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Compensation behaviour recognized in literature reports of selected heterogeneous catalytic reactions: aspects of the comparative analyses and significance of published kinetic data

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Abstract

A comparative analysis of selected examples of compensation behaviour, reported in the literature or identified here in published rate studies for heterogeneous catalytic reactions, showed that the isokinetic temperature often occurs within the interval of the kinetic measurements. (At the isokinetic temperature the rate constants for all reactions of the set are equal). Detailed comparisons of data for a diverse group of nickel metal catalyzed cracking-type processes showed significant variations of the magnitudes of the activation energies reported for ethane hydrogenolysis, though levels of reactivity were similar to other chemical changes in the set. It is also concluded that the factors determining the magnitude of Arrhenius parameters for many surface processes are insufficiently well understood to warrant the formulation of detailed mechanisms of the contributory surface reactions. It is also concluded here that the similarity of reactivities over a range of reaction temperatures, for a set of rate processes, is demonstrated by the existence of compensation behaviour. This observation may be useful in providing insights into the identity of common factors controlling reactivities within each group of isokinetically related reactions. A similar level of reactivity characterizes the compensation set. A theoretical explanation of the magnitudes of Arrhenius parameters for many surface processes is not at present practicable because we have insufficient knowledge of the conditions and controls prevailing. Mechanistic proposals are often based on presumed extensions of the theory accepted for homogeneous rate processes. © 1997 Elsevier Science B.V.

1. Introduction

The "compensation effect" is a pattern of kinetic behaviour recognized within groups of related heterogeneous reactions or catalyst: it is both well-known and theoretically enigmatic [1]. This behaviour is characterized by the systematic and interdependent variations of the magnitudes of calculated Arrhenius parameters (A–frequency factor and E–activation energy) for the individual members of a set of related rate processes, according to the isokinetic relation:

$$\ln A = B + eE \tag{1}$$

The isokinetic constants B and e ($B=\ln k_i$, $e=(RT_i)^{-1}$) quantitatively express a kinetic interrelationship between the reactions comprising the set. This is described as "compensation" because the reduction in rate which was expected to result from an increase in activation energy, however, did not occur for the set of reactions obeying Eq. (1), where

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there is a compensatory increase of A. Indeed, it is easily shown by the author [1] that all reactions within such a set proceed at identical rates (equal rate constants, k_i) at the isokinetic temperature T_i. It is always essential that considerations of compensation phenomena are based on comparisons using rate constants (k, A and E) expressed in identical units, appropriate to the system under consideration. In catalysis rates may often be reported as reciprocal time or, if known, expressed per unit area of active solid.

Isokinetic behaviour was first described by Constable [2] in the field of heterogeneous catalysis. Numerous further examples of this pattern of behaviour have since then been reported by the author, Cremer and Bond, [1,3,4] for many and varied surface reactions, though it must be pointed out that a similar pattern of behaviour occurs in other diverse physical and chemical rate processes [1]. Many and varied possible explanations of isokinetic behaviour have been proposed [1] but no satisfactory theoretical interpretation has yet been accepted generally. Consequently, the recognition of the existence of isokinetic behaviour for a set of related reactions has, so far, provided little theoretical insight into the understanding of the chemistry of the reactions involved or into identifying the factors controlling reactivity. It is probably true to say that most of the numerous reports of isokinetic behaviour in the literature implicitly regard Eq. (1) as an empirical relationship.

The purpose of the present article is to compare apparent Arrhenius parameters for a number of sets of related rate processes for which suitable kinetic measurements have been reported in the literature and to discuss the significance of the compensation trends discerned in these data. The system examined here in greatest detail, the set for which the most extensive measurements are available, is concerned with reactions resulting in the evolution of methane from nickel surfaces. Compensation trends recognized in 11 other systems are discussed more briefly. From these results it is concluded that the present theory provides no general mechanistic interpretation of the significance of apparent A and E values calculated for many heterogeneous catalytic reactions. It is concluded that the compensation trends reported arise because similar rate processes (within each set of reactions involving identical or closely related reactants and catalysts) exhibit similar reactivities. The reactions within each group of chemical changes proceed in comparable temperature intervals though the temperature coefficients for the individual reactions vary significantly for reasons that are incompletely understood at present. This conclusion may be applicable to a wider range of systems than those mentioned here and the present article contributes to the continued debate intended to provide an understanding of isokinetic behaviour [5–7].

2. Recognition of isokinetic behaviour

The iterative procedure in the kinetic calculations from which compensation behaviour is recognized has been described [5]. The pattern of fit to Eq. (1) is recognized from the individual points on a plot of log A against E, each point representing a distinct and different rate process. We are aware of no study in which controlled variations of identified factors results in continual progressive, predictable and reversible systematic changes in the magnitudes of A and E within the reactions that comprise a compensation set. There is no agreement as to which factors augment or diminish A and E values. Such information, if it could be reliably established, would be of value in providing a mechanistic basis for the phenomenon and, perhaps, controlling catalytic behaviour. Although examples of compensation behaviour are to be found widely dispersed throughout the catalytic literature, this often appears as a secondary objective of the study. Specific investigations of the effect itself are less common. Perhaps kinetic experiments undertaken to compare directly the magnitudes of Arrhenius parameters from well characterized related systems would enable the parameters controlling reactivities and the temperature coefficients of reaction rates to be more clearly identified and understood.

[We may note, in parenthesis, that reported magnitudes of A and E provide an important method of expressing levels of reactivity and enable comparisons to be made throughout the field of kinetics. This communication function is important, widely used and independent of any theoretical significance the terms may possess].

The contribution of experimental errors towards the appearance of isokinetic behaviour is difficult to assess [6]. Every rate coefficient measurement is subject to some uncertainty arising from the inaccuracies in each determination of extent of reaction, time and temperature. These errors are reflected in the precision of the calculated A and E values and ultimately in the B and e values [5]. Moreover, it is almost invariably assumed that the Arrhenius equation is strictly applicable [1], and the possibility of the fit of data to an alternative k/T functional relationships is not usually considered. We may, however, note that the Boltzmann energy distribution does not necessarily apply to surface bonded immobilized material. The Arrhenius constants calculated for heterogeneous processes do not, therefore, necessarily possess identical significance with the models developed in the theory of homogeneous rate processes.

3. Determination of a set of reactions exhibiting isokinetic behaviour

The provision of criteria which specify all possible reactions that constitute a set that exhibits isokinetic behaviour has rarely been attempted. In the absence of suitable chemical criteria, no reliable recognition of what constitutes a set is possible, comprehensively including all those systems that are relevant and excluding all others. At present it would seem that if the (A, E) values measured for a group of arbitrarily selected "similar" reactions fall close to a line expressed in the form of Eq. (1), then "there is isokinetic behaviour". Points remote from the line may be excluded for that and no other reason justified through chemical or theoretical factors. It has long been recognized [8] that this procedure involves an unacceptably large element of subjectivity and is not amenable to statistical consideration in delimiting the set that exhibits a compensation effect. We are aware of no studies in which attempts have been made to define the totality of the rate processes that constitute a set exhibiting isokinetic behaviour. Similarly, we are aware of no studies specifically directed towards delimiting the extreme range of possible A and E values or attempting to characterize the parameters that control their systematic variations within the overall limits.

Another feature of isokinetic behaviour that merits further critical consideration is the linearity of the Arrhenius plots in the vicinity of the isokinetic temperature [1]. This temperature represents the point of inversion of reactivity within the set of reactions that constitute the isokinetic relation and is sometimes outside, or at a limit of, the temperature interval of the kinetic measurements. It could be of considerable theoretical interest and, indeed, potential practical value, to determine whether or not such inversion occurs in practice, because the catalysts most active at high temperatures (large E) are expected to be those of relatively least activity at lower temperatures. If kinetic behaviour was not in accordance with this expectation from Eq. (1), whatever variations were found would be of value in formulating a theoretical explanation for isokinetic behaviour.

Isokinetic effects have been recognized and compensation parameters listed [1] for chemical changes proceeding on different catalysts, where the reactions of each set are related through common features of the catalyst, of the chemical transformation, of the reactants and/or of the products. The similarity of reactivity inherent in obedience to the isokinetic relation has been ascribed [7] to control through common features in the reaction mechanism. We believe that a profitable approach towards increasing understanding of isokinetic phenomena is by considering the effect itself rather than by regarding it as a subsidiary feature of other kinetic measurements or as a theoretical conundrum to be examined in isolation from the chemistry of the set of participating rate processes. Early studies (see, for example, Cremer [3]) investigated the influences of catalyst (thermal) pretreatments on the magnitudes of A and E (and, therefore, compensation behaviour) for a suitable heterogeneous reaction. Such experiments were designed to determine directly the effect of catalyst modification on magnitudes of Arrhenius parameters. Any changes were then expected to yield evidence that could be interpreted to provide a theoretical explanation for the fit of data to Eq. (1). More recently, it seems (at least to the author) that there have been fewer attempts to design experiments capable of resulting in controlled and perhaps predictable variations in A and E. Reports of kinetic studies now sometimes mention the existence of a compensation effect but reasons for the linked changes in Arrhenius magnitudes, and why values are high or low, are neither investigated nor discussed.

To illustrate the latent extent that isokinetic behaviour may exist in reported kinetic data for some selected reactions we now consider together some relevant features of system for which extensive and most reliable rate measurements are available: these may be loosely classified as "cracking reactions on nickel".

4. Cracking reactions on nickel

In the previous review 43 systems were included in the set exhibiting an isokinetic relation concerned with various types of cracking reactions on nickel [1]. The overall ranges of the Arrhenius parameter values were large, $35<E<244$ kJ mol^{-1} and $22<\text{Log } A<39$ (A/molecules m^{-2} s^{-1}) and the isokinetic temperature, T_i, was 527±20 K ([1], Fig. 2 and Table 1).

In the present analysis we now introduce a further requirement, that each rate process incorporated in the isokinetic relation records the temperature interval used for the measurement of the Arrhenius constants reported. Again, all frequency factors refer to unit area of catalyst surface (molecules m^{-2} s^{-1}). From the previous set of 43 systems, 31 of these (A, E) values were identified as conforming to the revised specification. (We recognize an inevitable subjective element of choice in this selection.) To these we add a further 12 acceptable kinetic reports, found in a further literature search, to give 43 rate measurements that constitute the set giving the isokinetic relation to be considered here, incidentally showing a somewhat greater scatter than previously [1], Fig. 1. The estimated isokinetic temperature, 540±30 K, also showed enhanced uncertainty though the previous value [1] can, perhaps, be regarded as remaining acceptable, 527±20 K.

In this isokinetic relation for the set of 43 reactions on nickel, the average temperature interval used for Arrhenius constant determinations was 48 K: 9 studies used a temperature range of 25 K or less and 8 studies used 70 K or more. The average ranges of measured reaction rates were X12 (logarithmic mean) and X37 (arithmetic mean). Thus, kinetic investigations were usually most concerned with an approximately 20-fold increase in reaction rate across a 48 K temperature range. The mean value of E was 113 kJ mol^{-1} (from $17<E<247$ kJ mol^{-1}).

5. Chemical characteristics of this set of cracking type reactions that exhibit compensation behaviour

Each of the 43 reactions of the present set was incorporated because it could be regarded as being chemically related to hydrocarbon cracking reactions on nickel. For most of the rate processes listed,

Table 1
Hydrocarbon cracking reactions on nickel: compensation set. Reaction sequence based on rate at compensation isokinetic temperature (T=527 K)

Reaction	Log k_T Isokinetic T=527 K	Log$_{10}A$ molecules m^{-2} s^{-1}	E kJ mol^{-1}
$CO+H_2$	21.1	31.3	103
Cyclopropane cracking	20.1	23.3	31.3
Cyclopropane cracking	19.9	28.5	67
CO_2+H_2	19.4	26.5	72
Ethane cracking	19.2	35.7	167
Ethane cracking	18.7	35.6	170
CH_4+D_2	18.6	26.0	75
i butane cracking	18.2	30.8	126
$Ni_3C + H_2 \rightarrow CH_4$	18.2	32.2	140
Propane exchange (III)	17.8	27.0	92
Ethane cracking	17.8	29.0	115
$HCN + H_2$	17.7	24.4	67
$C_2H_5NH_2 + H_2$	17.7	22.5	47.2
$Ni + C_2H_6 \rightarrow H_2$	17.7	25.7	81.5
Propane cracking	17.4	30.4	130
Ethane cracking	17.3	35.3	180
Ethane cracking	17.3	35.3	180
$(C_2H_5)_2O + H_2$	17.3	31.8	145
Ethane exchange	17.3	24.8	75.2
$CH_3NH_2 + H_2$	17.2	22.8	55.6
$CH_4 + Ni \rightarrow H_2$	17.2	26.6	96
Pentane cracking	17.1	30.1	130
Ethane exchange	17.1	24.8	75.2
n-Butane cracking	17.0	32.5	142
Pentane cracking	17.0	30.3	134
Methane exchange	16.9	29.3	124
Propane cracking	16.7	36.8	205
Ethane exchange	16.7	27.6	109
Cyclohexane decomposition	16.6	25.3	88
Propane cracking	16.5	22.8	62.7
$CO+H_2$	16.3	23.8	75
Methane exchange	16.2	26.2	100
Cyclohexane exchange	16.2	21.7	55
Ethane cracking	15.7	39.8	242
Ethane exchange(100)	15.7	24.4	88
$Ni_3C+H_2 \rightarrow CH_4$	15.7	17.5	17
CH_4+D_2 exchange	15.6	33.5	180

Table 1
(Continued)

Reaction	Log k_T Isokinetic T=527 K	$\mathrm{Log}_{10}A$ molecules $m^{-2}\,s^{-1}$	E kJ mol^{-1}
Ethane cracking	15.3	39.9	247
Ni+CO→Ni_3C	15.0	29.3	146
CH_4+D_2O exchange single	14.9	20.8	60
CH_4+D_2O exchange multiple	13.4	27.0	137
Ethane cracking	12.7	27.7	150
Ethane exchange	12.4	20.5	80

Kinetic data in Table 1 were obtained from the following **J. Catal**.

- 1 (1962) 227,
- 5 (1966) 250,
- 8 (1967) 48,
- 11 (1968) 326,
- 13 (1969) 345,
- 14 (1969) 148,
- 22 (1971) 226,
- 24 (1972) 187, 283,
- 30 (1973) 250,
- 37 (1975) 114, 449, 462,
- 39 (1975) 181.

Catal. Rev.

- 3 (1969) 175.

Proc. Roy. Soc. (Lond.)A

- 217 (1953) 376,
- 223 (1954) 361,
- 244 (1958) 398,
- 271 (1963) 402.

J. Phys. Chem.

- 67 (1963) 841,
- 68 (1964) 2962.

Trans. Faraday Soc.

- 54 (1958) 1692,
- 64 (1968) 1102,
- 68 (1972) 600.

Bull. Soc. Chim. Fr.

- (1966) 1369.

Int. Congr. Catal. 3rd

- (1964) 1048.

reactants and products contain both carbon and hydrogen though oxygen or nitrogen were present in some, and methane formation was often involved. The present section considers critically the problems of objectively classifying reactions that meaningfully constitute the isokinetic set. The available data are presented in the form of a composite Arrhenius plot in Fig. 2. The 35 lines included specify the temperature ranges used to determine the (A, E) values reported in the literature. The 8 lines omitted were outside the temperature range that permitted convenient comparative representation of behaviour in the vicinity of the estimated 'best' isokinetic temperature, 527 K.

Table 1 lists reactions of the set in the sequence of decreasing Log k_T values at the isokinetic temperature 527 K, estimated by extrapolation of the Arrhenius plots where necessary. All rate values reported below in brackets are defined as Log (k_T/molecules $m^{-2}\,s^{-1}$) The overall range of values was from (12.4) to (21.1) and the mean was (17.4). Magnitudes of A and E reported by authors have been used and no account has been taken here of the estimated error limits in preparing Fig. 2.

Two of the four most rapid processes at 527 K were $CO+H_2$ (21.1) and CO_2+H_2 (19.4), which are readily recognized as being chemically different from cracking reactions (despite CH_4 formation) and therefore can be excluded from the set. The other two relatively rapid reactions were cyclopropane hydrogenation, (20.1) and (19.9), involving opening of the strained ring and may similarly be omitted from the set.

At the other end of the range (Table 1), ten of the slowest rate processes (12.4)–(15.7) included a further four chemical changes that are recognizably different from cracking, despite yielding CH_4 product. The following are, therefore, deleted from the set: $Ni_3C + H_2$ (15.7), Ni_3C formation (15.0), and exchange $CH_4+ D_2O$ both single (14.9) and multiple (13.4).

The above arguments justify the exclusion on chemical criteria of eight reactions from the set originally identified, these are at the outer limits of indicated rates at the isokinetic temperature. With a single exception, ethane cracking (12.7), all 34 remaining values are between (15.3)–(19.2), or (17.1+2.1) and 24 of these are (17.0+0.8). The identification of this preferred value constitutes the justification for our continued consideration of this isokinetic behaviour. The 24 'best' selected points encompass a variety of diverse chemical processes and define the very satisfactory line (●) on Fig. 3, for which the isokinetic temperature is 522 K.

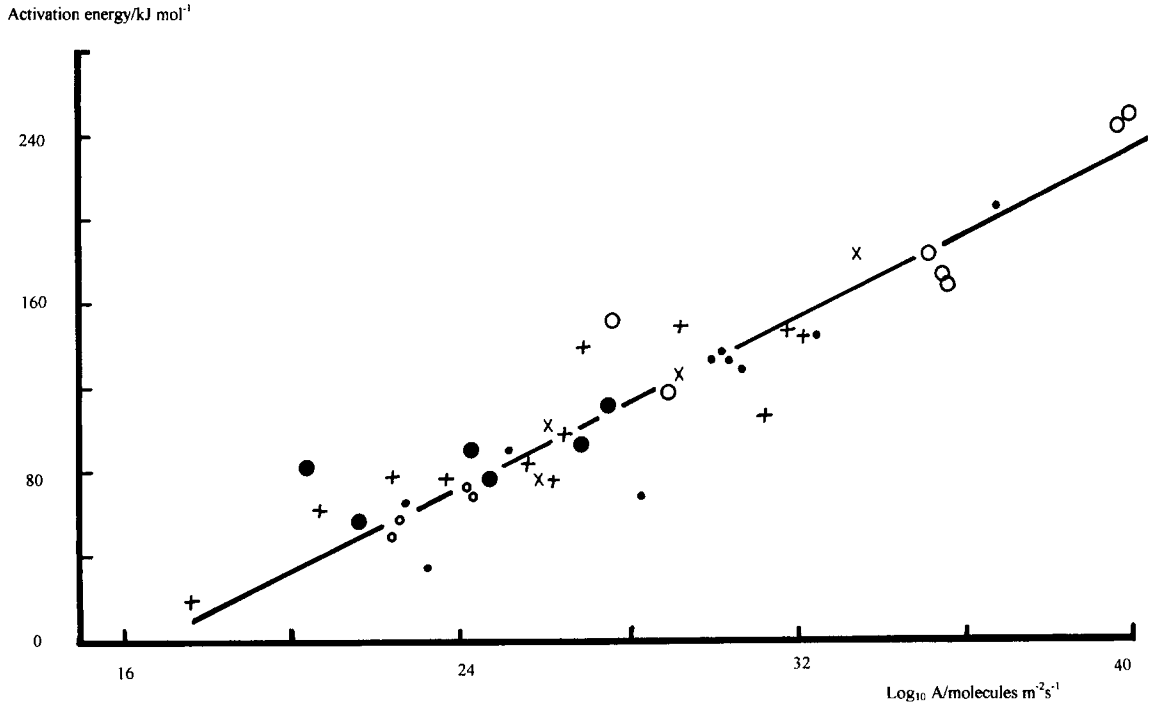

Fig. 1. Compensation plot for 43 related reactions classified as "cracking reactions on nickel". Methane exchange (×), ethane cracking (○), other hydrocarbon cracking (●), nitrogen compounds, (o), ethane and propane exchange (•), other reactions (+).

5.1. *Ethane hydrogenolysis*

The data in Table 1 include 8 kinetic studies of ethane hydrogenolysis on nickel. The Log (k_T) values for these, (12.7), (15.3), (15.7), (17.3), (17.3), (17.8), (18.7) and (19.2) extend across almost the overall range (12.4)–(21.1) characteristic of our total present isokinetic set. The scatter of these reported kinetic parameters make it difficult to state quantitatively an "absolute reactivity" because of the differences between the reported kinetic parameters from the several independent studies of the same chemical process. Moreover, the temperature intervals of the various chemical studies were significantly different, though many extended to ca. 520 K. The mean activation energy was 190±25 kJ mol^{-1} (seven values were between 150–247 kJ mol^{-1} and one was lower, 115 kJ mol^{-1}) and the mean Log A was 34.8 (values were 27.7–39.9). The isokinetic plot obtained from these data was unsatisfactory and indicated only an approximate isokinetic temperature of ca. 650 K.

While such large variations in kinetic parameters reported for the same apparently simple and well-studied reaction remain unexplained, the interpretations of the mechanistics significances of E and A values must be regarded as, at best, unreliable and, more realistically, as speculative. The wide range of A and E magnitudes reported by different workers, using diverse catalyst preparations and various reaction conditions, make it unreasonable to identify these parameters (on the usual transition state model) with the energy required for bond rupture and the frequency factor for surface rate processes, respectively. Indeed, the overall range of reported k_T values for ethane hydrogenolysis on nickel was comparable with that for the 43 more diverse chemical reactions incorporated in our original isokinetic set (Table 1).

5.2. *Constant experimentalist*

The present isokinetic set includes 10 kinetic studies, of distinct and different rate processes, studied by Kemball et al. and a further 13 by Anderson et al.,

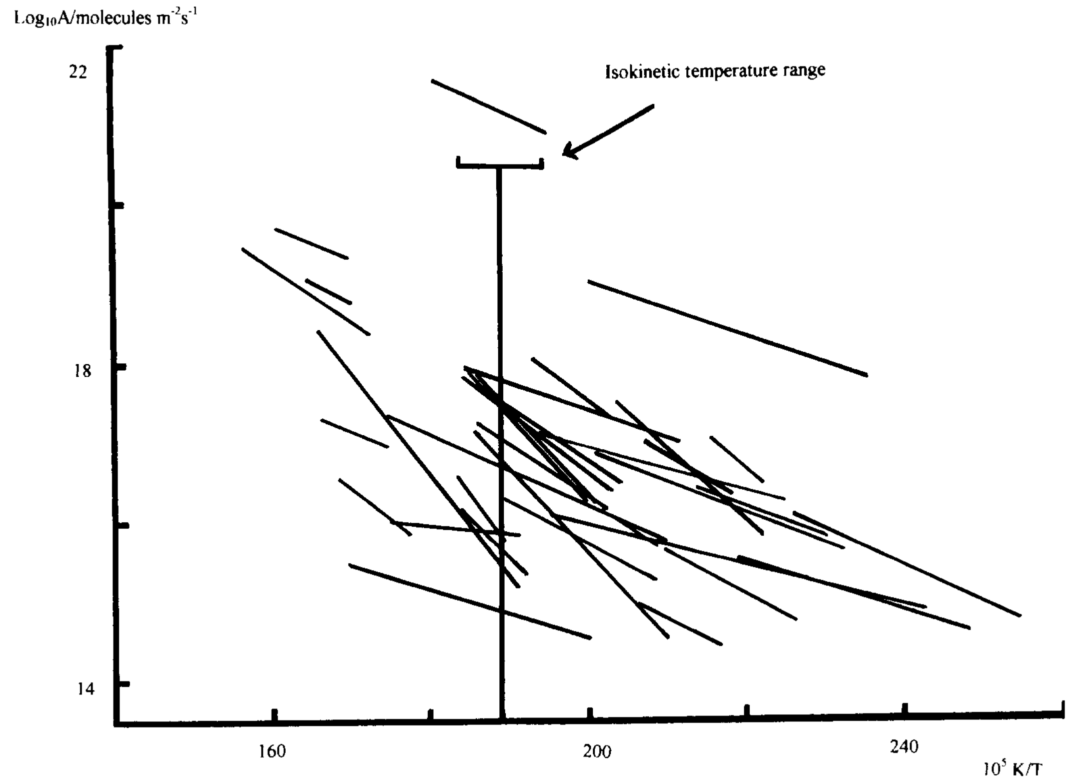

Fig. 2. Composite Arrhenius plot for 35 of the reactions incorporated in the set "cracking reactions on nickel". The remaining 8 results were beyond the temperature interval conveniently displayed here and have been omitted. The scatter illustrates the variation in reactivity found in what has been recognized as a compensation effect.

concerned with hydrocarbon exchanges and cracking on nickel. These 23 (A, E) values exhibit the very satisfactory isokinetic relation, shown in Fig. 4, for which the isokinetic temperature was 543 K, close to the upper limit of the range mentioned above for cracking reactions on nickel. A probable explanation is that the isokinetic pattern identified in the different reactions (incorporating constancy of reactivity) derives from common features of experimental technique, such as similarities in catalyst preparations, reactant pressures, purification of reactants, rates extending between comparable limits, etc. Furthermore, it is probably significant that Kemball and Anderson collaborated and used similar experimental methods.

It would appear therefore, that the more consistent isokinetic behaviour can be found between studies concerned with diverse reactions investigated by similar techniques than from the same reaction examined by different workers. Catalyst activity and kinetic behaviour may, therefore, be dominated by pretreatment, form (wire, foil, film etc.), reactant pressure, reaction conditions, etc. Until reliable and reproducible kinetic results can be obtained for a specified reaction between different studies, a considerable element of speculation must remain in the interpretation of rate data and apparent magnitudes of Arrhenius parameters for heterogeneous reactions. Perhaps catalytic chemists should direct more attention towards the attainment of reproducibility of kinetic behaviour and to establishing reasons for the large variations between different workers. Activation energy values reported in the literature show much greater relative variations than would be regarded as acceptable in other areas of chemistry, for example in reporting the magnitudes of reaction enthalpies in thermochemistry.

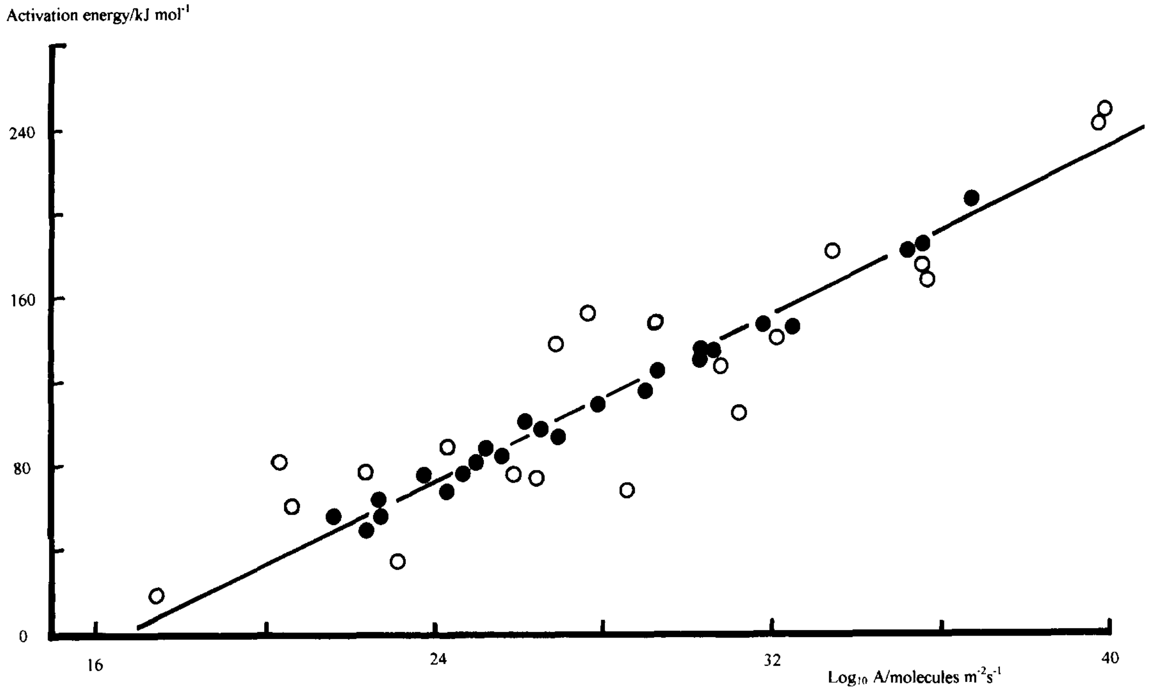

Fig. 3. Compensation plot for set of 'best 24' reactions (●) (as discussed in the text) from "cracking reactions on nickel" set. Other values shown in Fig. 1 have been included (○)

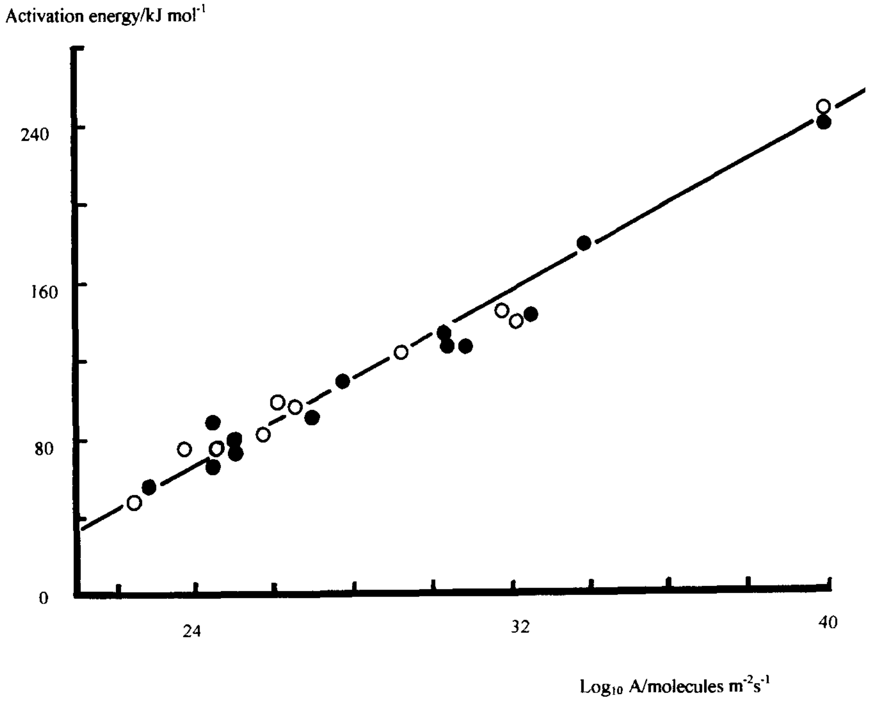

Fig. 4. Compensation plots for "cracking reactions on nickel" including only results by Kemball (○) and by Anderson (●) (see Table 1).

5.3. Other reactions on nickel

We note from Table 1 in [1] that the isokinetic temperature for cracking on nickel (527 K) is similar to values reported for other processes on the same metal, (dehydrogenation and hydrogenation)–500 K and formic acid decomposition –522 K. The value for (exchanges and hydrogenations) –607 K was somewhat greater. These temperatures are somewhat less than the mean value of T_i for cracking reactions obtained by including data for several metals (580 K, See Table 3A of [1]). This is consistent with the well-known relatively high activity of nickel in promoting hydrocarbon cracking, together with the possibility that it may exhibit similarly large reactivity for a number of other related heterogeneous reactions.

6. The isokinetic temperature and temperature interval of kinetic studies

It has been shown above for cracking reactions on nickel that the isokinetic temperature, T_i is within the temperature interval across which the kinetic measurements were made. Table 2 lists values of T_i for a variety of heterogeneous reactions, selected to include the diverse types of chemical changes that are broadly representative of current interests in the field. With one exception, ethanol on Cu, and one possible exception, C_3H_8 on Ru, T_i is within the interval used for kinetic measurements. Compensation behaviour occurs, therefore, where there are similar levels of catalyst reactivity, though within each set of chemically comparable rate processes the individual reactions exhibit significantly different temperature coefficients (*A* and *E* values).

7. Oxidation: $CO + 1/2\ O_2 \rightarrow CO_2$ on platinum

In a kinetic study [9] of $CO + 1/2\,O_2 \rightarrow CO_2$ on platinum between 460–520 K, the reported values were E=140–210 kJ mol^{-1} and *A* values were 10^{36}–10^{43} molecules $m^{-2}\ s^{-1}$, which is outside the expected [4] range for heterogeneous processes, maximum value ca. 10^{32}. The pressure dependencies [10] of reaction rate $(= kP_{CO}^{-1.0}P_{O_2}^{+1.2})$ are consistent with the conclusion that under the usual reaction conditions the metal surface is almost exclusively covered by CO and the oxygen occupancy is small.

In the absence of CO, oxygen is readily chemisorbed on clean platinum and desorption occurs [11] at ca. 585 K, above the temperature of the present catalytic reaction. In contrast, CO chemisorbed alone is thermally desorbed [12] at the lower temperature, ca. 525 K. The similarity of this value (525 K) leads to the conclusion that surface site vacancies resulting from CO desorption permit oxygen uptake. Subsequent reaction will then contribute towards further reduction in CO coverage. An increase in the relative effectiveness of these processes across the temperature interval studied is then expected to result in a high *A* value for the catalytic reaction. It has already been pointed out (appendix in [1]) that temperature dependent changes in the frequency of occurrence of the reaction situation can result in isokinetic behaviour and are a factor in determining the magnitudes of *A* and *E*.

In the absence of detailed quantitative data relating to surface occupancy for cracking reactions on nickel and without an extensive set of compensatory data for oxidation reactions on platinum, a detailed comparison between these two systems cannot be made. Isokinetic behaviour for oxidation reactions on platinum is apparently restricted in extent (refer Table 2, line H in [1]) and can be explained by variations in the temperature dependencies of the adsorption coverage by one or both participants [1].

8. Errors in measurements of reaction rates

Values of both *A* and *E* are subject to experimental uncertainty, often reported as $\mathrm{Log}\,A \pm 0.3$ and $E \pm 2.5$ kJ mol^{-1}. These errors are relatively small compared with the ranges of variations of these parameters usually found for the isokinetic relation. Two much larger potential sources of uncertainty, that are discussed much less frequently, are stable catalyst activity and the active catalyst surface area.

8.1. Stable catalyst activity

The activity of a catalyst often varies during initial usage, freshly prepared material sometimes being

Table 2
Comparison of isokinetic temperature and temperature intervals used to measure kinetic data in various reaction sets showing isokinetic behaviour

Reaction	Approximate temperature interval used in kinetic measurements (K)	T_iK	References
C_2H_5OH on Cu[a]	495–528	ca. 555	F.H. Constable, Proc. Roy. Soc. A (Lond.),108 (1923) 355.
N_2O on CuO[a*]	580–820	800	E. Cremer, Adv. Catal., 7 (1955) 75.
Formic Acid on ignited magnesite[a*]	606–735	690	E. Cremer, Adv. Catal., 7 (1955) 75.
C_3H_8 on Ru[*]	388–425	433	Po K. Tsjeng and R.B. Anderson, Canad. J. Chem. Eng., 54 (1976) 101.
Unsaturated alcohol hydrogenation on Ni[b*]	293–313	ca. 305	J.M. Campelo et al., J. Catal., 97 (1986) 108.
Exchange on WS_2 and MoS_2[c*]	195–553	464	A.K. Galwey, Adv. Catal., 26 (1977)247, Table 2 and p.287.
Cracking on WS_2 and MoS_2[d*]	389–578	532	A.K. Galwey, Adv. Catal., 26 (1977)247, Table 2 and p.287.
Hydrocarbon desorption from clays[e*]	400–570	517	M.C. Wilson and A.K. Galwey, J. Chim. Phys., 73 (1976) 441.
Ethene hydrogenation on Ru clusters[*]	345–515	345	R.B. Moyes et al., J.C.S., Faraday I, 82 (1986) 2719.
CO and CO_2 hydrogentation on Ru clusters[f*]	444-635	612	S.D. Jackson et al., J.C. S., Faraday 1, 83 (1987) 905.
N_2O on Pt/Al_2O_3[f*]	703–803	803	R.J. Mikovsky and R.F. Waters J. Phys. Chem., 59 (1959) 985.

[a] Early recognition of isokinetic behaviour concerned systems in which the same reaction was studied on catalysts subjected to heat pretreatments of varying severity. Isokinetic temperatures were often close to the upper intervals of the kinetic measurements.

[b] Campelo et al. report various isokinetic temperatures related to sets defined by the reactant alcohols (allyl, methallyl and crotyl) (T_i: 274–354 K) or by the differently supported nickel (T_i: 260–438 K). We find a fair isokinetic trend including all data for which we estimate T_i=305±10 K.

[c] For exchange reactions (D_2/H_2, methyl and ethyl thiols etc.) rate constants at T_i =464 K were all within (or extrapolated to) the narrow interval Log_{10} (k_i/molecules m^{-2} s^{-1}) 14.7–16.2 with thiophene appreciably lower at 13.7.

[d] For cracking reactions on the same catalysts as c, Log_{10} k_i values were 14.0–15.6 (thiophene 13.3) at the relatively higher T_i=532 K.

[e] The composite Arrhenius plots for hydrocarbon desorption reactions from clays is shown in Fig. 5. All Log k_i values at 517 K were within the very narrow interval 13.4±0.3.

[f] In these trends the scatter was somewhat greater than is usually accepted in compensation behaviour though this obedience was not discussed in detail by the authors. Compensation trends were even less evident in reactions catalyzed by osmium clusters (see J. Catal., 86 (1984) 342).

[*] For every entry (except 1) the value of T_i was within the temperature interval used in the determination of Arrhenius parameters from which isokinetic behaviour was found.

more active than the level subsequently maintained over a long period of use. Moreover, there may be a slow diminution in reactivity. It is not always clear from published reports whether kinetic observations refer to an initial active state or an aged material, the differences in rates of catalytic processes can be substantial. The possible contributions from such variations in catalyst activity, together with effects on the magnitudes of A and E, must be incorporated in all comparisons of kinetic data, including isokinetic behaviour.

8.2. Catalyst active surface area

Probably the most significant uncertainty in the rate data used to identify isokinetic relations is the effective area of the participating surface metal. The mobility of surfaces during catalytic reactions makes active area determinations uncertain. The area after usage may change from the value at preparation [9] and it is important to confirm that the value measured was that which actively participated during the chemical change. For many catalysts, however, the meaningful determination of this parameter presents both theoretical and practical difficulties due to surface heterogeneity and sintering [4].

9. Arrhenius parameters

The usually very close fit of rate constants for heterogeneous reactions to the Arrhenius equation has (inter alia) resulted in a wide acceptance of the view that the magnitudes of A and E have similar signficances to those developed in homogeneous reaction rate theory. Reaction models derived from collision theory and from transition state theory are routinely applied to discussions of surface processes. Some experimental support for these parallels is found from simple adsorption processes studied on well characterized surfaces. However, for reactions of the types discussed here as exhibiting compensation behaviour, the surface processes can be expected to be very much more complicated. Different adsorbed species including reactants, intermediates, products and constituents from the catalyst phase, are expected to participate actively so that the overall behaviour is the resolution of several chemical interactions under the directions of an even larger number of controlling parameters. While, in principle, one step may dominate the kinetics of the chemical change of interest, this simplification cannot be assumed, or indeed expected, for many of the reactions of greatest interest. The Arrhenius parameters are now considered individually.

9.1. Activation energy

Garn [13] has drawn attention to the shortcomings in the theory underlying the application of the Arrhenius equation to reactions of solids. The Boltzmann energy distribution function does not express the energy apportionment amongst the participating species, as in homogeneous reactions. This criticism is also applicable to the immobilized participants in heterogeneous catalytic reactions. Brown and Galwey [14] have considered the distributions of both electronic and phonon energies in solids and pointed out that the functions applicable (Fermi–Dirac and Bose–Einstein statistics respectively) approximate to the form of the Arrhenius equation at the higher energies of interest. Accommodation of energy in surface electron accepting (catalytic) levels may then be followed by chemical change. The numbers and energy values of such reaction precursor sites may be highly sensitive to condition prevailing, surface composition and structure.

The variations pointed out in Table 1 and Fig. 1 and Fig. 2 for the reported magnitudes of Arrhenius parameters for ethane cracking are considerable and call into question the theoretical significance to be attached to the reported magnitudes of E for reactions of this type. The extent of such irreproducibility is not known because critical surveys of this type are rarely completed and many systems lack comparable, comparative investigations. It appears to the present author that there is little point in formulating theoretical explanations directed towards providing a reaction model of a rate limiting step for any system where such irreproducibility of behaviour has been demonstrated. This conclusion has been based on the large number of kinetic studies of the highest quality from different highly-respected laboratories cited in the present survey. Some unpalatable conclusions emerge from these comparisons. It may be that these systems are too complicated for meaningful fundamental study at present. It is necessary first to characterize the factors responsible for these variations of behaviour, so that reliable values of A and E can be agreed which may then be capable of interpretation. A knowledge of the factors responsible for the variations in apparent Arrhenius parameters may be helpful in understanding factors controlling their magnitudes. One alternative to seeking more reliable kinetic evidence is to attempt to replace the present theoretical framework and thus to provide an alternative explanation for E.

9.2. Frequency factor

It has already been pointed out that some calculated values of A exceed the maximum possible theoretical magnitude [4]. This further confirms the evidence of the inadequacy of the present theory.

9.3. Question

If we accept that the rates of many heterogeneous reactions are not controlled by a single rate controlling step, uninfluenced by other factors, and that the magnitudes of A and E show unacceptable irreproducibility, how do we explain isokinetic behaviour? One possible approach is to reverse the accepted procedure. It is shown in Table 2 that the activities of the catalysts within each set are similar: T_i values fall within the temperature range of each study. This common feature of the chemical processes participating is evidence that there are similar, or even common, reactivity controls within each set which may be capable of interpretation to identify the factors influencing the magnitudes of A and E. Compensation behaviour is the demonstration of a comparable level of reactivity within the set, consideration of this conclusion may be developed to establish the significance of A and E values which are not, at present, adequately understood and for which no satisfactory theory has yet been provided[1].

10. Towards a theoretical explanation of compensation behaviour

For the present representative sets of reactions that exhibit compensation behaviour, the comparisons have shown similar levels of reactivity, within the experimentally investigated temperature ranges. This is apparent in Table 2. The same conclusion also applies to Table 1 and Fig. 2 where 24 of the 43 values of Log k_T were (17.0±0.8: overall change of rate ×40) at 527 K (and $22.5<\text{Log } A/\text{mol m}^{-2}\text{ s}^{-1}$ <36.8; $47<E(/\text{kJ mol}^{-1}) < 205$:see Table 1). These, and indeed all the other chemical processes listed in Table 1, were promoted by nickel under reducing conditions and, therefore, expected to involve the metal. Common features of the reactions include the making and breaking of C–H bonds involving species adsorbed on the metal, together with strongly retained adsorbed hydrocarbon fragments [16] and most reactions of the set resulted in CH_4 desorption. It is suggested that surface processes for all the reactions of this group are subject to the same kinetic controls. Catalytic activity becomes appreciable above a threshold temperature common throughout the compensation set. Below this temperature chemical changes are slow because catalyst surfaces are effectively deactivated by the presence of long-lived, relatively stable adsorbed species.

The ranges, and scatter, of A and E values for all the reactions in Table 1 overlap with those applicable to ethane cracking Fig. 1 (though some of the other reactions give lower magnitudes of Arrhenius parameters). This comparable level of reactivity within similar adsorbed phases may be explained by a common temperature of appearance of intrinsic catalytic activity by the metal surface. [The value of T_i for cracking on nickel is similar to those for hydrogenation/dehydrogenation (500 K) and formic acid decomposition (522 K) on the same metal: see Table 1 lines J and L [1]]. T_i is substantially below the Tammann temperature for $Ni_3C+H_2 \rightarrow CH_4$ reaction studied 523–573 [17], evidence of the ability of carbon to migrate within the boundary layer. All reactions in Table 1 are envisaged as involving interactions between species composed of C, H and possibly Ni, together with Ni_3C, Ni metal and surface hydride.

Two of the other systems discussed in the present article give evidence that catalytic properties appear in the temperature range of onset of reactivity of the solid. Hydrocarbon desorption occurs at temperatures characteristic of the commencement of clay dehydration [18]. Surface textural reorganisation accompanied the oxidation of CO on platinum [9]. [The isokinetic temperature for $Li_2SO_4.H_2O$ dehydration 377 K was also in the range of the kinetic studies: ca. 320–410 K [15]].

Expressing the rate of the reaction ($C_{ads}+D_{ads} \rightarrow$Products) in the conventional form of the Arrhenius equation applied to a surface process, we have

$$\mathrm{d}[\text{Product}]/\mathrm{d}t = A_s[C_{ads}][D_{ads}]\exp(-E_s/RT)$$

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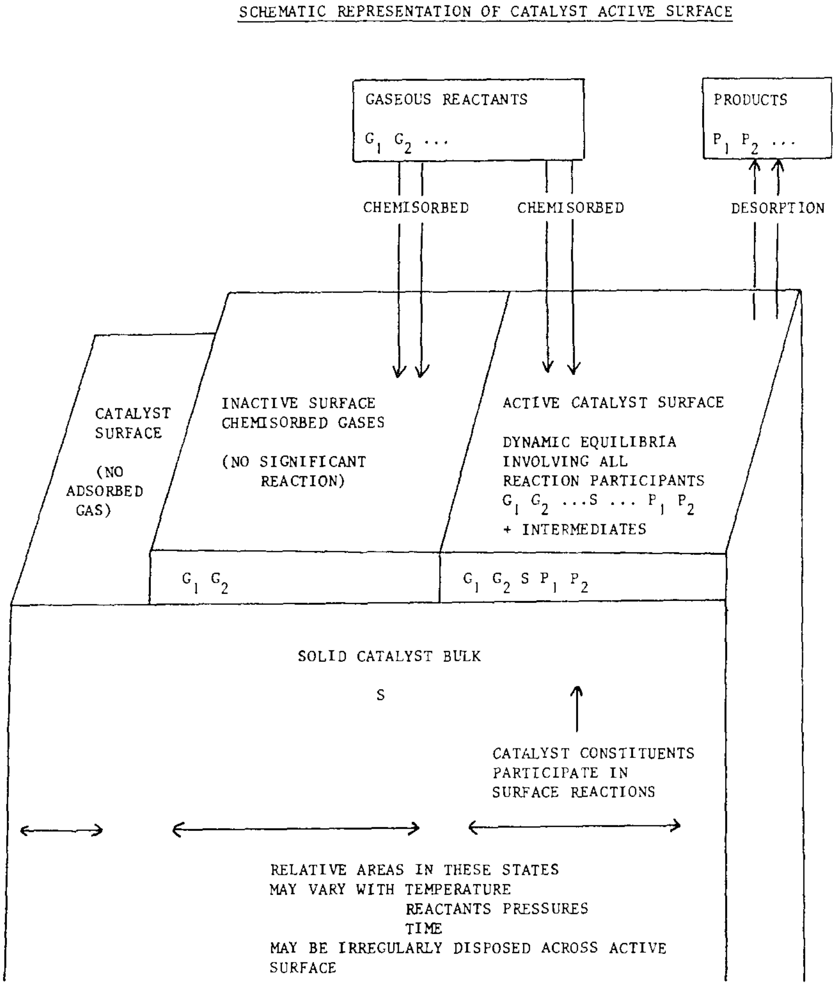
[1] It is worth mentioning that irreproducibility of kinetic behaviour is not confined to heterogeneous catalysis. Similar unsatisfactory irreproducibility concerning the magnitudes of A and E values has been found [15] for the dehydration of $Li_2SO_4.H_2O$. This solid state decomposition might appear to be mechanistically simpler than the reactions considered here, having been selected for comparative studies on the basis of a lack of complication (a forecast that was not confirmed by the observations). The scatter of reported magnitudes of Arrhenius parameters for this reaction is unacceptably large and compensation behaviour is observed [15]. Until satisfactorily reproducible and agreed values of A and E can be determined, and reasons for their apparent variations established, discussions of their theoretical significances must also remain sterile. Attempts to use this reaction as a standard for the quantitative comparison of kinetic measurements between different laboratories appear to have been abandoned. Perhaps catalytic chemists might undertake a similar initiative to establish reproducible, reliable and agreed kinetic parameters for cracking reactions on nickel.

It has been shown [1] that systematic variations with temperature of the effective area (in A_s) or of reactant concentrations $[C_{ads}]$ or $[D_{ads}]$ significantly influence the apparent activation energy, which is a composite parameter. Thus, reactions within a set exhibiting comparable reactivities, close to T_i (and, therefore, isokinetic behaviour) include rate processes exhibiting a range of A and E values. A number of factors may be expected to contribute towards different magnitudes of variations of A, $[C_{ads}]$ and/or $[D_{ads}]$ across the temperature interval. These include (inter alia) the chemical characteristics of the participating reactants and their adsorption followed by interactions on the surface, reactant concentrations (pressures) and the presence or absence of products, catalyst preparation and impurities. Thus, overall reactivities are similar within a set of surface processes involving common or similar intermediates but showing different values of E.

The above discussion includes features in common with a recent proposed explanation of compensation behaviour [19] which applies the transition state theory to surface processes by considering the entropy–enthalpy variations [20]. In the absence of knowledge of many aspects of the chemistry of the surface processes involved, we prefer the above approach as potentially more promising in advancing understand-



Scheme 1. Schematic representation of catalyst active surface.

ing at the present imperfect state of development of the subject.

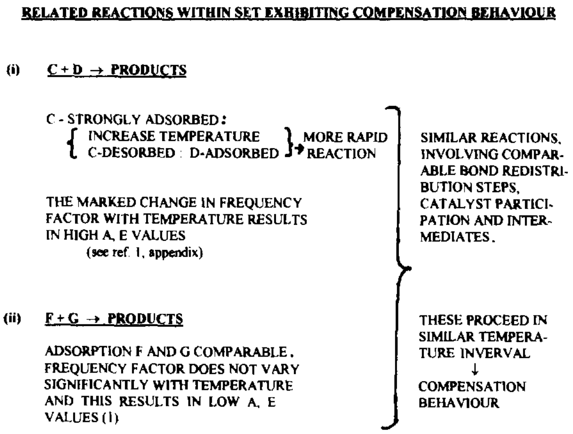
11. A proposed reaction scheme to explain compensation

The essential features of the proposed model, Scheme 1, is that the total available catalyst surface does not necessarily promote chemical change all the time and that components from the solid may be accepted into the active catalyst surface, the boundary phase or zone within which the catalytic chemical changes proceed. Mobility of metal atoms during catalysis has been demonstrated by the radical changes observed for platinum wire surfaces during promotion of carbon monoxide oxidation at 500 K, well below the melting point of the metal (2045 K) [9]. Metal atoms accommodated into the active zone of chemical change may leave the bulk, form surface intermediates (carboxyl, carbide, hydride, etc.) and be recycled many times within the active zone through the cycle of bond redistributions that yields the product. A possible chemical role for the metal from the catalyst is particularly mentioned here to emphasize the potential importance of this type of contribution to reactivity. The chemical properties of solid catalysts are often virtually ignored or are regarded simply as an array of immobile sites.

The active area participating in product formation may contain dynamic equilibria involving changes with (Scheme 1):

1. temperature (discussed previously ([1])),
2. every gas present (different kinetic parameters for adsorption and dissociation (A,E)) and active area controlled by the usually unknown amounts of adsorption of all reactants and intermediates participating,
3. readsorption of products,
4. extent of reaction (there may be catalyst sintering and possible initial activation),
5. strongly held impurities (poison) and/or inactive adsorbed material, and
6. catalyst crystal imperfections.

The essential point made here to explain the compensation behaviour is that all reactions of any set proceed on similar active phases (involving the same dynamic surface equilibria), through comparable chemical changes and react in a similar temperature interval. It is suggested that within each set reactions in the active phase are controlled by virtually identical bond redistributions, perhaps with a common intermediate and thus isokinetic behaviour is reached at the temperature of similar reactivity. This activity then extends to the greater portion of the available catalyst surfaces and reaction rates are similar, but not necessarily identical, probably requiring participation of comparable intermediates, catalyst components and precursors. Aspects of the variations in rates between related reactions within a particular set are represented in Scheme 2.



Scheme 2. Related reactions within set exhibiting compensation behaviour.

12. Conclusions

The above comparative analysis has focused attention on the possible conclusion that the compensation effect is the manifestation of a similarity of reactivity within a set of related (and, sometimes, subjectively selected) rate processes. Thus, the wide perception of the existence of isokinetic behaviour can be accepted as real effect. It is not to be regarded as an artefact or coincidence, a possibility that seriously concerned MacCallum and Monroe [21] because "*such a widespread artefact would seriously weaken the credibility of the basic data*".

Acceptance that the effect is real may enable reactions having similar kinetic controls to be grouped together for theoretical consideration of their detailed mechanisms. Comparisons of the relative magnitudes of A and E within each set should provide further insights into the factors determining reactivities. This approach inverts the more widely used sequence of interpretation of results through application of the theory developed for heterogeneous processes. However, the variations between different studies of the reported magnitudes of Arrhenius parameters suggests that their considerable sensitivity to unidentified features of experimental conditions has not yet been adequately recognized. This applied particularly, for example, to the ethane cracking reaction discussed above through consideration of the best kinetic data available from the literature. We conclude that the general application of the transition state theory to heterogeneous reactions of the types discussed above is premature. The collection of reliable, reproducible and agreed values of A and E for representative reactions must precede any detailed theoretical interpretation and the identification of the rate controlling parameters. In my view, therefore, the current problem in heterogeneous kinetics does not concern the existence of a compensation effect (which I accept as evidence of equivalence of reactivity) but is in the incomplete understanding of the reasons for irreproducibility of measured A and E values and their variations between related reactions of any compensation set. Compensation may therefore be explained as a set of reactions exhibiting common reactivity (isokinetic behaviour) because of a common mechanism whereby similar adsorbed intermediates undergo comparable changes in a dynamic active surface equilibrium in the same temperature interval.

A further paper is concerned with the significance of compensation behaviour in solid-state decompositions [22].

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