A FIELD GUIDE TO THE EXCESS FUNCTIONS

M.M. Abbott, M.V. Ariyapadi, N. Balsara,
S. Dasgupta, J.S. Furno, P. Futerko,
D.P. Gapinski, T.A. Grocela, R.D. Kaminsky,
S.G. Karlsruher, E.W. Kiewra, A.S. Narayan,
K.K. Nass, J.P. O'Connell,* C.J. Parks,
D.F. Rogowski, G.S. Roth, M.B. Sarsfield,
K.M. Smith, M. Sujanani, J.J. Tee, N. Tzouvaras
Rensselaer Polytechnic Institute
Troy, NY 12180

Over the past thirty-five years, a substantial data base has become available for the principal "energetic" excess properties (g^E, h^E, and c_P^E) of binary liquid mixtures. A major use of these numbers is for incorporation into group-contribution techniques (*e.g.,* ASOG, UNIFAC) for estimating liquid-phase activity coefficients. The application here is quantitative; the ultimate goal is to predict the composition and temperature dependence of the activity coefficient, γ_i, in binary and multicomponent mixtures.

The excess-property data can also serve another, more qualitative, purpose. Because they reflect differences between energetic and structural effects in a solution relative to those in the unmixed components, the excess properties serve as probes for elucidating phenomena at the molecular level. The signs and relative magnitudes of the excess properties can therefore, with judicious interpretation, be used to support or disqualify molecular theories. The desired generalizations, however, must be based on a large number of experimentally based results.

This "explanatory" role of the excess properties demands that the most rational and communicative way of organizing the data base be found. What simple ways exist to display g^E, h^E, and c_P^E which could highlight patterns and trends? How best can we use these plots as aids for modeling and as props for qualitative discussions of phase equilibria? Are there patterns and trends that suggest important generalizations connected to the chemical natures of the species involved?

Early work suggests that there is at least a qualified "yes" answer to these questions. Malesinski[1] proposed classifications based on the signs of g^E, h^E, and s^E; it is this simple idea that all subsequent schemes share. Kauer, Bittrich, and Krug[2] used a plot of g^E vs. Ts^E to display the then small g^E/h^E data base; they also proposed classifications and generalizations based on signs and mixture type. Gaube and coworkers[3-5] employed a plot of g^E vs. h^E and also a modified diagram in which g^E is replaced by $g^E + Ts_c^E$, where s_c^E is the combinatorial excess entropy. In these later efforts, the g^E/h^E data base comprised about 200 points.

Most recently, Shukla, Chialvo, and Haile[6] studied the h^E vs. g^E and h^E/RT vs. g^E/RT diagrams. While no data were displayed, the authors discussed the classical-thermodynamic features of these plots for miscible and immiscible systems and also noted how molecular theory with different size and energy ratios for the intermolecular potentials can lead to various diagrams.

Since 1983, when the paper of Kohler and Gaube first became known to us,[7] we have explored the use of excess-property diagrams for organizing data and for discussing observed property and phase behavior. The diagrams are particularly helpful as visual aids in the classroom. In fact, early experiences with them were so positive that they subsequently became vehicles for two comprehensive classroom projects in which students scoured the literature for excess-property data and then participated in the posing of explanations and generalizations based on the results of their searches. Thus, most of the coauthors of this paper are former Rensselaer students who participated in these exercises, and many of the data reported herein were gleaned by them.

***Michael M. Abbott** and **John P. O'Connell** are Professors of chemical engineering at, respectively, Rensselaer Polytechnic Institute and The University of Virginia. They share interests in thermodynamics and in chemical-engineering education. Their twenty co-authors are former BS, MS, and/or PhD students from Rensselaer who participated in the collection, evaluation, and organization of the data upon which this paper is based.*

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* *University of Virginia, Charlottesville, VA 22903*

EXCESS-PROPERTY DIAGRAMS

At modest pressures, the excess properties of liquid mixtures depend only on composition and temperature. Isothermal data allow separation of these effects; many data are reported at 298 K. At this temperature, comparison among systems may be most representative at equimolar composition (the choice we make), but the way to display data still must be chosen.

The excess Gibbs energy, excess enthalpy, and excess entropy are related by

$$g^E = h^E - Ts^E \tag{1}$$

The experimentally accessible quantities are g^E (via activity coefficients from vapor-liquid equilibria) and h^E (from calorimetry and temperature variations of g^E). When these are measured or estimated at the same conditions, a value for s^E can be found at the same conditions (there is no entropy meter!). Equation (1) shows that only two of these properties are independent, so any pair from the set $\{g^E, h^E, s^E\}$ can be used as the coordinates. The three types of diagrams (g^E vs. h^E, g^E vs. s^E, and h^E vs. s^E) convey exactly the same information.

Equivalent to Eq. (1), we may write

$$\frac{g^E}{RT} = \frac{h^E}{RT} - \frac{s^E}{R} \tag{2}$$

which suggests choices from the set $\{g^E/RT, h^E/RT, s^E/R\}$ as alternatives with exactly the same information.

We favor dimensionless ("scaled") coordinates (*i.e.,* pairs from the second of the above sets) for the following reasons:

- The quantity g^E/RT is the most natural dependent variable for phase-equilibrium applications, because $\ell n\ \gamma_i$ is a partial molar property with respect to g^E/RT.
- The quantity h^E/RT is cleanly related to g^E/RT via the Gibbs-Helmholtz equation

$$\frac{h^E}{RT} = -T\left(\frac{\partial\left(g^E/RT\right)}{\partial T}\right)_{P,x} \tag{3}$$

- One can establish temperature-independent upper bounds for g^E/RT of a stable liquid mixture.
- By scaling, values for g^E and/or h^E at different temperatures are put on a more comparable basis.
- Experience shows that important generalizations and rules-of-thumb are more easily grasped and retained when expressed in dimensionless terms.

TABLE 1
Definition of Regions on the $\hat{g}$ vs. $\hat{h}$ Diagram

Region	Sign $\hat{g}$	Sign $\hat{h}$	Sign $\hat{s}$
I	+	+	+
II	+	+	-
III	+	-	-
IV	-	-	-
V	-	-	+
VI	-	+	+

Again, which scaled coordinates should be used? For everyday work, we favor the first (g^E/RT vs. h^E/RT) and the last (h^E/RT vs. s^E/R), which we call "engineering" and "modeling" coordinates, respectively. Engineering coordinates represent experimental quantities; they facilitate discussion of phase equilibria, expecially liquid/liquid equilibria (see Shukla, *et al.*[6]). Modeling coordinates represent directly the enthalpic and entropic contributions to g^E/RT; they facilitate explanations of system-to-system trends in g^E/RT. Our goal in this paper is to present the data base we have accumulated and demonstrate the engineering patterns it shows. Thus, we will focus on the g^E/RT vs. h^E/RT diagram.

For convenience, we introduce the following notation for equimolar binaries:

$$\left.\begin{aligned} \hat{g} &\equiv g^E/RT \\ \hat{h} &\equiv h^E/RT \\ \hat{s} &\equiv s^E/R \\ \hat{c} &\equiv c_P^E/R \end{aligned}\right\} \quad \text{At} \quad x_1 = x_2 = 0.5$$

Equations (2) and (3) then become

$$\hat{g} = \hat{h} - \hat{s} \tag{4}$$

$$\frac{\partial \hat{g}}{\partial T} = -\frac{\hat{h}}{T} \tag{5}$$

We also have, from classical thermodynamics,

$$\frac{\partial \hat{s}}{\partial T} = \frac{\hat{c}}{T} \tag{6}$$

and thus, by Eqs. (4) through (6), we have

$$\frac{\partial \hat{h}}{\partial T} = \frac{\hat{c} - \hat{h}}{T} \tag{7}$$

Equations (4) through (7) are useful for analyzing the features of the $\hat{g}$ vs. $\hat{h}$ diagram.

According to Eq. (4), there are just six possible combinations of sign for $\hat{g}$, $\hat{h}$, and $\hat{s}$. These are listed in Table 1. Each sign combination defines a region on the $\hat{g}$ vs. $\hat{h}$ diagram (see Table 1 and Figure 1) We number the regions from I (counterclockwise) to VI.

The diagonal line on Figure 1 corresponds to $\hat{s} = 0$. In regions to the right of the diagonal (V, VI,

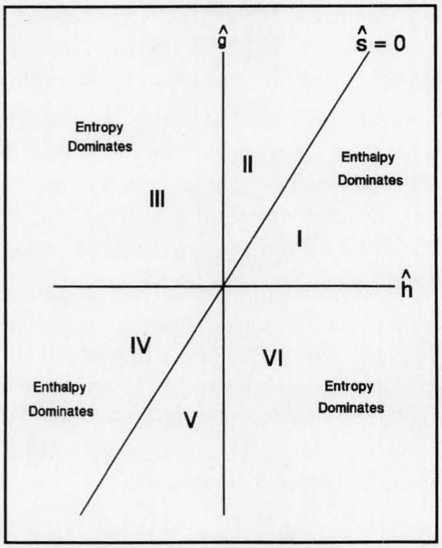

***Figure 1.** The $\hat{g}$ vs. $\hat{h}$ diagram.*

and I), $\hat{s}$ is positive, and for regions to the left of the diagonal (II, III, and IV), $\hat{s}$ is negative. Lines of constant (nonzero) $\hat{s}$ are parallel to the $\hat{s} = 0$ diagonal.

In Regions II and V the signs of $\hat{g}$ are preordained by the signs of $\hat{h}$ and $\hat{s}$ according to Eq. (4). This is not so for the rest of the diagram. Consider Region I where $\hat{g}$, $\hat{h}$, and $\hat{s}$ are all positive. According to Eq. (4), the sign of $\hat{g}$ is ambiguous, but the definitions actually require that in Region I *enthalpy dominates* since $\hat{h}$ must be greater than $\hat{s}$. Similar arguments show that enthalpy also dominates in Region IV, while entropy dominates in Regions III and VI. (This pretty line of reasoning, used by Malesinski,[1] is purely classical and model-independent.)

So far, we have said nothing about magnitudes. How large is large? We begin with $\hat{g}$, defining a "large" $\hat{g}$ as one for which phase-splitting (here, LLE) is likely. In the simplest approximation (with $g^E/RT = Ax_1x_2$), $\hat{g} = 1/2$ yields LLE; this *model-dependent* result constitutes a *practical lower bound* on $\hat{g}$ for phase-splitting. A *greatest upper bound* for stability obtains for $\hat{g} = \ell n2 = 0.6931\ldots$, corresponding to the Gibbs energy change of mixing Δg being zero for an equimolar binary mixture. Values in the range $0.50 < \hat{g} < 0.69$ are thus "large," with $\hat{g} = \ell n2$ chosen as the concrete limit on "largeness."

What of $\hat{h}$ and $\hat{s}$? Suppose that $\hat{h} = 0$, as for an "athermal" solution. According to Eq. (4), if $\hat{g}_{ath} = \ell n2$, then $\hat{s}_{ath} = -\ell n2$. Thus $\hat{s} < -\ell n2$ is a "large" negative $\hat{s}$. In fact, if $\hat{s} < -\ell n2$, $\hat{h}$ must be *negative* to produce a stable liquid mixture. (Notice that the entropy change of mixing Δs is negative for $\hat{s} < -\ell n2$. This perhaps counterintuitive, but occasionally observed, behavior suggests "unusual" phenomena in action.)

Suppose that $\hat{s} = 0$, as for a "regular" solution. According to Eq. (4), if $\hat{g}_{reg} = \ell n2$, then $\hat{h}_{reg} = \ell n2$. Hence $\hat{h} = \ell n2$ is a "large" positive $\hat{h}$; if $\hat{h} > \ell n2$, $\hat{s}$ *must* be positive to produce a stable liquid mixture.

We thus establish $\hat{g} > \ell n2$, $\hat{s} < -\ell n2$, and $\hat{h} > \ell n2$ as criteria of "largeness"; this is about as far as purely classical reasoning can take us. The missing bounds (practical lower bounds on $\hat{g}$ and $\hat{h}$, and a practical upper bound on $\hat{s}$), if they exist, must be supplied by Nature.

The temperature dependence of the excess properties for a given mixture defines a *trajectory* on the $\hat{g}$ vs. $\hat{h}$ diagram. Figure 2 shows a few examples. Some kinds of trajectories are forbidden. For example, Eq. (5) requires that $\hat{g}$ *increase* with T in Regions III, IV, and V (where $\hat{h}$ is negative), and that $\hat{g}$ *decrease* with T in Regions VI, I, and II (where $\hat{h}$ is positive).

From Eq. (6), the sign of $\partial\hat{s}/\partial T$ is determined solely by the sign of $\hat{c}$. On the other hand, Eq. (7) shows that both $\hat{c}$ and $\hat{h}$ contribute to $\partial\hat{h}/\partial T$. (We will show later that negative $\hat{h}$ usually implies positive $\hat{c}$, so both $\hat{s}$ and $\hat{h}$ normally increase with T for systems in Regions III, IV, and V.)

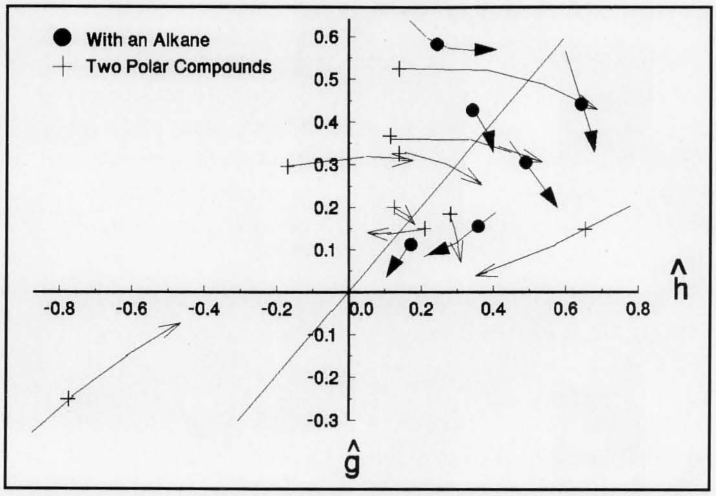

Figure 2. *Trends with temperature for equimolar mixtures. Symbols at 298 K; ranges are at least 100 K.*

TABLE 2
The g^E/h^E Data Base
Classification by Region and Mixture Type

	Region						
Mix Type	**I**	**II**	**III**	**IV**	**V**	**VI**	**Total**
NP/NP	46	4	2	1	10	32	95
NA/NP	80	16	7	5	2	0	110
A/NP	29	54	0	0	0	0	83
NA/NA	11	6	6	24	0	1	48
A/NA	28	15	11	5	0	0	59
A/A	8	6	4	6	1	1	26
Totals	202	101	30	41	13	34	421

In any case, $\hat{c}$ is important in the analysis and prediction of trends with T on the $\hat{g}$ vs. $\hat{h}$ diagram. Thus, we seek effective ways of graphically displaying data for $\hat{c}$. (We will show later that a plot of $\hat{c}$ vs. $\hat{s}$ has advantages as an organizational and explanatory aid.)

MIXTURE TYPES AND DATA BASE

For organizing and discussing the data base, we (like many others) find it convenient to classify mixtures by "type." We use a *coarse* classification based on separate identification of the components as nonpolar (NP), polar but nonassociating (NA), or polar and associating (A). Here, "association" means association only by hydrogen-bonding—though other association mechanisms exist. Hence, by our convention, acetonitrile/n-hexane is an NA/NP mixture, whereas ethanol/n-hexane is an A/NP mixture. Notice that this scheme gives us the same number of binary mixture types (six) as there are regions on the $\hat{g}$ vs. $\hat{h}$ diagram. (This handy six-

TABLE 3

The "Extended" $g^E/h^E/c_P^E$ Data Base

Classification by Region and Mixture Type

	Region and Sign of c_P^E												
	I		II		III		IV		V		VI		
Mixture Type	$c_P^E\oplus$	$c_P^E\ominus$	$c_P^E\oplus$	$c_P^E\ominus$	$c_P^E\oplus$	$c_P^E\ominus$	$c_P^E\oplus$	$c_P^E\ominus$	$c_P^E\oplus$	$c_P^E\ominus$	$c_P^E\oplus$	$c_P^E\ominus$	TOTAL
NP/NP	3	25	0	0	0	0	0	0	1	1	1	15	46
NA/NP	10	13	3	0	1	2	0	1	0	0	0	0	30
A/NP	1	0	28	0	0	0	0	0	0	0	0	0	29
NA/NA	5	4	4	1	2	0	22	0	0	0	0	0	38
A/NA	6	1	7	0	3	0	0	1	0	0	0	0	18
A/A	1	0	1	0	3	0	0	1	0	0	0	0	6
Totals	26	43	43	1	9	2	22	3	1	1	1	15	167

TABLE 4

The "Extended" $g^E/h^E/c_P^E$ Data Base

Classification by Signs and Mixture Type

	$c_P^E\oplus$				$c_P^E\ominus$			
Type Mixture	$h^E\ominus$	$s^E\ominus$	$h^E\oplus$	$s^E\oplus$	$h^E\ominus$	$s^E\ominus$	$h^E\oplus$	$s^E\oplus$
NP/NP	1	0	4	5	1	0	40	41
NA/NP	1	4	13	10	3	3	13	13
A/NP	0	28	29	1	0	0	0	0
NA/NA	24	28	9	5	0	1	5	4
A/NA	3	10	13	6	1	1	1	1
A/A	3	4	2	1	1	1	0	0
Totals	32	74	70	28	6	6	59	59

by-six mnemonic has no special thermodynamic significance.)

Data were collected in two separate sweeps of the literature. In the first effort we sought systems for which both g^E and h^E had been measured (or could be estimated) at or near to 298 K. In the second search, we also looked for c_P^E data. Both primary and secondary sources were consulted.

Table 2 summarizes the *makeup* of our g^E/h^E data; the data themselves are in an Appendix that is available from the senior authors (Abbott and O'Connell). In addition to the approximately four hundred organic and aqueous/organic mixtures classified in Table 2, equimolar g^E/h^E data were found for twenty-two cryogenic mixtures at temperatures ranging from 0.9 K (helium-3/helium-4) to 184 K (ethylene/nitrous oxide and nitrous oxide/xenon). These data are also available and can be obtained by writing the authors.

Although the c_P^E data base is reasonably large (*ca.* 350 different mixtures), the overlap of systems with the g^E/h^E data base is relatively modest. In many cases, however, the *sign* of c_P^E (if not the magnitude) can be unequivocally fixed by interpolation, by analogy, or by inspection of the temperature variation of the data for h^E. For example, available data show that c_P^E is always positive for 1-alkanol/n-alkane systems at 298 K. Similarly, c_P^E is always positive for solvating NA/NA mixtures. (Here, "solvation" means that strong unlike attractions occur even though association may not be found for one or both of the unmixed components.) Thus, we can define an "extended" $g^E/h^E/c_P^E$ data base comprising about 150 systems for which g^E, h^E, and either c_P^E or its sign are known; it is summarized in Tables 3 and 4.

Before presenting our findings, we offer a few words of caution:

- ❑ *First:* We make no claims of completeness. This collection is largely the result of two classroom (*i.e.,* time- and resource-limited) searches of the mostly post-1960 literature.
- ❑ *Second:* Our ground rules were to include only miscible mixtures of nonelectrolytes at temperatures near to 298 K. This delimits and biases the data base. Partially-miscible mixtures are, of course, of great concern to designers of separation processes, yet our collection excludes such systems.
- ❑ *Third:* Although the relative proportions of data for the various mixture types should reflect the relative numbers of available g^E/h^E sets for these types, one must recognize that the kinds of systems reported actually reflect the individual and collective biases of thermodynamic experimentalists and their customers. As a result, some classes of mixtures have received disproportionately intense attention because of their interest to correlators and theoreticians, and not because they are particularly "representative" of Nature.
- ❑ *Fourth:* We note that many of the g^E and/or h^E values for 298 K are determined by extrapolation or derivation via the Gibbs-Helmholtz equation. Such estimates are of course better than no estimates at all, but they *are,* in the end, only estimates.

With these caveats in mind, we can briefly review the statistical makeup of our data collection. For the g^E/h^E and extended $g^E/h^E/c_P^E$ data bases, mixture types are represented approximately as follows (see Tables 2 and 3 for details):

Mixture Type	% of g^E/h^E	% of Extended $g^E/h^E/c_P^E$
NP/NP	23	27
NA/NP	25	18
A/NP	20	17
NA/NA	12	23
A/NA	14	11
A/A	6	4

Hence, about 65% of our mixtures contain a nonpolar species, 50% a nonassociating polar species, and 35% an associating polar species. Of the binary mixture types, A/A mixtures are the most poorly represented, accounting for only about 5% of the whole.

PATTERNS AND TRENDS

Figure 3 is a $\hat{g}$ vs. $\hat{h}$ plot for the complete g^E/h^E data base. Although this picture appears at first glance to be a scene from an experimentalist's nightmare, it (and its companion Table 2) delivers some important messages:

1. Regions I and II are very heavily represented, accounting for 48% and 24% of the data base: positive g^E and h^E are "the norm."
2. Region V is very sparsely represented. Nature appears to abhor the most inherently stable of liquid mixtures—the systems with negative h^E and positive s^E.
3. Only 59% of our mixtures have positive s^E, whereas 80% have positive h^E. Thus, in a very gross statistical sense, the regular solution ($s^E = 0$) is a better approximant to reality than is the athermal solution ($h^E = 0$).
4. Negative h^E implies negative s^E, and positive s^E implies positive h^E about 90% of the time. The converses are true only about half of the time:

   $h^E\ominus \rightarrow s^E\ominus$ (85% valid)
   $s^E\oplus \rightarrow h^E\oplus$ (95% valid)
   $h^E\oplus \rightarrow s^E\oplus$ (70% valid)
   $s^E\ominus \rightarrow h^E\ominus$ (41% valid)

5. Nature seems to provide some of our missing bounds for "largeness" of $\hat{g}$ and $\hat{s}$. Very approximately, according to Figure 3, we may consider $\hat{g} < -0.4$ and $\hat{s} > 0.4$ as additional criteria of "largeness." When combined with the criteria presented earlier, these bounds define the rectilinear region denoted by the dashed line in Figure 3. Systems falling outside this region may be considered "unusual."

Figure 4, the modeling plot of $\hat{h}$ vs. $\hat{s}$ for the complete g^E/h^E data base, without most of the "unusual" cases, conveys the same messages as Figure 3.

Plots of $\hat{g}$ vs. $\hat{h}$

It is instructive to examine $\hat{g}$ vs. $\hat{h}$ relations for each of the six binary mixture types. We do them in order of increasing molecular complexity

NP/NP Mixtures

These are shown by the open circles of Figure 3 (and separately in Figure 6 of the Appendix, available from the authors). The systems fall mainly in Regions I and VI; $\hat{g}$ is small to modest in size, rarely exceeding 0.2 in absolute value. The Region VI mixtures mostly contain alkanes or other "inerts" of greatly different molar volume; here, the negative $\hat{g}$ results from a relatively large positive $\hat{s}$ ("entropy dominates"). The Region I mixtures mostly contain two alkanes or two aromatics of modest molar-volume ratio, or mixtures of an alkane with an aromatic hydrocarbon. Heat effects can be quite large for the alkane/aromatic systems, but these tend to be compensated by a large positive value of $\hat{s}$, leading to small or modest $\hat{g}$.

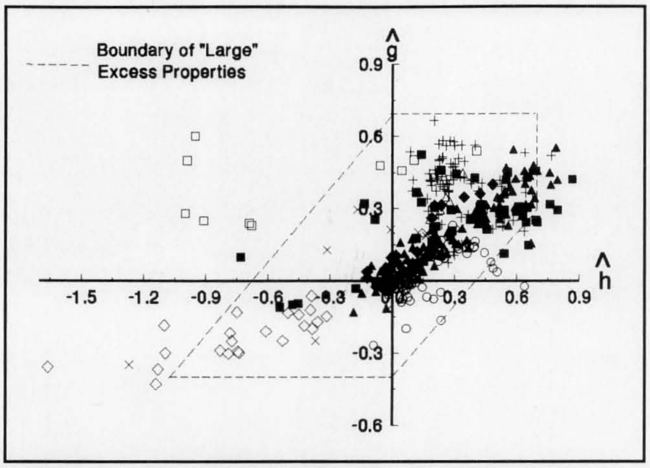

Figure 3. *The complete g^E/h^E data base for binaries at 298 K and equimolar composition.*

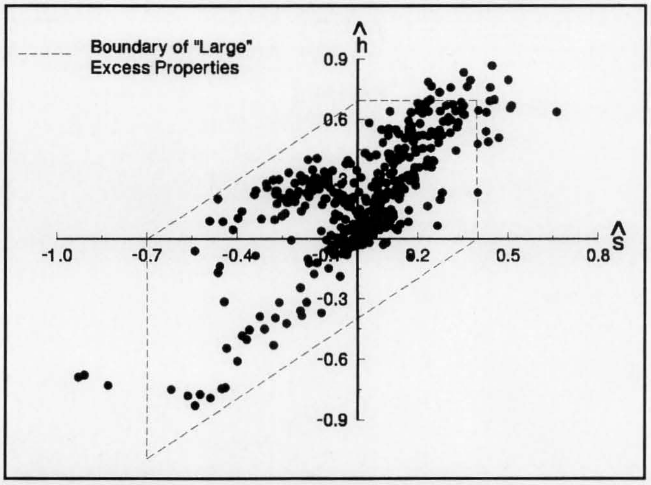

Figure 4. *The complete h^E/s^E data base for binaries at 298 K and equimolar composition*

NA/NP Mixtures

These are shown by the triangles in Figure 3 (and separately in Figure 7 of the Appendix. Region I behavior is the norm ("enthalpy dominates"), but one finds occasional excursions into Regions II through V. Most of the latter cases are systems in which one of the substances is an aromatic hydrocarbon, a tertiary amine, CCl_4, or acetonitrile. Mixtures containing acetonitrile tend to fall in Region II; their location makes them appear to be "weak" relatives of A/NP mixtures (see below). Notice that for NA/NP mixtures, both $\hat{g}$ and $\hat{h}$ can be quite large.

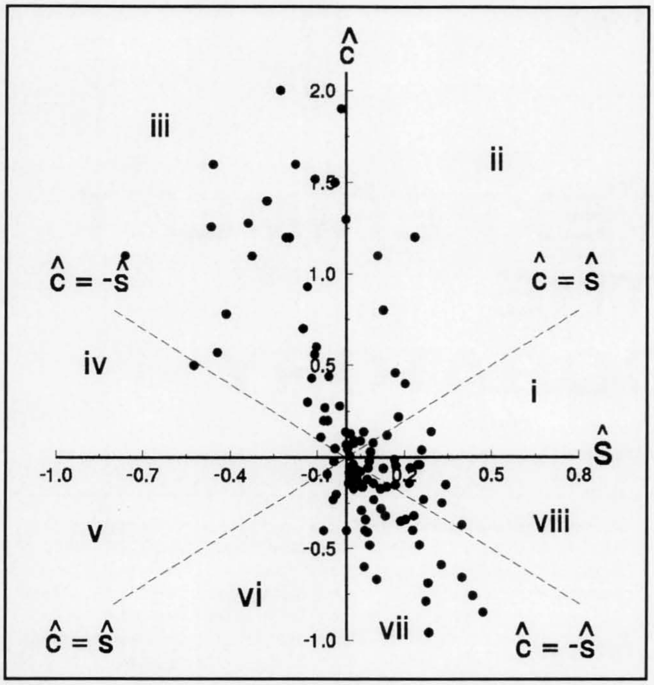

Figure 5. *The complete c^E/s^E data base for binaries at 298 K and equimolar composition.*

A/NP Mixtures

Data for these systems are the crosses in Figures 3 (and are plotted separately in Figure 8 of the Appendix). All data fall in Regions I or II. The stronger associators (alcohols and carboxylic acids) tend to show Region II behavior when mixed with alkanes. Here, $\hat{s}$ is negative and $\hat{g}$ is large and positive: so large as to lead to phase splitting in extreme cases. Mixtures of strong associators with aromatics exhibit smaller values of $\hat{g}$, owing to smaller negative, or even large positive, values of $\hat{s}$. Mixtures of secondary amines with hydrocarbons behave similarly to NA/NP systems: $\hat{h}$ and $\hat{s}$ are positive and sufficiently comparable in magnitude so as to produce small to modest values for $\hat{g}$.

NA/NA Mixtures

As the diamond symbols of Figure 3 (and Figure 9 of the Appendix) show, these systems exhibit one of two general kinds of behavior, depending on whether the unlike species can solvate by hydrogen bonding. If solvation occurs (acetone/chloroform is the classical example), then g^E, h^E, and s^E are all negative, and Region IV behavior obtains (open diamonds). If both species are proton donors or both are proton acceptors, then Region I or Region II behavior is common (solid diamonds). Quasi-ideal mixtures (very small $\hat{g}$, $\hat{h}$, and $\hat{s}$) are possible when the two species both have high effective polarity.

A/NA and A/A Mixtures

Data for the A/NA systems are the box symbols in Figure 3 (plotted separately in Figure 10 of the Appendix). A diversity of behavior is seen, but $\hat{g}$ is usually positive and is often large. Generalization is difficult because of the complex molecular effects in operation; association or electrostatic interactions between like molecules may be partially compensated by solvation between unlike species. Region III behavior is not uncommon, especially at low temperatures. Aqueous systems are the open boxes in Figure 3, principally in Region III.

The x symbols in Figure 3 (plotted separately in Figure 11 of the Appendix) show the very small data base for A/A mixtures. Association or solvation can occur between all pairs, sometimes leading to a near cancellation of polarity or association effects (as in many alcohol/alcohol mixtures), and sometimes not. No easy generalization can be made.

Relationships with c_P^E

Finally, we consider the excess heat capacity. The statistics in Table 4 suggest a strong correlation between the signs of s^E and c_P^E. Thus a negative s^E (or c_P^E) gives a positive c_P^E (or s^E) about 90% of the time, while a positive s^E or (c_P^E) implies a negative c_P^E (or s^E) about 70% of the time:

$$s^E\ominus \rightarrow c_P^E\oplus \qquad \text{(93\% valid)}$$

$$c_P^E\ominus \rightarrow s^E\oplus \qquad \text{(91\% valid)}$$

$$s^E\oplus \rightarrow c_P^E\ominus \qquad \text{(68\% valid)}$$

$$c_P^E\oplus \rightarrow s^E\ominus \qquad \text{(73\% valid)}$$

Hence, we have the *approximate* equivalence

$$\text{Sign}\,(c_P^E) = -\,\text{Sign}\,(s^E)$$

Searching for correlations between the signs of h^E and c_P^E, we find

$$h^E\ominus \rightarrow c_P^E\oplus \qquad \text{(84\% valid)}$$

$$c_P^E\ominus \rightarrow h^E\oplus \qquad \text{(91\% valid)}$$

$$h^E\oplus \rightarrow c_P^E\ominus \qquad \text{(46\% valid)}$$

$$c_P^E\oplus \rightarrow h^E\ominus \qquad \text{(31\% valid)}$$

Negative signs on h^E (or c_P^E) imply positive signs on c_P^E (or h^E) about 85% or more of the time, whereas positive signs on h^E (or c_P^E) imply negative c_P^E (or h^E) only about 40% of the time. Thus, we have the relatively strong implications that a negative h^E (or c_P^E) gives a positive c_P^E (or h^E). The converse statements are not generally true, however.

These arguments lead us to consider a plot of $\hat{c}$ vs. $\hat{s}$ (Figure 5). Quantitative judgments are aided if one adds to Figure 5 the dashed parity lines $\hat{c} = \hat{s}$ and $\hat{c} = -\hat{s}$. These lines, with the axes $\hat{c} = 0$ and $\hat{s} = 0$, divide the $\hat{c}/\hat{s}$ plane into

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EXCESS FUNCTIONS

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octants, denoted by numerals I through VIII. We make the following observations:

1. c_P^E is usually *larger* in absolute value than is s^E; for the systems shown in Figure 5, $|\hat{c}| > |\hat{s}|$ about 85% of the time.
2. Octants IV, V and VI are very sparsely occupied. Thus the following behaviors are *unusual:*

   $$s^E \ominus \text{ with } c_P^E \ominus$$

   and

   $$s^E \ominus \text{ with } c_P^E \oplus \textit{ and } c_P^E < -s^E$$

   Other octants have reasonable representation.
3. $\hat{c} < -1$ is an unusually large negative $\hat{c}$; positive values of $\hat{c}$ can, however, be considerably larger than unity.

The above observations lead to a few generalizations. Mixtures with negative h^E and s^E usually have positive c_P^E; mixtures with negative c_P^E usually have positive s^E and h^E. For NP/NP mixtures, c_P^E is *usually* negative, though exceptions are observed (*e.g.,* for mixtures of CCl_4 with an aromatic hydrocarbon). For NA/NP mixtures, c_P^E is *often* negative, though exceptions occur (*e.g.,* when the polar species is a ketone). For all other mixtures, positive c_P^E is the norm; exceptions obtain, *e.g.,* for quasi-ideal mixtures of components with similar effective polarity.

THE EXCESS-PROPERTY DECK OF CARDS

To stimulate interest in this method, a card game has been devised for use in class. Each card has the name of a common chemical written on one side, and the other side is blank. There are 52 cards in the deck, with representations of possible mixture types approximately as indicated above. The cards are shuffled and someone pulls out two cards without looking at the compounds. The signs on g^E and h^E for the mixture are then guessed. (The best guesses are $\oplus$.) Then, an "entropy coin" is taken out to determine the sign on s^E. (Since the chances are about even, a coin flip is as good as any other guess.)

At this point the compounds are revealed and the mixture behavior predicted based on the probabilities and connections given in the tables. Finally, if the Appendix is available and it has the system (or a related one), it is possible to see how good the predictions are; if not, one of the group contribution methods for activity coefficients could be used to predict the sign on g^E.

This is one of those exercises where quick students can often surpass the instructor in accuracy, though good fun is almost always had by all involved.

CLOSURE

The $\hat{g}$ vs. $\hat{h}$, the $\hat{h}$ vs. $\hat{s}$, and the $\hat{c}$ vs. $\hat{s}$ diagrams are effective props for displaying and categorizing the excess-property behavior of binary liquid mixtures. The six-type mixture-classification scheme, when used in conjunction with the diagrams, allows one to make some broad generalizations about liquid-mixture behavior. Thermodynamic arguments are few and classical in nature.

It would be foolish to ignore molecular concepts as aids for further organizing and explaining the results presented in this paper. In fact, the required level of molecular argument seems to be relatively modest, and precedents exist. We are preparing a "molecular exegesis" of this Field Guide which will be a second paper in this study.

The Appendix, which is available to interested readers by writing the senior authors, contains an enormous amount of information, which we use in various ways. For example, one can employ selected data in conjunction with the $\hat{g}$ vs. $\hat{h}$ or the $\hat{h}$ vs. $\hat{s}$ diagrams to illustrate and explain trends in families of binary mixtures containing a common component with a series of homologs. Educators will have no difficulty devising their own examples with this data collection and finding variations on the card game. There are a thousand stories here!

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