

# ON ERROR PREVENTION

## On Error Prevention\*

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**A plan is presented for catching various types of errors in reported physical property data before they enter the permanent literature. Execution of the proposed checks by means of existing or easily constructed computer programs should be straightforward and, with the exception of thermochemical data, require very little, if any, expert guidance.**

The analysis of error incidence and control in the chemical literature by the participants in this symposium has directed attention to three major error sources: incorrect nomenclature, incorrect data, and unsatisfactory methods to connect the few errata notices submitted with their original errors.

The incidence of other than typographical errors in a journal is basically a failure of its primary error filter: the editor and the reviewers. Both of these are extremely busy and can hardly be expected to catch every incorrect chemical name or structure or property datum, unless really blatant. Yet, in an age where an increasing fraction of scientific and technological work depends on literature information, even "minor" errors can lead to serious waste of effort. Typically, an erroneous thermochemical datum can persuade a chemist or group of chemists to undertake a completely hopeless synthesis or, conversely, discourage the pursuit of what would have been a most lucrative synthetic venture.

The economic cost of the rapidly accumulating errors in the literature has not been evaluated, and it is unlikely that many scientists keep track of or will readily admit the time wasted with incorrect information from the literature. On the most trivial level as little as two hours per chemist man-year spent on chasing down an error represents a direct loss of three million dollars per year (in salaries and overhead) for the U. S. economy, not estimating the several times higher cost of the work left undone or done incorrectly. Potential or actual costs of this magnitude amply justify a massive assault on the error sources so far uncovered.

Preferably errors should be caught at the source, and ultimately the same means, proposed here for use by journal editors, will be employed by the chemist or engineer who originates the information. Specifically, I shall propose the use of computers by editorial staffs as checking devices for the correlation between names and structure and for physical property data before a paper is ever submitted to the reviewers. The results of this preliminary check would be submitted to a reviewer simultaneously with the manuscript since it should be axiomatic that only a scientist and not a machine be entrusted with the final judgment regarding the merits of a paper.

The machine encoding of chemical structures by Wiswesser's and several other codes, proposed by Addelston (see p.126 this issue), is a well-established procedure and could be used with little modification for the checking scheme which he described. Hence the balance of this paper will be primarily concerned with error prevention in the physical property field.

### PURPOSE AND SCOPE

The purpose of the present paper is to review the principles which could be used to reduce the number of errors creeping into the literature on the physical properties of liquids and gases and to assemble some of the mathematical treatments and programs to implement these principles.

The scope of the present proposals is set by the task of the present symposium to develop an error prevention scheme applicable to "physical and thermochemical properties of pure chemical substances." The scope of the present paper is further restricted to treatments many of which may be applicable only to organic substances, or possibly include those inorganic substances held together in the condensed state by molecular forces. The reason for this restriction is the large amount of work which has been done on the correlation of the properties of these substances in contrast to the absence of such treatments for predominantly ionic (inorganic) substances.

### GENERAL PRINCIPLES OF ERROR PREVENTION

Error prevention in the present context is the comparison of experimental data or of relations between different experimental data of a given composition with the existing information in the form of theories or correlations and with the (interproperty) relations demanded by the rules of thermodynamics. The underlying supposition is that large deviations from the numerical values estimated by theories or correlations could indicate either that the data are unreliable or that a rather novel situation exists which could not have been contained in the existing theories or correlations. The latter is, of course, always possible but would have to be rationalizable in order to be acceptable. No exceptions are possible in the case of inconsistency with the rigorous relations of thermodynamics. Failure here is fatal to whatever data have been produced.

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An advantage of computer handling of the problem is that the laborious process of salvaging seemingly questionable data can be undertaken at little expense. A regression program can be arranged to show how far the data have to be adjusted in order to be consistent with the demands of thermodynamics or with well-established correlations. When the proposed changes are within the error limits of the experiment, the regression program would be asked to provide numbers which meet the demands of internal or external consistency and at the same time fall within or very close to the error limits of the experiments. If the error limits are wide enough to accommodate that possibility, it would be futile to repeat the experiment. In that case the error prevention procedure may justly be said to have improved the data.

Where no such accommodation is possible, economic considerations of the consequences of uncertainty will determine whether to repeat the experiment or to live with the uncertainties of results obtained from an estimating method. The assumption here is that experimental measurements of physical properties will nowadays be carried out only if the uncertainties of estimating methods are economically unattractive—e.g., make process design too expensive or a product unsaleable—or if the precise knowledge of the numerical value of a property is of intrinsic scientific value.

**Test Plan (for all but Thermochemical Properties).** A typical plan to check the probable correctness of a datum proposed for publication might proceed by the following route:

- (a) Screening by comparison with results from general property estimation or from upper and lower limit estimates. If the comparison is satisfactory and no high degree of accuracy is claimed by the author, the test is completed, but if high accuracy is claimed by the author, the next tests should be applied.
- (b) Fit into multiple regression of the family of compounds of which the compound under consideration is a member. This fit will generally supply a measure of the accuracy of the proposed datum.
- (c) Internal consistency tests of thermodynamics should then be applied, if the datum under consideration is an equilibrium (thermodynamic) property.

**Comparison with General Property Estimation.** If the property and the compound under consideration are of a kind for which insufficient data are available to use any of the tests under (b) and (c), the questioned datum should be produced by a physical properties computer program such as the A.I.Ch.E. program (APPES) (1) or the thermodynamic network generator program by Reid (9), if applicable.

This program calculates the physical properties described in Table I from molecular structure and the atmospheric boiling point as data input, and gives an estimate of the expected error limit of its own calculation, the combined error of the correlation schemes used in the calculation. The accuracy of the questioned datum

Table I. Physical Properties Calculated by A.I.Ch.E. Physical Properties Computer Program

	Gas Phase	Liquid Phase
Critical constants	X	X
Density	X	X
<i>P-V-T</i> relations, equations of state	X	...
Vapor pressure, $\Delta H_{\text{vap}}$	...	X
Heat capacity	X	X
Surface tension	...	X
Viscosity	X	X
Thermal conductivity	X	X
Diffusion coefficient	X	X

should be declared "doubtful" if it falls outside the error limits of the computer estimate.

The indicated use of APPES presupposes a high degree of reliability of the correlation selection system appropriate for given types of compounds built into that computer program. Such a degree of reliability is achievable in principle for many types of compounds. Properties of compounds outside the scope the correlations built into the program may be checked by means of a limit system outlined in the following section.

**Limit System.** A lower limit can be set for the numerical value of physical properties of compounds for which the previously described checking scheme cannot be used. The scheme is based on the supposition that the physical property of the hydrocarbon homomorph of any polar organic compound at the same "reduced temperature" is the lower limit to the numerical value of that property of the compound under consideration.

The reduced temperature is ideally the ratio  $T/T_c$ , so that the scheme presupposes existence of a method to estimate  $T_c$  for the compound in question (unless its  $T_c$  is known). If that is not the case, the ratio  $T/T_b$  could be used as reduced temperature. If  $T_b$  is neither known nor estimable by means of any boiling point estimating method, recourse can be had to another corresponding states method—namely, comparison at the same packing density,  $\rho V_w M$ . This supposes that the density,  $\rho$ , of the compound under consideration is available for the temperature at which the property is to be checked. The van der Waals volume,  $V_w$ , can be calculated for both the compound under consideration and for its hydrocarbon homomorph from published increments (6).

The hydrocarbon homomorph property under consideration is then taken from the American Petroleum Institute Research Project 44 Tables, "Selected Physical Properties of Hydrocarbons" (2), for the reduced state value of the compound under consideration. The result should be considered as lower limit for the numerical value of that property.

Automation of this scheme is feasible only when a structure code is available which can translate any molecular structure of a polar compound into the structure of its hydrocarbon homomorph. The method cannot be used for nonpolar nonhydrocarbons such as per halides, per cyano compounds and the like.

**Multiple Regression.** The availability of extensive information on the property under consideration for several members of the chemical family of the compound under consideration permits the construction of a very powerful filter,

the multiple regression. In that type of regression one represents a given property not only as a function of a state variable ( $T, p$ ) but also as a function of chemical composition (12). This presupposes guidance from theory or experience regarding the most useful functional relation between coefficients and the important elements of molecular structure.

"Family of compounds" in the present context can mean any regular progression of structure changes, such as in homologous series, or the successive substitution of hydrogen atoms by a given functional group, as in mono-, di-, tri-, etc., halobenzene, -ethane (taking due account of molecular geometry) or the series monofluoro-, -chloro-, -bromo-, or -iodobenzene, or a series of isomers of a given compound, etc. (1).

Degree of fit or misfit of a set of data under scrutiny into such a regression is easily established. On the other hand, sight should not be lost of the cumbersome procedure of setting up the original regression, an effort which can only be justified by frequent use of such program.

**Internal Consistency Tests (Other Than Thermodynamic).** Whenever data of two or more different physical properties are submitted for a given compound or composition and these data are entered into the APPES, the program output will state whether the input data were mutually consistent in terms of the correlations contained in the system. One case not contained in APPES, refractivity, illustrates this principle rather well. If the refractive index and the density (and molal weight) of a compound are given, these can be combined in the Lorentz-Lorentz molar refractivity and compared with the refractivity calculated for that particular molecular structure from one of the well-established refractivity-structure correlations (25). Deviation of the experimental from the calculated refractivity by more than the very narrow error limits of the correlation makes density and refractive index suspect. Since the latter is more easily determined with high accuracy, the major doubt will fall on the density datum.

#### Internal Consistency Tests for Thermodynamic Properties.

(a) The internal consistency tests of vapor phase  $P$ - $V$ - $T$  data can be obtained from textbooks of thermodynamics (for example, Barnett F. Dodge, "Chemical Engineering Thermodynamics," McGraw-Hill, New York, N. Y., 1944), and will therefore not be recounted here except to say that not many experimental data yield smooth first derivatives and hardly any survive the requisite direct second differentiations with respect to the state variables. Hence, it is generally more realistic to fit the data to an appropriate equation of state and to test their quality and internal consistency by observing the error pattern in the least square fitting to that equation of state. This procedure permits the simultaneous application of external consistency tests by comparing the coefficients of the equation of state with well-established patterns, especially in terms of reduction with the critical constants.

(b) An internal consistency test for vapor pressure data of individual compounds is the set of inequalities at  $\theta_D < T < T_b$ ;

$$\left. \frac{d}{dT} \left( R \frac{d \ln p_i}{d(1/T)} \right) \right|_{\text{sat. liq.}} = C_s(g) - C_s(l) < 0 \text{ because of } C_p(l) > C_p(g)$$

and

$$\left. \frac{d}{dT} \left( R \frac{d \ln p_i}{d(1/T)} \right) \right|_{\text{sat. solid}} = C_s(g) - C_s(s) < 0 \text{ because of } C_p(s) > C_p(g)$$

at  $T < \theta_D$ :

$$\left. \frac{d}{dT} \left( R \frac{d \ln p_i}{d(1/T)} \right) \right|_{\text{sat. solid}}$$

$> 0$  because  $C_s(s) < C_s(g)$  since  $C_p(s) \rightarrow 0$  as  $T \rightarrow 0^\circ \text{K}$ .

if either measured or reliably estimated values of  $C_s(l)$  and  $C_s(g)$  or of  $C_s(l) - C_s(g)$  are available (produced by the program), the consistency test can be made more precise by testing

$$\left. \frac{d}{dT} \left( R \frac{d \ln p_i}{d(1/T)} \right) \right|_{\text{sat. liq.}} - \Delta H_i = 0; \text{ and } \left. \frac{d}{dT} \left( R \frac{d \ln p_i}{d(1/T)} \right) \right|_{\text{sat. solid}} - \Delta H_i = 0.$$

against the values of  $C_s(g) - C_s(l)$ . In the range  $T_c < T < T_b$ ,  $d^2 \ln p_i / d(1/T)^2$  may change sign due to vapor imperfections. The location of this inflection and the absolute value of  $d^2 \ln p_i / d(1/T)^2$  in that region can be checked by combining the heat capacity with the equation of state data.

When calorimetric or reliably estimated data are available for the heat of vaporization,  $\Delta H_i$ , or for the heat of sublimation, one can test at  $T < T_b$ .

$$\left. R \frac{d \ln p_i}{d(1/T)} \right|_{\text{sat. liq.}} - \Delta H_i = 0; \text{ and } \left. R \frac{d \ln p_i}{d(1/T)} \right|_{\text{sat. solid}} - \Delta H_i = 0.$$

at higher temperatures the test involves also the equation of state because then

$$\left. R \frac{d \ln p_i}{d(1/T)} \right|_{\text{sat. liq.}} = \frac{\Delta H_i}{\Delta Z}.$$

(c) Critical constants. The correctness of determined or estimated  $T_c$  and  $p_c$  can be assessed by testing their consistency with known or estimated values of  $\Delta H_i$  (at  $T = T_b$ ) and of  $T_b$ , as suggested by Edwards (8).

**Thermochemical Properties.** Proposed thermochemical property data should preferably be checked on two levels: First, the conversion of the raw experimental heat of combustion, or of other heat of reaction data, to the usually desired standard heat of formation datum should be executed with a suitable computer program. If that test is met, or if the raw data had not been given,\* the second test should be applied—namely, consistency of the proposed datum with other well-established thermochemical information [for example, N.B.S. Bull. 500 (13) and the other forthcoming N.B.S. bulletins on thermochemical data]. All of these should become available as data banks on magnetic tape. A computer program for the execution of such consistency tests should also become available from the National Bureau of Standards. A major difficulty in the interpretation of deviations from "consistency" with other heat of formation data is the incidence of true effects in either direction, due to steric strain or to resonance stabilization.

\* Absence of the original experimental data should in general be considered as reason for rejection of a proposed publication of thermochemical information.

A recent review of the available correlations of thermochemical data by Somayajulu (20) gives one great confidence in the use of the best existing schemes as means to check experimental data. Mathematical programs are also available for strain energy calculations (10, 24).

Stabilization of chemical bonds by aromaticity and other conjugated multiple bonds also leads to well-known corrections, sharp deviations from which should always be viewed with suspicion. Here strain effects are much less well understood, however, than in the case of saturated hydrocarbons and can give only qualitative leads in consistency tests.

Thanks to the extensive work of API-Project 44 one knows so well how to expand data from those of a parent compound to those of its various alkyl, etc., derivatives, that a datum for a derivative can be checked reliably even if prior experimental data are available only for the parent compound.

**Properties That Cannot be Checked by Calculation.** Computational check of the accuracy of a reported datum requires either the availability of structural additivity relations for the property under consideration, or that the property can in some way be related to other experimentally available properties or to other additive properties. A typical set of properties for which no such relation applies is the melting point ( $T_m$ ), the first order solid/solid transition temperatures ( $T_{tr}$ ), the heat of fusion ( $\Delta H_m$ ), if  $T_m$  is unknown, and the heat of transition, if  $T_{tr}$  is unknown. The sum of the entropy of fusion and of the entropy of transition is rather well correlated with molecular structure (5). Fortunately,  $T_m$  is also obtainable without very great effort. Hence, the inability to check the accuracy of a reported melting point is not a great handicap. The transition points,  $T_{tr}$ , are more difficult to determine, and with few exceptions (23), even more difficulty to rationalize. Hence, there is at present no way to check a reported value of  $T_{tr}$ .

## MIXTURES

The properties of mixtures can be divided into three groups from the point of view of the present objectives:

1. Mixture vapor pressure and solubility of liquids in liquids; mixture vapor pressure and solubility of solids in liquids;  $P$ - $V$ - $T$  properties of gas mixtures.

2. Equilibrium properties of mixtures other than those named under 1.

3. Transport properties of mixtures.

The thermodynamics of the Class 1 system properties have been very highly developed and the internal consistency of reported data can be checked to a high accuracy. The thermodynamics and molecular theories of Class 2 system properties are far less well developed and only limit checks may be possible in many instances. Among Class 3 system properties only those of very simple gases can be checked by reference to well-founded theory. The transport properties of liquid mixtures and of solid solutions can be checked only by reference to empirical rules.

**Internal Consistency Tests for Multicomponent Phase Equilibria.** (a) LIQUID-VAPOR AND LIQUID-LIQUID PHASE EQUILIBRIA. The internal and external consistency of

vapor-liquid equilibrium data should be tested by the method proposed by Tao (22) once its awkward data plotting procedure will have been replaced by a regression analysis. The latter would also set the error bound more precisely than any graphical procedure.

An important supplement for Tao's internal consistency program is the demand for external consistency; for example, the consistency of the heat of mixing calculated from the slope of the curve of activity coefficient *vs.* temperature with existing molecular structure correlations of the heat of mixing, or with known heats of mixing of similar systems entered into the data bank of the appropriate computer program.

The minimum internal consistency requirement on vapor-liquid and liquid-liquid phase equilibria is that they meet the Redlich-Kister criterion (16)

$$\int_{x_1=0}^{x_1=1} \log (\gamma_1/\gamma_2) dx_1 = 0$$

which is more easily done on the computer than by hand. Given the error bounds determined by regression analysis of the experimental data or entered as primary information with the data (based on the known performance of the equipment) the computer program should print out a diagnostic report saying how far the data have to be adjusted away from their own mean within their error envelope in order to meet the Tao or at least the Redlich-Kister consistency criteria, or whether and how far the adjustment required would carry the data outside their error envelope.

(b) SOLID-LIQUID EQUILIBRIA. Straightforward internal consistency tests are far more difficult to apply in this case. A first try has been made very recently by Null (14). His simplest result is for the rare case of an ideal liquid solution at constant temperature:

$$\int x_1 d \ln \left( \frac{Y_1}{\theta_1} \right) + \int x_2 d \ln \left( \frac{Y_2}{\theta_2} \right) = 0$$

where  $x_i$  = mole fraction of component  $i$  in the solid phase, and  $y_i$  = mole fraction of component  $i$  in liquid phase,

$$\theta_i \equiv \exp \left\{ \frac{1}{R} \left[ \Delta S_m(i) \left( 1 - \frac{T}{T_m(i)} \right) + \Delta C_i \left( y - \frac{T_m(i)}{T} - \frac{T}{T_m(i)} \right) \right] \right\},$$

$\Delta C_i = C_p(l) - C_p(s)$  for compound  $i$ ,  $\Delta S_m(i)$ ,  $T_m(i)$  are entropy and temperature of fusion of component  $i$ . When the liquid solution cannot be assumed as ideal, the internal consistency test becomes rather involved and not enough experience has been gained in its use to recommend it for routine applications at this time.

Since neither APPES nor the API-Technical Data Book (3) contains a basis for external consistency tests of solid-liquid equilibria, at least an upper limit solubility ( $x_2$ ) equation might be added to the repertoire:

$$\ln x_2 (\text{ideal}) = -\frac{\Delta S_m}{R} \left( \frac{T_m}{T} - 1 \right)$$

where the entropy of fusion  $\Delta S_m$  and the melting point  $T_m$ , must be known. While  $\Delta S_m$  can be obtained from molecular structure correlation (5)  $T_m$  can only be determined by experiment. The upper limit  $x_2$  (ideal) can be exceeded if the solute has a much higher molecular weight than the solvent (10), or if the solvent forms a molecular compound with the solvent. The molecular weight correction is straightforward and rarely large (11). While many new molecular compounds will still be discovered, the likelihood for compound formation in a given case can almost always be recognized by an experienced chemist. Programming of the molecular structure combinations known to lead to compound formation should not be difficult because of the availability of extensive reviews on the subject (4, 21).

A lower limit of solubility cannot be given. However, exact or nearly exact solubility estimates will be possible once activity coefficients can be estimated from molecular structure increments more broadly than is possible to date (7).

**P-V-T Properties of Gas Mixtures.** Here two different criteria apply: internal consistency and absolute magnitude. The internal consistency of the data is tested by the rigorous partial differential equations of thermodynamics with the special requirement of differentiation at constant composition added.

The absolute magnitude of volume and enthalpy at given  $p, T$  can be checked only through use of equations of state. Since no rigorous theory produces mixture rules for the coefficients of equations of state, only limit checks can be made for particular assumed mixture rules. Computer programs are available for several such multi-component equations of state. Only few of these can be used to check the reliability of  $P$ - $V$ - $T$  data for polar gases (17, 18), while several can be used for nonpolar gases and vapors.

**Equilibrium Properties of Mixtures.** To a first approximation linear additivity prevails in the volume functions of liquids ( $v, \alpha, \beta$ ) so that these mixture properties are checked easily. High precision checking is unattainable because the excess volume  $V^E$ , cannot be predicted. Volume functions of solutions of gases or solids in liquids are more difficult to check, unless the liquid state properties of the substances are known. Similarly, the specific heat of liquids is to a first approximation linearly additive in weight fractions. Higher approximations are inaccessible to check by calculation because the heat capacity change on mixing cannot be predicted at present.

In general, only an upper limit check (linear volume fraction additivity) can be given for the surface tension of liquid mixtures. More accurate estimates (15) generally falter over the difficulty of defining the surface area per molecule required in the calculation.

**Transport Properties of Mixtures.** The transport properties (thermal conductivity, viscosity, and diffusion) of nonpolar gas mixtures at low to medium pressures can be checked to within  $\pm 30\%$  by suitable variants and simplifications of equations derived from kinetic gas theory, some of which are available in programmed form (1). Checks of higher precision are possible only for mixtures of the low molecular weight gases. Only limit checks can be given for mixtures of polar gases with each other or with nonpolar gases.

An upper limit check of the thermal conductivity of liquid mixtures is the weight fraction linear combination of the component conductivities. The downward deviation from this average is generally small and can be estimated only by means of empirical correlations (3, 5, 19).

There is no safe check for the viscosity of liquid mixtures. Approximate mixture rules are contained in the A.I.Ch.E. computer program, but their utility for checking purposes is very limited.

**Basically Unpredictable Properties.** While the melting point of mixtures can often be estimated from the component melting points by means of the solubility relation quoted earlier, the upward and downward deviations due to specific effects are too frequent to consider any quantitative relation as safe for checking of proposed data. The same applies to first order solid/solid transition temperatures of mixtures.

**Testing Program for Mixture Properties.** The most convenient first check of the properties of mixtures, as of pure compound properties other than phase equilibria, is by way of APPES (1).

## ERROR INDICATORS

The purpose of the set of programs discussed here is to prevent the entry of "gross errors" into reports, literature, and foremost into engineering or scientific calculations. Gross errors are those differences between the presented numerical value of a property and its "true" value which can be clearly discerned from the "background noise" of inevitable experimental and calculating errors, and/or which are outside the accepted error range of the calculating method that produces the standards of comparison.

The magnitude of experimental error and of the reliability of a calculating method, therefore, occupy a decisive place in the whole field of error control. This is quite aside from the method selection in the A.I.Ch.E. Physical Properties Program, which is guided entirely by the principle of minimum error propagation and hence by the built-in statements regarding the reliability—*i.e.* error—level of each correlation where applied to a particular group of chemical substances.

The importance of error statements is recognized in all textbooks of experimental physics, etc., but blithely ignored by a large fraction of those reporting experimental data or data correlations in the literature. (Random checks in current issues of ACS and A.I.P. journals will disclose that about 10% of all experimental papers contain adequate error characterization.) Experimental data should be accepted for publication only if they include the requisite error statements. Error range statements for correlations by their authors are perhaps only moderately useful because, having undoubtedly employed all data available to them for generating the correlation, their test would only reveal the quality of fit to the original data. Tests by a second author using wisely different data would generally be more representative of the true error range of a correlation.

## PLANNING FOR THE PROPOSED DATA TESTING PROGRAMS

As indicated in the introduction, the primary purpose

of the present assembly of testing methods is to assist journal editors in their task of making the contents of their journals as reliable an information source as possible. Journal editors are as a rule too busy to check new data as thoroughly as they would do if they had to use them. Nor can they be experts in all of the property fields for the editorial supervision of which they are responsible.

Hence it is essential that the program be operable by clerical help with a minimum of instruction. Experience with the A.I.Ch.E. Computer Program has shown that this goal is achievable, at a price. That price is an elaborate scheme to connect the various parts of the program into a self-connecting whole. The example of the internal consistency test on vapor pressure *vs.* temperature curves presented earlier shows the need for such connecting links. Part (a), testing the slope of the curves, must be connected with a source of heat of vaporization data, and part (b), testing their curvature, must be connected with a source of  $C_p(l) - C_p(g)$  information if the test is not to remain purely qualitative (in many cases, alas, the only applicable test).

Similarly, the internal consistency tests for phase equilibria must be linked with a source of vapor pressure data for the individual components as well as with a source of heat of mixing information.

The multiple regression testing system, by contrast, need be linked to no other information source but the equalized data tables which must be built into it in order to be useful. The Test Plan makes the use of this program optional for those data which have survived the less demanding external consistency tests. Switching of the data into that test could therefore be either manual or automatic. The switch into the internal consistency tests, on the other hand, should be automatic if the data have proven sufficiently accurate by external test criteria.

Experience has shown that the desired foolproof combination of already existing programs into a single interconnected computing system is costly to develop. Hence the question arises: Who besides journal editors could benefit from its use? An obvious employer of such a scheme would be those engineering organizations which lack the personnel to examine the validity of data taken from the literature. Engineering schools fall into the same category, since they often lack access to physical chemistry departments on their own university campus to have data checked by experts.

Experimentalists, on the other hand, will as a rule prefer highly specialized testing programs that obtain their reference data input together with the original experimental data under review to the more automatic system which relies on correlations as reference information.

This survey indicates that most of the individual consistency testing programs are either in existence or can be produced at modest expenditure. As such they will be immediately useful in the hands of experts or of scientists or engineers who have the necessary background to apply them when appropriate. However, the combination of the enumerated consistency tests into a fully automatic testing system has not yet been carried out and is going to be costly. The reward for the expenditure should be its routine foolproof employment by nonprofessional or semi-professional personnel.

## NOMENCLATURE

$C_p(g)$	= heat capacity of gas at constant pressure
$C_p(l)$	= heat capacity of liquid at constant pressure
$C_s$	= heat capacity along the saturation curve
$\Delta H_m$	= heat of fusion
$\Delta H_s$	= heat of sublimation
$\Delta H_v$	= heat of vaporization
$P_i$	= vapor pressure
$R$	= gas constant
$\Delta S_m$	= entropy of fusion
$T$	= temperature, ° K.
$T_b$	= atmospheric boiling point, ° K.
$T_c$	= critical temperature, ° K.
$T_m$	= melting point, ° K.
$T_r$	= transition temperature, ° K.
$v$	= specific volume
$V^E$	= excess volume of mixing
$x$	= mole fraction (in liquid)
$y$	= mole fraction (in vapor)
$\Delta Z$	= compressibility coefficient difference between vapor and liquid
$\alpha$	= thermal expansion coefficient
$\beta$	= compressibility
$\gamma$	= activity coefficient
$\theta_D$	= Debye temperature of a crystal

## LITERATURE CITED

- (1) A.I.Ch.E.-Physical Properties Computation Program, 1965.
- (2) American Petroleum Institute Res. Proj. 44-Tables, "Selected Values of Properties of Hydrocarbons and Related Compounds" (available in punched card form).
- (3) American Petroleum Institute Technical Data Book, 1965.
- (4) Andrews, L. J., Keefer, R. M., "Molecular Complexes in Organic Chemistry," Holden-Day, New York, N. Y., 1964.
- (5) Bondi, A., "Physical Properties of Molecular Crystals, Liquids and Glasses," Wiley, New York, 1966.
- (6) Bondi, A., *J. Phys. Chem.*, **68**, 441 (1964).
- (7) Deal, C. H., in "Techniques of Organic Chemistry," Vol. "Distillation," 2nd Edition, Wiley, New York, N. Y., 1965.
- (8) Edwards, D. G., UCRL-7167 Rev. I (1964) and UCRL-7843 Rev.
- (9) Gruber, G., Mohr, C. M., Reid, R. C., *Proc. Am. Petrol. Inst.*, **45**, III (1965).
- (10) Hendrickson, J. B., *J. Am. Chem. Soc.*, **83**, 4537 (1961); **84**, 3355 (1962).
- (11) Hildebrand, J. H., Scott, R. L., "Solubility of Non-Electrolytes," Reinhold Publishing Co., New York, N. Y., 1951.
- (12) Lundberg, G. W., Bondi, A., *Proc. Am. Petrol. Inst.*, **44**, III (1964).
- (13) National Bureau of Standards, Washington, D. C., Bulletin 500, ed. 1965.
- (14) Null, H. A., *A.I.Ch.E. Journal*, **11**, 780 (1965).
- (15) Prausnitz, J. M., Eckert, C. A., *Ibid.*, **11**, (1965).
- (16) Redlich, O., Kister, A. T., *Ind. Eng. Chem.*, **40**, 345 (1948).
- (17) Redlich, O., Kwong, J. N. S., *Chem. Revs.*, **44**, 233 (1949).
- (18) Redlich, O., Dunlop, A. K., *Chem. Eng. Progr., Symposium Ser.*, **44**, 95 (1963).
- (19) Reid, R. C., Sherwood, T. K., "Properties of Gases and Liquids," McGraw-Hill, New York, N. Y., 1958, 1966.
- (20) Somayajulu, G. R., Kudchadker, A. P., Zwolinski, B. J., *Ann. Rev. Phys. Chem.*, **16**, 213 (1965).
- (21) Schlafer, H. L., "Komplexbildung in Lösung," Springer, 1961.
- (22) Tao, L. C., *Ind. Eng. Chem.*, **56**, (2), 36 (1964).
- (23) Trappenniers, N., *Changement de Phase*, p. 241, Paris, 1952.
- (24) Wiberg, K. B., *J. Am. Chem. Soc.*, **87**, 1070 (1965).
- (25) Batsanov, S. S., "Refractometry and Chemical Structure," Consultants Bureau, 1961.