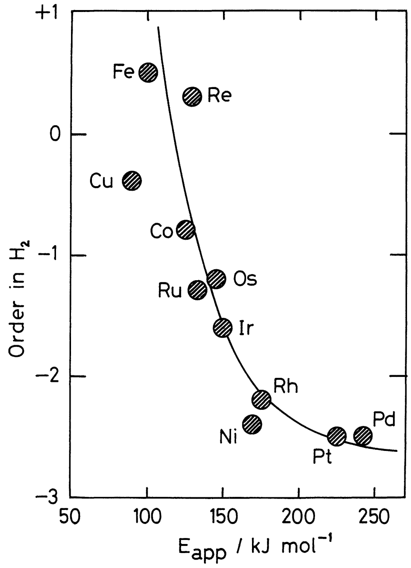

Fig. 8. Dependence of the order of reaction in H_2 on E_{app} for the hydrogenolysis of C_2H_6 on various SiO_2-supported metals [6].

tried this approach with a number of systems, but the problem is that E_{app} is not constant while a pressure P_i is being altered to measure the order, nor is n_i constant when temperature is being changed to obtain E_{app}. The results obtained may therefore have qualitative but not quantitative significance.

There are, however, a number of reports in the literature of correlations between E_{app} and n_i (n_H). As expected, the sense of the dependence is that higher values of E_{app} accompany more negative values of n_H. Fig. 8 shows the familiar data of Sinfelt [6] on C_2H_6 hydrogenolysis: the trend is in the expected sense, i.e. for those metals on which H_2 is strongly adsorbed and θ_H is high, orders in H_2 are most negative and values of E_{app} are highest. Major differences in activity, however, necessitate the use of widely different temperatures for measuring n_H and E_{app}.

6. A general explanation for kinetics and compensation

We may now propose a hypothesis to account for the occurrence of compensation either (i) by changing the reaction, but keeping the catalyst constant, or (ii) by changing the catalyst, but using the same reaction.

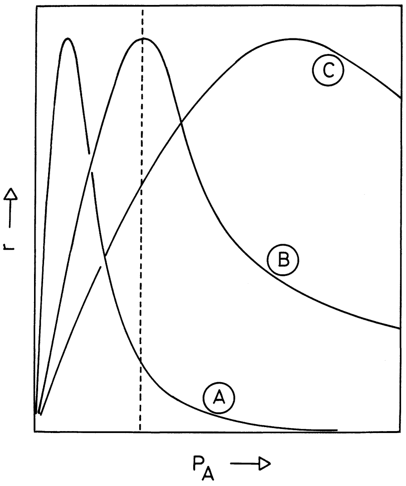

Fig. 9. Schematic diagram showing rate dependence on reactant pressure P_A for three different values of b_A such that $b_A > b_B > b_C$.

In the context of alkane hydrogenolysis, we must recall that: (i) E_{app} is a function of the pressure of each reactant, although H_2 (being more strongly adsorbed than the alkane) has the dominant effect; (ii) it is necessary to use Langmuir–Hinshelwood rather than Power Rate Law formalism; and (iii) the unifying factor is the surface coverage by H atoms (θ_H).

Let us imagine a series of curves of rate vs. P_H (Fig. 9; A, B and C) for convenience normalised to the same maximum rate. The order n_H measured in any constant P_H range will decrease in the sequence C>B>A, so that these curves could represent either (a) the use of metals or catalysts A, B and C arranged in order of decreasing strength of H_2 adsorption [20] or (b) increasing temperature [11,18] or (c) the use of a series of alkanes A, B and C which show increasing strength of adsorption or ease of activation [11].

Now corresponding to each curve there will be adsorption isotherms for each reactant, that for H_2 being the more important: the three curves can be condensed into one by adjustment of the θ_H scale, and the ranges of θ_H (or P_H) over which each of the situations A, B and C are met can be identified (Fig. 10). The value of E_{app} will be a function of θ_H as before. If one elects or is constrained to work near the tail of the curve (situation A) one will find high E_{app}, low rates and a negative order in H_2; working close to the maximum (situation B) one finds a lower

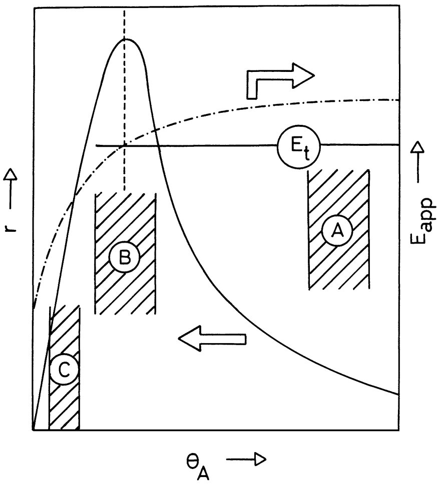

Fig. 10. Schematic diagram for dependence of rate and of E_t on θ_A showing the locations of the three different values of b.

E_{app} ($\cong E_t$), faster rates and an order n_H close to 0; and at low θ_H one obtains low E_{app}, low to medium rates and a positive value of n_H. The values of E_{app} obtained using a fixed P_H under situations A, B and C (see broken line in Fig. 9) will differ because the range of θ_H scanned by the temperature change will differ in each case. So, e.g. the values found with different alkanes (Fig. 1) are not the same *because the* θ_H *ranges differ*; the same may be true for Sinfelt's values of E_{app} and orders in H_2 for C_2H_6. This form of analysis ought to apply to any reaction following Langmuir–Hinshelwood kinetics, but so far it is only for alkane hydrogenolysis that sufficient data are available to test the concept.

7. Isokinetic parameters

It was noted at the outset that precise obedience of a set of Arrhenius lines to the compensation Eq. (5) implied that they would all intersect at exactly the same point, the co-ordinates of which are the *isokinetic temperature* and the *isokinetic rate* (or rate constant): the isokinetic temperature T_i is given by

$$T_i = (mR)^{-1}, \qquad (7)$$

where R is the gas constant, and the isokinetic rate by the antilog of c [22]. However, there are numerous examples in the literature, some of which are shown in this paper, in which E_{app} varies widely and is *approximately* compensated by changes in ln A_{pp}. One example will suffice to make the point: the model calculations performed by changing P_H [10] (see Figs. 3–5) generate E_{app} values that are compensated by ln A_{app} over a considerable range (Fig. 5), the slope m corresponding to T_i=422 K. Individual pairs of the Arrhenius plots do not, however, intersect at a unique isokinetic point (see Fig. 2 of [10]). The existence of such a point would imply a temperature at which the rate was quite independent of P_H, but this is not possible (see Fig. 3). Corma et al. [23] have distinguished between *isokinetic phenomena* (where there is a precise isokinetic point) and *compensation phenomena* (where such a point is absent, although the Arrhenius parameters vary sympathetically). It is with these latter phenomena that this paper is concerned.

The occurrence of compensation, defined in this way, is inevitable if the exponential term $\exp(-E_{app}/RT)$ varies more than the rate. The approach to the understanding of compensation adopted in this paper is to analyse the significance of E_{app}, using established kinetic formalism.

If it were desired to see whether this led to the expectation of an *isokinetic* point, it would be necessary to perform a similar analysis on the ln A_{app} term to see how it is affected by variations in the adsorption energies, but this is less easy because it comprises a number of factors including the surface area or the number of active sites, as well as the entropies of activation and of adsorption of the reactants. Such an exercise, while not impossible, is beyond the scope of this paper: intuitively it seems likely that the origin of compensation will be traced to the equations that define free energies of activation and of adsorption.

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