a different blend. (b) The pertinent π^*, α, and β values might not yet have been determined at the time TAK carried out their correlation. (c) The TAK correlation may have involved data from an earlier literature reference, where the SSPA correlation took data from a later paper in which the data base had been expanded. Again, this appears to be the case with the $E_T(30)$ results. (d) TAK may have specifically mentioned that we were using a limited data set, e.g., only select solvents or only nonprotonic aliphatic solvents, to exclude hydrogen bonding or variable polarizability effects.

Fortunately, the information necessary to test the above allegation is readily at hand. As a specific instance, SSPA state in their footnote 60, "As a typical example, in Table II, we (SSPA) retain E_T data for triethylamine, methyl ethyl ketone, nitromethane, ethyl ether, hexane, and cyclohexane, all omitted by Kamlet et al. We (SSPA) use 47 E_T data whereas they use only 31." It is true that we (TAK) excluded these data. The reasons were (a–c) above. However, we have now repeated the correlation including all the additional solvents for which the solvatochromic parameters are known; n becomes 39, and the multiple linear regression equation is given by eq 6. The above

$$E_T(30) = -0.51 + 14.3(\pi^* - 0.23\delta) - 15.5\alpha \tag{6}$$

$$n = 39;\ r = 0.986$$

correlation coefficient compares with $r = 0.985$ for our earlier correlation involving the 31 solvents.

The free energies of transfer of the $Et_4N^+I^-$ ion pair is another example. SSPA commented that their 21 solvents gave $r = 0.984$, while our 10 solvents gave $r = 0.987$. Here, the reason for the exclusion of data was (d) above. Accordingly, we have rerun our correlation using the same 21 data as SSPA. The result is given in eq 7. Thus, in

$$\Delta G_t(Et_4N^+I^-) = 3.15 - 12.8(\pi^* - 0.17\delta) - 4.60\alpha \tag{7}$$

$$n = 21;\ r = 0.988$$

both cases, inclusion of the additional data have not worsened but very slightly improved the statistical goodness of fit of the TAK correlations. We consider this to be prime facie evidence that the SSPA allegation was incorrect.

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Substituent and Solvent Effects on Chemical Reactivity

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This is a comparison of the procedures of five research groups using multiple correlation analyses for assessing the components of substituent and solvent effects. Advantages and problems of each procedure are indicated.

In 1983 our papers reevaluating components of substituent effects[1] and solvent effects[2] were published. After three papers[3-5] critical of the first and one[6] critical of the second were submitted, editors F. D. Greene and W. J. le Noble generously invited us to contribute this paper. The four omit any mention of the weaknesses of the approach being promoted; therefore, we shall try to put all five approaches into perspective and compare their strengths and weaknesses.

General Problems with Multiple Linear Free-Energy Relationships

Linear free-energy relationships are based on the fact that free-energy differences (or spectral frequencies or logarithms of rate or equilibrium constants) for numerous reactions denoted by i can be expressed as linear functions ($a_ix_j + b_i$) of a common set of constants (a vector x_j) when common structural modifications denoted by j are made in a reactant or solvent. The first ones were the Brønsted laws for catalysis by acids ($\alpha_i(pK_A)_j + c_i$)[7] or bases ($\beta_i(pK_B)_j + d_i$).[8] The best known is the Hammett equation ($\rho_i\sigma_j + e_i$).[9] We first suggested the use of *multiple*, e.g., dual ($a_ix_j + b_iy_j + c_i$), linear free-energy equations when structural changes influence the overall effect in multiple but nearly independent ways, as when both electrophilic (x_j) and nucleophilic (y_j) properties of a solvent affect logs of solvolytic rate constants.[10] Such dual vector representations were subsequently adopted by Edwards and Pearson,[11] Winstein,[12] Yukawa and Tsuno,[13] and many others. It often does happen that two factors are important and

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[2] Swain, C. G.; Swain, M. S.; Powell, A. L.; Alunni, S. *J. Am. Chem. Soc.* **1983**, *105*, 502.

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[4] Hoefnagel, A. J.; Oosterbeek, W.; Wepster, B. M. *J. Org. Chem.*, second article in this series.

[5] Charton, M. *J. Org. Chem.*, third article in this series.

[6] Taft, R. W.; Abboud, J. M.; Kamlet, M. J. *J. Org. Chem.*, previous paper in this issue.

[7] Brønsted, J. N. *J. Am. Chem. Soc.* **1927**, *49* 2582.

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[11] Edwards, J. O.; Pearson, R. G. *J. Am. Chem. Soc.* **1962**, *84*, 16.

[12] Winstein, S.; Fainberg, A. H.; Grunwald, E. *J. Am. Chem. Soc.* **1957**, *79*, 4146.

[13] Yukawa, Y.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 971.

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operate nearly independently (e.g., resonance and inductive effects of substituents, or anion solvation and cation solvation by solvents), and a major improvement in fit or predictability results when they are allowed for explicitly by two separate vectors.

In physics or chemistry it is usually possible to vary one structural or environmental variable j at a time, and the variables usually exert their influence by not more than two major independent (unrelated) factors or modes of action. When two factors are sufficient, it becomes possible to sort out the two factors by a factor analysis of the data. In phase 1 of such an analysis the optimum least-squares fit between observed and calculated data (with two vectors) is obtained, but the vectors x_j' and y_j' are not unique (reproducible from the same data) unless phase 1 includes six subsidiary conditions (4 to set references and scales, and two critical ones). The fits (correlation coefficients) do not depend at all on the choice of any of these conditions. However, whether or not the vectors x_j' and y_j' have simple physical significance depends entirely on the assumptions represented by the two critical ones. In phase 2 of any analysis one can replace these two by *valid* (true) critical subsidiary conditions to transform the a_i', b_i', c_i', x_j', and y_j' values, *without any changes of fit*, into new values that have a clear meaning or interpretation at the molecular level. Thus if x_j and y_j represent anion and cation solvating tendency, phase 1 might have yielded $x_j' = x_j + y_j$ (or $2x_j + 3y_j$) and $y_j' = x_j - y_j$ instead of x_j and y_j, but phase 2 can then yield x_j and y_j, with no change in the overall or any individual correlation coefficient.

If two vectors are so much better than one, why not use three or more? This has been tried many times, but such attempts typically[14] have suffered from three errors or difficulties. First, standard deviations between observed and calculated data have been used to evaluate goodness of fit, whereas proper correlation coefficients should be used instead to put deviations into proper perspective by dividing by the range of the data and to incorporate the proper number of degrees of freedom.[2] Such correlation coefficients must be higher with three vectors than with two to justify three vectors. Second, the vectors have often had different dimensions (energy, frequency, or none) and units (kcal, cal, s^{-1}, cm^{-1}, or none) so that their relative importance is obscured, but no correction for this (such as our weights[1] w_i) has been applied. Third, application of phase 2 is much more difficult when three or more vectors are involved because then many more critical subsidiary conditions must be identified, justified, and incorporated in phase 2 (0 for 1 vector, 2 for 2 vectors, 6 for 3 vectors, 12 for 4 vectors).[15] This has never been done with 3 or more vectors, and usually not even with two.

There are other factor analysis procedures developed and used by psychologists, political scientists, economists, statisticians, and others confronted by factors that cannot be varied one at a time, but these generally incorporate unjustified and invalid subsidiary conditions in their transformations and are not equivalent to our phase 2. When applied to a problem with accurately known answers, they all give grossly wrong answers and conclusions.[16] We conclude that such factor analyses are misleading and should be abandoned, but recognize that we have not provided an easy alternative when three or more factors need to be considered. Fortunately, we believe that we at least have a generally valid and practicable method (DOVE, dual obligate vector evaluation) for evaluating two meaningful factors when two are sufficient.[15]

As might be expected, the most controversial part is the choice of the two critical subsidiary conditions used in phase 2. Ours are as follows: For substituents, one of them states that trans 4-substituents in cyclohexane derivatives exert no influence *by resonance* on a reacting center at position 1, while the other states that a $(CH_3)_3N^+$ substituent is never either more electron donating nor more electron attracting than H *by resonance*.[1] For solvents, one of them states that hexamethylphosphoric triamide (HMPA) is as poor at anion solvation as *n*-heptane, while trifluoroacetic acid (TFA) is at the other extreme, as poor at cation solvation as *n*-heptane.[2] We are concerned that no one of these subsidiary conditions is 100% accurate, but there is abundant evidence that each is close enough to the truth to serve well until more suitable substituents or solvents for these conditions are identified. These conditions yield reasonable resonance ($y_j = R$) and nonresonance ($x_j = F$, field or inductive) constants for 43 substituents and sensitivities ($b_i = r$ and $a_i = f$) to these for 14 reactions (220 data) used to evaluate R and F and 32 others (271 more data),[1] and reasonable anion solvation ($x_j = A$) and cation solvation ($y_j = B$) constants for 61 solvents and sensitivities (a and b) for 77 reactions (1080 data) on which A and B are based and 11 others (75 more data).[2]

Linear free-energy relationships should be expected to fail if pushed to extremes where the mechanism of reaction changes (e.g., by a change in rate-determining step) or the reactants undergo a major change in their state of aggregation in solution (e.g., from solvated monomer in methanol to hydrogen-bonded dimer in benzene). Although we found 1155 solvent effects apparently free from such difficulties, we found many others that did not fit well but where these or other special complications could be identified as very likely in one or more of the solvents used. Actually it seems rather remarkable that as many as 1155 solvent effects can readily be found where only two solvent factors (expressed by two constant vectors x_j and y_j need to be considered.

When a new reaction of small related group of reactions fails to fit with two vectors (x_j and y_j) one has at least three choices: (1) One can use a different set of values for one or both of the two vectors (x_j and y_j). (2) One can use three vectors ($a_ix_j + b_iy_j + c_iz_j + d_i$) instead of two. (3) One can introduce no new vectors, but instead use the deviations to suggest likely special effects as above. The second (2) is very difficult to implement because six critical plus six reference or scale-factor conditions are then required. We favor the third choice (3).

The first choice (1) has been most popular and of course gives better fits because one is free to change "constants" at will. However, this multiplicity of parameters has several disadvantages. It makes the better fits less noteworthy. It allows a subjective or arbitrary choice between vectors by the user, which may allow more rationalization after data are known but probably less to be predicted before, owing to doubt about which vectors to use. It is no longer clear how many different kinds of factors are involved. If one has accumulated 12 vectors, one is likely to draw the incorrect inference that 12 different factors or properties are all important. One might think that 1 is not very different from 3 because each recognizes that something is different about the ill-fitting reaction and very similar reactions. However, the inference under 1 is likely to be that the mechanism is constant but another kind of

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[15] Strong, P. F.; Swain, C. G.; Swain, M. S. *J. Chem. Inf. Comput. Sci.* 1979, *19*, 13.

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factor needs to be considered, whereas the inference under 3 is the more probable one that there is a discontinuity in the mechanism, e.g., a change in complexing or a change in rate-determining step.

The clearest way to spot abnormalities is to do as we have done, i.e., evaluate solvent (or substituent) constants that represent average or normal behavior for the solvents (or substituents) in a wide variety of reactions, then compare observed vs. calculated rates for new reactions using these constants, and then use the direction (sign) and magnitude of deviations as a direct and quantitative measure of abnormalities or of breakpoints in a reaction mechanism. This can be done from a *single* plot or table using two constant vectors, without the need for trial and error correlations with different sets of parameters and consequently greater uncertainty about what the different sets represent and what the different correlations imply.

The Reynolds and Topsom Paper[3]

Following Charton who refers to our substituent paper as SURS (Swain, Unger, Rosenquist, Swain)[1] and Taft who refers to his correlations as TAK and our solvent paper as SSPA (Swain, Swain Powell, Alunni),[2] we shall refer to Reynolds and Topsom[3] as RT, to Hoefnagel, Oosterbeek, and Wepster[4] as HOW, to Charton[5] as C, and to Taft, Abboud, and Kamlet[6] as TAK.

RT criticize our assumption that $(CH_3)_3N^+$ is not a significant electron donor by resonance. However, references that they cite as evidence refer to H_3N^+ rather than to $(CH_3)_3N^+$. For example, for electron donation their references show that H_3N^+ directs only 62% meta in nitration (presumably because the minor fraction of free H_2N is ortho,para directing and much more reactive), but $(CH_3)_3N^+$ in fact directs 89% meta. Then (under ii) they suggest that 4-substituted quinuclidinium ions or 3-substituted pyridinium ions would be more appropriate for defining F than any saturated carboxylic acid because "both are predicted to have insignificant resonance contributions." This is an odd suggestion after their contention that ammonium ions are significant resonance donors.

In connection with our use of a single resonance constant (criticized under iii), our fits to σ_p^+ and σ_p^- are good in spite of this (correlation coefficient = 0.994), just as good for such extreme substituents as H_2N, HO, and CH_3O as for other substituents in the σ_p^+ series and just as good for such extreme substituents as NO_2 and CN as for 15 other substituents in the σ_p^- series. There do appear to be data for σ_p^- for a few other substituents that we missed. However, the slightly higher % r for σ_p^+ than for σ_p^- accommodates them and is consistent with the degree of curvature in their consequently inappropriate plot (RT, Figure 1).

More important is the matter (discussed under iv) whether substituent constants should be constant or whether their values should be adjusted to fit each special application or type of reaction being correlated. The major objective of RT, HOW, C, and TAK has been to obtain good fits and they have allowed themselves multiple vectors and used, for any application, whatever vector or vectors fit best. This is a different objective from SURS or SSPA (see last section of this paper) but certainly reasonable and worthwhile. However, this multiplicity of parameters has all the disadvantages noted for choice 1 under "General Problems" above.

The Hoefnagel, Oosterbeek, and Wepster Paper[4]

This paper is unique among the five in presenting new experimental data by the authors themselves, as well as reviewing their previous experimental work, and it emphasizes clear-cut examples of deviations from average behavior of the sort that we discussed at the end of the "General Problems" section above. This is quite useful. We expect that the main use of our F,R treatment will become the assessment of such deviations, just as the principal use of the Hammett $\rho\sigma + e$ equation became the study and interpretation of deviations from it as soon as constant substituent constants σ were tabulated.

Although it is a (remarkable) fact that one set of R constants suffices adequately for many purposes, including correlating σ_p, σ_p^+, and σ_p^- and all the reactions correlated separately or collectively by σ_p, σ_p^+, and σ_p^-, it is obvious and inevitable that if there is enough stronger electron demand or electron repulsion by the reaction center the electron response of substituents will vary significantly and may even change sign. For example, if one considers substituents *directly* attached to a reaction center, phenyls on a carbocation (as in Ph_3C^+) are obviously electron supplying by resonance but on a carbanion (as in Ph_3C^-) are electron withdrawing by resonance (relative to H_3C^+ or H_3C^-). Of course our correlation will not accommodate such large effects.

From other data HOW claim that we have overestimated the resonance tendency of a nitro group relative to its nonresonance effect (as about equal, from Wheland's phenol data). HOW estimate only 12% and 1% resonance effects in *p*- and *m*-nitrobenzoic acids. However, these effects can be correct and still consistent with our treatment because the effect depends not only on F and R but also on sensitivities f and r, which are different for *p*- and *m*-substituents and also different for phenols and benzoic acids. These are not discrepancies or abnormalities.

The discrepancies with charged substituents noted in their Table I are real but small (correlation coefficients still generally above 0.965). Failure of our F values to fit their theoretical dipole treatment more accurately may raise more doubt about their theoretical treatment than about our F's, which are more empirically based.

"Through-resonance effects" is the name HOW give to the variation of resonance influence of a substituent depending on its environment, for which the evidence, although not nonexistent, now at least seems much weaker and less general than before. Our empirical fits to σ_p, σ_p^+, σ_p^-, and a wide range of related reactions with a constant set of R values is certainly very good. These fits are even more significant because the larger range of σ_p^+ data results in a lower weight for them than for σ_p^- data, i.e., the weight in our nonlinear least-squares analysis for any series i is the reciprocal of the variance of data for that series.

The principal weakness of the HOW work is that it stops with phase 1 (see General Problems section) and does not do the phase 2 separation of substituent effects into nonresonance (field, inductive, or localized) and resonance (delocalized) components. Their correlations using two different experimental σ sets as x_j and y_j fit just as well, but none of these experimental series is free from nonresonance influences.

The Charton Paper[5]

Under his section on Methods, C states only slightly incorrectly the critical subsidiary conditions that we used to separate F and R (our r is actually set at 0 for one reaction, not many, and R for $(CH_3)_3N^+$ is set at 0 regardless of whether it is bonded to a benzene ring or not), but he completly fails to state the critical subsidiary conditions that Taft or he use to separate the calculated vectors σ_I and σ_R. His main focus in this paper is on whether F or σ_I gives the better fit in correlating substituent effects in reaction series where we and everyone will agree that π-bond resonance plays little or no role. (It is possible to find a large number of such reactions, whereas we agree that no reaction series exhibits substituent effects free from a significant field or nonresonance component.) However, C arbitrarily excludes all substituents that are ionic ($(CH_3)_3N^+$, COO^-, O^-, SO_3^-, etc.) or hydroxylic (OH, COOH, CH_2OH, etc.). These should not have been excluded (see below). His main conclusion is that σ_I is superior because it gives better fits than F in simple correlations with this specially chosen remaining group of substituents.

One weakness in this argument is that this is a poor way to decide whether F or σ_I is superior because, in fact, both fit well even with this chosen group (both averaging between 0.971 and 0.986 for his 16 reactions).

We noted[1] that some polar or hydroxylic substituents (OH, NH_2) do have measurably different effects in protic and aprotic solvents (OH more like O^-, NH_2 more like NH_3^+, in protic solvents), but the variation is generally by less than 0.2 in log k, not enough to interfere with assigning useful average values for these substituents nor to warrant their exclusion from correlations.

A much more series weakness of the C paper is its failure to state the critical subsidiary conditions that Taft or C use to evaluate σ_I and σ_R. As discussed in the "General Problems" section above, whether users realize it or not, the evaluation of physically significant factors or vectors x_j and y_j for any linear dual vector expression or equation $a_ix_j + b_iy_j + c_i$ depends on identifying, justifying, and incorporating into the analysis two valid critical subsidiary conditions.[15] This is an essential difference from one-vector treatments like the Hammett equation, where no critical subsidiary conditions are involved. Many proponents of dual linear free-energy relationships (including Charton) do not appear to appreciate this, but have arrived at their numbers in undefined and thus unreproducible ways, using their fit to experimental data as sufficient justification.

Two critical conditions are required and involved whether stated or not. Originally Taft and co-workers were careful about this and their conditions were clearly stated to be (1) equal steric and resonance effects in acidic and basic rates of hydrolysis of saturated carboxylic esters and (2) transmission of resonance influence only 33.3% as effective from a meta position in a benzene derivative as from a para position, but field influence 100% as effectively transmitted. However, the 33.3% and 100.0% values lack any rigorous justification and for some reactions fits were better with 10% or 60% than 33.3%. More recently some σ_I values appear to have been derived from acid dissociation constants rather than rates of ester hydrolysis. Still more recently it appears that values have been varied arbitrarily or subjectively simply to improve the fit. Certainly it is no longer clear what the two critical subsidiary conditions are.

It would be most helpful if Charton or Taft would state all their current subsidiary conditions clearly and also assemble all the data on which their constants are now based in one table so that everyone will understand exactly how the present σ_I and σ_R values are obtained. At the moment it is not clear how one could reproduce the σ_I and σ_R values. The σ_I and σ_R can hardly be any more valid than the unfortunately now obscure subsidiary conditions on which they are based. As noted above, the fits with F and σ_I are good, similar, and not really the problem. The problem is specifying the conditions necessary for a phase 2 transformation or its equivalent to make the final constants physically significant without changing any of the correlation coefficients. This problem was stated clearly by Jack Hine in 1975,[17] but it is still not generally appreciated.

We previously calculated that σ_I has a 9% resonance component (9% r by multiple linear least squares based on our F and R values). This is supported, for example, by the positive σ_I assigned to SO_3^- (+0.15, in spite of its full negative charge), whereas our F is −0.05. One expects SO_3^- to be electron withdrawing by resonance (R = +0.53), but not by its field effect. Most reaction series have resonance contributions between 0% and 50% r, so +9% r is not at all unusual or unexpected. C turns this around and calculates that our F has a negative (−15%) contribution from σ_R based on his σ_I and σ_R values. However, a mix with negative % r still implies that F includes a *smaller* contribution from R or σ_R than does σ_I. F, σ_I, and R (or σ_R) are still in the same rank order. Only the reference point has shifted.

The Taft, Abboud, and Kamlet Paper[6]

The procedure that TAK use is to try simple (one-vector) linear correlations with their various parameter sets (π^*, α, β) before trying multiple linear correlations. This is a reasonable procedure and quite sufficient if the correlation coefficient with one of these vectors alone exceeds 0.965. Simple linear correlations are much easier to do or plot than multiple linear correlations. They are less controversial when they fit well than dual linear correlations because simple linear correlations require no critical subsidiary conditions to be identified, justified, and incorporated, but only the one trivial reference (zero) condition and the one standard (unit) condition, whose arbitrary assignment changes only the reference solvent and scale unit size.

However, there are many more venerable sets that could also be tried singly for correlating new reactions, such as Winstein's Y based on *tert*-butyl chloride solvolysis rates, Kosower's Z, Reichardt's and Dimroth's E_T30, or log k_2 for the Menschutkin reaction $Et_3N + EtI$ (which unfortunately tends to be ignored because it has not been assigned a letter symbol). If one tries three of these, E_T30, Y, and this log k_2, one has a fair chance of finding one of them that fits, because collectively they represent a wide range of different responses to changing solvent. One could easily draw the incorrect inference from this that three solvent factors or properties are affecting the reactions used for evaluating these different single vectors, i.e., that these different reactions are responsive to three different factors or different combinations of three factors. In fact SSPA showed that *only two* solvent factors are involved in E_T30, Z, Y, and log k_2 for $Et_3N + EtI$ because each can be expressed as a different linear combination of only two other vectors (A and B) for all the solvents studied, with a correlation coefficient above 0.983.[2] These simply form a graded series in which E_T30 gives the most weight to A, and log k_2 for $Et_3N + EtI$ gives the most weight to B. In fact, SSPA showed that 88 single reactions can be so expressed. Therefore in principle one could do a simple linear correlation ($ax + b$) of any new reaction against each of the 88 in succession separately and have a very good

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(17) Hine, J. "Structural Effects on Equilibria in Organic Chemistry"; Wiley: New York, 1975; pp 74–75.

chance of finding a good fit with at least one of them. However, this would be so excessively time consuming that no one is likely to choose more than three along the graded series.

TAK try only π^*, α, and β separately before resorting to multiple linear correlation with various pairs and triads of their three vectors. Usually at least some combination of them yields a correlation coefficient above 0.965. The reason that TAK assign a third vector (β) is the reasonable desire to improve the fit for some reactions that do not fit without β. Also for this reason they use whatever multiple combination of however many of the three vectors is needed to fit any given reaction or application best. They also often restrict the choice of solvents used according to clearly stated rules in order to improve the fit further, but the "rules" are of course just descriptions of what has been or is being done to get the best fit.

Although we agree that "best fit" is a worthwhile goal, it should not be considered so important that three solvent vectors are used in a multiple correlation when two are generally adequate. In fact the overall improvement in fit with three variable vectors is slight compared to two constant vectors and does not warrant a third vector.[2] Our deviations with two constant vectors are already about as small as the likely experimental errors.

The greatest weakness of the TAK approach is that phase 2 is not done right. Whether a user realizes it or not, *six* valid critical subsidiary conditions must be identified, stated, justified, and incorporated into any analysis involving three solvent vectors (in addition to the six trivial ones that fix zero reference points and scale unit sizes) to assure that the derived vectors not only are unique (reproducible from the same data) but also physically significant (in the right rank orders for the factors that they purport to measure).[15] The constants can be no more valid than the six critical subsidiary conditions so identified and used. As a practical matter it is extremely difficult to find, justify and incorporate six critical subsidiary conditions. If one uses two solvent vectors instead of three, the number of required critical subsidiary conditions drops to two, which is more manageable. TAK have understood and quite correctly stated our two critical subsidiary conditions in their abstract and first three paragraphs. What is missing in the subsequent discussion is a statement of all the subsidiary conditions built into TAK's two-vector and three-vector analyses. If their emphasis had been on phase 2 (assigning correct physical meaning to the solvent vectors) TAK would have identified and emphasized the 2 (or 6) critical subsidiary conditions rather than just good correlation coefficients (which are determined in phase 1 and *do not change* in phase 2, see "General Problems" above).

Optimizing the fits by adjustment of the vectors is not enough. Optimizing fits is a phase 1 operation and has *nothing* to do with physical significance of the component vectors. That is totally determined in phase 2 (which can be accomplished either by a subsequent transformation that changes no correlation coefficients but does change all the constants, or by any equivalent procedure), which must embody 6 or 12 subsidiary conditions (2 valid, defensible, critical + 4 trivial for two vectors or 6 valid, defensible, critical +6 trivial for three vectors). If TAK can state, justify, and incorporate valid critical subsidiary conditions, they may be able to remedy this deficiency and make their analyses physically significant as well.

TAK assign special roles to the hydrogen-bond donor and hydrogen-bond acceptor solvents, which are used to evaluate their α and β parameters. However, there is no experimental series that measures a hydrogen-bonding influence of the solvent free from other influences of the solvent. Also, SSPA found no convincing evidence that solvations involving hydrogen bonding are qualitatively different or require different treatment than solvations involving other kinds of polar or polarizable solvent molecules. They did not exclude hydrogen bonders, but mixed all types together. Reactants in their series 35–41, 69, and 70 are all what TAK call "hydrogen bond donors", many others are Lewis acids, and there is also no shortage of what they call "hydrogen bond acceptors". There are many excellent fits over a wide range of reactant types as well as the whole range of solvents. The fact that two solvent vectors are generally quite adequate for all these data shows that only two solvent factors are important. When significant deviations do occur, we therefore think that it is better to look for and test the cause rather than to define additional solvent vectors.

There are indeed many reactions that do not fit either TAK's equations or ours. TAK do not discuss these in general, but SSPA have. In many cases it is clear why they do not fit. For example, there may be a breakpoint due to a change in rate-determining step. The solvolysis of *tert*-butyldimethylsulfonium ion is abnormally slow in acetic acid because the rate-determining step changes from $(CH_3)_3C^+$ formation in more polar solvents to reaction of the cation with acetic acid in acetic acid. There may be a significant change in state of association of a reactant. The IR stretching frequencies of CH_3OD fit well enough in the more polar solvents but in less basic and less polar solvents the shifts with changing solvent are less than expected. Evidently CH_3OD stops associating predominantly with the solvent and begins to self-associate because it is then a better base than the solvent. Deviations occur exactly where expected and are perfectly understandable. Similarly understandable deviations arise when charge transfer complexes form or when the reactants or mechanism change for any other reason. Such reactions should not be used for defining new solvent vectors because each may be unique. We are in fact surprised that so many (88) reactions have a constant mechanism over such a wide range of solvents, which makes our correlation with two constant vectors (A and B) more useful than anticipated for detecting such points of mechanistic change when they occur. The deviations then are and should be the focus of our scrutiny because they are direct measures of the direction and magnitude of the unexplained departure from average, normal, or previously expected behavior.

TAK conclude that our B measures solvent "dipolarity/polarizability" rather than basicity. This cannot be true. B is a maximum for HMPA ($((CH_3)_3N)_2PO$), *n*-butylamine, and aniline, solvents hardly noted for their high polarity or polarizability. Ethanol, on the other hand, has a B value less than half as large as these amino compounds. However, we do provide a perfectly good measure of solvent polarity (a combination of anion-solvating ability and cation-solvating ability) in $A + B$, which of course is much higher for water or ethanol than for HMPA. The TAK π^* and α hybrid parameters are correlated with each other (correlation coefficient = 0.52). Our independent parameters A and B are not.

The Swain, Unger, Rosenquist, and Swain[1] and Swain, Swain, Powell, and Alunni[2] Papers

Our principal goals have been to determine how many significant factors have to be included to account for about 95% of all the effects considered (it appears to be two), and to identify the factors qualitatively and evaluate them quantitatively. We think that we have confirmed that they are field (and/or inductive) and resonance factors for the 491 substituent effects that we considered and anion- and cation-solvating tendency for the 1155 solvent effects considered, and have provided reasonable, constant, and generally useful values for them.

A strength of this approach is that it considers a wide range of data and reaction types simultaneously so that the derived constants represent an average or norm from which deviations are then more apparent and more easily measured. Other strengths are that it works over the whole range with only *two constant* vectors, and that the two critical subsidiary conditions are clear, as is, consequently, the physical significance of the constants. There is value in learning that only two significant factors are involved. The range of data fitted is large enough to challenge the general previous view about the necessity or desirability of using variable parameters or maintaining three or more discrete sets of solvent constants to cope with these same applications. For any new reaction we do only a *single* correlation, always with the same constant substituent or solvent vectors, and then focus attention on the deviations.

A weakness is the fact that correlations may be slightly poorer than when more vectors are used, or when vectors are selected or adjusted to make the fits better. We have deliberately avoided special vectors or special rules for particular applications. Our choices of critical subsidiary conditions are no doubt more subject to criticism because we stated them so clearly, and they are so easily understood. We chose them so that the solvent factor measured by A becomes a property that TFA has but HMPA and n-heptane lack ($A = 0$, hence A = "anion-solvating tendency"), while B becomes a property that HMPA has but TFA and n-heptane lack ($B = 0$, hence B = "cation-solvating tendency"). Although these solvents appear to be the most extreme ones among the group we studied, more extreme solvents may be found or sought in the future. If they are, it fortunately requires only a simple one-step transformation to recalculate all A, B, a, and b values, whereupon HMPA, TFA, and n-heptane will no longer be the extremes, but probably still close to extremes with all changes relatively minor.

A practical weakness is that our procedure always involves multiple (dual) least-squares correlations to determine a, b, and c for any new reaction, or x and y for a new substituent or solvent. These are certainly more trouble than simple least squares, but at least one needs only to do a single *linear* least-squares fitting to evaluate a, b, and c if one accepts the x and y values for the substituents or solvents used, or a single *linear* least-squares to get x and y if one accepts the a, b, and c values for the reactions used. (In the original assignments we had to use a *nonlinear* least-squares procedure, original with us,[15] on all 220 or 1080 basis data, which is admittedly much more difficult but should not as often need repeating.)

Our assertion that it is easier to recognize, measure, and correctly interpret deviations if one knows what average or normal behavior is requires that there be a well-defined average without much spread for a wide range of data. Our 1155 solvent data include an especially diverse collection of rates, equilibria, distribution coefficients, and spectral (IR, VIS, UV, ESR, NMR) data. They all fit well with the same constant tabulated A's and B's because the overall correlation coefficient between data and predictions is 0.991, no individual solvent is below 0.970 and no reaction is below 0.975. Evidently, there is a remarkable parallelism between three neat (bulk) solvent properties, i.e., anion-solvating tendency, hydrogen-bonding acidity, and electrophilicity (all represented by the constant solvent vector A) and also a remarkable parallelism between three other neat solvent properties, i.e., cation-solvating tendency, hydrogen-bonding basicity, and nucleophilicity (all represented by the constant solvent vector B). Many combinations of hydrogen-bonding reactants and solvents prove to be unexceptional and do not require special treatment. No special vectors or special rules excluding particular reactants or solvents are needed. Thus there are evidently only two solvent factors involved, and there is a significant average or norm from which deviations for at least these 88 reactions and 1155 data are in fact rather small.

Finally, we suggest that physical organic chemists would be wise to ignore most effects or deviations that are less than a factor of two, (0.3 in log k or 0.5 kcal in ΔG at 0–100 °C) not only because of possible experimental error, but because too many interpretations for such small effects can be devised. Detailed rationalizations of smaller deviations are likely to be about as reliable as the elaborate interpretation of the battle of Bravalla from scratches on a Swedish rock, which later turned out to be natural lines and cracks.[18] Bigger deviations from these two-vector relationships should be the focus of interest because they can serve to indicate more interesting discontinuities of mechanism, e.g., significant changes in state of association or complexing of reactants or changes of rate-determining step.

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[18] *Chem. Eng. News* **1983**, *61* (35), Aug. 29, p 72.