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CHEMICAL THERMODYNAMICS AND THEORETICAL MODELS

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ABSTRACT

This paper presents a brief discussion of the relationship between classical thermodynamics and theoretical models of chemical systems. Applications of thermodynamics to real chemical systems and to related theoretical models concerning "complexes in nonelectrolyte solutions" and "substituent and solvent effects in organic chemistry" are described, with particular emphasis on research that my colleagues and I have done in these areas. This paper concludes with a brief autobiographical section on "people and places".

INTRODUCTION

It was a pleasure to accept the Editor's invitation to write this partial "thermodynamic autobiography" for Thermochimica Acta. One reason is the personal pleasure of writing about some of the research that has occupied an important part of my life. I also appreciate the opportunity to acknowledge some of the help that I have received from many people for many years.

Much of my research has focussed on applications of chemical thermodynamics (often based on calorimetric measurements) to several different kinds of scientific problems involving solutions, and I have chosen to write about two applications that I hope will interest a variety of readers. Finally, this paper will conclude with a brief section on People and Places that I hope will also be of some interest.

THERMODYNAMICS AND MOLECULAR THEORIES

Thermodynamics was originally formulated in a purely macroscopic way, with no explicit mention of atoms and molecules. One of the advantages of such classical thermodynamics is that it can be applied usefully to a variety of systems for which we have no detailed molecular knowledge. As might be expected, there is a corresponding limit on the microscopic or molecular information that we can obtain by application of strictly classical thermodynamics to chemical problems. Stated informally, classical thermodynamics is a very dull tool for probing (directly) into the molecular characteristics of any chemical system.

Although classical thermodynamics alone is of little value for learning about molecular properties of any chemical system, it is well known that classical thermodynamics can be combined with various molecular theories to obtain microscopic understanding, to aid in convenient treatment of experimental data for various systems, and to permit logical development of correlations and predictive schemes. Looked at another way, thermodynamics provides means of testing various theories against experimental results, thereby leading to rejection of theories or models that are demonstrably inadequate at any specified level of accuracy.

In this paper I will describe results of experimental investigations that can be related to appropriate theoretical models. Because the chemical solutions under consideration here are very complicated at the molecular level, it is unreasonable to expect that any theoretical model will be exactly right, but it is possible that we can use our experimental results in combination with thermodynamic analyses of various models to improve our understanding and develop better theoretical models, in ways that I will be describing. It should also be recognized that even a poor theory can provide a useful guide to measurements that should be made.

COMPLEXES IN NONELECTROLYTE LIQUID SOLUTIONS

My graduate student research under W.M. Latimer led me to a general interest in hydrogen bonding and hydrogen bonded complexes. Then, more than ten years later, equilibrium measurements [1] with undergraduate student B.J. Hales and post-doctoral G.L. Bertrand on the effect of chloroform on the mutual solubilities of water and triethylamine indicated strong interaction (presumably hydrogen bonding) between chloroform and triethylamine and I thought it would be entertaining to use an old-fashioned classical method to prove or disprove the existence of a “real” 1 : 1 compound of chloroform and triethylamine in the solid state. Cooling curve measurements with G.W. Stapleton (visiting high school teacher), M. Bellay (undergraduate student), and C.A. Wulff (post-doctoral) led to a solid–liquid phase diagram [2], which showed that the 1 : 1 chloroform–triethylamine complex is a “real” solid compound that melts at 191 K, and thereby provided support for the proposed existence of a reasonably stable complex in the liquid state.

Various theoretical models in chemistry begin by distinguishing between “chemical” and “physical” interactions, and proceed by postulating that one of these kinds of interaction is relatively large and the other kind is relatively small for a specified system. It may then be a useful approximation to take the small kind of interaction to be negligible so that only the large kind of interaction need be considered. Contrasting examples are gaseous N_2 and NO_2/N_2O_4. Deviations of properties of $N_2(g)$ from $pV=nRT$ are attributed to "physical" effects of molecular size and intermolecular attractions. On the other hand, it is a useful first approximation to analyze the pVT properties of gaseous NO_2/N_2O_4 solely in terms of the "chemical" interaction represented by the equilibrium $N_2O_4(g) = 2NO_2(g)$.

The purely "chemical" or "ideal associated solution" model or theory for nonelectrolyte solutions originated long ago. For example, Dolezalek tried to account for deviations from ideal solution properties solely in terms of chemical equilibria between like and/or unlike molecules, with activity coefficients for all chemical species taken to be unity and the implication that all "physical" interactions were negligible.

When I was on sabbatical leave at the University of Otago in New Zealand, working with D.V. Fenby, we measured [3] enthalpies of mixing chloroform with triethylamine, intending to test the ideal associated solution model and possibly evaluate the equilibrium constant and ΔH^0 for the reaction between chloroform and triethylamine that is represented by

$$\mathrm{A} + \mathrm{B} = \mathrm{AB} \tag{1}$$

We began our analysis by considering a mixture of N_A moles of A with N_B moles of B, with $(N_A + N_B) = 1.0$ mole so that N_A and N_B are numerically equal to the stoichiometric mole fractions x_A and x_B. We let r represent the number of moles of AB at equilibrium. Use of these quantities with the ideal solution model (activity coefficients of equilibrium species equal to unity) then led [3] to

$$K = r(1-r)/\left(x_A x_B - r + r^2\right) \tag{2}$$

The enthalpy of mixing x_A moles of A with x_B moles of B is the molar excess enthalpy (H^E) that is attributed (from the postulate that activity coefficients are unity over a range of temperature) to the enthalpy of reaction (1), which leads to

$$H^E = r\Delta H^0 \tag{3}$$

Combination of eqns. (2) and (3) then yielded

$$x_A x_B/H^E = -\left[(K+1)/K(\Delta H^0)^2\right] H^E + (K+1)/K\Delta H^0 \tag{4}$$

according to which a plot of $x_A x_B/H^E$ against H^E should be linear. Our experimental results were plotted as suggested by eqn. (4) and did indeed lead to a straight line with slope and intercept that permitted evaluation of K and ΔH^0 for reaction (1).

T. Matsui (post-doctoral), Fenby, and I then showed [4] that the ideal associated solution model leads to

$$\Delta H^0 = L_A^0(K+1)/K = L_B^0(K+1)/K \tag{5}$$

in which L_A^0 and L_B^0 are partial molar enthalpies of solution of A into B and of B into A at infinite dilution, respectively. Our calorimetric values of L_A^0 and L_B^0 were shown to be reasonably consistent with eqn. (5) and our previous [3] results. We also considered [4] more complicated systems containing A_2B complexes.

Fenby and I then applied the ideal associated solution model to vapor pressures and enthalpies of mixing for the chloroform + dimethylsulfoxide system [5] for which it was necessary to consider both AB and A_2B complexes. We obtained K and ΔH^0 values for both equilibria. N.F. Pasco (graduate student at the University of Otago), Fenby, and I then used the ideal associated solution model in comparing results of thermodynamic investigations with those of spectroscopic investigations of various chloroform + ether systems, again with results [6] indicating that the model is a usefully accurate approximation.

Fenby and I also wrote a review [7] about calorimetric investigations of hydrogen bond and charge transfer complexes in which we considered some of the thermodynamic consequences of the ideal association solution model.

Shortly after my return to Canada from New Zealand, I became interested in heat capacities of aqueous electrolyte solutions. E.M. Woolley (former post-doctoral, then with me as a visiting professor from Brigham Young University) and I considered [8] the heat capacities of solutions in which solutes were involved in some temperature-dependent equilibrium and derived equations for separating the measured heat capacities into contributions from the chemical species (needed for some purposes) and the "relaxation" effect associated with the temperature-dependent equilibrium. A few years later I applied these same general ideas to the ideal associated solution model and derived some interesting equations, which were extended following a useful suggestion from Fenby. A little later J.-P.E. Grolier came from France to visit me, during which time we talked about the ideal associated solution model and the desirability of further applications and tests. At about this same time, G.J. Mains (visiting professor), J.W. Larson (former graduate student, then a visiting professor), and I developed a convenient general procedure [9] for dealing with the "relaxation" contribution to heat capacities of ideal associated solutions.

Z.S. Kooner (post-doctoral) and I then measured L_A^0 and L_B^0 values at three temperatures for chloroform + triethylamine while Grolier and G. Roux-Desgranges measured heat capacities and densities to provide a further test [10] of the ideal associated solution model as applied to this system, as summarized below.

Because researchers at the University of Otago had measured [11,12] vapor pressures for the chloroform + triethylamine system since Fenby and I had done our earlier work [3] on enthalpies of mixing, we used [10] these newer results for evaluation of K alone, which is better than our previous procedure [3] for obtaining K and ΔH^0 simultaneously from one set of H^E

values. Then the resulting K was used (eqns. 2 and 3) with H^E values to obtain an improved value of ΔH^0 of reaction (1). We also used V^E values similarly to obtain ΔV^0 for this reaction.

The heat capacities measured by Roux-Desgranges and Grolier were expressed [10] in terms of excess heat capacities defined by

$$C_p^E = C_p - x_A C_{p,A}^0 - x_B C_{p,B}^0 \tag{6}$$

in which C_p represents the heat capacity of a solution containing one mole of stoichiometric A + B and $C_{p,A}^0$ and $C_{p,B}^0$ are the molar heat capacities of the pure liquids A and B. We then used these C_p^E values with

$$\Delta C_p^0 = \left[C_p^E - (\Delta H^0)^2/(RT^2Q)\right]/r \tag{7}$$

and

$$Q = [-1/(1-r)] + [1/r] + [1/(x_A - r)] + [1/(x_B - r)] \tag{8}$$

as derived earlier [9] to obtain ΔC_p^0 for reaction (1). We also used [10] our calorimetric values of L_A^0 and L_B^0 in

$$\Delta C_p^0 = \left[(\mathrm{d}L^0/\mathrm{d}T) - (L^0)^2/(RT^2K)\right][(K+1)/K] \tag{9}$$

to obtain other values of ΔC_p^0 for reaction (1).

As explained in detail in our previous paper [10], the good consistency of the results (K, ΔH^0, ΔV^0, ΔC_p^0) we have summarized here has shown that there is no empirical reason to reject the relatively simple ideal associated solution model in favor of some more complicated model that will allow for "physical" interactions as well as the "chemical" interactions we have been considering.

Although we think that the results summarized here show that the ideal associated solution model is a usefully accurate representation of the chloroform + triethylamine system in which the complexes are relatively stable, we also recognize that neglect of "physical" interactions will become less satisfactory as we consider systems (such as chloroform + benzene) in which the complexes are less stable. We (Kooner, Roux-Desgranges, Grolier) have therefore undertaken further calorimetric measurements leading to $\mathrm{d}L^0/\mathrm{d}T$ and C_p^E values for several other systems and are now analyzing the results in terms of the ideal associated solution model with the intention of establishing guides as to the kinds of systems for which this model is internally consistent and therefore probably sufficiently realistic to be useful.

Graduate student J.F. Smith and I are now working on a purely thermodynamic method (no model for "physical" interactions) for using vapor pressures to obtain activity coefficient products and a "true" thermodynamic equilibrium constant for reaction (1). If this work is successful, we will then have a practical improvement on the ideal associated solution model so that we can investigate systems for which the simple model is not a satisfactory approximation. Smith is also making measurements that are intended to provide a link between properties of complexes in binary systems (A + B, no solvent) and similar properties of dilute solutions (A + B in an "inert" solvent).

SUBSTITUENT AND SOLVENT EFFECTS IN ORGANIC CHEMISTRY

It has been known for a long time that nitrophenols are stronger acids than phenol in aqueous solution at or near 25°C. Similarly, it has been known for a long time that *p*-nitrophenol is a stronger acid than *m*-nitrophenol. A traditional explanation for these facts is that the nitrophenols are stronger acids than phenol because the electronegative (relative to hydrogen) nitro group substituent makes it "easier" to remove a proton from the phenolic oxygen, and that *p*-nitrophenol is a stronger acid than *m*-nitrophenol because the anion of the former is reasonance stabilized much more than is the anion of the latter. Hammett and a few others had recognized that such traditional explanations of substituent effects were based on energy (rather than the more relevant free energy) considerations and that these explanations might be valid because of nearly constant contributions from entropies.

Sometime about 1955 it occurred to me that there might be an inconsistency in the idea of nearly constant entropy of ionization and the "resonance stabilization explanation" mentioned above. According to the resonance theory (or a more modern molecular orbital treatment), the charge distribution is different in the anions derived from *p*-nitrophenol and *m*-nitrophenol, with the charge on the latter anion being more localized on the phenolic oxygen. I expected this difference in charge distribution to lead to differences in ion–water interactions and thence to different entropies of ionization, which ought to be considered in explanations of substituent effects.

Graduate student L.P. Fernandez then joined me in making calorimetric measurements leading to ΔH^0 values for ionization of phenol and the nitrophenols in aqueous solution at 298 K. Results of these measurements were combined with ΔG^0 values from already known acid ionization equilibrium constants to obtain [13] the thermodynamic properties summarized in Table 1. Just as expected on the basis of considerations of different charge distributions in the anions, it is seen that ΔS^0 values for ionization of phenol, *m*-nitrophenol, and *p*-nitrophenol are considerably different. It was of special interest to us to note that well over half of the acid-strengthening effect of the nitro group (either *para* or *meta*) arose from $T\Delta S^0$ rather than from ΔH^0 and that nearly all of the difference in free energy of ionization of the two nitrophenols was due to the difference in $T\Delta S^0$ rather than an "energy difference" in ΔH^0 values. After some specific discussion that I think still looks good some 25 years later, we

TABLE 1

Thermodynamics of ionization of aqueous acids at 298 K [a]

Acid	$K \times 10^{10}$	ΔH^0 (cal mol^{-1})	ΔS^0 (cal K^{-1} mol^{-1})
Phenol	1.05	5650	−26.7
m-Nitrophenol	45.1	4705	−22.5
p-Nitrophenol	720	4700	−16.9

[a] The values given here are taken directly from Fernandez and Hepler [13]. Some slightly different and probably better values have been reported [14,15] later.

summarized [13] our conclusions as follows: "...emphasize that a satisfactory correlation of strengths and structures of organic acids in aqueous solutions must not be based solely on energy (or even free energy) changes *within* the acid and its anion. It is equally important that differences in solute–solvent interaction be considered in as much detail as possible".

Graduate student W.F. O'Hara and I then worked on an explicit method for considering the separate "*int*ernal" or "*int*rinsic" and "*ext*ernal" or "*env*ironmental" contributions to the total measurable thermodynamic changes associated with ionization of organic acids in solution. Later, King [16] clearly described these contributions as follows: "*Internal effects* are those intrinsic to the molecules of the acid and base. *Environmental effects* are those which result from interaction of the acid and base with the solvent."

O'Hara and I began [17] by writing the following equations to represent the ionizations of a parent or unsubstituted acid (HA) and a substituted acid (HAx):

$$\mathrm{HA(aq)} = \mathrm{H^+(aq)} + \mathrm{A^-(aq)} \qquad (10)$$

$$\mathrm{HAx(aq)} = \mathrm{H^+(aq)} + \mathrm{Ax^-(aq)} \qquad (11)$$

Combination of (10) and (11) leads to

$$\mathrm{HAx(aq)} + \mathrm{A^-(aq)} = \mathrm{Ax^-(aq)} + \mathrm{HA(aq)} \qquad (12)$$

The equilibrium constant for (12) is related to equilibrium constants for (10) and (11) by

$$K_{12} = K_{11}/K_{10} \qquad (13)$$

and the increment in some standard thermodynamic property (ΔY^0) for the composite equilibrium represented by (12) is related to corresponding quantities for (10) and (11) by

$$\Delta Y_{12}^0 = \Delta Y_{11}^0 - \Delta Y_{10}^0 \qquad (14)$$

Here it is convenient to define and later use

$$\delta \Delta Y^0 = \Delta Y_{12}^0 \qquad (15)$$

O'Hara and I then expressed [17] the idea that the measurable $\delta\Delta Y^0$ quantities for composite reactions of type (12) could be expressed as sums of internal and environmental contributions as indicated explicitly by

$$\delta\Delta H^0 = \delta\Delta H_{\text{int}} + \delta\Delta H_{\text{env}} \tag{16}$$

and

$$\delta\Delta S^0 = \delta\Delta S_{\text{int}} + \delta\Delta S_{\text{env}} \tag{17}$$

At the time of our work Pitzer [18] had already investigated entropies of ionization of weak acids by methods that allowed us to show that $\delta\Delta S_{\text{int}}$ is very close to zero for reactions of type (12) for which there are no steric complications, leading from (17) to the simpler

$$\delta\Delta S^0 = \delta\Delta S_{\text{env}} \tag{18}$$

We then presented arguments [17] that $\delta\Delta H_{\text{env}}$ and $\delta\Delta S_{\text{env}}$ are directly proportional to each other as in

$$\delta\Delta H_{\text{env}} = \beta_{\text{env}}\delta\Delta S_{\text{env}} \tag{19}$$

in which β_{env} is a parameter with the dimensions of temperature. A few years later graduate student J.W. Larson and I showed [19] that the simple proportionality or "compensation" expressed in eqn. (19) should be modified to

$$\delta\Delta H_{\text{env}} = \beta_{\text{env}}\delta\Delta S_{\text{env}} + \gamma\Delta H_{\text{int}} \tag{20}$$

in which γ depends on the solvent and the temperature.

Considerable evidence has been presented in our papers [14,15,17,19–23] and in others we have cited that

$$\beta_{\text{env}} \simeq T \tag{21}$$

For simplicity in what follows we take (21) to be an equality instead of an approximation.

Combination of equations (16, 18, 20, and 21) with

$$\delta\Delta G^0 = \delta\Delta H^0 - T\delta\Delta S^0 \tag{22}$$

leads to

$$\delta\Delta G^0 = \delta\Delta H_{\text{int}} + \gamma\delta\Delta H_{\text{int}} = \delta\Delta H_{\text{int}}(1+\gamma) \tag{23}$$

Equation (23) is immediately satisfying because it provides justification for the traditional explanations of effects of substituents on acid strengths (free energies or related equilibrium constants) primarily in terms of "internal energy" effects, in spite of the facts that solvation effects and entropy effects are certainly neither negligible nor generally constant. Terms involving $\delta\Delta H_{\text{env}}$ and entropies are absent from eqn. (23) because of what has come to be called "compensation" of part of the total enthalpy by $T\delta\Delta S^0$.

The next step in applying the model described here began [19–21] with recognition that eqn. (12) represents the kind of equilibrium to which the Hammett equation

$$\log K_{12} = \rho\sigma \tag{24}$$

is applicable. In this Hammett equation ρ is a parameter that depends on the class of reaction under consideration, on the solvent, and on the temperature, while σ is a parameter that depends only on the substituent. The impressive empirical successes of this simple Hammett equation make it worthwhile to consider this equation in relation to our model for substituent and solvent effects. To do so we combine eqns. (23) and (24) with

$$\delta\Delta G^0 = -RT \ln K_{12} = -2.3RT \log K_{12} \tag{25}$$

to obtain

$$\rho\sigma = [C(1+\gamma)/2.3RT][-\delta\Delta H_{\text{int}}/C] \tag{26}$$

in which C is an arbitrary constant. We identify $[C(1+\gamma)/2.3RT]$ with the Hammett ρ and $[-\delta\Delta H_{\text{int}}/C]$ with the Hammett σ. According to this identification, the Hammett ρ parameter varies with $1/T$ and depends on the solvent (because of γ), while the Hammett σ parameter is independent of both solvent and temperature.

Application of equations of classical thermodynamics to the model-based equations presented here has shown [22] that both $\delta\Delta H^0$ and $\delta\Delta S^0$ are proportional to the Hammett σ parameter and has also led [22] to

$$\delta\Delta H^0 = [\beta_{\text{env}} - (1+\gamma)/(\mathrm{d}\gamma/\mathrm{d}T)]\,\delta\Delta S^0 \tag{27}$$

Although proportionality of both $\delta\Delta H^0$ and $\delta\Delta S^0$ to the Hammett σ has been observed for several classes of reaction, the proportionality of $\delta\Delta H^0$ to $\delta\Delta S^0$ that is predicted by eqn. (27) is of greater present interest. Several investigators have observed such proportionality of $\delta\Delta H^0$ to $\delta\Delta S^0$ as indicated concisely by

$$\delta\Delta H^0 = \beta_{\text{iso}}\delta\Delta S^0 \tag{28}$$

in which β_{iso} is what has been called the isoequilibrium (or isokinetic) temperature. Because the distinction between β_{iso} and β_{env} has been missed or confused by some investigators of substituent effects, we explicitly write

$$\beta_{\text{iso}} = \beta_{\text{env}} - (1+\gamma)/(\mathrm{d}\gamma/\mathrm{d}T) \tag{29}$$

In the special case when $(1+\gamma)/(\mathrm{d}\gamma/\mathrm{d}T)$ is small compared to $\beta_{\text{env}}(\simeq T)$, we see that $\beta_{\text{iso}} \simeq T$ as observed for several classes of reaction. On the other hand, there is no necessary requirement that $(1+\gamma)/(\mathrm{d}\gamma/\mathrm{d}T)$ be small compared to T, so it is entirely possible for β_{iso} to be considerably larger or smaller than T, as also sometimes observed.

As discussed in detail in several of the papers already cited, there have been various comparisons of experimental results with equations based upon the "internal–environmental model". One such comparison led to introduction of the γ parameter, without which the model predicted incorrectly that the Hammett ρ parameter should be independent of solvent. We (and others) have made various other comparisons of consequences of the model with experimental results, leading to the conclusion that this simple model is generally (in the absence of steric or other "special" effects) a close enough representation of the unknown and complicated truth to be useful.

Another way in which thermodynamics has proven useful in connection with substituent and solvent effects in organic chemistry was provided by a detailed thermodynamic analysis [22] of what might be called the "derivative consequences" of the Hammett equation.

Because it is a general empirical observation that the Hammett equation "works" about as well at one temperature as another, the starting point of my thermodynamic analysis [22] was to combine eqns. (24) and (25) to obtain

$$\Delta G^0 = -2.3RT\rho\sigma \qquad (30)$$

and to pretend that this equation is exactly valid over a range of temperatures. Differentiation of this equation (30) with respect to temperature and combinations with the equations of classical thermodynamics then led [22] to the following

$$\delta\Delta H^0 = 2.3RT^2(\mathrm{d}\rho/\mathrm{d}T)\sigma \qquad (31)$$

$$\delta\Delta S^0 = 2.3R[\rho + T(\mathrm{d}\rho/\mathrm{d}T)]\sigma \qquad (32)$$

$$\delta\Delta H^0 = \{[T^2(\mathrm{d}\rho/\mathrm{d}T)]/[\rho + T(\mathrm{d}\rho/\mathrm{d}T)]\}\delta\Delta S^0 \qquad (33)$$

$$\delta\Delta C_p^0 = 2.3R\sigma[T^2(\mathrm{d}^2\rho/\mathrm{d}T^2) + 2T(\mathrm{d}\rho/\mathrm{d}T)] \qquad (34)$$

Because accuracy of most experimental data on substituent effects limits us to considering both $\delta\Delta H^0$ and $\delta\Delta S^0$ as temperature independent constants, I set $\delta\Delta C_p^0$ in eqn. (34) equal to zero and solved the differential equation to obtain the general two-constant equation that is written as

$$\rho = C_1 + C_2/T = \rho^*(1 - \beta_{\mathrm{iso}}/T) \qquad (35)$$

Differentiation of eqn. (35) with respect to temperature and substitution of the result in eqn. (33) gives $\delta\Delta H^0 = \beta_{\mathrm{iso}}\delta\Delta S^0$ (previously written as eqn. 28), which shows that the negative of the slope of ρ against $1/T$ is the same as the isoequilibrium temperature obtained from the slope of $\delta\Delta H^0$ against $\delta\Delta S^0$. The purely thermodynamic treatment presented here, in which β_{iso} appears as a constant of integration, requires no particular numerical value or even sign for β_{iso}.

It is known that data for several reaction series are in good accord with the exact thermodynamic consequences summarized by the equations given here. Possibly of greater interest than this common but not universal agreement of experimental results with what I have called the derivative consequences of the Hammett equation is the empirical observation that the

Hammett equation "works pretty well" even when there is poor agreement of experimental results with these derivative consequences. An explanation for the success of the Hammett equation as a good approximation in such cases is provided by the "internal–environmental model", which includes the idea that there is partial compensation of $\delta\Delta H_{\mathrm{env}}$ by $T\delta\Delta S^0$ even when $\delta\Delta H^0$ and $\delta\Delta S^0$ vary in ways that are contrary to the exact thermodynamic requirement of proportionality to σ.

The empirical successes of the Hammett equation at correlating equilibrium constants (also rate constants) for many reactions have led to many attempts to improve or extend the original equation, often by introducing new sets of σ parameters. Several researchers, including Swain and Lupton [24], have considered the question of how many such sets of substituent constants are really needed and might therefore have some general significance. The statistical analysis by Swain and Lupton [24] provided convincing evidence that all of the various sets of substituent constants can be expressed as linear combinations of two terms, each of which can be regarded as representing one kind of interaction of substituent with reaction center. L.D. Hansen (visiting professor) and I then pursued this idea by writing a linear free energy equation of the form

$$\delta\Delta G^0 = a_{\mathrm{e}}t_{\mathrm{e}} + a_{\mathrm{r}}t_{\mathrm{r}} \tag{36}$$

in which a_{e} and a_{r} are substituent constants for electrostatic field and resonance effects, respectively, with t_{e} and t_{r} representing corresponding transmission coefficients. Our detailed thermodynamic analysis of this model was carried out in the same general "spirit" as several of the other investigations already cited in this discussion. I hope that a few readers will carefully consider the detailed conclusions of this paper [25] in relation to efforts to extend, improve, or interpret substituent and solvent effects.

At the time graduate students L.P. Fernandez and W.F. O'Hara began our work on substituent effects, there was no experimental method for obtaining a separation of some measured thermodynamic quantity for a reaction in solution (represented generally by $\delta\Delta Y^0$) into its "internal–environmental" components ($\delta\Delta Y_{\mathrm{int}}$ and $\delta\Delta Y_{\mathrm{env}}$). A few years later, however, the pioneering work of Kebarle, McMahon, and others permitted measurements of equilibrium constants of ionization reactions in the gas phase. These gas phase results (no solvent so that $\delta\Delta Y_{\mathrm{env}} = 0$) permitted identification of measured $\delta\Delta Y^0$ quantities with the theoretically important $\delta\Delta Y_{\mathrm{int}}$ quantities. Arnett, Aue, Hopkins (former graduate student), Taft, and others have improved our understanding of both solution chemistry and substituent effects by considering properties in solution (including "environmental effects") in relation to properties in the gas phase (only "internal" or "intrinsic" effects).

My last work in this general area was carried out with post-doctoral T. Matsui. We developed an electrostatic theory [26] of substituent and solvent effects that was intended to be consistent with the Hammett equation and various thermodynamic treatments already mentioned here; we also considered the relationship of our theory to gas phase data.

The focus of my discussion of substituent and solvent effects has been on thermodynamic and theoretical analysis, with the implied assumption that reliable experimental results for reactions of interest are well established. Unfortunately, several experimental investigations of thermodynamics (mostly by way of measurements of equilibrium constants at several temperatures) of important reactions have led to results that are now known to be substantially mistaken. In this connection I call attention to work done [27] with post-doctorals T. Matsui and H.C. Ko on the thermodynamics of ionization of benzoic acid and substituted benzoic acid, which are basic to many discussions of the Hammett equation. Because of the practical appeal of measuring equilibrium constants for acid ionizations with the glass electrode (possibly at several temperatures to obtain enthalpies and entropies) I also call attention to work [28] done with J.G. Travers (an outstanding undergraduate student) and faculty colleagues K.G. McCurdy and D. Dolman from which we obtained useful data for benzoic acid over a wide range of temperature and also established that the glass electrode can be used satisfactorily for such measurements.

To conclude this discussion of substituent and solvent effects I offer the following generalizations about kinds of investigations that are likely to be useful in the future. (i) We now have many reliable data for reactions in the gas phase; I suggest that further efforts to relate these data to data for the same reactions in solution will be fruitful. (ii) Developments in calorimetry now make it practical to obtain $\delta\Delta C_p^0$ values that I think are likely to turn out to be interesting and useful; the $\delta\Delta V^0$ values that are often obtained with the heat capacities will probably also be useful.

PEOPLE AND PLACES

As an undergraduate at the University of Kansas I first became interested in chemistry as a result of courses taught by C.A. Van der Werf and P.W. Gilles. My interest was also stimulated by Walter Conrad (graduate student/lab instructor) and Hardy Scheuermann (undergraduate friend). Following completion of my undergraduate studies in 1950, I went to the University of California (Berkeley) for graduate work under the direction of Professor W.M. Latimer. At Berkeley I was especially influenced by Latimer, by Professors L. Brewer, R.E. Connick, W.F. Giauque, and K.S. Pitzer, by Z Z. Hugus, Jr. (then an instructor in Chemistry) and by graduate students O.G. Holmes and J.W. Kury. After completing my Ph.D. in 1953, I went to the University of Minnesota for a year of post-doctoral research with Hugus.

My first faculty position was at the University of Virginia (1954–1961).

Faculty colleagues J.S. Belew, T.I. Crowell and R.B. Martin deserve special thanks for the help and encouragement they gave me there.

In 1961 I moved to Carnegie Institute of Technology (later Carnegie-Mellon University). I am pleased to acknowledge the help and stimulation that I received from several faculty colleagues, especially S.W. Angrist in Mechanical Engineering and A.K. Colter and G.J. Mains in Chemistry.

I then worked at the University of Louisville for one year (1967–1968) before moving in 1968 to the University of Lethbridge, which was a new and small university. My first research in Lethbridge was done alone, but I was soon helped by some undergraduate students and in 1969 E.M. Woolley came to me as a post-doctoral. I was very fortunate to have such an excellent colleague with me then and I am pleased to express my appreciation for all that he did.

In late 1975 I started a little part-time work for the newly formed Alberta Oil Sands Technology and Research Authority (AOSTRA). Then in mid 1976 I was appointed AOSTRA Professor at the University of Lethbridge and began nearly full-time work for AOSTRA; this work involved research related to oil sands and heavy oils and also various organizational duties.

It is appropriate here to acknowledge the help and encouragement provided by several colleagues in Lethbridge—especially C.O. Bender, D. Dolman, K.G. McCurdy, R.M. McKay, and S.F. O'Shea.

In 1983 I concluded 15 happy and productive years in Lethbridge when I moved to my present position as AOSTRA Professor of Chemistry and Chemical Engineering in the University of Alberta.

During my long association with AOSTRA, several people have taught me a lot about oil sands and have helped my research along in various ways. I thank them all, and especially mention C.W. Bowman, T.J. Cyr and C. Hsi at AOSTRA and J. Liu at Syncrude.

I was fortunate to have two sabbatical leaves from regular academic duties. The first (1963–1964) took me from Carnegie to Australia, where I worked with R.H. Stokes at the University of New England and with S.D. Hamann at CSIRO in Melbourne. The second (1972–1973) took me from Lethbridge to the University of Otago in New Zealand, where I worked with D.V. Fenby.

Among the people I have done research with who have not yet been mentioned are R.S. Roche at the University of Calgary, P.D. Bolton at the University of Wollongong, A.R. Katritzky at the University of East Anglia, V.A. Medvedev and M.E. Efimov at the Academy of Sciences in Moscow, H.A. Skinner at the University of Manchester, J.E. Desnoyers and C. Jolicoeur at the Université de Sherbrooke, P.R. Tremaine and J.A. Barbero at the Alberta Research Council, and C.E. Bamberger and D.M. Richardson at Oak Ridge. In addition, I have been associated with the CODATA Task Group for Key Values for Thermodynamics, headed by J.D. Cox of the NPL in England.

Finally, I have saved until last my most important acknowledgments and thanks. I'd like to go into detail about all of the excellent work done by the students (undergraduate and graduate), post-doctorals, and visiting faculty who have come to "my" places to work with me, but the best I can do here is list all of their names in Table 2 and hope that they all realize how much I appreciate their work and the many personal kindnesses they have shown me.

TABLE 2

My students, post-doctorals and visiting research collaborators

M.N. Ackermann[a]
J.C. Ahluwalia[c]
G.C. Allred[c]
A. Apelblat[d]
L. Barta[b]
M. Bellay[a]
G.L. Bertrand[c]
M.M. Birky[b]
O.D. Bonner[d]
T.E. Burchfield[c]
R. Cassis[a]
P.J. Cerutti[a,c]
Y.S. Choi[d]
L.J. Danielson[a]
I. Dellien[c]
C. Dobrogowska[c]
U. Eichelbaum[a]
O. Enea[d]
B.P. Erno[a,c]
G.J. Ewin[c]
L.P. Fernandez[b]
N. Fuller[a]
H.K. Garber[a]
L.M. Gedansky[b]
R.N. Goldberg[b]
R.L. Graham[b]
R.B. Grigg[c]
J.-P.E. Grolier[d]
B.J. Hales[a]
F.M. Hall[d]
W.K. Hannan[d]
L.D. Hansen[d]
O.E. Hileman, Jr.[d]
J.O. Hill[c,d]
H.P. Hopkins, Jr.[b]
J.K. Hovey[b]
T. Hu[b]
C.Y. Huang[b]
D.G. Hurkot[a]
R.A. Jesser[a]
L.H. Johnson[a]
K.L. Kasperski[b]
J.-H. Kim[d]
H.C. Ko[b,c]
Z.S. Kooner[c]
J.W. Larson[b,d]
A. Leung[c]
M.G. Lowings[a]
G.J. Mains[d]
T. Matsui[c]
I.R. McKinnon[d]
R.J.C. McLean[a]
F.J. Millero[b]
C. Moss[a]
C.N. Muldrow, Jr.[b]
T. Nelson[a]
W.F. O'Hara[b,c]
G. Olofsson[d]
I.V. Olofsson[b]
D.E. Oyler[c]
P.J. Pearce[c]
M. Peterson[a]
S.R. Rao[c]
R.A. Reichle[a]
P.J. Reilly[c]
R.G. Riddell[e]
J.B. Rosenholm[d]
M. Roth[a]
H.P. Singh[b]
P.P. Singh[d]
A. Skauge[c]
J.F. Smith[b]
D. Smith-Magowan[c]
J.G. Spencer, Jr.[b]
J.J. Spitzer[c]
N.S. Srinivasan[c]
G.W. Stapleton[e]
J.R. Sweet[a]
J. Tomkins[a]
J.G. Travers[a]
R.W. Wilton[a]
M.R. Wingard[e]
E.M. Woolley[c,d]
I.G. Worsley[c]
C.-H. Wu[b,c]
C.A. Wulff[c]
H.-K. Yan[c]
S. Yariv[d]
K.G. Zeeb[a]
Z.-L. Zhang[c]
T.A. Zordan[b]

[a] Undergraduate student.
[b] Graduate student.
[c] Post-doctoral.
[d] Visiting faculty.
[e] High-school teacher, summer visitor.

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