

THE VALIDITY OF LINEAR FREE ENERGY RELATIONSHIPS AT VARIOUS TEMPERATURES

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The validity of the Hammett equation — or of any other one-parameter relation of free energies (LFER) — at various temperatures is conditioned by the validity of the isokinetic relationship, Eq. (4). The simultaneous dependence of the rate constants on temperature and on substituent constant is then given by the isoparametric relationship, Eq. (3). Calculations on 20 examples have shown that the later equation is obeyed with the same precision as the unconstrained LFER's for each temperature, the isokinetic relationship itself being always more precise. It follows that LFER's can be used safely at variable temperatures within a reasonable interval, *i.e.* as far as the activation parameters are temperature independent at least. When data at several temperatures are available, the isoparametric relationship should always be applied. Its theoretical corollary, the temperature independence of the reaction rate for a particular value of σ , is of no significance, since this critical value is experimentally not accessible in kinetics.

The broad significance of the Hammett equation (1) depends among others on its applicability to reaction series studied at different temperatures; it means that the fixed scale of substituent constants σ retains its validity when changing temperature, and the reaction constant ρ is only affected. The same applies to all correlation equations of the similar type, called Linear Free Energy Relationships (LFER). Further conclusions of this paper are restricted to those relationships of this type, which involve only one empirical constant characterizing substituent, or solvent, reagent *etc.*; they can be written in the form

$$(\forall T) \log k_{\sigma,T} = \log k_T^0 + \rho_T \sigma. \quad (1)$$

In this equation the logarithm of the rate (equilibrium) constant (k) depends on temperature and on substitution, the proportionality constant (ρ) and the rate of the unsubstituted compound (k^0) depend only on temperature, and the generalized substituent constant (σ) only on substitution (or on another variable parameter); the symbol ($\forall T$) denotes explicitly that the equation is valid for any fixed temperature.

Simultaneously, for any given σ , $\log k$ depends on temperature. When the temperature interval is not too broad and the highest precision not required, the Ar-

Arrhenius equation may be assumed to hold

$$(\forall \sigma) \log k_{\sigma, T} = \log A_{\sigma} - (E_{\sigma}^*/2.3R) T^{-1}, \quad (2)$$

in which the preexponential factor A and the activation energy E^* depend only on σ . Further conclusions of this paper are restricted to the approximation with the exactly valid Arrhenius equation and temperature independent activation parameters, but they apply to equilibria (with ΔH^0 instead of E^* and $\Delta S/2.3R$ instead of $\log A$) as well as to kinetics.

It can now be deduced that the simultaneous validity of equations (1) and (2) is equivalent to the equation (3), firstly derived by Miller¹ and called the isoparametric relationship² (IPR)

$$\log k_{\sigma, T} = y_0 + \varrho_0(\sigma - \vartheta)(1 - \beta T^{-1}). \quad (3)$$

Of the four empirical constants involved, β – the isokinetic temperature³ – represents the fictive temperature at which the rate constant is independent of substitution^{3,4}; ϑ – the critical value of σ (denoted² $\hat{\sigma}$) – is the fictive value of the substituent constant at which the rate is independent of temperature^{1,2}; y_0 – the isoparametric value², or the isokinetic point⁵ – is the value of $\log k$ at $T = \beta$ or at $\sigma = \vartheta$; ϱ_0 represents the limiting value of ϱ at the infinite temperature. When the dependence on σ is disregarded, equation (3) reduces to the form

$$\log k_{i, T} = y_0 + b_i(T^{-1} - \beta^{-1}), \quad (4)$$

which simply means that several Arrhenius lines have a common point of intersection (β^{-1}, y_0) . This statement is equivalent⁴ to the linear relationship between the activation parameters

$$\Delta H_i = h_0 + \beta \Delta S_i, \quad (4a)$$

or

$$E_i^* = e_0 + 2.3R\beta \log A_i.$$

Either of the equations (4), (4a) is called the isokinetic relationship^{3,4} (IKR). Taking into account the symmetry of equation (3) with respect to the variables σ and T^{-1} , one can deduce thereof another equation

$$\log k_{\sigma, j} = y_0 + \varrho_j(\sigma - \vartheta), \quad (5)$$

which means that several Hammett lines intersect in one point with the coordinates (ϑ, y_0) . Equations (4) and (5) together imply equation (3); however, one of them is

a necessary but not sufficient condition. *E.g.* from (4) one can deduce (3) only with the additional premise that the LFER equation is valid at one temperature at least. Hence the IKR is a sufficient condition for any LFER to hold at various temperatures, provided that it holds at one temperature^{6,7}. With respect to the symmetry of the model another combination of sufficient premises may be formulated, it is the equation (5) combined with the validity of the Arrhenius equation at least for one value of σ .

Finally, by comparing equations (1) and (3), the expression for the temperature dependence of the reaction constant ϱ follows^{4,6-8}

$$\varrho_T = \varrho_0(1 - \beta T^{-1}). \quad (6)$$

Most of these equations have been already derived¹⁻⁸, some are even well known. However, they have been usually treated in the framework of pure algebra and the fact has not been paid proper attention that they are only approximately valid. Hence, testing their validity and determining the values of constants are problems of mathematical statistics, and the results must be formulated and treated accordingly. *E.g.* the values of constants are estimates, related to the given statistical model; they cannot be obtained from arbitrary equation neither treated as a simple algebraic quantity. The object of the present paper are the pertinent statistical considerations and comparison with experimental data on typical reaction series.

THEORETICAL AND RESULTS

Let us have a series of l reactions ($l \geq 3$) differing only in substituents or any other single factor; the i -th reaction has been kinetically followed at m_i temperatures T_{ij} ($i = 1, 2, \dots, l; j = 1, 2, \dots, m_i; \sum m_i = N$ number of all data) and the values of $\log k_{ij}$ determined.* These data may now be correlated: A) by the separate Arrhenius equations (2) for each reaction without any assumption concerning the substituent effects, B) by the separate LFER's (1) for each set of $\log k_{ij}$ related to the same temperature, using a proper set of fixed substituent (or structural) constants σ and making no assumption as to the temperature dependence, C) by the IKR (4) irrespective of the substituent effects, D) by the set of LFER's expressed by equation (5) with no assumption as to the temperature dependence of the constant ϱ , E) by the IPR (3).

These possibilities are summarized in Table I, giving the equations which hold in each case, the constants to be estimated, standard deviations, and the pertinent degrees of freedom. The least-squares problem of estimating constants reduces

* It is assumed that the same values T occur in several reactions; for a significant correlation B it is necessary that each value T is encountered at least in three reactions. Most conveniently, of course, all the reactions are studied at the same set of temperatures, see the Appendix.

TABLE I
Statistic Models for Correlation of Reactivity Data at Variable Temperature

Model	Equations fulfilled	Degrees of freedom	Standard deviation	Constants to be determined
<i>A</i> independent Arrhenius equations	(2)	$N - 2l$	s_{00}	$A_i E_i^*$
<i>B</i> independent LFER's	(1)	$N - 2m$	s_{LF}	$\rho_j k_j^0$
<i>C</i> isokinetic relationship (4)	(2) (4)	$N - l - 2$	s_0	$\beta y_0 b_i$
<i>D</i> LFER's with constraint (5)	(1) (5)	$N - m - 2$	—	$\vartheta y_0 \rho_j$
<i>E</i> isoparametric relationship (3) with variables T^{-1} and σ	(1)–(5)	$N - 4$	s_{IP}	$\beta \vartheta y_0 \rho_0$

in the cases *A* and *B* to a series of simple regressions, whereas in the case *C* it is non-linear⁹ and can be solved generally only by approximation¹⁰; in the case *D* the problem is quite analogous. The most constrained case *E* is again simpler from the statistical point of view and is solved by multiple regression with some possible simplifications given in the Appendix.

In further considerations we shall raise the symmetry of the model with respect to σ and T^{-1} , supposing that the Arrhenius equation is always fulfilled. This assumption is reasonable within small temperature intervals as usual in solution kinetics. Hence the corresponding standard deviation s_{00} is taken merely as an estimate of the experimental error than of the imperfection of the model. By comparing s_{00} with other standard deviations by appropriate *F*-tests (not strictly applicable to models *C* and *D*, see^{9,10}) the validity of other models may be now tested.

It follows further that the model *B* is highly improbable and may be considered for comparison only; the less probable is the model *D* which will be further disregarded. Attention will be focused to testing model *E* by comparing with *C* or even with *B*; testing of the IKR in the model *C* was dealt with in another place¹¹.

The results obtained on 20 reaction series are listed in Table II. Data from recent literature^{12–28} have been mostly selected containing the sufficient number of constants in a not too narrow temperature interval. Most examples concern the Hammett equation in its classical range of validity²⁹; otherwise the selection was not quite systematic.

The correlations have been restricted to simple one-parameter equation and little attention was paid to the choice of proper σ constants. It follows that in some cases the fit could be improved but the overall pattern would not change. Some specific features of certain reaction series are mentioned in the foot-notes in Table II.

In addition to the statistics explained in Table I the standard deviation¹¹ s_R is listed in Table II, representing the variability of reactivity between the individual reactions of the series (*i.e.* due to substitution). The ratio of any standard deviation, resulting from a particular correlation, to s_R is the recommended measure of the goodness of fit^{11,30} (denoted ψ); the values of 0.44 and 0.14 correspond to correlation coefficients 0.9 and 0.99, respectively, in the case of simple regression.

DISCUSSION

Validity of LFER and IKR. Although the validity of IKR is a necessary condition for any LFER to hold at variable temperature, the experimental evidence has been somewhat puzzling. Ritchie and Sager³¹ distinguished three types of reaction series according to whether the Hammett equation or the IKR is obeyed, or both. Since the first possibility is theoretically inadmissible, it was assumed that it comes into existence only by improper statistical treatment²⁹. This assumption is now confirmed by the data of Table II. In most cases the fit of the LFER may be denoted⁸ as "excellent" (comparison of s_{LF} to s_R); the three cases where it is only "fair" are caused by the too small differences in reactivity (reaction series 5 and 12), or in addition by the low accuracy expressed by s_{00} (reaction series 19). In 18 of 20 reaction series the IKR is fulfilled better — usually much better — than the LFER (comparison of s_0 with s_{LF}). In the two exceptions, reaction series 16 and 19, the experimental error s_{00} is relatively large and all the standard deviations are in the same range; hence these cases do not invalidate the general conclusion.* It follows further that when the isokinetic constraint is added to a LFER, the resulting IPR (model E) yields as good fit as the original LFER (comparison of s_{IP} and s_{LF}). Usually the fit is even somewhat improved ($s_{IP} < s_{LF}$) since there are more degrees of freedom; the two apparent exceptions (reaction series 16 and 19) are explained as above.*

The main conclusions of this paper may thus be formulated as two mutually dependent postulates; although their validity has been proved directly on small samples of data, it is consistent with all the available evidence: 1. The IKR is more common and in general more precise than any LFER. 2. The proper LFER can be used at any temperature without additional problems. When data at several temperatures are available, the united correlation by equation (3) is preferable to separate ones.

The preference of IKR to LFER's is in accordance with the common feeling: The similarity between related reaction series should be still exceeded by the similarity within one series at different temperatures. On the other hand the validity of the two postulates is clearly restricted to a temperature interval "not too broad"; intervals usual in solution kinetics fall into this range.

* If s_{00} is assumed to represent the estimate of the experimental error, then any standard deviation smaller than s_{00} may only arise by chance and is of no significance.

TABLE II
Results of LFER Correlations at Variable Temperature

No	Reaction	Constants	l	N	Tempera- ture °C	Standard deviations 10 ³					β from Eq. (4), K	Constants of Eq. (3)	
						s_{00}	s_0	s_{LF}	s_{IP}	s_R		β, K	β
1	pK benzoic acids ^{12,a}	$\sigma_{m,p}$	9	36	15-30	2	3	15	14	360	-40	2.08	0.875
2	pK anilines ¹³	σ, σ^-	15	75	20-40	7	7	101	96	1 310	-938	2.33	0.760
3	pK benzal-4-methoxy- anilines ^{14,b}	σ, σ^+	6	24	15-50	39	36	159	144	1 270	-39	18.59	1.913
4	pK anisalanilines ^{14,c}	$\sigma_{m,p}$	6	24	15-50	23	34	114	104	760	91	87	3.566
5	equilibration of anti- pyridine dyestuffs ^{15,d}	$\sigma_{m,p}$	6	24	20-50	25	36	73	68	680	803	746	-1.218
6	benzoic acids + DDM ^{16,e}	$\sigma_{m,p}$	18	54	25-45	22	38	98	96	950	-1 546	-1 332	4.75
7	subst. DDM's + benzoic acid ^{16,e}	$\sigma_{m,p}$	8	24	25-45	27	22	104	99	1 020	-444	-433	-0.694
8	hydrolysis of dinitrophenyl thiobenzoates ¹⁷	$\sigma_{m,p}$	10	30	10-30	57	64	98	97	620	174	170	-6.79
9	methanolysis of allyl arenesulfonates ¹⁸	$\sigma_{m,p}$	8	24	30-50	3	6	20	19	530	-2 598	-2 482	11.99
10	malachite G. dyestuffs + OH ^{19,f}	$\sigma_{m,p}$	5	50	10-75	7	14	27	22	80	335	334	2.61 ⁿ
11	ditto ^g	$\sigma_{m,p}$	13	91	10-40	5	24	76	72	300	399	388	3.87
12	esterification of thiobenzoic acids ^{20,h}	$\sigma_{m,p}$	8	24	10-30	25	38	76	73	230	229	221	-2.87

13	alkylation of anilines ²¹	$\sigma_{m,p}\sigma_o$	15	45	30-40	20	15	82	80	540	545	540	-1.80	2.569
14	methylation of thiobenzamides ²²	$\sigma_{m,p}$	7	21	25-40	17	18	38	36	260	-257	-165	-28.31	-0.676
15	aryliselenocyanates + butylamine ²³	$\sigma_{m,p}$	5	20	15-30	29	30	54	47	590	105	116	-9.07	2.164
16	N-aryl-2-chloroacetamides + DMA ^{24,j}	$\sigma_{m,p}$	10	30	146-188	56	42	15	37	110	468	468	2.35	-4.059
17	dinitromethanes + MVK ^{25,k}	$\sigma_{m,p}^o$	11	44	5-50	12	13	45	43	140	141	136	37.80	-0.541
18	coupling of diazonium salts ^{26,l,m}	$\sigma_{m,p}$	11	44	0-25	5	17	249	236	1 460	1 005	963	1.06	-1.778
19	bromination of cyclohexanones ^{27,m}	σ_l	11	44	15-50	76	66	75	81	160	-1 027	-1 251	-29.57	-0.118
20	hydrolysis of benzoates ²⁸	σ^*	8	32	15-50	17	27	201	186	1 040	-28 824	6 915	4.96	-0.0709
	Approximate median values						20	30	80	80	500			

^a The temperature interval has been restricted to 15°C with respect to the non-linear Arrhenius plots; ^b substitution in the benzaldehyde moiety; correlation with $\sigma_{m,p}$ gives poorer results; ^c substitution in the aniline moiety; correlation with σ^- gives poor results; ^d equilibrium triaryl-methylation \rightleftharpoons triarylcarbinol, one aryl replaced by the antipyrine moiety; ^e DDM = diphenyldiazomethane; ^f reaction of triarylmethylations with hydroxide anion to yield carbinols; selected substituents with respect to the validity of IKR, full temperature interval; ^g all substituents investigated, restricted temperature interval, the IKR is fulfilled less accurately; ^h esterification reaction with 2,4,2',4'-tetranitrodiphenyl ether; ^j DMA = dimethylaniline; ^k MVK = methyl vinyl ketone; only *meta* and *para* derivatives have been selected; ^l coupling of benzene diazonium salts with Brønner acid; ^m one of the 44 rate constants has been estimated by extrapolation in order to facilitate the mathematical treatment; ⁿ in reference² this value is given with the opposite sign as -2.54.

Fig. 1 compares the correlations according to the equation (3) and that by unconstrained Hammett lines in the case of reaction series 16, where the difference is by chance very distinct; in typical examples the two models B and E are indistinguishable in the graph.

Meaning of the constant ϑ . This constant is of analogous physical meaning as the isokinetic temperature β . It represents a fictive value of the constant σ at which the reactivity is independent of temperature; when passing over this value the temperature dependence changes its sign. This consequence is easily understandable in the case of equilibria, which can shift with temperature to any side. *E.g.* the acidity of substituted anilines increases with temperature¹³; from Table II, line 2, one can predict that a substitution with $\sigma = 2.33$ would cause the temperature independence and at a still higher σ the acidity would drop with temperature. The prediction is confirmed by the behaviour of *ortho*-nitro derivatives³², even if these, of course, do not obey the Hammett equation.

On the other hand, such a reversal is an inadmissible corollary in kinetics, since the reaction rate can depend on temperature in one direction only. The question thus arises, whether the value of ϑ can be in principle reached experimentally and what will happen in such a case; the question is still more pressing than the similar one concerning the isokinetic temperature^{4,9,10}. From the 13 reaction series from Table II concerning kinetics, in at least 10 cases the constant σ lies far outside the range of possible values of σ and may be viewed as the product of extrapolation without any physical meaning. In fact the only possibility to surpass the value of ϑ is given

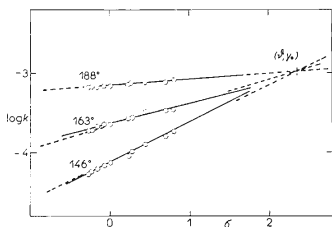


FIG. 1

The Isoparametric Relationship in the Coordinates $\log k$ vs σ (reaction²⁴ 16 from Table II; full lines — unconstrained Hammett equations, dashed lines — the isoparametric relationship)

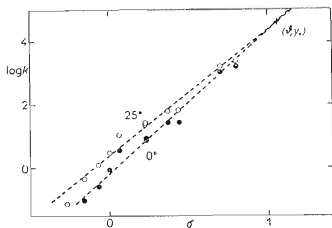


FIG. 2

The Isoparametric Relationship with a Near Critical Value ϑ and Large Scatter (reaction²⁶ 18 from Table II)

Symbols as in Fig. 1; ● at 0°C, ○ at 25°C.

in reaction series 18 (e.g. with 3,5-dinitrobenzenediazonium salt, $\sigma = 1.40$), but Table II and Fig. 2 show that just in this series the scatter is rather bad and the behaviour in the neighborhood of $\vartheta (= 1.06)$ cannot be predicted. In the reaction series 16 (Fig. 1) the fit is much better but the value $\vartheta = 2.35$ lies rather far and cannot be realized within the limits of the classical Hammett equation. In conclusion, there is no evidence that the value of ϑ could be reached (or even surpassed) experimentally in kinetics and a reaction with zero (or even negative) activation enthalpy thus realized. Of course, detailed studies of the border-line cases would be desirable.

Determination of β . The isokinetic temperature β is involved in both equations (3) and (4), but the least squares procedures yield different estimates from either (see the appropriate columns in Table II). It was suggested³³⁻³⁵ to determine β from equation (3) even when only the IKR is being investigated; still easier is the plotting, or correlating ϱ against T^{-1} according to equation (6). However, the two procedures are not equivalent generally, but only in a special case (see Appendix). Furthermore, both are principally incorrect, since they make the value of β dependent on a fixed scale of σ constants, the result may change when an inappropriate type of constants has been chosen, etc. Table II shows that the error is usually not very large but there are exceptions (e.g. reaction series 2, 14). It is also true that the exact value of β is not fundamental in the analysis in terms of the IKR, the values of s_0 , s_{00} , s_R being more important^{4,9,10}. Nevertheless, the unobjectionable statistical procedures are available^{4,9,10} to obtain unbiased values of β , hence it would not be logical to use the indirect procedures and replace the more precise equation (4) by the less precise equation (3).

Meaning of remaining constants. The constant y_0 , denoted the isoparametric value² or isokinetic point⁵, represents the value of $\log k$ at such a value of σ when it is independent of T , or *vice versa*. In principal it can be attained in two ways, either at the σ constant equal to ϑ , or at the temperature equal to β . The first possibility was considered on p. 522 to be realistic only with equilibria, while the second was discussed previously^{4,11} with the result that it is very rare but not completely excluded.

The constant ϱ_0 represents the fictive value of ϱ at the infinite temperature and its possible physical meaning, or use in mechanistic discussions are still obscure. The signs of ϱ_0 and ϱ_{exp} at the experimental temperature may be even opposite if β is positive and higher than T_{exp} ; in other cases the signs agree. All the possible combinations are listed in Table III, columns 2-4. As far as only kinetics are concerned, the values and signs of ϑ and y_0 are also interrelated and all the six possibilities are given in Table III and visualized in Fig. 3 in the coordinates $\log k$ vs T^{-1} . In the same graph also the dependence of ϱ on T^{-1} is shown. This classification unables us to discuss once more the validity of the so-called reactivity-selectivity relationship^{29,36}. No doubt that this principle accords with chemist's common feeling but it has not

been deduced theoretically, not is the experimental evidence unambiguous. In the case under consideration the principle would require the smaller differences between individual reactions the higher their reaction rates, *i.e.* the constant γ_0 should be

TABLE III
Relations between Constants in the Isoparametric Relationship (3)

Case	β	ϱ_0	ϱ_{exp}	ϑ		Examples from Table II	Reactivity-selectivity relationship
				ϑ	γ_0		
<i>a</i>	$>T_{\text{exp}}$	pos.	neg.	neg.	$>\text{exp.}$	5, 13	fulfilled
<i>b</i>	$>T_{\text{exp}}$	neg.	pos.	pos.	$>\text{exp.}$	10, 11, 16, 18, 20	fulfilled
<i>c</i>	negative	pos.	pos.	pos.	$>\text{exp.}$	1, 2, 3, 6, 9	fulfilled
<i>d</i>	negative	neg.	neg.	neg.	$>\text{exp.}$	7, 14, 19	fulfilled
<i>e</i>	$<T_{\text{exp}}$	pos.	pos.	neg.	$<\text{exp.}$	4, 8, 12, 15	violated
<i>f</i>	$<T_{\text{exp}}$	neg.	neg.	pos.	$<\text{exp.}$	17	violated

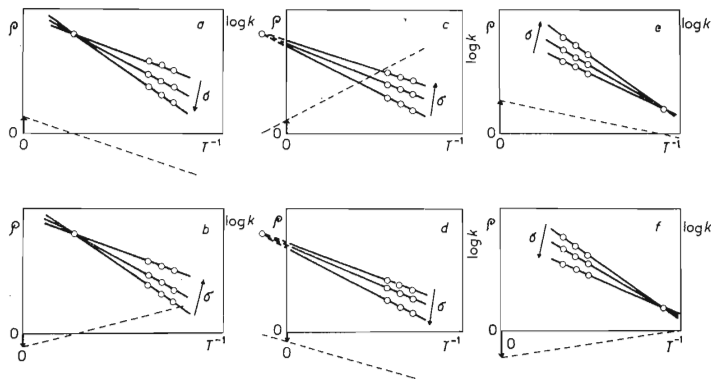


FIG. 3

Schematic Representation of Signs of Constants in the Isoparametric Relationships in the Coordinates $\log k$ vs T^{-1} ;

a-f Possible combinations from Table III, \circ point of intersection with coordinates (β^{-1}, γ_0) , dashed line — dependence of ϱ on T^{-1} , heavy arrow — ϱ_0 .

higher than experimental values of $\log k$ and represent some limiting value of reactivity. According to Table III the prediction is fulfilled in the cases $a - d$ which include 15 from the 20 experimental examples. It follows that even in this case the reactivity-selectivity relationship gives a true picture of typical, prevailing cases but is not without exceptions. Fig. 3 and the above considerations do not concern equilibria which may depend on temperature in both senses even within one reaction series.

APPENDIX

When equation (3) is rewritten

$$\log k_{\sigma, T} = \varrho_0 \beta \vartheta T^{-1} + \varrho_0 \sigma - \varrho_0 \beta T^{-1} \sigma + y_0 - \varrho_0 \vartheta \quad (3a)$$

it can be treated as a multiple regression with independent variables T^{-1} , σ , and $T^{-1}\sigma$ and dependent variable $\log k$; from the four coefficients of the regression the four constants β , ϑ , ϱ_0 , and y_0 are obtained univocally. The computation does not even require the set to contain values at several temperatures for each substituent, nor *vice versa*. However, the comparison with equations (1)–(4) makes this condition necessary; a reasonable set of data would involve, say, three values for each substituent and four for each temperature at least.

The most advantageous case arises, of course, when each of the l reactions (with σ_i , $i = 1, 2, \dots, l$) has been followed at each temperature T_j ($j = 1, 2, \dots, m$); it corresponds to the so-called special case⁹ in the computation of parameters of the isokinetic relationship (4). The regression is significantly simplified in this case and the constants are obtained directly according to the formulae

$$\begin{aligned} \vartheta &= (\sum_i \sigma_i - A_{11} A_{23} / A_{123}) / l, \\ 1/\beta &= (\sum_j T_j^{-1} - A_{22} A_{13} / A_{123}) / m, \\ \varrho_0 &= -A_{123} / \beta A_{11} A_{22}, \\ y_0 &= (\sum_{ij} \log k_{ij} - A_{13} A_{23} / A_{123}) / ml \end{aligned} \quad (7)$$

where the A 's have the usual meaning

$$\begin{aligned} A_{11} &= \sum_i \sigma_i^2 - (\sum_i \sigma_i)^2 / l, \\ A_{22} &= \sum_j T_j^{-2} - (\sum_j T_j^{-1})^2 / m, \\ A_{13} &= \sum_{ij} \sigma_i \log k_{ij} - \sum_i \sigma_i \sum_{ij} \log k_{ij} / l, \\ A_{23} &= \sum_{ij} T_j^{-1} \log k_{ij} - \sum_j T_j^{-1} \sum_{ij} \log k_{ij} / m, \end{aligned} \quad (8)$$

$$A_{123} = \sum_{ij} \sigma_i T_j^{-1} \log k_{ij} - \sum_i \sigma_i \sum_{ij} T_j^{-1} \log k_{ij}/l - \sum_j T_j^{-1} \sum_{ij} \sigma_i \log k_{ij}/m + \\ + \sum_i \sigma_i \sum_j T_j^{-1} \sum_{ij} \log k_{ij}/ml.$$

In this case, and only in this case, the constants β and ϱ_0 may be also obtained by the linear regression according to equation (6); this indirect procedure is clearly cumbersome and of little value, when a complete analysis is desired.

The residual sum of squares is given by

$$S_{IP} = \sum_{ij} (\log k_{ij})^2 - (\sum_{ij} \log k_{ij})^2/ml - A_{13}^2/mA_{11} - A_{23}^2/lA_{22} - A_{123}^2/A_{11}A_{22} \quad (9)$$

and has, according to Table I, $ml - 4$ degrees of freedom. It can be compared to the residual from unconstrained LFER's

$$S_{LF} = \sum_{ij} (\log k_{ij})^2 - \sum_j (\sum_i \log k_{ij})^2/l - \sum_j (\sum_i \sigma_i \log k_{ij} - \sum_i \sigma_i \sum_{ij} \log k_{ij}/l)^2/A_{11} \quad (10)$$

(with $ml - 2m$ degrees of freedom) and to residuals S_0 and S_{00} computed by the appropriate formulae^{9,10}.

The computations have been programmed for the Hewlett-Packard calculator 9820 A. In the input are given: temperatures in °C, σ values, rates constants either as $\log k$ or $k \cdot 10^x$. In the output one obtains: T^{-1} in reciprocal K, σ 's, values of $\log k$, unconstrained ϱ 's for each temperature, β in K, $1/\beta$, ϱ , ϱ_0 , γ_0 , s_{IP} , s_{LF} . The data of Table II have been obtained in this way.

LIST OF SYMBOLS

$A_{11} \dots A_{23}$	auxiliary symbols defined by Eq. (8)
b	slope of the Arrhenius line, Eq. (4)
i	subscript pertinent to a reaction (substituent)
j	subscript pertinent to a temperature
k	symbol for rate or equilibrium constant
k^0	intercept of the LFER
l	number of reactions
m, m_i	number of temperatures
N	number of all data
$s_0, s_{00}, s_{IP}, s_{LF}$	standard deviations defined in Table I
$S_0, S_{00}, S_{IP}, S_{LF}$	residual sum of squares corresponding to the respective standard deviations
s_R	standard deviations expressing difference between reactions
γ_0	isoparametric value of $\log k$, Eq. (3)
β	isokinetic temperature
δ	critical value of σ , Eq. (3)
ϱ, ϱ_T	temperature dependent reaction constant
ϱ_0	reaction constant at the infinite temperature, Eq. (3)
σ	generalized substituent constant

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