The Isokinetic Relationship

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1 Introduction

If we assume that we have available rate constants for some reaction measured at different temperatures, then these can readily be correlated by means of the Arrhenius equation

$$k = A. \exp(-E_a/RT) \tag{1}$$

Let us further assume that we have similar data for a series of *closely related* reactions (denoted by an index i). We then have a series of values of rate constants (k_i), pre-exponential factors (A_i), and activation energies ($E_{a.i}$) individually related by equation 2

$$k_i = A_i. \exp(-E_{a.i}/RT) \tag{2}$$

Since the reactions are closely related we are tempted to look for an empirical relationship linking these data.

In fact this has been done many times in many fields, often independently. One of the first was Constable[1] who found a linear relationship between the logarithm of the pre-exponential factor and the activation energies of the dehydrogenation of alcohol using different copper oxide catalysts. Many other catalytic studies involving this effect were reviewed by Schwab[2], by Cremer[3], by Galwey[4] and by Ranganathan[5]. However, compensation effects are found in most processes that involve activation, for example in vaporization;[6] solid state interdiffusion;[7-9] thermal dissociation of carbonates;[10] electron diffusion in

[1] F. H. Constable, *Proc. R. Soc. (London)*, 1925, **A108**, 355.
[2] G. M. Schwab, *Adv. Catal.*, 1950, **2**, 251.
[3] E. Cremer, *Adv. Catal.*, 1955, **7**, 75.
[4] A. Galwey, *J. Catal.*, 1983, **84**, 271.
[5] R. Ranganathan, N. N. Bakhshi, and J. F. Mathews, *Can. J. Chem. Eng.*, 1977, **55**, 544.
[6] R. Bjorklund, J. Lester, and K. Spears, *J. Chem. Phys.*, 1977, **66**, 3426.
[7] P. Winchell, *High Temp. Sci.*, 1969, **1**, 200.
[8] T. Dosdale and R. J. Brook, *J. Am. Chem. Soc.*, 1983, **66**, 392.
[9] S. Wach, *Diffus. Defect Monogr. Ser.*, 1983, 454.
[10] Z. Adony and G. Körösi, *Thermochim. Acta*, 1983, **60**, 23.

organic semiconductors;[11,12] pharmaceutical and biochemical systems;[13–16] electrode kinetics;[17] life times for thin film semiconductor interconnects;[18] chemical adsorption;[19] viscosity of liquids;[20] *etc.* A large number is found in homogeneous reactions and equilibria, either in the gas phase or in solution.[21–32]

Correlations of this type have been given many names, for example the compensation effect,[33–35] the enthalpy–entropy relationship,[29,36–39] the theta rule in heterogeneous catalysis,[2] the Meyer–Neldel rule in conductivity of metals,[11] the Zawadzki–Bretsznajder rule,[40] the Smith–Topley effect,[41] and the isokinetic relationship,[24,30,36–39,42] *etc.* For reasons that will become clear we will confine this review to the isokinetic relationship or IKR (which we define below, carefully distinguishing it from the compensation effect with which it shares a common origin).

Many of these rules and correlations have been reviewed extensively in the past. Among the most important reviews are those of Leffler and Grunwald,[29,30] Cremer,[3] Galwey,[34] Lumry,[43] Ritchie and Sager,[44] Hughes,[45] Hammett,[46] and Tomlinson.[13] From these reviews we get a general picture of an effect which, if

[11] W. Meyer and H. Neldel, *Z. Tech. Phys.*, 1937, **18**, 588.
[12] F. Gutmann and L. E. Lyons, 'Organic Semiconductors', Wiley, New York, 1967, pp. 428– 435.
[13] E. Tomlinson, *Int. J. Pharm.*, 1983, **13**, 115.
[14] E. Tomlinson and S. S. Davis, *J. Colloid Interface Sci.*, 1980, **76**, 563.
[15] S. S. Davis and E. Tomlinson, *Stud. Phys. Theor. Chem.*, 1982, **27**, 295.
[16] M. R. Eftink, A. C. Anusiem, and R. L. Biltonen, *Biochemistry*, 1983, **22**, 3884.
[17] R. Tamamushi, *Denki Kagaku*, 1980, **48**, 603.
[18] J. A. Schwarz and L. E. Felton, *Solid State Elect.*, 1985, **28**, 669.
[19] A. Tsiatsios and A. Lycourghiotis, *Chim. Chronika, N.S.*, 1978, **7**, 149.
[20] M. I. Shakhparonov and V. S. Sperkach, *Z. Fiz. Khim.*, 1980, **54**, 312.
[21] S. Wold, *Chem. Scr.*, 1972, **2**, 145.
[22] O. Exner, *Prog. Phys. Org. Chem.*, 1973, **10**, 411.
[23] O. Exner, *Prog. Phys. Org. Chem.*, 1964, **29**, 3133, 1094.
[24] W. Linert, A. B. Kurdjavtesv, and R. Schmid, *Aust. J. Chem.*, 1983, **36**, 1903.
[25] W. Linert, *Aust. J. Chem.*, 1985, **38**, 677.
[26] W. Linert, *Aust. J. Chem.* 1986, **39**, 199.
[27] W. Linert, *Chem. Phys.*, 1989, **129**, 381.
[28] S. Wold and O. Exner, *Chem. Scripta*, 1973, **3**, 5.
[29] J. E. Leffler and E. Grunwald, 'Rates and Equilibria of Organic Reactions', Wiley, New York, 1963.
[30] J. E. Leffler, *J. Org. Chem.*, 1955, **20**, 1020.
[31] O. Exner, *Collect. Czech. Chem. Commun.*, 1975, **40**, 2762.
[32] W. Linert and V. N. Sapunov, *Chem. Phys.*, 1988, **119**, 265.
[33] W. Linert and A. B. Kudrjawtsev, *Aust. J. Chem.*, 1984, **37**, 1139.
[34] A. Galwey, *Adv. Catal.*, 1977, **26**, 247.
[35] R. K. Agraval, *J. Therm. Analysis*, 1986, **31**, 73.
[36] O. Exner, *Collect. Czech. Chem. Commun.*, 1974, **39**, 515.
[37] O. Exner, *Collect Czech. Chem. Commun.*, 1966, **31**, 3222.
[38] O. Exner, *Collect. Czech. Chem. Commun.*, 1972, **37**, 1425.
[39] O. Exner, *Collect. Czech. Chem. Commun.*, 1973, **38**, 781, 799.
[40] J. Pysiak and B. Sabalski, *J. Therm. Analysis*, 1979, **17**, 287.
[41] E. P. Manche and B. Carroll, *Thermochim. Acta*, 1979, **31**, 387.
[42] L. G. Hepler, *Can. J. Chem.*, 1971, **49**, 2803.
[43] R. Lumry and S. J. Rajander, *Biopolymers*, 1970, **9**, 1125.
[44] C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, 1964, **2**, 323.
[45] E. A. M. Hughes, 'The Chemical Statics and Kinetics of Solutions', Academic Press', London, New York, 1971.
[46] L. P. Hammett, 'Physikalische Organische Chemie', Verlag Chemie, Weinheim/Bergstrasse, 1973.

valid, calls for an explanation. However, the physical significance (reality) of a simple linear relationship between $\ln(A_i)$ and $E_{a,i}$ has often been questioned,[22–29,36–39,47–57] and indeed it may all-too-often be an artifact arising from the means of evaluation of these parameters from the kinetic data (see below). Peterson[49] demonstrated that the related linear enthalpy–entropy plot can also be extremely deceptive and that it is not by itself a demonstration of any significant effect.

It was Exner[31,36–39] who realized that the problem lies in the fact that in testing the validity of the compensation effect, which is a linear correlation between activation energy and the logarithm of the pre-exponential factor, one encounters difficulties in that *both quantities are derived from the same data set* and are thus *statistically not independent*. He showed how this problem can be avoided, by means of different variables, as follows:

The linear relationship between E_a and $\ln A$ can be written in the form (3)

$$\ln A_i = \ln k_{iso} + E_{a,i}/RT_{iso} \tag{3}$$

Inserting (3) into (2) we get (4):

$$k_i = k_{iso}. \exp[-E_{a,i}(1/RT - 1/RT_{iso})] \tag{4}$$

which gives in the $\ln k$ *versus* $1/T$ plane (which we will refer to as the Arrhenius plane) a family of straight lines (5) intersecting at an ordinate position of $\ln(k_{iso})$

$$\ln(k_i) = \ln(k_{iso}) - E_{a,i}(1/RT - 1/RT_{iso}) \tag{5}$$

and an abscissa value of $1/T_{iso}$. Exner suggested that this single point of intersection of lines in the Arrhenius plane could be used for a sound statistical test since $\ln k$ and T are *statistically independent*; this is the basis of the **Isokinetic Relationship** or **IKR**. Note that for *actual experimental data* one may infer from such a point of intersection linearity between $\ln(A_i)$ and $E_{a,i}$, *but not the reverse* (*cf.* Exner[47])!

Both of these effects, namely the compensation effect and the IKR, can of course be expressed in differential form. Using Leffler's operator δ,[29] (δ refers to the variation of discrete values within the considered series) we have, for a single interaction mechanism, a linear plot of $\ln(A_i)$ *versus* $E_{a,i}$ with a slope given by

[47] O. Exner, *Nature*, 1964, **201**, 488.
[48] S. Wold and O. Exner, *Chem. Scr.*, 1973, **3**, 5.
[49] R. C. Peterson, *J. Org. Chem.*, 1964, **29**, 3133.
[50] B. E. C. Banks, V. Damjanovic, and C. A. Veron, *Nature (London)*, 1972, **240**, 147
[51] C. G. Swain, M. S. Swain, A. L. Powell, and S. Alunni, *J. Am. Chem. Soc.*, 1983, **105**, 502.
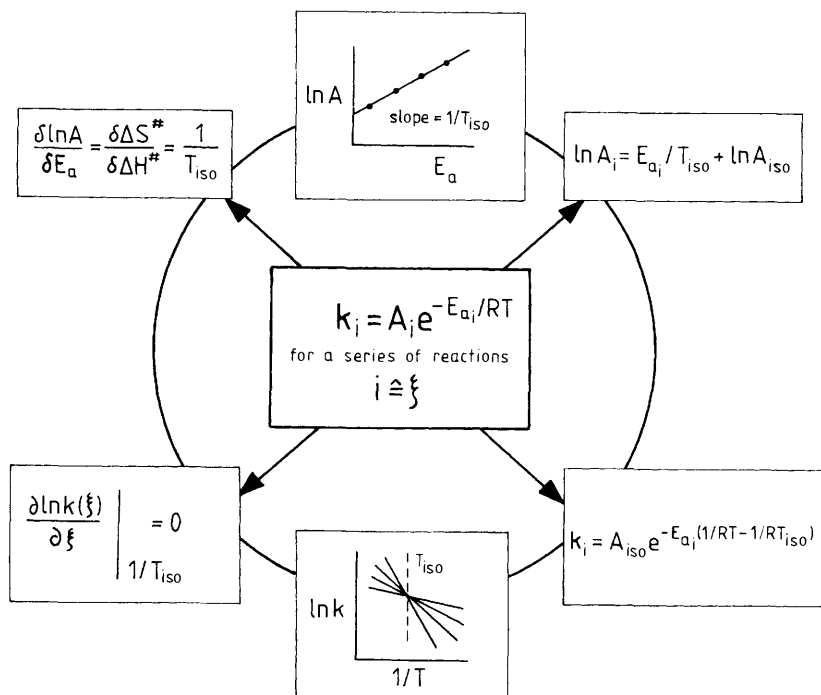[52] V. I. Shimulis, *Kinet. Katal.*, 1969, **10**, 1026.
[53] V. I. Shimulis, E. G. Guseva, and B. A. Giuntini, Deposited Doc., Viniti No. 4826 - 80, (1980).
[54] J. Sesták, *Therm. Analysis*, 1980, **1**, 29.
[55] J. M. Criado and M. Gonzalez, *Thermochim. Acta*, 1981, **46**, 201.
[56] V. A. Logvinenko, B. I. Peshchevitsky, and O. V. Gegola, *J. Therm. Analysis*, 1980, **18**, 463.
[57] A. K. Galwey and M. E. Brown, *J. Catal.*, 1979, **60**, 335.

Figure 1 *Different representations of the compensation effect (upper part) and the isokinetic relationship (lower part) in differential form (left hand side) and an integral form (right hand side)*

$$\delta \ln A / \delta E_a = 1/T_{iso} \tag{6}$$

and (6) can be used as a definition of the compensation effect.

In the same way, by using a *continuous* parameter, ξ (instead of the discrete i-values), we may write the IKR as

$$\frac{\partial \ln k(\xi)}{\partial \xi}\bigg|_{1/T_{iso}} = 0 \tag{7}$$

meaning that a temperature exists where differences between $\ln k$ within the series show a minimum, *i.e.* that there is a minimum in *selectivity* (see also Giese [58–61]).

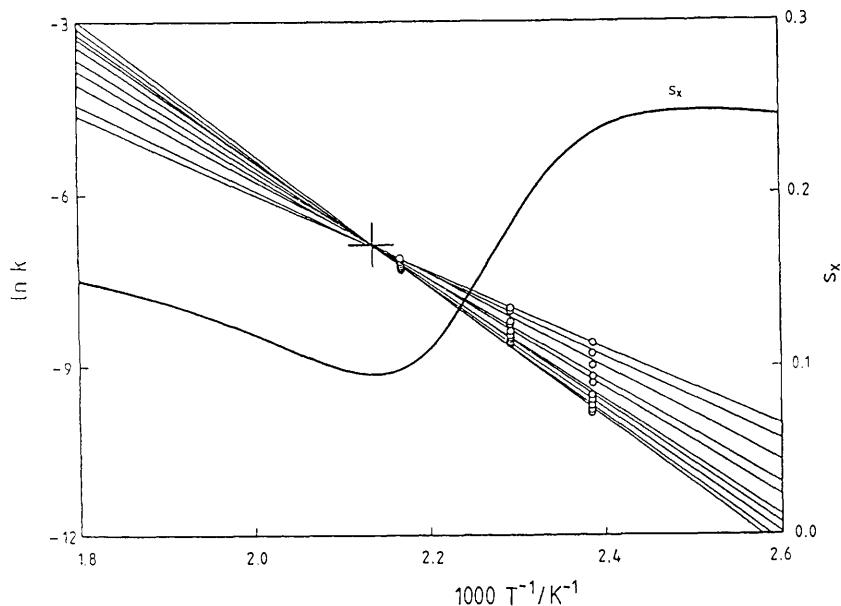The formulations and interrelations between various representations of the effect are summarized in Figure 1.

A good example of a statistically sound IKR, which we will refer to again in

[58] B. Giese, *Acc. Chem. Res.*, 1984, **17**, 438.
[59] B. Giese, *Angew. Chem.*, 1976, **88**, 161.
[60] B. Giese, *Angew. Chem.*, 1977, **89**, 162.
[61] O. Exner and B. Giese, *Angew. Chem.*, 1978, **90**, 816.

Figure 2 *Arrhenius plot of the formation of anilides of* N-*phenylsarcosine*[26,62] *from dimethylaniline with substituted chloroacetanilides in octanol. (Substituents in sequence of decreasing rate constant at the mean experimental temperature:* p-NO_2, p-CH_3CO, m-NO_2, m-I, p-Br, H, m-Br, m-CH_3, p-CH_3, 3,4-$(CH_3)_2$, p-OCH_3) (T_{iso} = 467 K; $\ln k_{iso}$ = 6.9)

this review, is the reaction of dimethylaniline with substituted chloroacetanilides (see Figure 2).[26,62] The information contained in such plots (which can be in either the Arrhenius or the van't Hoff planes—see below) exhibiting a common point of intersection lies at the centre of the Isokinetic Relationship.

2 Statistical Tests

Unfortunately, it is often not realized that the compensation effect itself, *i.e.* the linear relationship between $\ln(A_i)$ and $E_{a,i}$, is not open to sound statistical evaluation, despite the fact that Exner in fact made the point extremely clearly in a note to *Nature* as early as 1964.[47] To this day the problem of the existence of linear relationships between the mutually dependent enthalpic and entropic variables continues to be discussed[49,50] and this has unfortunately led to a profound distrust of the whole concept of an isokinetic relationship.

As has been pointed out above, however, this problem of interdependence can be avoided by expressing the effect as an intersection in the Arrhenius plane (or van't Hoff plane) and it is now necessary to demonstrate for any specific example that this is statistically significant and not a drafting artefact (it is all-too-easy to persuade oneself that such a point exists if the only test is trying to draw it!).

[62] Yu. V. Svetkin and M. M. Murza, *Reakts. Sposobn. Org. Soedin.*, 1971, **8**, 875.

There are two main statistical procedures for analysing the existence of an IKR from given data, namely that of Krug[63] based on a variation analysis of a ΔG and ΔH relationship, and a procedure based on the work of Exner,[36-40] showing that a common point of intersection exists in the Arrhenius or van't Hoff plot (or any other plot of straight lines which should be analysed in terms of an isoparametric relationship[64,65]). It should also be pointed out that these methods give the same results for T_{iso} and $\ln(k_{iso})$ and are about equal in their ability to accept or to reject the IKR if one is careful when setting up the statistical hypotheses to be rejected by the tests. (Some of the original papers unfortunately lay down incorrect statistical testing criteria for this problem, see references 64 and 65.)

In many ways the use of a slightly modified Exner method is much to be preferred as it gives directly (in contrast to Krug's method) the position of the characteristic parameters of the IKR, *viz.* T_{iso} and $\ln(k_{iso})$. Furthermore, Exner's test is not restricted to the values and the number of temperatures at which the members of the series are measured. In this procedure one compares the residual sum of squares for the *unconstrained lines* (*i.e.* summing up the square deviations for all straight lines as they are and without any connection) with that one of the *constrained lines* (*i.e.* the sum of square deviations when assuming a common point of intersection of the lines). T_{iso} is then defined by the minimum of the residual sums of the constrained lines when varying the abscissa of the intersection point along the $1/T$ axis. For the statistical F-test this common point is treated almost as a new measurement point, being the same for all lines. The basis of the F-test can then be described in two more-or-less equivalent ways: (i) does the inclusion of a common point of intersection adversely effect the mean deviation of measured points from the straight lines[21-28,47] or (ii) can the point of intersection be treated as if it was an experimental point within all the sets?[64,65] A modification of these tests has been developed that enables them to be carried out using a simple programmable calculator.[64]

From our point of view, the important outcome of these statistical studies is that they not only show that the isokinetic effect is real (*i.e.* highly significant) but also that they enable one to pin-point the conditions for such an effect to exist. We can summarize the position to date as follows: It has now been possible, using recently developed sound statistical tests, to re-examine an enormous range of kinetic and equilibrium data published over many years. This has been done, in part by Exner[36-40] and continued by Linert[27,64,65] and from this collection of—now statistically sound—T_{iso} values the following points may be deduced:
1. The IKR exists and is not merely the fulfilment of wishful thinking.
2. It is possible to find T_{iso} values close to or within the experimental range. (This is an important point when developing a theory to explain the effect.)
3. Gas-phase reactions very often show *isoentropic* behaviour.
4. In condensed-phase reactions: (i) Different reaction series very often show the

[63] R. R. Krug, *Ind. Eng. Chem. Fundam.*, 1980, **19**, 50.
[64] W. Linert, R. W. Soukup, and R. Schmid, *Comp. Chem.*, 1982, **6**, 47.
[65] W. Linert, *Inorg. Chim. Acta*, 1988, **141**, 233.

same T_{iso} value when performed in the same solvent or at the same catalyst. This is true even when the reactions have very different rate constants. (ii) The same reaction series performed in different solvents very often exhibit either different T_{iso} values, or no IKR at all.

5. Isosolvent relationships, that is an IKR for one reaction carried out in different solvents or on different catalysts (isocatalytic relationships) are *rarely statistically sound.*

6. A change in the mechanism is reflected by a change in the IKR (in accordance with Leffler's suggestion).[29]

Any successful theory must therefore be able to explain to some extent these six observed features of the isokinetic relationship. However, before describing and appraising such theories it will be helpful to discuss the more general problems of linear free energy relationships and their connection to the IKR.

3 Linear Free Energy Relationships or LFERs

The isokinetic relationship or IKR, when represented by the common point of intersection of lines in the Arrhenius plane is, as mentioned above, described by two parameters, namely $\ln k_{iso}$ (*i.e.* the ordinate position) and T_{iso} (*i.e.* the reciprocal of the abscissa position). It is important to note, however, that not only kinetic data are expressible in this way, but equilibrium data plotted as $\ln K$ *versus* $1/T$ graphs (or van't Hoff diagrams) are of the same mathematical form. In other words, kinetic and thermodynamic data may be treated in the same way— at least from the phenomenological point of view. Furthermore, it is always possible to derive thermodynamic information from kinetics. Thus we must expect to find a close connection between the IKR and the more general *linear free energy relationship* or *LFER* (see Appendix p. 504).

Broadly speaking, linear free energy relationships or LFERs are produced when rate constants or equilibrium constants (or related parameters describing kinetic and/or thermodynamical chemical behaviour) of a series of reactions are plotted against a characteristic quantity measured by means of another reaction series.[29,66,67] Typical examples would be the Brønsted[68,69] and Hammett[70] relationships, correlations with solvent parameters such as Gutmann's Donor Number (DN)[71] and Reichardt's E_t values,[72] and correlations with spectroscopic data like Goulden's rule,[73] *etc.* Excellent reviews of linear free energy relationships are to be found in the monograph by Wells[66] and that of Shorter.[74]

Figure 3 illustrates one of the most important relationships between a LFER

[66] R. P. Wells, 'Linear Free Energy Relationships', Academic Press, New York, 1968.
[67] R. D. Levine, *J. Phys. Chem.*, 1979, **83**, 159.
[68] J. N. Brønsted, *Chem. Rev.*, 1929, **5**, 238.
[69] R. D. Levine, *J. Chem. Rev. B*, 1979, **5**, 159.
[70] L. P. Hammett, 'Physikalische Organische Chemie', Verlag Chemie, Weinheim, 1973.
[71] V. Gutmann, 'The Donor–Acceptor Approach to Molecular Interaction', Plenum Press, New York, 1978.
[72] C. Reichardt, 'Solvent Effects in Organic Chemistry', Verlag Chemie, Weinheim, 1979.
[73] T. M. Krygowski and J. Guillemè, *J. Chem. Soc., Perkin Trans 2*, 1982, 531.
[74] J. Shorter, 'Correlation Analysis in Organic Chemistry: Introduction to LFER', in Oxford Chemistry Series, Vol. 42, Oxford University Press, Oxford, 1973.
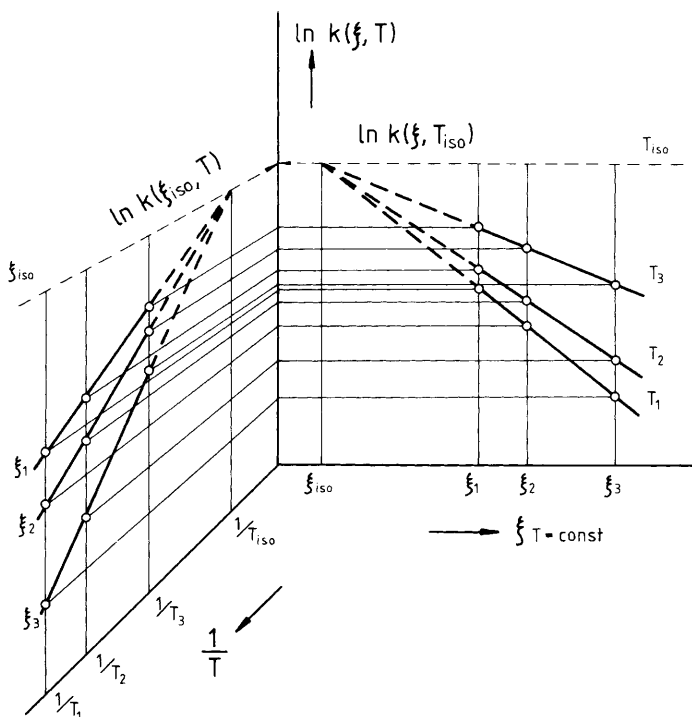
Figure 3 *Temperature-dependence of a well behaved LFER. Left-hand side: Arrhenius plot. Right hand side: Hammett plot*

and its associated IKR (for experimental examples see references 24, 25, 32, and 114). It can be shown that, whenever a LFER holds for at *least two* (or more) different temperatures, these LFER lines show either a common point of intersection or parallel lines.[25,26,29,32] (The latter can be considered to have an intersection point at infinity, corresponding to the 'isoenthalpic' case with $T_{iso} = 0$.) On the other hand, this means that plotting the *same data* in their Arrhenius or van't Hoff forms will *yield an IKR* with the *same ordinate* of the intersection point. To give an example for this situation the reaction series given in Figure 1 is plotted in its Hammett representation in Figure 4. This is the source of several relationships, which are mathematically based on transformations between different planes [32] (see Figure 5). In general it can be concluded, that whenever an IKR (or IER) is found a LFER with a single parameter must exist and *vice versa* (although the physical meaning of this parameter is often unknown, a representation of this parameter can always be found from the IKR).

From the chemical point of view these relationships are of importance because they have high predictive value as well as leading to conclusions with important consequences (for example it follows that Hammett parameters, σ, must be
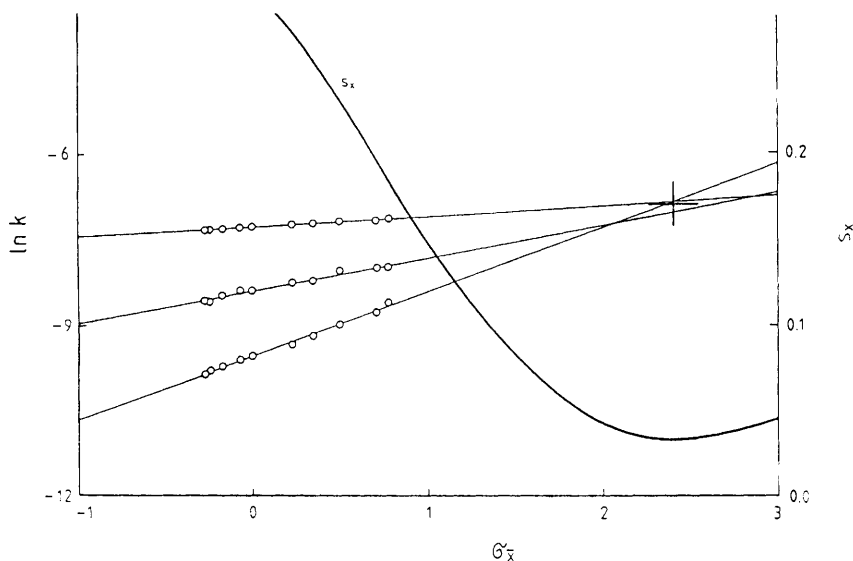
Figure 4 *Hammett plots at three different temperatures (146 °C, 167 °C, and 188 °C for increasing experimental k) for the formation of anilides of* N-*phenyl sarcosine* [26,62] *from dimethylaniline with substituted chloroacetanilides in octanol.* (σ_{iso} = 2.4; $\ln k_{iso}$ = −6.9)

temperature dependent and that the associated dissociation of substituted benzoic acids will show IKR behaviour). Note that in this respect the differences between the dissociation constants of the substituted benzoic acids are entropy controlled. Despite this σ can be correlated with enthalpy controlled reaction series, *which is only possible when isokinetic relationships exist.*[25,26] Analogously this is valid for the enthalpy-controlled Donor Number (negative ΔH value of the adduct between SbCl$_5$ and solvents dissolved in 1,2-dichloroethane) which can be correlated with free energies (*e.g.* redox potentials of metal ions in non-aqueous solvents, Gutmann[71]).

As pointed out above, illustrated in Figure 3, and exemplified in Figure 4 for a given reaction series, $\ln k_{iso}$ is the same in the Arrhenius- and in the more commonly used LFER-plane (in the latter the abscissa contains no temperature-dependent term). However, $\ln k_{iso}$, even when showing the same value, is not of the same physical origin as in the Arrhenius plane it represents the point where *different reactions* (*i.e.* changing ξ) show the same rate constant at a defined temperature, namely T_{iso}, whereas in the LFER-plane the *same reaction* (*i.e.* a defined ξ_{iso}) shows a temperature-independent rate constant at the corresponding point. The transformations between these various representations, as shown in Figure 5, have been described by Linert and Sapunov,[32] and will be summarized below yielding the possibility of predictions of both the temperature dependence as well as the ξ dependence (for example the substituent or solvent dependence).
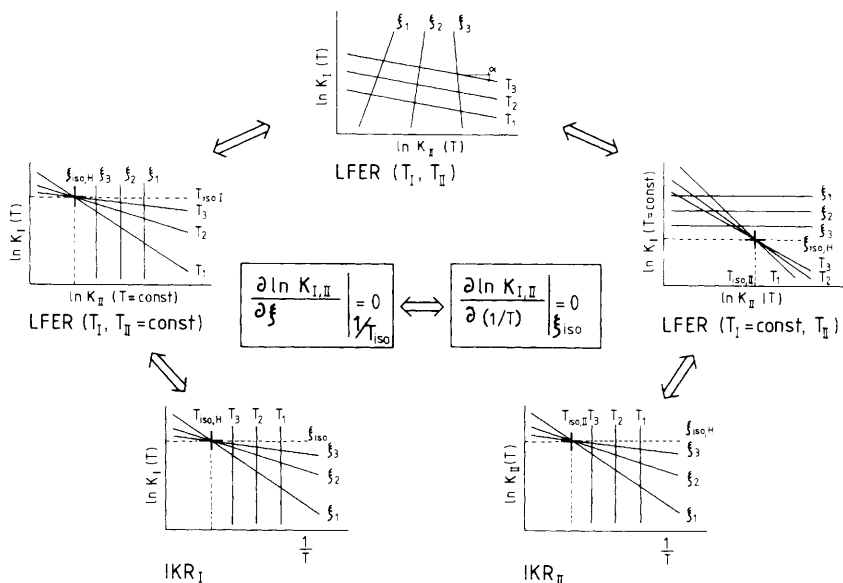
Figure 5 *Various graphical representations of the temperature dependence of LFER-plots*

Consider a LFER based on a test reaction series (represented by I) measured at temperatures T_I and a reference reaction series (represented by II) measured at temperatures T_{II}. The LFER is then given by

$$\ln\left(\frac{k_I(\xi)}{k_I(\xi_0)}\right)_{T_I} = \alpha_{T_I,T_{II}} \ln\left(\frac{k_{II}(\xi)}{k_{II}(\xi_0)}\right)_{T_{II}} \tag{8}$$

namely straight lines with different slopes for different temperatures. Obviously test and reference reaction series may be taken at different temperatures. (For example, with respect to Hammett's relationship, the ionization constants of benzoic acids, which yield the reference reaction series, are those measured at 25 °C, independently of the test reaction series.)

$\alpha_{T_I,T_{II}}$ can be related to a temperature-independent quantity of physical meaning, namely with

$$\alpha_{T_I,T_{II}} = \alpha_0 \frac{\left(\dfrac{1}{T_I} - \dfrac{1}{T_{iso,I}}\right)}{\left(\dfrac{1}{T_{II}} - \dfrac{1}{T_{isi,II}}\right)} \tag{9}$$

and

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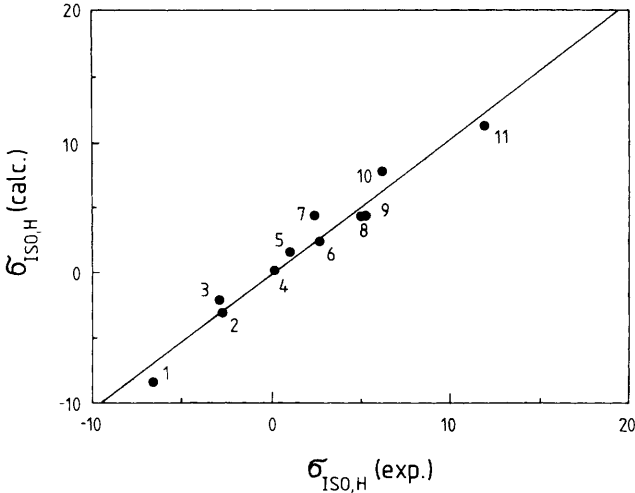
Figure 6 *Experimental* versus *calculated* σ_{iso} *values:* 1, *alkaline hydrolysis of dinitro-thiophenylbenzoates;* 2, *formation of quarternary ammonium salts;* 3, *decomposition of* m-*dinitrobenzene complexes;* 4, *ionization of nitroanilines;* 5, *coupling of phenyldiazonium salts with Brenner acid;* 6, *protonation of 3,5-disubstituted anilinium ions;* 7, *formation of anilides of* N-*phenylsarcosine;* 8, *alkaline hydrolysis of ethyl-acetates;* 9, *alkaline hydrolysis of methyl acetates;* 10, *alkaline hydrolysis of aromatic amides;* 11, *alkaline hydrolysis of benzyl acetates* (*for details see references* 26 *and* 32)

$$\alpha_0 = \frac{\delta \Delta H_I}{\delta \Delta H_{II}} = \frac{\delta \Delta S_I T_{iso,II}}{\delta \Delta S_I T_{iso,I}} \tag{10}$$

where $\delta \Delta H$ and $\delta \Delta S$ represent the differences of the enthalpy and entropy of the reaction ξ minus those for the reference reaction ξ_0 (for example, values for the unsubstituted acid when dealing with Hammett LFERs). Knowing this, any $\ln k_{iso}$ in each one of the representations can be calculated by using equation 11.

$$\ln\left(\frac{k_{iso,II}}{k_{0,II}}\right) = \frac{\Delta H_0}{\alpha_0}\left(\frac{1}{T_{II}} - \frac{1}{T_{iso,II}}\right) \tag{11}$$

For example, the iso-substituent Hammett parameter, σ_{iso}, is given, when using $T_{iso} = -255$ K for the ionization of the substituted benzoic acids, by (12):

$$\sigma_{iso} = \Delta H_{0,I}/2630 \, \alpha_0 \tag{12}$$

where α_0 is given by (10) and represents the temperature-independent slope (13)

$$\alpha_0 = \Delta H_{0,I}/(\Delta H_{0,II} - \Delta H_{iso,II}) \tag{13}$$

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of a Hammett plot where both coordinates are taken to be in their temperature-dependent form. Figure 6 shows that this indeed works extremely well for a series of reactions collected in order to examine this relationship

4 Theories
Although the IKR or LFERs that we have described above are largely used in an *ad hoc* manner it should be possible to find some theoretical explanation for them—especially since their statistical significance has now been established. Some important steps towards this goal are discussed in this section.

A. Overview of Theories.—One of the earliest attempts at an explanation was due to Schwab[2] who proposed the theta-rule and believed that T_{iso} equalled the temperature at which a catalyst had been prepared. From this it is to be concluded that T_{iso} has always to be above T_{exp}, but there are examples showing clearly that this is not always true (*cf.* Kral reference 75).

Thorn,[77] in 1969, analysed entropic and energetic aspects of chemical bonding and showed the monotonicity of the relationship between ΔS and ΔH. However, the results of this investigation are much too general to explain or even to describe the IKR. At this point it might be of interest to draw attention again to the fact that a monotonicity between the entropic and enthalpic factors is not enough by far to explain the IKR (which is connected—mathematically, but not statistically—with a linear relationship). The argument used in several papers, where an attempt is made to explain the IKR or the compensation effect on the basis of transition-state theory, requires that for small variations in the pre-exponent and/or in the activation energies a linear approximation (based on a truncated Taylor expansion) is possible. This is not very satisfactory, however, because there are several experimental examples where T_{iso} is near to the mean experimental temperature and in this case the variation is too large to allow for such linear approximations. In fact this means that all theories based largely on partition function arguments are unlikely to describe accurately the IKR since any parameter which may be interpreted as being ξ appears in one functional form in the temperature-dependent term and in another (mainly in a logarithmic) form in the temperature-independent terms of the rate equation.

A theory based on Hinshelwood's[78-80] description of unimolecular reactions has been used to describe the IKR independently by Linert[24,33] and Schwab.[81] Similar modelling, including anharmonicity effects, was used by Ruetschi.[82] Unfortunately, however, on going to the more advanced Rice–Ramsperger–

[75] H. Kral, *Chem.-Ing.-Tech.*, 1987, **59**, 795.
[76] H. Kral, *Chem. Eng. Technol.*, 1988, **11**, 113.
[77] R. J. Thorn, *J. Chem. Phys.*, 1969, **51**, 3582.
[78] C. N. Hinshelwood, *Proc. R. Soc. (London)*, 1927, **A113**, 230.
[79] G. N. Lewis and D. F. Smith, *J. Am. Chem. Soc.*, 1925, **47**, 1508.
[80] R. H. Fowler and E. K. Rideal, *Proc. R. Soc. (London)*, 1926, **A113**, 570.
[81] G. M. Schwab, *J. Catal.*, 1983, **84**, 1.
[82] P. Ruetschi, *Z. Phys. Chem.*, 1958, **14**, 277.

Kassel (RRK)[83-85] or the Rice–Ramsperger–Kassel–Marcus (RRKM)[86,87] treatments the properties exhibiting IKR character vanish from the rate equations! This is because absolute rate theory does in general not allow for T_{iso} to equal T_{exp} when considerable changes of E_a and $\ln A$ are found in the reaction series. Nevertheless this work made it clear that any description of the physical background of the IKR should be based on a description of an energy distribution within osciallatory degrees of freedom because only then will partition functions be forthcoming that exhibit the necessary temperature dependence.

Likhtenstein[88] built his model on a chain of different states of solvation of both reactants and products. Approximating the changes in rate constants between all these states as equal certainly yields an isokinetic relationship, but the model is still not restrictive enough to enable it to pin down the origins of the IKR. Peacock-Lòpez and Suhl[89] later attempted to explain the compensation effect by counting the way in which a heat bath can furnish the energy necessary to surmount the barriers. This involved counting the number of excited states available at a solid-state catalyst, and one of their conclusions was that the Arrhenius lines of the members of the series should all exhibit a sharp change of slope at the point corresponding to T_{iso}. Although such behaviour might be recorded in the literature in very rare cases,[90] it is certainly not a general observation.

Galwey[4] suggested that surface heterogeneity and/or two concurrent reactions were the most reasonable explanation for compensation. Bond[91] used the concept of active centres on catalytic surfaces for his explanation of the compensation effect. More recently[34] Galwey has suggested that a common temperature may exist for the onset of a specific (presumably related) reaction, but the physical significance of this idea is not clear. Much more recently, Larrson[92] explains the IKR as a resonance effect between reactants and catalysts. His T_{iso} values (taken from the compensation plot) should be related to *reactant* frequencies. Although this is an extremely interesting approach, it cannot be a general explanation of the isokinetic relationship as it contradicts the observed variation within a series of reactants.

In 1988, Estrup *et al.*[93-95] suggested that the isokinetic temperature may be related to a phase transition for reactions on single crystals. They note that the

[83] L. S. Kassel, *J. Phys. Chem.*, 1928, **32**, 225.
[84] O. K. Rice and H. S. Ramsperger, *J. Am. Chem. Soc.*, 1927, **49**, 1616.
[85] O. K. Rice and H. S. Ramsperger, *J. Am. Chem. Soc.*, 1928, **50**, 617.
[86] R. A. Marcus, *J. Chem. Phys.*, 1952, **20**, 359; 1965, **43**, 2658; 1962, **37**, 1835.
[87] W. Tsang, *Int. J. Chem. Kinet.*, 1973, **5**, 947.
[88] G. I. Likhtenstein, *Russ. J. Phys. Chem.*, 1970, **44**, 1079.
[89] E. Peacock-Lòpez and H. Suhl, *Phys. Rev. B.*, 1982, **26**, 3774.
[90] A. V. Grabazhiu, K. A. Vyunov, and A. I. Ginak, *Kinet. Katal.*, 1986, **27**, 215.
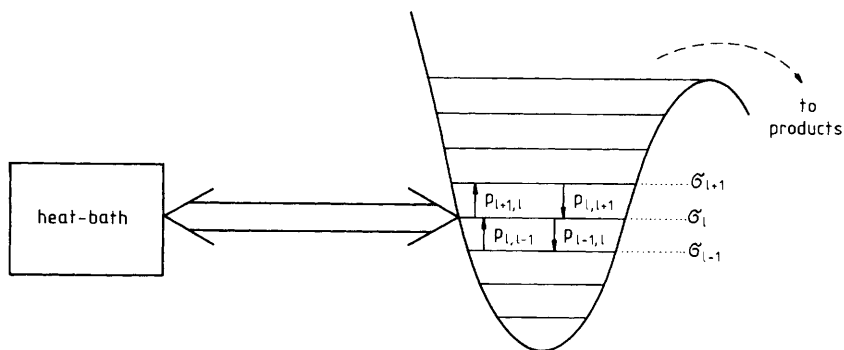[91] G. C. Bond, *Z. Phys. Chem. N.F.*, 1985, **144**, 21.
[92] R. Larrson, *Catalysis Today*, 1987, **1**, 99.
[93] P. J. Estrup, E. F. Greene, M. J. Cardillo, and J. C. Tully, *J. Phys. Chem.*, 1986, **90**, 4099.
[94] P. J. Estrup, R. A. Barker, and A. H. Smith, *Surf. Sci.*, 1984, **136**, 327.
[95] J. W. Erickson and P. J. Estrup, *Surf. Sci.*, 1986, **167**, 5.

Figure 7 *Random walk of reactants in a potential well connected to an energy reservoir*

phase transitions are reflected in the phonon spectra of metal catalysts, and they suggest[95] that the interaction between the reaction complex and the 'heat bath' for the system might play a role in the explanation of isokinetic behaviour.

Conner[96] explained in a qualitative way the IKR as an effect based on availability and accessibility of energy in a reaction. Although only qualitative, there is little doubt that in citing the latter point, Conner had realized where a solution of the problem should be sought, and we will now trace the course towards such a solution.

As pointed out above, we should look to non-transition-state rate theories to guide us. A way in which this can be achieved is through stochastic theories, which indeed would seem to yield a way towards an understanding of the isokinetic relationship. We therefore begin with a short outline of the necessary background required in order to understand the main points of such theories.

B. Stochastic Modelling of Chemical Reactions.—In Kramers' theory[97] of rate constants reactant molecules are supposed to become activated through their collision with other molecules of the surrounding medium, which act as a constant temperature 'heat-bath'. After a random walk over discrete energy levels of the reactants they reach, at the highest point of the barrier, a point of no return. The crossing of this barrier constitutes the chemical reaction rate. Figure 7 and equation 14 explain this in some detail.

$$d\sigma_l(t)/dt =$$
$$Z\left[-\sum_{l<m} P_{ml}N^-\sigma_l(t) + \sum_{l<m} P_{ml}N^+_{ml}\sigma_l(t) + \sum_{m<l} P_{lm}N^+_{lm}\sigma_m(t) + \sum_{m>l} P_{lm}N^-\sigma_m(t) \right] \quad (14)$$

In this σ_l represents the time-dependent density of the reactants to the discrete

[96] W. C. Conner, *J. Catal.*, 1982, **78**, 238.
[97] H. A. Kramers, *Physica*, 1940, **7**, 284.

levels l. The $P_{l,m}$ are the transition probabilities per collision for the transition from m to l (with $P_{0,-1} = 0$); Z is the collision number and $N_{l,m}^+$ are the concentrations of heat bath molecules which have 'sufficient energy' to excite a molecule from a given level l to a higher level m $(m > l)$ and N^- is the concentration of heat bath molecules able to de-excite a reactant molecule from m to l (m,l). In the limit of long times equilibrium should be reached as represented by

$$d\sigma_l(t)/dt = 0 \qquad (15)$$

This yields the condition

$$N_{l,m} = \exp(\Delta E/kT) \, N_{m,l} \qquad (16)$$

which (if ΔE is the energy difference between two heat bath energy levels) represents a Boltzmann distribution for the heat bath. The basic concept is now to keep this equilibrium assumption *even when the reaction is going on*. The non-equilibrium approach, therefore, is only to be applied to the reactant distribution with reactants able to exchange energy with their molecular surroundings and assumed to be always in thermal equilibrium.

After several advances in this theory, McCoy[98] has rewritten this representation of a Markoff process in the form of a Langevine equation, by assuming l to be continuous and therefore making possible a change from a *difference* equation to a *differential* equation, namely:

$$\frac{\partial\sigma(t)}{\partial t} = \frac{\partial}{\partial l} R(l) \left[\frac{\partial\sigma}{\partial l} + \frac{1}{k_{\mathrm{B}}T} h \frac{\partial}{\partial l} \omega(l)\sigma \right] + g(l) \qquad (17)$$

Based on investigations of Kramers,[97] Shuler[99,100] and Schwartz,[101] a quantum–statistical description of chemical reaction rates has been developed by McCoy[98] by considering a system with internal degrees of freedom in thermal contact with a heat bath. A steady-state solution of the master equation 17 has been obtained under the condition of large barriers for a non-equilibrium distribution of reactant molecules among discrete energy levels, with a point of no return at an energy barrier, and connected with a surrounding heat bath. It has been assumed that during a reaction a non-equilibrium steady-state distribution of reactant particles is present so that the solution of the differential equation 17 takes the form:

$$k = \varphi(s_N) \left\{ \int_0^{s_N} \mathrm{d}l \exp\left(-\frac{h}{RT} \int_0^l \omega(l'')\mathrm{d}l'' \right) \int_0^{s_N} \mathrm{d}l' \frac{\exp\left(\dfrac{1}{RT} \displaystyle\int_0^{s_N} \omega(l'')\mathrm{d}l'' \right)}{P(l')} \cdot \varphi(l') \right\}^{-1} \qquad (18)$$

This integral may be solved by partial integration and thereupon yields,

[98] B. J. McCoy and R. G. Carbonell, *Chem. Phys.*, 1977, **20**, 227; *J. Chem. Phys.*, 1977, **66**, 4564.

[99] E. W. Montroll and K. E. Shuler, *Adv. Chem. Phys.*, 1986, **1**, 361.

[100] I. Oppenheim, K. E. Shuler, and G. E. Weiss, *Adv. Mol. Relax. Processes*, 1967, **1**, 13.

[101] R. N. Schwartz, Z. I. Slawsky, and K. F. Herzfeld, *J. Chem. Phys.*, 1952, **20**, 1591.

assuming that the energy barrier is much larger than kT, the following simple form:

$$k = A_0(h\omega/kT)P_{s_N,s_{N-1}}\exp(-s_Nh\omega/kT) \qquad (19)$$

The terms A_0, $s_Nh\omega$, T_{exp}, and $P_{s_N,s_{N-1}}$ represent a constant involving mainly the collision number, the energy barrier height, and the temperature of the molecular surroundings of the reactants (*i.e.* the heat bath) and the quantum-mechanical transition-probability of a transition between the reactant level s_{N-1} to the highest reactant level (*i.e.* the point of no return) s_N, respectively. McCoy tried to derive IKR behaviour from his equations when solving the master equations by assuming anharmonicity terms which vary within the considered reaction series [102] (this anharmonicity parameter can be identified with ξ). Unfortunately his equations do not reduce to harmonic form when the anharmonicity parameter goes to zero so that this description of the IKR seems to be rather a mathematical artefact. [103]

Kreuzer *et al.*[104,105] also found compensation behaviour for physisorption processes when using a similar approach, *i.e.* the Smoluchowski–Champnam–Kolomogorov equation for the description of heterogeneous kinetics.

Although flawed, the above methods of approach did provide a key to the understanding of the IKR, as has been shown by the work of Linert.[27,103]

C. Application to the IKR.—The problem of understanding the IKR is at this point transferred to the problem of quantum-mechanical transition probability $P_{s_N,s_{N-1}}$.[103] When using, like McCoy,[98] or earlier Kramers,[97] the Landau–Teller transition probabilities [106] which are based on a translational energy exchange between a non-vibrating particle (*i.e.* a member of the heat bath) and an harmonic vibrator, isoentropic behaviour is found. In condensed phases, however, it must be assumed that the heat bath also contains energy stored in the form of vibrational degrees of freedom. This situation is now that given in Figure 8 and note that the (molecular) structure of the heat bath is not now included in its required properties.

The appropriate transition probabilities for a vibrational–vibrational energy transfer [101,107–109] are calculated in [103] and shown to yield:

$$P_{l,m} = l\exp(\omega/v) \qquad (20)$$

where a resonance condition of the form

$$vm = \omega l \qquad (21)$$

[102] B. J. McCoy, *J. Chem. Phys.*, 1984, **80**, 3629.
[103] W. Linert, *J. Chem. Phys.*, 1987, **116**, 381.
[104] H. J. Kreuzer, *Applications Surface Sci.*, 1982, **11/12**, 793.
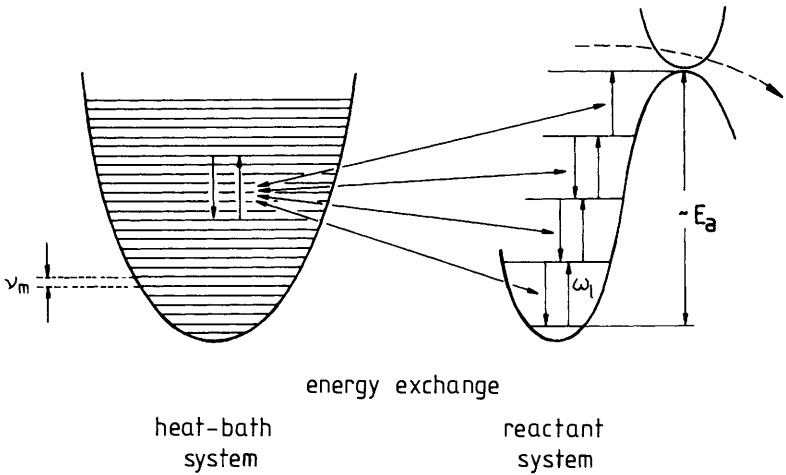[105] E. Sommer and H. J. Kreuzer, *Phys. Rev. Lett.*, 1982, **49**, 61.
[106] L. Landau and E. Teller, *Phys. Z. Sowietunion*, 1936, **10**, 34.
[107] D. Rapp and P. Englander-Golden, *J. Chem. Phys.*, 1964, **40**, 573.
[108] K. N. C. Bray, *J. Phys. B*, 1970, **3**, 1515.
[109] B. J. McCoy and R. G. Carbonell, *J. Chem. Phys.*, 1977, **66**, 4564.

energy exchange

heat-bath   reactant
system   system

Figure 8 *Random walk of reactants distributed in a potential well with a point of no return (i.e. a reaction barrier) coupled to a heat bath storing energy in vibrational levels*

is included implying that energy is exchanged with the highest probability at equal energies (m represents the number of the heat bath level, ν the associated frequency, and the resonance condition is given in its form for harmonic oscillators). Combining equation 20 with equation 18 yields the following form of the rate constant:

$$k = A_0 s_N (h\omega/k_B T_{exp})^2 \exp[-s_N(\omega/\nu - h\omega/k_B T_{exp})] \qquad (22)$$

In this ν represents a vibrational heat bath frequency predominantly active in the energy exchange with the reactants. From this the IKR follows naturally.

When, for example, considering the reactants, the frequency ω associated with a vibration along the reaction coordinate can be identified with ξ from equation 7

$$[\partial \ln k(\omega)/\partial \omega]_{T_{iso}} = 0 \qquad (23)$$

Applying this condition to equation 16 a relation is found between T_{iso} and the vibrational frequency predominantly exchanging energy with the reactants present in their molecular surroundings:

$$1/RT_{iso} = 1/E + 1/N_L h\nu \qquad (24)$$

where h = Planck's constant; N_L = Avogadro's number; k_B = Boltzmann's constant; ν = the predominantly active heat bath frequency. (The first right-hand term is associated with collision activation and may be neglected for reaction series where vibrational activation is possible.) In this case equation 25 should be valid:

$$1/RT_{iso} = 1/N_L h\nu \qquad (25)$$

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It should be pointed out at this point that ξ may also be identified with s_N yielding the same result. This means that *in whatever form the members of the series are represented* they exhibit the same rate at T_{iso} or show a minimum in selectivity at this temperature. It might be significant for this approximation that in the gas phase, where the energy exchange is by individual collisions, the experimental results show $1/T_{iso}$ values near zero, *i.e. isoentropic* behaviour is observed. At T_{iso} the dependence upon ξ vanishes from the rate equations and the members of the reaction series therefore cannot be identified by means of their rate constants, *i.e.* they exhibit *isoselective behaviour*.

The following assumptions built into the theory should be pointed out: The heat bath frequency, ν, should be much smaller than the reactant frequency, ω, which is always the case—at least for condensed phase reactions.

(i) The resonance condition between ω and ν given in equation 21 should be fulfilled.

(ii) The energy barrier should be much larger than kT.

(iii) No group-theoretical selection rules have been explicitly built into the model as the heat bath was assumed to be structureless, containing only vibrational frequencies.

(iv) With regard to the last point, specific selection rules are in any case highly unlikely to apply to the question of predicting the active heat bath frequency because solvent molecules are assumed to be not orientated in the solution outside the inner coordination-sphere. This is particularly important as the theory is based on a heat bath for which the only physical requirement is the existence of discrete energy levels which can exchange energy with defined energy levels of the reacting system and therefore no particular information about the actual chemical systems acting as heat baths is implied, or indeed required. However, in some sense, because the reacting species have a real chemical identity, selection rules have been implicitly invoked, *i.e.* because most chemical reactions involve a change in polarity rather than in polarizability, IR-active vibrations—as opposed to Raman active ones—are more likely to be involved in exciting the reacting species.

D. Negative T_{iso} Values.—There are, in the literature, several examples of statistically significant *negative* T_{iso} values, for example the above mentioned ionization constants of substituted benzoic acids.[25,26,32] Obviously such a T_{iso} cannot be related to a frequency of vibration as is required by a theory such as that of Linert which has been outlined above.

The first point to be made is that these theories have all been developed for elementary steps and a negative isokinetic temperature bears a similar relationship to these theories as does a calculated negative energy of activation to, say, collision theory. In fact, whenever the extrapolation of Arrhenius or van't Hoff lines yields a negative T_{iso}, it is better to interpret this in terms of the slope of the ΔH *versus* ΔS plot since negative values of T_{iso} are then readily accommodated in the framework of anti-compensation, *i.e.* ΔH and ΔS are shifted in opposite directions within the considered reaction series. This effect can be explained in

terms of processes that can be dissected into *two* steps, one of which more strongly affects the overall energy and the other the overall entropy. Both steps are affected in oppposite sense by varying reactants or substrata. For example, when investigating Hammett reaction series (*i.e.* reaction series with substituent variation described by Hammett's relationship) several series are found[26] exhibiting negative T_{iso} values. (The ionization of substituted benzoic acids—used to define the Hammett relation—themselves show this behaviour.) All these reactions are performed in water and either one of the reactants or one of the products are *charged* large organic (*i.e.* hydrophobic) molecules, and negative T_{iso} values can now be explained in such series as follows:[26] the intrinsic ionization affects the *overall energy* whereas the hydration of the anion affects the *overall entropy* with both steps oppositely affected by the substituents. Thus electron withdrawal from the reaction site (for example a hydrogen-binding oxygen) brings about a decrease in ΔH and a less negative ΔS. Finally, since the entropic contribution dominates the free energy changes, it follows that hydration in many cases effectively disfavours the process of ionization.

5 Experimental Tests of the Theory and its Significance

A. Isokinetic Relationships.—A general outcome of the theory is that the Boltzmann energy of T_{iso} should exist as a frequency in the vibrational spectrum of the heat bath, *i.e.* of the solvent or catalyst. Or, reversing the argument, for a given solvent an isokinetic temperature may only be found within discrete regions corresponding to the absorption bands of the vibrational spectrum of the solvent. Figure 9 gives as an example the temperature dependence of the rate constants of the oxidation of substituted phenylmethyl sulphides with *N*-bromo-acetamide[110,111] and far infrared spectrum of acetonitrile. The bars included represent T_{iso} values found for various reactions performed in this solvent. The far infrared spectrum of acetone is given in Figure 10 (given in the commonly used scaling) also including T_{iso} values found for a collection of reaction series measured in this solvent. Both figures show the range of frequencies corresponding to the range of experimentally found T_{iso} superimposed on the IR-spectra of the solvents concerned.

This phenomenon has been confirmed by examination of some 150 reaction series, all established by means of a proper statistical analysis, and chosen under the condition that (a) they are statistically highly significant IKRs and (b) their T_{iso} value is within $\pm 5\%$ (even when extrapolated).[27,112] The data may be further divided into three groups according to (i) IKRs in homogeneous reactions with a variation in the reactants, (ii) IKRs in solutions when solvents are varied (*i.e.* isosolvent relationships), and (iii) IKRs found in heterogeneous catalysis.

The data for the first two categories are quoted by Linert[27] and are

[110] R. Schmid and L. Han, *Inorg. Chem. Acta*, 1983, **69**, 127.
[111] L. S. Prangova, E. G. Linrina, I. Ya. Kvitko, and L. S. Efros, *Reakts. Sposobn. Org. Soedin.*, 1984, **8**, 127.
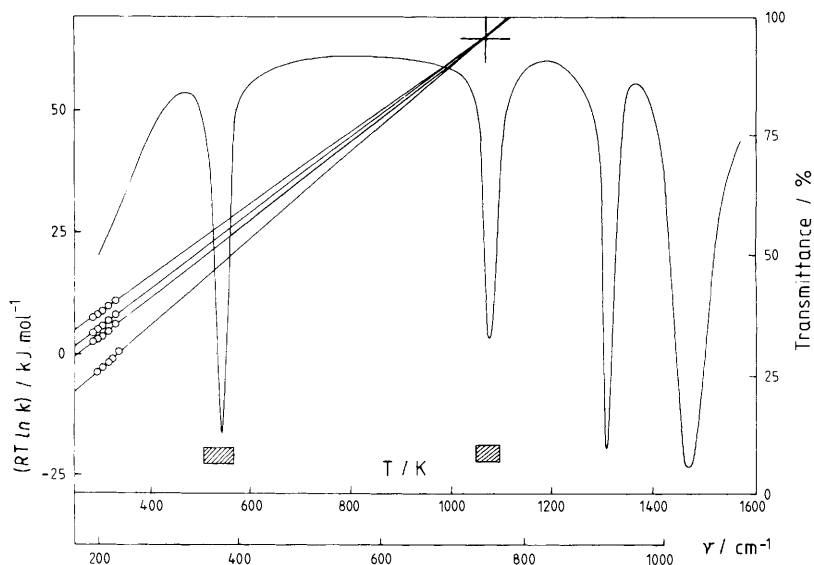
Figure 9 *Temperature dependence of the rate constants of the oxidation of substituted phenylmethyl sulphides with* N-*bromoacetamide* [111] *given in the RT*ln*k versus T plane and the far infrared spectrum of acetonitrile with bars representing* T_{iso} *values found for various reactions performed in this solvent*
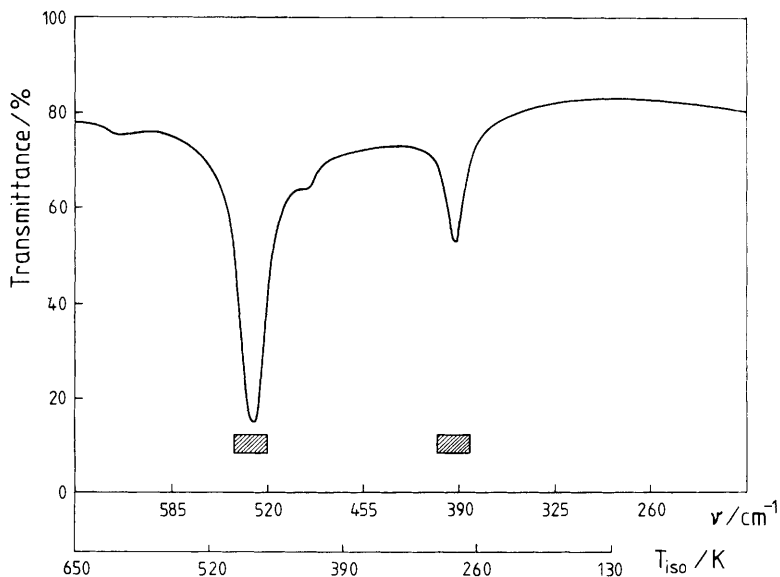
Figure 10 *Far IR-spectrum of acetone with bars representing* T_{iso} *values found for various reactions performed in this solvent*
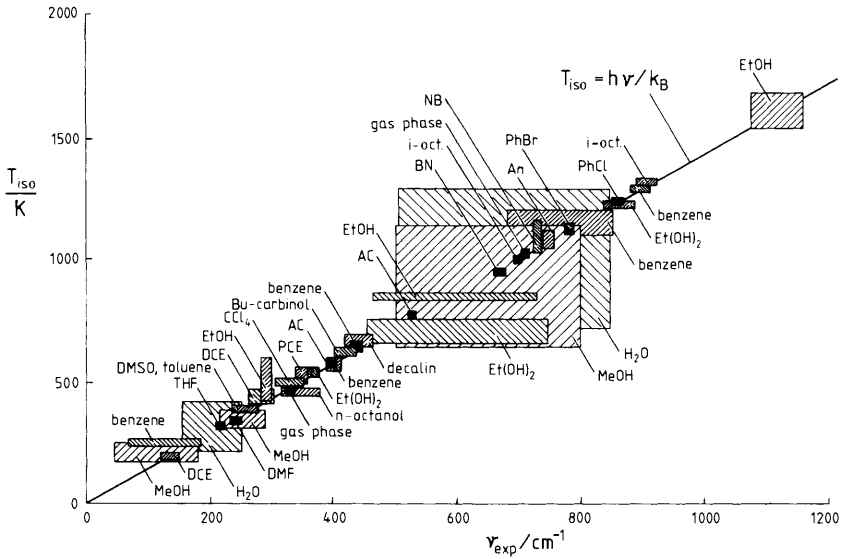
Figure 11 *Experimentally found isokinetic temperatures, T_{iso}, of various chemical reaction series versus the absorption bands observed in the infrared spectra of the solvents. The given straight line and its slope refer to the theoretical expectation*
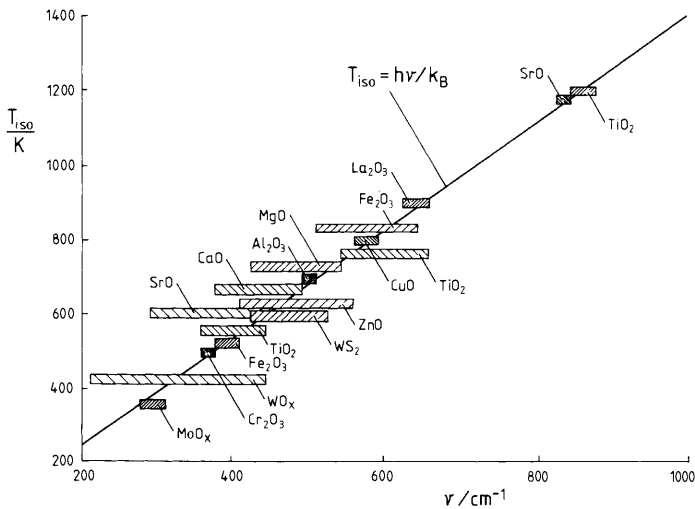
Figure 12 *Isokinetic temperatures T_{iso} of various chemical reaction series versus the absorption bands observed in the infrared spectra of the solid catalysts. The given straight line and its slope refer to the theoretical expectation*

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summarized graphically in Figure 11, and those for category (iii), *viz.* for reactions involving heterogeneous catalysis, were collected [112] and are displayed in Figure 12.

Although the broadness of some absorption bands makes a coincidence of theory and practice inevitable in these cases, the other systems show a relatively strict accordance with theory (Figures 11 and 12).

When analysing IKR series in heterogeneous systems it is remarkable that almost all analyses in the literature are based on the statistically wrong compensation plot (*i.e.* E_a versus $\ln A$) and that very often the original data are not published. Figure 12 has therefore been based in part on a ΔG versus ΔS representation according to Krug's test.[63] Furthermore, IR bands of solids are often very broad. This explains that, contrary to the case of homogeneous systems where isosolvent relationships are rare because of the condition of overlapping frequencies of all solvents of the series, IKRs with a catalyst variation, *i.e.* a variation of the heat bath, are often found. In fact, many scientists working in heterogeneous catalysis associate with the terms compensation effect or IKR merely a catalyst variation rather than a reactant variation.

Figure 11 indicates particularly clearly a linearity between T_{iso} and an observed IR frequency as required by equation 24 and this relationship will be examined in more detail below. The data pertinent to heterogeneous catalysis (Figure 12) are, as might well be expected, less convincing because more of the IR bands are of necessity generally very broad in the required region. Nevertheless, a general correlation is evident.

Noting that to date no frequency calculated from a T_{iso} value lies in an IR window of the solvent concerned, a major problem requiring examination remains—namely to examine to what extent it is possible to predict which band in the infra-red spectrum of the solvent is the 'active' one. Furthermore, a change in solvent can sometimes yield a new T_{iso} for a given reaction series—or fail to give an IKR.

Similarly it should also be possible to obtain examples for cases when the *IKR breaks down or moves to another T_{iso} when the active frequency is removed*, this is of crucial importance to the theory. Consider the case where an IKR reaction is performed in *solvent mixtures* with T_{iso} related, as long as one solvent is in excess, to a frequency corresponding to an *IR band* of this solvent, but at the same time corresponding to an *IR window* of the other solvent. Changing the relative concentrations of these solvents should then lead to either a shift in the IKR (to accommodate the new exciting frequency) *or* disappearance of the IKR since a suitable exciting frequency does not exist. *Both types of behaviour are known* and are illustrated in Figure 13 for complex formation between nickel(II) and 2,2′-bipyridyl in water–methanol mixtures [113] when the IKR breaks down completely, and in Figure 14 for nickel(II) complex formation in acetonitrile–methanol mixtures [113] where there is a clear change to a new T_{iso} (frequency) when

[112] W. C. Conner and W. Linert, *Orient. J. Chem.*, 1989, **5**, 204.
[113] H. P. Bennetto, *J. Chem. Soc. A*, 1971, 2207, 2211.
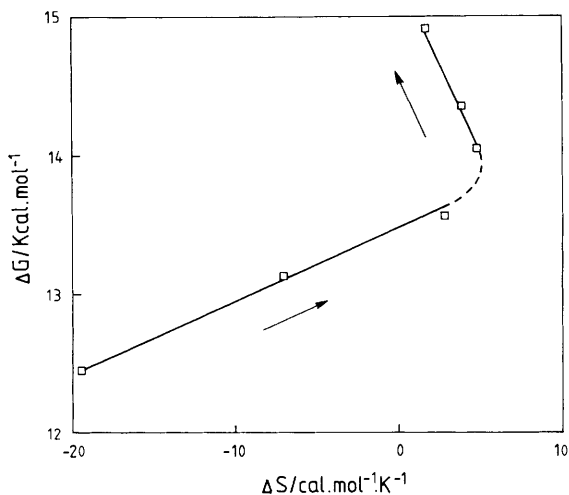
Figure 13 $\Delta G^{\neq}$ versus $\Delta S^{\neq}$ *(according to Krugs's IKR test [63]) for the rate constants of the complex formation of* Ni^{2+} *with 2,2'-bipyridine ligands in acetonitrile–methanol mixtures [113,114] (arrows represent increasing methanol content)*
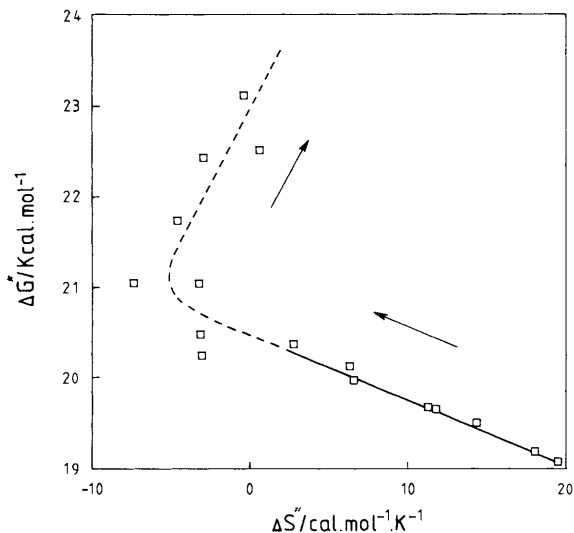
Figure 14 $\Delta G^{\neq}$ versus $\Delta S^{\neq}$ *for the rate constants of solvolysis of t-butylchloride in water–alcohol (ethanol, propanol, and t-butyl alcohol mixtures [114,115] (arrows represent increasing alcohol content)*

[114] H. Mayr, R. Schneider, and E. Grabis, *Angew. Chem.*, 1986, **96**, 1034.

[115] R. E. Robertson and S. E. Sugamori, *J. Am. Chem. Soc.*, 1969, **91**, 7254.

[116] S. Winstein and A. H. Fainberg, *J. Am. Chem. Soc.*, 1957, **79**, 5937.

increasing the alcohol content. Note that in these figures ΔG *versus* ΔS plots are used to show the effect—Krug's treatment[63] of such data shows this to be statistically proper. In this case the slope refers to $T_{exp} + T_{iso}$. Taking into account that (according to Krug), for T_{exp} the harmonic mean of the experimental temperature range has to be inserted, a change in slope reflects directly a change in T_{iso}. Another example of a reaction system exhibiting this effect is the solvolysis of t-butylchloride in solvent mixtures.[115,116] In both cases the change in T_{iso} (*i.e.* the change in slope) falls into the region of about 30% addition of the second solvent.[128] When running the former reaction in water–methanol mixtures the same effect is found, with a second change in T_{iso} at 70% addition of methanol (*i.e.* 30% when adding water to methanol). It has been argued that such a behaviour may be associated with a breakdown of solvent structures due to dilution which is also reflected in specific heat measurements.

B. Isosolvent Relationships.—A variation of the heat bath itself (*i.e.* solvent variation) may also yield isokinetic relationships but under the *strong restriction that all solvents of the series have the same vibrational frequency*. It is obviously not often the case that for a collection of solvents the necessary frequencies overlap. From this point of view the electro-reduction of quinones[117] showing an *isosolvent* relationship is of importance. The reduction potentials of four different quinones have been measured in five different solvents. It was found that the different quinones did not show isokinetic (isoequilibrium) behaviour: they are obviously different in more than one parameter and do not fall into one series. However a *solvent variation* yielded for each of the quinones highly significant common points of intersection. The isokinetic temperatures are found to be almost the same for the different quinone series and correspond to available IR frequencies of the solvents. The plot for only one of the solvents (namely that for acetonitrile) does not meet the common point of intersection and it is significant that this solvent has no absorption frequency in the appropriate region. Similar situations are found for isosolvent relationships for the electro-reduction of some solvatochromic nickel(II) complexes[118] and copper(II) complexes,[119] imine–enamine tautomerism,[120] chlorine isotopic exchange reaction, and olefine cycloaddition[121] as given in references.[27]

All these observations of IR absorption bands being linked in some way to T_{iso} through an IKR may be taken as a hint that a resonance condition determines the 'chosen' IR frequency corresponding to an isokinetic relationship. The fact that in the study of the electro-reduction of quinones in various solvents (above) the reactants themselves exhibit IR absorption at these frequencies might reinforce this conclusion.

[117] W. Linert and J. S. Jaworski, *Electrochim. Acta*, 1988, **33**, 1713.
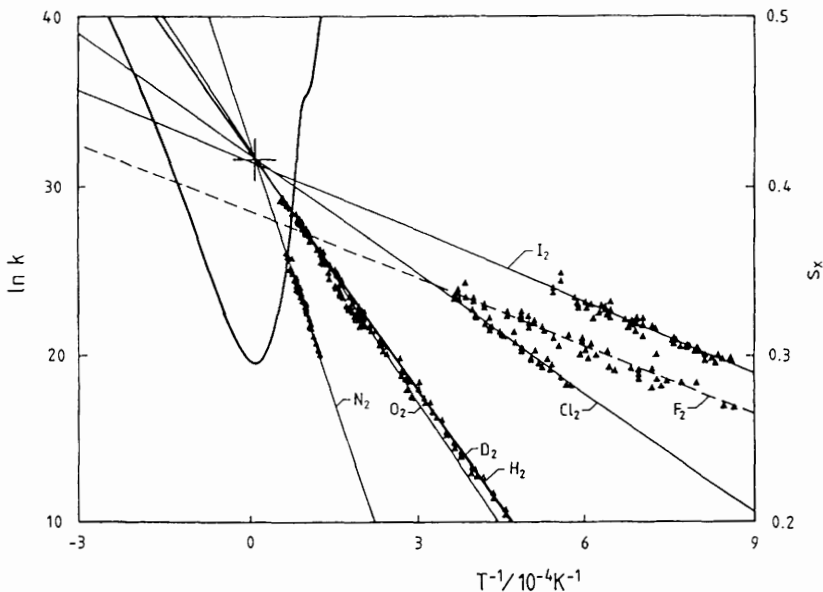[118] W. Linert, B. Pouresmaeil, and V. Gutmann, *J. Coord. Chem.*, 1988, **17**, 15.
[119] W. Linert, B. Pouresmaeil, and V. Gutmann, *Electrochim. Acta*, 1988, **33**, 975.
[120] H. Albrecht and R. D. Kalas, *Liebigs Ann. Chem.*, 1979, 102.
[121] X. K. Jiang, C. J. Wu, and Z. Z. Wu, *Acta Chim. Sin.*, 1983, **41**, 354.

**Figure 15** *Arrhenius plots of thermal dissociation of diatomic molecules in large excess of argon*

C. Changes in Reaction Mechanism.—Several authors, for example Leffler and Grunwald,[29,30] suggested that from the appearance of an IKR it may be concluded that only one reaction mechanism is present. The present theoretical description supports this as no general changes in the reaction profile (for example by including a new minimum or maximum according to an intermediate or a new barrier) are allowed for.

In fact the IKR analysis has brought to light several, sometimes unexpected, examples of a change in mechanism. Some examples follow:

(i) The gas-phase dissociation of diatomic molecules such as Cl_2, Br_2, I_2, N_2, H_2, D_2, and F_2. This series shows an excellent IKR (based on an enormous experimental temperature range), which is illustrated in Figure 15. The series is isoentropic and in fact is coincidentally a good example for the isoentropic behaviour of gas-phase reactions. However, note that the line for F_2 does not meet the intersection point and because the reactions were performed with argon as diluting gas this may be explained in terms of a reaction between F_2 and Ar which indeed takes place over this temperature range[122,123]—in contradistinction to all other members of the series.

(ii) Another example is given by the partitioning of pyridylalkylamides in

[122] J. H. Kolts and D. W. Setser, *J. Phys. Chem.*, 1978, **82**, 1766.

[123] H. C. Brashears, D. W. Setser, and Y. C. Yu, *J. Phys. Chem.*, 1980, **84**, 2495.
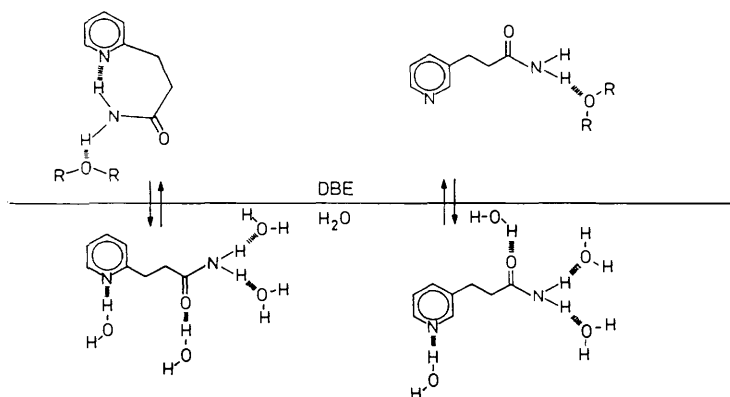
Figure 16 *Structural changes of pyridylalkylamides in dibutylether–water systems*[126]

cis – anti   trans – anti   trans – syn
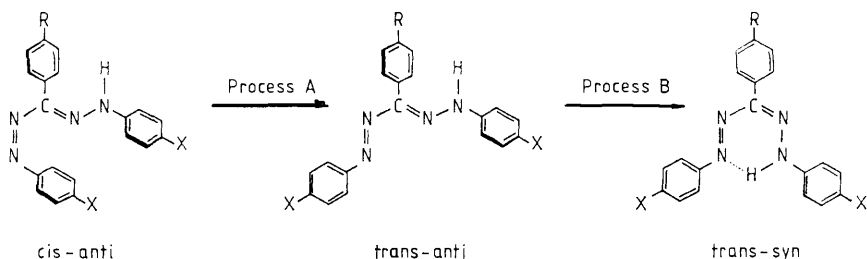
Figure 17 *Chemical pathway of the isomerization of substituted formazanes in a two-step reaction after excitation by radiation of the* trans-syn *species to the* cis-anti *species*[78]

octanol–water and di-n-butylether–water systems (Figure 16)[124,125] The partition coefficients of a series of 12 isomeric and homologous pyridylalkylamides split, rather surprisingly perhaps, into two groups when analysed for an IKR. This can be explained by noting that one group is able to form intramolecular N$\cdots$H–N bonds while the other, on steric grounds, is not.

(iii) A third example is given with the isomerization of formazanes where with two IKRs two pathways according to a rotational and an inversional mechanism are found[126] (Figure 17).

The third example is of particular importance because the authors originally found only one straight line on the basis of a ΔG *versus* ΔS plot and argued that—*contrary to their chemical expectations*—only one reaction mechanism is present in this series. (The alternative would of course be that the test is unreliable!) A statistically sound IKR analysis[65] later clearly demonstrated the

[124] C. Repond, J. M. Mayer, H. van de Waterbeemd, B. Testa, and W. Linert, *Int. J. Pharm.*, 1987, **38**, 47.

[125] C. Repond, H. van de Waterbeemd, J. M. Mayer, B. Testa, and W. Linert, in 'QSAR in Drug Design and Toxicology', ed. H. Hadzi and B. Jerman-Blazic, Elsevier Science Publishers, 1987, pp. 141.

[126] Y. Sueishi and N. Nishimura, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 2598.

existence of *two* intersection points for this series of reactions. In other words two mechanisms are indeed present—in agreement with both chemical intuition and the test!

6 Conclusions

We conclude from all the evidence so far collected that for a given solvent an isokinetic temperature may only be found within discrete regions corresponding to the absorption bands of the vibrational spectrum of the solvent. The rules for predicting this region for a given reacting system are, however, unknown. What is perhaps most important, however, is the inescapable conclusion to be drawn from Linert's theory that an isokinetic relationship is a natural outcome of an interplay between solvent and system and *ought to be expected* unless solvent molecules have a specific part to play in the reaction.

It is therefore obvious that further experimental results on both the IKR itself and the measurement and interpretation of far IR-spectra are necessary to provide more evidence for the given relationship. Either way the results would be of vital importance in elucidating both the nature of this isokinetic effect and the role played by the solvent.

A final observation: Many reaction series have been investigated but only a proportion of them contain the required original data. Many authors, mainly one suspects in order to reduce the space occupied by tables in publications, just give $\ln A$ and E_a or related data. But it is necessary, in order to make publications meaningful for later scientists, to give original data without losing a large amount of information by strong reductionism. Thankfully many journals have a system for archiving this essential extra data that avoids overloading the journal itself—unfortunately at present its use seems almost confined to crystallographers!

7 Future Work

Several points are open to further investigation and may yield a large field of exciting scientific work in the future.

From the theoretical point of view it seems to be possible either to go into some more details, or to try a more generalized approach. For example, the former path could be followed by including non-next-neighbour transitions and anharmonic behaviour of the reactant energy distribution. Both effects would possibly yield more information about $\ln k_{iso}$, but—as far as we can see from the present state of the art—no significant changes of the actual position of T_{iso}.

Following the latter path, we should mention that a generalized approach towards the IKR might well be based on a Markoff theory. Remembering the form of equations 3, 4, and 5, the IKR is seen to be based on an exponential form of separate temperature-dependent and temperature-independent terms containing the parameter ξ. The exponential character of the temperature-dependent part naturally results from the properties of Markoff processes when energy distributions to discrete reactant levels, allowing for transitions without any

memory effects, are investigated.[127] In the same way it might be possible to investigate the number of reactants distributed to discrete 'boxes' defined by the parameter ξ. As a simple *Gedanken* experiment one might ask for the number of reactants with a given substituent which are at a certain moment at the barrier height in a mixture of different substituents. In other words, the generalized potential 'energy', related to the parameter 'experimental temperature', may be replaced by a generalized potential according to different reactants related to the parameter 'ξ'. This would in fact be an interpretation of the high symmetry between T, ξ T_{iso}, and ξ_{iso} for example depicted in Figures 3 and 5.

Still open is the question as to which one of the IR bands within the given region is selected by an IKR series. Many points are leading us to look for an answer to this question through a resonance argument, but if the resonance explanation is basically sound, then one troublesome feature is likely to be the fact that a given reaction series can *change* its T_{iso} value to suit a change in solvent. (There is little problem associated with the destruction of an isokinetic relationship when the solvent is changed.) To gain more information about this question, far IR-spectroscopy performed on the heat bath (*i.e.* solvents, catalysts) and the reactants is necessary. Both theoretical and practical work in this field is continuing in our Institutes.[128]

APPENDIX
Linear Free Energy Relationships (LFERs)
For the purpose of this Review we can define linear free energy relationships as follows:
(i) Kinetic Data
If we have two series of closely related reactions i and j for which the rate constants are k_i and k_j and the corresponding equilibrium constants are K_i and K_j the relationships (A1) often hold:

$$k_i = c_1 k_j^\pi$$
$$k_i = c_2 K_i^\pi \qquad \text{(A1)}$$
$$k_i = c_3 K_j^\pi$$

This relationship can also be expressed, for example, in the form (A2)

$$\log k_i = \log k_0 + \sigma\rho \qquad \text{(A2)}$$

that was proposed by Hammett[70] when comparing the rate of reaction of

[127] K. Linderberg, K. E. Shuler, J. Freeman, and T. J. Lie, *J. Stat. Phys.*, 1975, **12**, 217.
[128] W. Linert, Han-liang Fang, and I. Lukovits, *Chem. Phys.*, in the press.

benzoic acid with those acids with *meta* and *para* substituents on the benzene ring. Thus α in (A1) is identical to ρ in (A2) and σ is the ratio of the acid ionization constant of the substituted benzoic acid to that one of benzoic acid itself.

That relationships of type (A2), or more generally type (A3)

$$\log k_i = m \log k_j + c \tag{A3}$$

are indeed linear free energy relationships can be established as follows:

An equilibrium constant is related to the free energy change accompanying the reaction by (A4);

$$\log K = -\Delta G^0/2.303 \, RT \tag{A4}$$

the specific rate constant can be expressed by (A5)

$$\log k = \log(k_B T/h) - \Delta G^{\neq}/2.303 \, RT \tag{A5}$$

in terms of a free energy of activation, $\Delta G^{\neq}$, by making use of transition-state theory, and therefore the combination of (A3), (A4), and (A5) yields the LFER (A6)

$$\Delta G_i^{\neq} = m' \, \Delta G_j^{\neq} + c' \tag{A6}$$

(ii) Equilibrium Data

In this case the parallel equation to (A2) is (A7),

$$K_i = c_4 \, K_j^{\alpha} \tag{A7}$$

and this can be expressed in logarithmic form (A8) which, in view of (A4) is again a linear free energy relationship.

$$\log K_i = \alpha \log K_j + c'' \tag{A8}$$

Finally, two points remain to be made:
(a) Since equilibrium data are independent of the path taken by the reaction whereas kinetic data are wholly dependent on the pathway, it is not immediately apparent that this simultaneous correlation should occur.
(b) It is important to note that LFERs remain *empirical relationships* despite the fact that thermodynamic arguments often go a long way towards justifying them in specific cases.