(27%) acids, together with smaller amounts of homologous degradation products of these acids. The equivalent chain length of the fragment tentatively identified as 2-hydroxyoctanedioate was 19.3 on an R-446 column.

A 40-mg portion of IIb was oxidized exactly as was Ib. The recovered acids were esterified with diazomethane, and glpc analyses gave the following results: hexanedioic (30%), octanedioic (17%), and 2-hydroxynonanedioic (24%) acids, together with smaller amounts of homologous degradation products. The equivalent chain length of the fragment tentatively identified as 2-hydroxynonanedioate was 20.1 on an R-446 column.

A 59-mg portion of III (containing 4% IV) was oxidized exactly as was Ib. The recovered acids were esterified with diazomethane, and glpc analyses gave the following results: heptanoic (43%), heptanedioic (28%), octanedioic (3%), and 2-hydroxyoctanedioic (11%) acids, together with smaller amounts of homologous degradation products of these acids.

Lithium Aluminum Hydride Reduction of Ib.—A 69-mg portion of Ib in 3 ml of dry ether was added to a suspension of 400 mg of lithium aluminum hydride in 8 ml of ether, and the mixture was refluxed for 3 hr. After cooling, excess hydride was destroyed by the addition of moist ether followed by 10 ml of 5% sulfuric acid. The mixture was extracted with ethyl ether, and the combined ether extracts were dried over anhydrous sodium sulfate. The crude material (43 mg) was recrystallized from hexane to give 21 mg of a diol, mp 56–57°. Infrared showed maxima at 2.72 (OH), 6.12 (C═C), 10.13 (*trans,trans*-diene), and 10.93 μ (CH_2═CH–). The ultraviolet spectrum gave λ_{max}^{EtOH} 231 mμ (ε 28,600).

Anal. Calcd for $C_{17}H_{30}O_2$: C, 76.64; H, 11.35. Found: C, 76.0; H, 11.5.

Conversion of V to Heptadecanoic Acid.—A 65-mg portion of V was refluxed 17 hr with 37 mg of red phosphorus and 3 ml of hydriodic acid (sp gr 1.7).[12] The reaction mixture was then diluted with 10 ml of water and extracted repeatedly with ethyl ether. Combined ether extracts were washed with 5% sodium metabisulfite, then dried over sodium sulfate. Upon evaporation, 61 mg of a clear oil remained. This was reduced by heating at reflux 4 hr with 200 mg of granular zinc, 5 ml of methanol, and 1 ml of concentrated hydrochloric acid. The mixture was then diluted with water and extracted repeatedly with ether. After drying over sodium sulfate and removing solvent, 42 mg of methyl heptadecanoate remained (mp 27–28°). A 40-mg portion was then refluxed 1 hr with 5 ml of 1 *N* potassium hydroxide in ethanol. Heptadecanoic acid was recovered by acidifying with hydrochloric acid and extracting with ether; 34 mg of product was obtained, mp 59.5–60.5°, undepressed upon admixture with authentic heptadecanoic acid.

Reaction of Ib with Methanolic Hydrochloric Acid.—A 113-mg portion of Ib was dissolved in 15 ml of 0.1 *N* methanolic hydrochloric acid and refluxed for 1.5 hr. Infrared and ultraviolet spectra of the product, after recovery by ether extraction, showed essentially no reaction. By extending the reaction period to 18 hr, Ib (80 mg) was converted to a mixture of products as shown by tlc. Allene was present in the product (infrared maximum at 5.1 μ), as well as ether (9.0–9.1 μ), and the carbonyl peak (5.72 μ) had a pronounced shoulder, suggesting the presence of a ketone. Maxima appeared at 228.3, 267.2, 277.6, and 289.0 mμ in the ultraviolet spectrum of the product mixture. No further characterization of these materials was attempted, as they were apparently present only in minor amounts.

Reaction of Ib with Methanolic Sulfuric Acid.—A 103-mg portion of Ib was added to 10 ml of 1.2 *N* sulfuric acid in methanol. The flask was flushed with nitrogen, then stoppered, and held at 50° for 22 hr. The mixture was then diluted with 20 ml of water and extracted repeatedly with ethyl ether. The combined ether extracts yielded 97 mg of product. Examination of the product by tlc gave three spots (R_f 0.83, 0.52, and 0.25). These components were separated by column chromatography on silica gel. The first fraction, 26 mg, had the following absorption maxima: infrared, 4.52 (C≡C), 6.13 (C═C), 9.03 (OCH_3), 10.95 (CH_2═CH–), and 10.48 μ (*trans*-enyne); ultraviolet, $\lambda_{max}^{cyclohexane}$ 229 mμ ($E_{1\,cm}^{1\%}$ 510).

Anal. Calcd for $C_{19}H_{30}O_3$: 2OCH_3, 20.2. Found: OCH_3, 18.8.

The second fraction (11 mg) had the following spectral characteristics: infrared, 5.11 (allene), 6.13 (C═C), 9.05 (OCH_3), 10.95 (CH_2═CH–), and 11.40 μ (allene);[27] ultraviolet, $\lambda_{max}^{cyclohexane}$ 178 mμ ($E_{1\,cm}^{1\%}$ 935).

Anal. Calcd for $C_{20}H_{34}O_4$: 3OCH_3, 27.5. Found: OCH_3, 24.8.

Nmr spectra of these first two fractions are discussed in the text. The third fraction (most polar), 42 mg, was primarily unreacted Ib.

Acknowledgment.—We thank J. E. Cluskey for spectropolarimetric data, J. W. Hagemann and G. F. Spencer for glpc analyses, Mrs. B. R. Heaton for microanalyses, and Dr. Quentin Jones, Crops Research Division, Agricultural Research Service, U. S. Department of Agriculture, for making available the *Acanthosyris* seed.

[27] This peak is tentatively assigned to the allene grouping on the basis of the spectra of other known allenes examined in this laboratory.

The Interpretation of Enthalpy and Entropy Data

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Practical criteria are described for using enthalpies and entropies of reaction or activation and for assessing the possible relations among them.

Some Definitions.—The close analogy between standard enthalpies or entropies of reaction and enthalpies or entropies of activation makes it possible to discuss them in a unified way, and in this paper the symbol ΔH (ΔS) will be used to represent either $\Delta \bar{H}°$ ($\Delta \bar{S}°$) or ΔH^* (ΔS^*). Some substituents and some solvents probably exert their influence on reactions by very similar mechanisms, but even when this is not the case the formal treatment of substituent and medium effects can always be the same. In this paper the operator, δ, will serve for both δ_M (now almost a standard symbol for the effect of a change in reaction medium) and δ_R (effect of a change in structure or substituent).[1] The operator, δ, is convenient not only because it eliminates unwanted quantities analogous to constants of integration, but also because it avoids confusion with the reaction operator, Δ, which might otherwise be used.

$$\delta \Delta H = \Delta H - \Delta H_{\text{ref structure or solvent}}$$
$$\delta \Delta S = \Delta S - \Delta S_{\text{ref structure or solvent}}$$

Isokinetic Temperature.—It is often enlightening to display enthalpy–entropy data as points on a graph of enthalpy as ordinate *vs.* entropy as abscissa. The slope of a line in such a graph has the dimensions calories per mole over calories per mole degree, hence absolute temperature. At a temperature correspond-

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[1] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963.

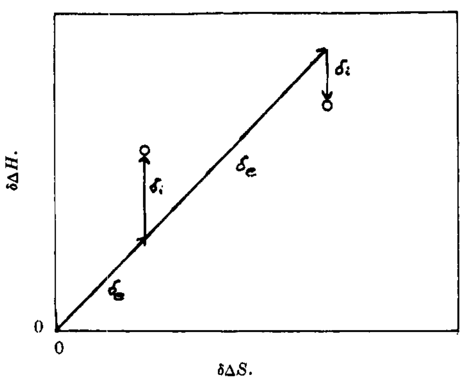

Figure 1.

ing to the slope, the quantity ΔF would appear to have a constant value for any reactions corresponding to points on the line and nearly constant for points very near the line. If $\delta\Delta H/\delta\Delta S = T$, then $\delta\Delta F$ and

$$\Delta F = \Delta H - T\Delta S$$
$$\delta\Delta F = \delta\Delta H - T\delta\Delta S$$

$\delta \log k$ equal zero. This property suggested the mnemonically convenient term *isokinetic temperature*,[2] symbol β, defined as the slope of a line in the enthalpy-entropy plane. If the enthalpies and entropies are sufficiently insensitive to temperature changes, or if the required change in temperature is small, the isokinetic temperature will be a real temperature at which the variation in $\log k$ among the set of correlated reactions is a minimum, if not zero. However, since these requirements are not generally met, the term *isokinetic temperature* is defined mathematically as the slope rather than phenomenologically as an experimental temperature. For reactions in which ΔC_p is appreciable, theory[1] predicts that isokinetic relationships are still to be expected, but that β will depend on the mean temperature used in obtaining the data.

Interaction Mechanisms.—In favorable cases it should be possible to analyze or separate the net effect of a substituent or medium change into independent components corresponding to different *interaction mechanisms*,[1] *i.e.*, mechanisms of the interaction between the substituent or solvent and the actual site of the reaction. Examples of interaction mechanisms are steric, inductive, resonance, or solvation effects. Simple relationships between two series of quantities, $\delta\Delta F$, are predicted in the most straightforward way when all of the substituent or medium effects, $\delta\Delta F$, are the results of just a single interaction mechanism. Similarly, when $\delta\Delta H$ and $\delta\Delta S$ are caused by a change in the strength of an interaction involving just a single interaction mechanism, a simple proportionality between these quantities is to be expected. Simple proportionality between more complex quantities is *not* generally to be expected, as can be seen from the following example in which the substituent effect is the resultant of two interaction mechanisms. In such a case

$$\delta_1\Delta H = \beta_1\delta_1\Delta S$$

$$\delta\Delta H = \delta_1\Delta H + \delta_2\Delta H$$

and

$$\delta\Delta S = \delta_1\Delta S + \delta_2\Delta S$$

$$\delta_1\Delta H = \beta_1\delta_1\Delta S \text{ and } \delta_2\Delta H = \beta_2\delta_2\Delta S$$

but $\delta\Delta H$ is not equal to $\beta\delta\Delta S$.

Although the most general theory allows for any number of independent interaction mechanisms each with any isokinetic temperature β_1, β_2, etc., many examples can be understood quite well in terms of simpler models such as those of Hepler, *et al.*,[3] and Lee.[4] Hepler's model uses two interaction mechanisms for substituent effects, corresponding to *internal* and *external* contributions to ΔH and ΔS. The internal effects, particularly in a rigid molecule, should contribute only to the enthalpy so that $\beta_{\text{internal}} \cong \infty$. The external effects, consisting mostly of constraints on the motion of solvent molecules, are expected to contribute to both the enthalpy and entropy, with β in the experimental temperature range. Using this model, $\delta\Delta H = \delta\Delta H_{\text{internal}} + \delta\Delta H_{\text{external}}$, $\delta\Delta S = \delta\Delta S_{\text{external}} = \delta\Delta H_{\text{external}}/\beta_{\text{external}}$. If we are permitted to assign a value to β_{external} based on studies of medium effects, it is obviously possible to extract $\delta\Delta H_{\text{internal}}$ from the observed $\delta\Delta H$ and $\delta\Delta S$ values. The resulting $\delta\Delta H_{\text{internal}}$ frequently makes more sense and fits simpler theories than does the composite experimental $\delta\Delta H$.

Interaction Mechanism Vectors.—If individual interaction mechanisms are truly independent to a usable degree of approximation, their effects have to add vectorially. Thus the point ($\delta\Delta H$, $\delta\Delta S$) in the $\delta\Delta H$, $\delta\Delta S$ plane is a vector representing the displacement of ΔH, ΔS from the origin by the operation denoted by δ. If there are two interaction mechanisms δ_1 and δ_2, each pair of quantities, $\delta_1\Delta H$, $\delta_1\Delta S$ and $\delta_2\Delta H$, $\delta_2\Delta S$, is also a vector, and their vector sum is the observed net effect ($\delta\Delta H$, $\delta\Delta S$). This is illustrated in Figure 1, using Hepler's special case of only two interaction mechanisms, internal and external, although the treatment will extend to any number of component vectors of any slope. It is clear that, if there is only a single interaction mechanism, variation in the magnitude of its vector can only generate a straight line. With two or more independent interaction mechanisms whose vectors vary independently in magnitude *and which have two different slopes*, a scatter diagram or any other pattern can be generated. Interaction mechanisms of constant magnitude representing constant features of the reagent structure will cancel out in the δ quantities. If two groups of substituents (or two classes of solvent) are characterized by different values of the constant vector, a pair of parallel lines will result.

If a scatter diagram is the result of the independent variation of the magnitudes of only two interaction mechanisms, it is clear that it could be reduced to a straight line if one of the two sets of vectors could be obtained in some other way. For example, trial and error methods might uncover a single set of vectors that could convert two scatter diagrams into two linear relationships, perhaps using a constant scalar multiplier to adjust the magnitude as in the use of

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[2] J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

[3] L. G. Hepler and W. F. O'Hara, *J. Phys. Chem.*, **65**, 811 (1961); W. F. O'Hara, T. Hu, and L. G. Hepler, *ibid.*, **67**, 1933 (1963); L. G. Hepler, *J. Am. Chem. Soc.*, **85**, 3089 (1963).

[4] I. Lee, *J. Korean Chem. Soc.*, **7**, 211, 238, 264 (1963).

ρ in the Hammett equation. In practice, however, it turns out that the available data are not quite good enough.

Error Contours for Enthalpy and Entropy.—The error in ΔH and ΔS depends on the accuracy of the rate constants and on the size of the temperature interval. If there are enough individual rate constants, the best procedure is probably to calculate a least-squares fit of log k/T as a function of $1/T$ with the probable error of the slope and intercept as a by-product.[5a]

However, it is not possible to judge whether two pairs of ΔH, ΔS data are significantly different, even if the probable errors are given, without taking into account the shape and orientation of the *error contours* surrounding the ΔH, ΔS points in the ΔH, ΔS plane. The error contour can be approximated as follows.

The calculation of ΔH and ΔS is equivalent to solving a pair of simultaneous linear equations in ΔH and ΔS as variables and ΔF_{T_1}, ΔF_{T_2}, T_1 and T_2 as known constants. The solution is shown graphically

$$\Delta H = \Delta F_{T_1} + T_1\Delta S$$
$$\Delta H = \Delta F_{T_2} + T_2\Delta S$$

in Figure 2 for a hypothetical case using typical numbers. Figure 3 shows what happens if error has changed the rate constants by ±10% (range 20%, 3a) or ±5% (range 10%, 3b). With no error in the rate constants, the lines intersect in the middle of the figure, as before. A rate constant 10% too low at temperature T_1 raises ΔF_{T_1} and displaces the corresponding line upward without changing the slope. If we now make the rate constant at temperature T_2 10% too high, that line is lowered and the intersection of the two lines is displaced from its correct position to the point marked $-+$. The reverse combination of errors would produce the point marked $+-$ at the other end of the error contour. The error combinations 00, +10%,+10%, and −10%,−10%, however, all fall within the small circle centered on the correct solution. The other half of the figure is drawn to the same scale and shows what happens if the accuracy of the rate constants is ±5%.

Although the matched extreme error combinations $+-$ and $-+$ would introduce a possibly disasterous amount of noise into the signal, the situation is not quite so bad as might at first be thought, because such combinations should be considerably rarer than those in which the errors are random or of the same sign.[5b]

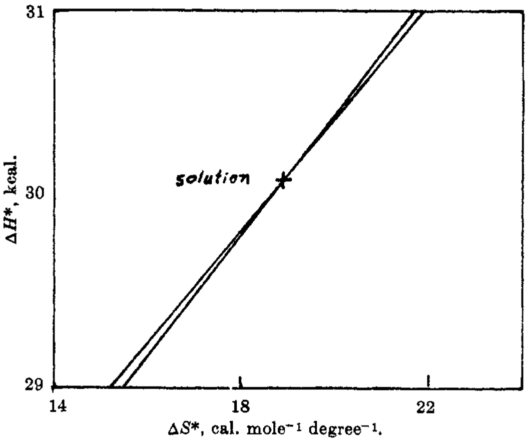

Figure 2.—$k_{300} = 10 \times 10^{-6}$ sec^{-1}, $\Delta F_{300} = 24.42$ kcal, $\Delta H = 24.42 + 300\Delta S$; $k_{320} = 250 \times 10^{-6}$ sec.$^{-1}$, $\Delta F_{320} = 24.04$ kcal, $\Delta H = 24.04 + 320\Delta S$.

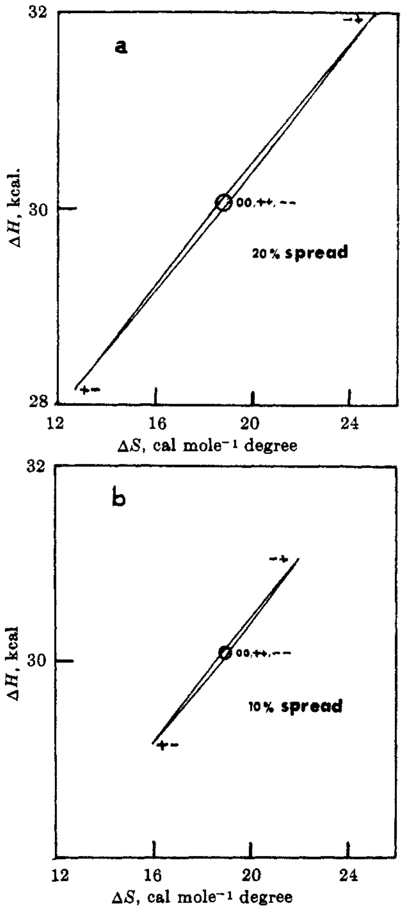

Figure 3.—$k = 10 \times 10^{-6}$ at 300°; $k = 250 \times 10^{-6}$ at 320°.

Reducing the temperature range from 20 to 10° has about the same effect on the accuracy of ΔH and ΔS as doubling the percentage error in the rate constants. As a rule of thumb the error in ΔH is roughly proportional to the percentage error in k and to the reciprocal of the difference in temperatures. Enthalpies based on *single pairs* of rate constants with the accuracy (*unusually good*) of ±5% and measured 20° apart (too often a range of 10° is used) should be accurate to within about ±1 kcal/mole, as illustrated in Figure 3b. If the error is systematic rather than random or if it can be reduced by replication of the runs, the enthalpy might be accurate to within tenths of a kilocalorie. The errors in the entropy will always be equal to those of the enthalpy times $\bar{T}$.[6]

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[5] (a) During the calculation of the enthalpy and entropy and their probable errors it will be found necessary to retain what may seem a ridiculously large number of significant figures in order to avoid serious rounding errors. A related problem is the fact that a pair of ΔH and ΔS values that have been rounded off in a reasonable way for the comparison of the enthalpy with other enthalpies and for comparison of the entropy with other entropies cannot be used to calculate a rate constant with the same accuracy as the rate constants originally used in the calculation of the ΔH and ΔS. For example, if the rounding happens to introduce *no* error into ΔS, but introduces a 0.5-kcal error into ΔH, the rate constant calculated with these numbers will have a rounding error of 130% at ordinary temperatures. To calculate rate constants within ±5% it is necessary to have either a rate constant of the desired accuracy at one temperature and a value of ΔH (which may be rounded) *or* the unrounded results of the calculation of ΔH and ΔS in which the ΔH figures are kept to at least the nearest 0.1 kcal and the ΔS figures to the nearest 0.3 eu. (b) This, of course, depends on the presence of *systematic* error; the various combinations due to *random* error would occur with equal frequency.

[6] Although it is useful to describe errors in k in terms of per cent error, per cent error of ΔH or ΔS is meaningless.

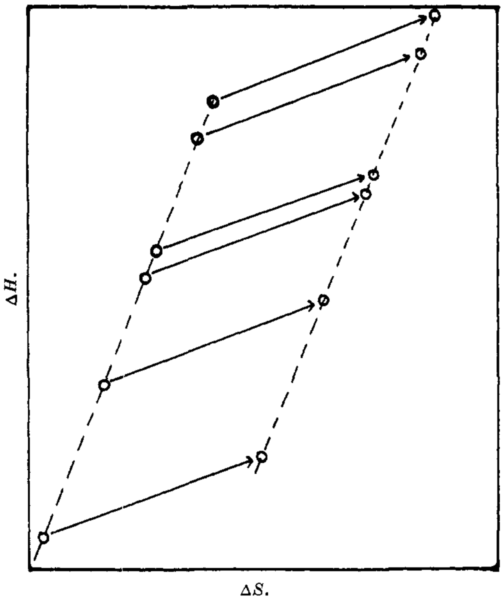

Figure 4.

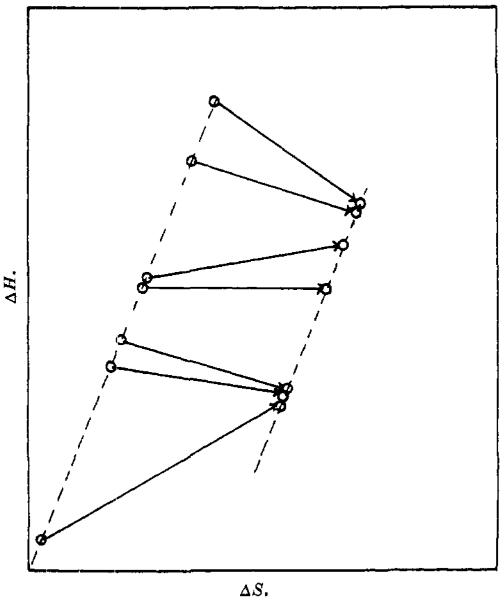

Figure 5.

The Error Vector.—An important property of the error contour (Figure 3) is that the slope of the major axis is always equal to $\bar{T}$, the mean experimental temperature. This means that experimental error superimposes upon the true distribution of enthalpies and entropies in a graph of ΔH against ΔS an effect that *looks* like an interaction mechanism whose β is equal to $\bar{T}$. This would not be nearly so troublesome if it were not for the fact that there are real interaction mechanisms, solvation effects particularly, whose β values are equal to $\bar{T}$ or at least are in the easily accessible range of experimental temperatures.[1,3]

Interpretation of Data When $\beta = \bar{T}$.—How can a real effect, $\beta = \bar{T}$, be distinguished from what is essentially no effect, *i.e.*, a single point spread out by error into a line of slope $\bar{T}$? There are two ways. If the real range of ΔH and ΔS is large enough, it may be possible to get precise enough data to reduce the size of the error contours enough so that they no longer overlap. If this is not feasible, the data should be tested for randomness. If the sequence of points along the presumed isokinetic line is random when compared with (a) every property of the substituent or solvent such as its σ, dielectric constant, internal pressure, Y value, polarizability, etc., and (b) the sequences observed along the lines for related series of reactions, then the effect of the error vector is much larger than the effects of any real vectors of $\beta = \bar{T}$, and no such real effects need be present. However, there are many series of reactions in which the sequence of points along the isokinetic line is rational rather than random.[1] For example, solution of gaseous *n*-alkanes and *n*-alkanols in water at 25° gives parallel isoequilibrium lines corresponding to the two classes of solute, and the sequence of points along the line is rational in two ways: it is the same as the sequence of increasing number of carbon atoms in the solute and it is the same as the sequence of points on the other line. To give a different kind of example, the solvolysis of a series of *para*-substituted benzoyl chlorides in acetone–water or in ether–alcohol gives two parallel isokinetic lines corresponding to the two solvents. The sequence of points is the same on each line and also the same as the sequence of the σ values.[7]

Separation of Vectors.—If it were not for the error vector we should observe patterns like that of Figure 4, in which the corresponding points on two lines of $\beta = \bar{T}$ can be related by a constant vector. This vector would be attributed to some interaction mechanism whose vector has a different constant magnitude in the two series of reactions. However, because of the uncertainty in the position of the points along a line whose slope is nearly the same as that of the error vector, an actual experimental result is more likely to look like Figure 5, in which the sequence of points is preserved but not their exact position and not the magnitudes and directions of the vectors connecting corresponding points on the two lines. If this were not the case with almost all data available today, it would be very easy to assign β values to interaction mechanisms and to discover what change in the magnitude of the interaction mechanism vector is caused by a given change in structure or medium. It would also be possible to resolve the kind of scatter diagram that is the result of only two interaction mechanisms of independently varying importance. Given two such scatter diagrams, a careful trial and error search should be able to find a set of vectors and one scalar parameter capable of converting both scatter diagrams into straight lines. No such resolution has ever been achieved except in special cases such as acid ionization equilibria.[3,8] The reason that the acid ionization data were analyzable is that one of the two interaction mechanisms does not affect the entropy at all and the other has $\beta = \bar{T}$. Under those circumstances it does not matter whether the interaction mechanism re-

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[7] The ρ values tend to be small simply because of the exclusion of examples with very large or very small β values, hence β is not far enough from $\bar{T}$ for the effects on the rate constants to be large. When $\beta = \infty$, for example, the error vector will cross the isokinetic line at a large angle and have the maximum scattering effect. The resulting pattern would probably be interpreted as a case of randomly varying entropy rather than constant entropy.

[8] L. P. Hammett, Symposium on Linear Free Energy Correlations, Durham, N. C., Oct 1964.

sponsible for the apparent $\delta\Delta S$ includes experimental error, because the appropriate correction to the observed enthalpy will be $\bar{T}$ times the observed $\delta\Delta S$ in any case.

Some Limitations on the Effects of Error.—Although the effect of experimental error in currently available data very seriously limits the usefulness of enthalpies and entropies, the data do not leave us completely ignorant and we can always *exclude* certain patterns from the range of the possible. Perhaps it is worthwhile to illustrate this with some specific examples.

Case I.—The ostensible enthalpies and entropies form a good isokinetic line with $\beta = \bar{T}$. The possible patterns in the absence of error might be (a) the observed pattern, (b) a longer or shorter line with the same slope but with a different sequence of points, or (c) a cluster of points, provided that the cluster can be made to fit within the narrow confines of the error contour. Large-scale scatter diagrams, sets of widely separated parallel lines, and lines of β very different from $\bar{T}$ are definitely excluded.

Case II.—The ostensible pattern consists of several parallel lines of $\beta = \bar{T}$. If the lines overlap in enthalpy, the true pattern might be a single line with β very different from $\bar{T}$. It could not be a single line with $\beta = \bar{T}$.

Case III is a scatter diagram on a large scale. The actual pattern could be a single isokinetic line or set of lines provided that the β values are nowhere near $\bar{T}$.

Case IV.—The ostensible pattern is a rough isokinetic line with $\beta \cong \bar{T}$, but the σ values correlate with vertical (enthalpic) distances *from* the line rather than with position along it. This is essentially what Brown[9] does when he passes lines of slope $\bar{T}$ through each point and examines the intercepts with the line $\Delta S = 0$. The true pattern might be the ostensible one with a second interaction mechanism of $\beta = \bar{T}$ present, or it might be a rather short line of very large or very small β. Brown[9] is correct in not interpreting such cases as *single* isokinetic lines due to a *single* mechanism of $\beta = \bar{T}$ when the deviation of points from the line exceeds the thickness of an error contour.

Further narrowing of the possible interpretations of the data requires some knowledge of the size of the error contour. Except when it is desired to compare rate constants with another set at a different temperature, it is probably a waste of time to do the experiments necessary to determine ΔH and ΔS unless the accuracy of the rate constants is unusually good, the expected effects are unusually large, or the experimenter is willing to do an unusually large number of replicate runs.

The High Frequency of β Values in the Experimental Range.—Spurious instances in which the real effect is actually negligible will of course always give $\beta = \bar{T}$, but there are many apparently reliable instances with small error contours, usually involving solvation. In most of the examples, the temperatures are in the rather narrow popular range of experimental temperatures, but, on the other hand, they are not identical. For some interaction mechanisms, there are theoretical grounds for expecting β to *remain* equal to $\bar{T}$ even when the experiments are repeated at a different $\bar{T}$.[3,8,10] Hammett,[8] who has discussed this problem from the most general point of view, has pointed out that, when a reagent is involved in rapid subsidiary equilibria with various subspecies (for example, solvation isomers), the equilibria can be expected to shift in response to temperature changes in such a way that their contribution to $\delta\Delta F$ remains very small, even though their contributions to $\delta\Delta H$ and $\delta\Delta S$ may be large and quite dependent on the temperature. The β values associated with such an effect would follow $\bar{T}$ closely.

Finally, it should be pointed out that early searches for enthalpy–entropy correlations like that of Leffler[2] would tend to classify cases of very large or very small β as examples of constant enthalpy or constant entropy and not assign β values to them. It should also be noted that, although almost all specific models for interactions seem to predict positive β values, there is no general theory excluding negative values. A negative value of β would easily pass unnoticed unless the data were unusually good, since the error vector would cause the maximum possible amount of scatter.

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(9) R. F. Brown, *J. Org. Chem.*, **27**, 3015 (1962).

(10) D. J. G. Ives and P. D. Marsden, *J. Chem. Soc.*, 649 (1965).