

CLASSICAL THERMODYNAMICS

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RESEARCH IN CHEMICAL ENGINEERING thermodynamics is often inspired by the practical importance of vapor/liquid equilibrium (VLE). This is certainly true at Rensselaer, where we specialize in VLE data collection and correlation for systems at low to moderate pressures. Since experiment is necessarily conditioned by theory, we first consider the relevant thermodynamic equations.

LOW-PRESSURE VLE AND EXCESS FUNCTIONS

As shown in numerous textbooks, VLE in a system of uniform T and P requires uniformity of the component fugacity \hat{f}_i of each distributed species:

$$\hat{f}_i^l = \hat{f}_i^v \quad (1)$$

This notorious equation, while suitably general, is not especially useful as it stands. In particular, one wishes to display explicitly the compositions x_i and y_i of the phases. We do this by *definition*, through one or the other of two secondary quantities: the component fugacity coefficient $\hat{\phi}_i$, or the activity coefficient γ_i .

The conventional description of low-pressure VLE treats the liquid phase through activity coefficients, and the vapor phase through fugacity coefficients. Introducing these quantities, we rewrite Eq. (1) as

$$x_i \gamma_i \hat{f}_i^\circ = y_i \hat{\phi}_i P \quad (2)$$

Here, \hat{f}_i° is the standard-state fugacity of species

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i as a liquid, and all quantities are evaluated at the system T and P. The fugacity coefficients are determined from an equation of state for the vapor phase, and the activity coefficients are derived from an expression for the excess Gibbs function G^E for the liquid mixtures. For obvious reasons, we describe formulations based on Eq. (2) as "gamma/phi" approaches. ["Gamma/gamma" and "phi/phi" approaches are also used for two-phase equilibria, the former for liquid/liquid equilibria (LLE), and the latter for VLE at high pressures.]

Equation (2) applies for both subcritical and supercritical species, provided that appropriate interpretations are put on γ_i and \hat{f}_i° . When all species in a system are subcritical, the state of pure liquid is accessible for all i, and it is conventional to eliminate each \hat{f}_i° in favor of the vapor/liquid saturation pressure P_i^{sat} of pure i. Moreover, convenience dictates the referral of each activity coefficient to a fixed reference temperature T^+ and pressure P^+ . Consistent with these requirements, we may write Eq. (2) in the equivalent form [1]

$$x_i \gamma_i^+ P_i^{\text{sat}} = y_i \Phi_i P \quad (3a)$$

where the correction factor Φ_i (a quantity of order unity) is defined as

$$\Phi_i \equiv \frac{\hat{\phi}_i}{\phi_i^{\text{sat}}} \Pi_i \quad (3b)$$

Here, function Π_i depends on liquid properties only, specifically, on the molar volume of pure i, and on the partial molar excess functions \bar{H}_i^E and \bar{V}_i^E .

Equations (3) find two distinct but complementary uses: in the *reduction* of VLE data, the goal of which is to provide correlations for G^E , and in the *computation* of VLE, which requires the availability of appropriate numerical expressions for G^E . In either case, the connection between the activity coefficient and the excess Gibbs function is made through the partial-property relationship

$$\gamma_i = \exp(\bar{G}_i^E/RT) \quad (4)$$

Equation (4) in effect establishes the composition dependence of G^E through reduction of VLE data; the T and P dependencies are related to H^E (the "heat of mixing") and V^E (the "volume change of mixing"):

$$H^E = G^E - T \frac{\partial G^E}{\partial T} \quad (5)$$

$$V^E = \frac{\partial G^E}{\partial P} \quad (6)$$

In principle, the T dependence of G^E can be determined by analysis of isothermal VLE data taken at several different temperatures; in practice, it is far more easily established through Eq. (5), by use of a single set of isothermal VLE data and one or more directly measured sets of data for H^E . The volume change of mixing is small for liquids at low pressure levels and is easily measured; the correspondingly small effect of P on G^E is always determined through Eq. (6).

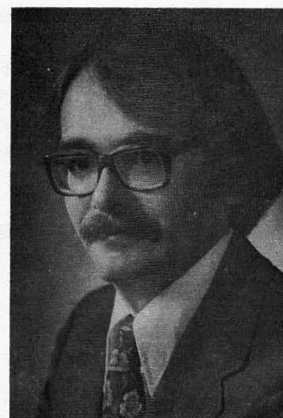
DATA COLLECTION AND REDUCTION

OUR RESEARCH PROGRAM IN thermodynamics, initiated by H. C. Van Ness, is an effort of some 25 years' standing. The thermodynamics is "classical," and largely centers on the exploitation of Eqs. (3) through (5); that is, on the measurement, reduction, and correlation of low-pressure VLE data and of the excess functions, particularly G^E and H^E . The immediate goals of our research are severalfold:

- To derive and expose the classical thermodynamic theory relating measurable variables to functions of practical interest.
- To develop the tools (equations of state and expressions for the excess functions) required for implementation of technical thermodynamic calculations.
- To devise experimental methods that are as accurate, quick, and "technique-proof" as possible, and to demonstrate their feasibility.
- To produce high-quality data suitable for formulation and testing of theories of solutions.

We regard the last two items as particularly significant, and consider them in the following paragraphs.

Apart from a few special techniques, VLE data at low pressures (ca. 1 bar or less) are mainly collected on one of two types of apparatus: dynamic circulation stills, and static equilibrium cells. Because of their simple construction and ease of operation, we favor the use of static cells. By this technique, a liquid mixture is charged to



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an evacuated cell immersed in a constant-temperature bath. Equilibration of the phases is brought about by stirring, and the equilibrium pressure is read from a high-precision gauge. In an older design [2], we determined liquid compositions gravimetrically; with our present equipment [3], liquids are metered into the cell with calibrated piston-injectors.

There are two potential problems associated with static cells: possible errors in measured pressures because of incomplete degassing of the liquids before charging, and errors arising from disturbance of the equilibrium state on withdrawing vapor samples for analysis. We have solved the first problem by a novel distillation technique [4]. The second problem is in fact avoidable because, if an accurate equation of state is available for the vapor phase (the usual case for low-pressure VLE), then the vapor compositions actually represent redundant information. Thus we measure only P and x, and reduce the data either by integration of the coexistence equation [2, 5], or by applying a technique known as Barker's method [6, 7]. Barker's method presumes the availability of an expression for G^E of sufficient flexibility to represent the P-x data to within their precision, and of an efficient computer program for nonlinear regression. We have built up a library of such equations and programs, and reduction of our VLE data is now normally straightforward: we can collect and correlate (via an expression for G^E) VLE data for a binary system in two to three days, an exercise that at one time constituted half the effort for a Master's degree.

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Next to G^E , the liquid-phase excess function of major interest is H^E , for, by Eq. (5), it establishes the often significant effect of T on G^E , and is an indispensable tool for computation of isobaric VLE from isothermal VLE measurements [1]. Moreover, knowing both G^E and H^E , one can compute the excess entropy and the entropy change of mixing, quantities of importance to solution theorists:

$$S^E = (H^E - G^E)/T \quad (7)$$

$$\Delta S = S^E - R \sum x_i \ln x_i \quad (8)$$

We measure H^E by isothermal dilution calorimetry, a technique in which amounts of a component (or solution) are successively injected into a vessel containing another component (or solution), sufficient amounts of heat being added or extracted in the meantime so as to keep the contents of the vessel at constant temperature. The quantitative transfer of heat under these conditions is an extremely exacting task, subject to some fairly subtle sources of error, and the measurement of heats of mixing is thus inherently more difficult than the taking of isothermal VLE data. On the other hand, the reduction of the calorimetric data is trivial—unlike the reduction of VLE data—because the quantity measured is directly related to the quantity sought.

Our dilution calorimeters have gone through several stages of development. The prototype device of Mrazek and Van Ness [8] demonstrated the suitability of the technique for producing high-quality data on endothermic systems, quickly and with a minimum of effort. The second- and third-generation designs [9, 10], which followed closely upon one another, incorporated (then) state-of-the-art electronics and circuitry, and accommodated exothermic as well as endothermic systems. These devices have been widely copied and are thus, directly or indirectly, the source of many of the world's published heat-of-mixing data. Inevitably, the most recent electronics revolution has caught up with us, and we recently [11] constructed and tested a fourth-generation calorimeter, incorporating the latest in solid-state

microcircuitry. A photograph of the new device is shown in Figure 1.

As already noted, thermodynamics at R. P. I. is of the classical variety, directed mainly at the measurement and empirical description of macroscopic properties of solutions. We endeavor, however, to keep abreast of developments in molecular thermodynamics, and the tone of our experimental program reflects and complements trends in this area. It was once hoped, for example, that thermodynamic properties of mixtures could somehow be estimated from properties of the constituent pure

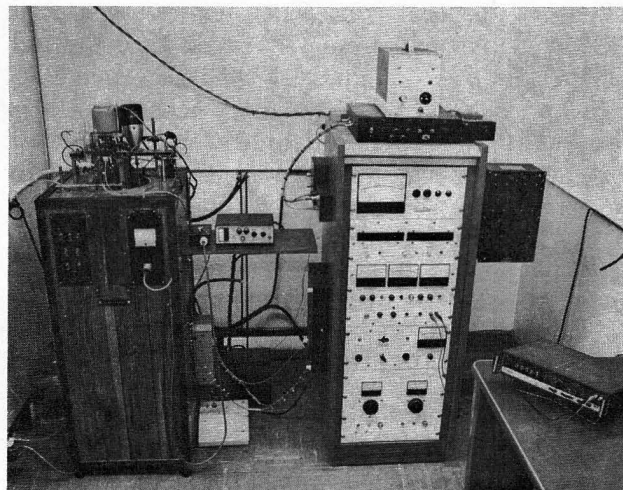


FIGURE 1. The fourth-generation heat-of-mixing calorimeter.

species. This hope has been abandoned and replaced by a more realistic goal: that of predicting properties of multicomponent mixtures from those of the constituent binaries, either through models for G^E based on the "local composition" concept [12, 13, 14], or by "group contribution" techniques [15, 16]. For such approaches, *binary* data form the data base, but *multicomponent* data are required for testing and fine-tuning the correlations. The simplest multicomponent system contains three chemical species, and thus for the past eight years we have conducted a program of collecting precise VLE and H^E data for ternary systems and their constituent binaries. This program is still in progress. □

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volved in the main reactions (i.e., C-H, C-O, etc.). Each process is described in terms of the chemistry involved, thermodynamics, and kinetics aspects. Emphasis is given to the catalyst activity, selectivity and deactivation in relation to process operation and reaction engineering aspects. Cross reference is made to the fundamental aspects discussed in Part I whenever possible.

The typical enrollment in the course is ten to fifteen graduate students from chemical engineering and science. The material is presented in two, 75 minute lectures, and about one laboratory session per week. Grades are assigned on the basis of a written exam and a term paper. The latter consists of a written report and an oral presentation which provides stimulating discussion as well as fresh references and new ideas on specialized topics. The research papers focused on energy related catalytic processes with emphasis in fossil fuel and coal processing.

No text is available which covers all the material included in Table 1. Hence I prepared a set of notes based on more specialized books and papers dealing with specific subjects and techniques as well as information and experience accumulated in our own laboratory.

The combination of theory and experiments has a strong impact on the students, even though in some cases they do not directly operate the equipment due to its complexity and specialization. The majority of the engineering students have not been exposed to surface analysis and electron microscopy techniques, and thus feel that they acquired new knowledge in the course. The combination of principles, industrial application and experiments equips the students with a new perspective of catalysis and catalytic reaction engineering which enables them to face a larger variety of problems with a larger diversity of tools.

I enjoyed teaching the course because it provides an opportunity for interaction with colleagues from other disciplines, which enriched my own knowledge and perspective of the subject. □

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