

## The role of experimental data in chemical process technology\*

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**Abstract:** Experimental data have served two critical roles in chemical process technology: (1) by providing the definitive quantitative basis to evaluate competing processes, to optimize designs, and ultimately to guarantee plant performance; and (2) by guiding the form and structure of applied-thermodynamics correlations. This paper first presents two representative applications to highlight the role of thermodynamic and transport properties in chemical process technology: ammonia recovery from syngas using water as solvent, and design of a caustic-guard system to eliminate small residual concentrations of SO<sub>2</sub> from a gas stream. These applications illustrate the first role of experimental data. The paper next studies the second role by examining the historical contribution of experimental data—over two centuries—in guiding the development of key concepts and correlations, such as Henry’s law (1802), group-contribution methods (Kopp, 1842), Raoult’s law (1878), second-virial-coefficient correlation (Berthelot, 1907), surface-tension correlation (Macleod, 1923), the use of one property to estimate another (Othmer, 1940), cubic equations of state (Redlich and Kwong, 1949), electrolyte systems (van Krevelen, 1949), acentric factor (Pitzer, 1955), and highly accurate equations of state (Span and Wagner, 2003). The analysis reveals that careful, accurate, and wide-ranging experimental data have identified the patterns of the underlying phenomena.

**Keywords:** ammonia recovery; chemical process technology; engineering correlations; property estimation; SO<sub>2</sub> removal; syngas; thermodynamic properties; transport properties.

### INTRODUCTION

The process industries spend an estimated US\$500 billion annually on conceptual design, construction, startup, plant operations, and maintenance for chemical, refining, polymer, and power plants. In order for chemical technologists to successfully execute these projects, they perform process modeling of the chemical systems they work with [1]. In these industries, technologists enhance the decision-making processes by using engineering software products that are easy-to-use, effective, and accurate. An essential component of this software is the suite of integrated and validated property correlations that describe the thermodynamic and transport properties and the chemistries of the relevant chemical systems. The quality and efficiency of the chemists’ and engineers’ pursuits in the process industries are dependent on the accuracy and reliability of the underlying thermodynamic and transport property models [2].

Thermodynamic and transport property models, in turn, rely upon three methods of knowledge acquisition (experiment, theory, and simulation), and the greatest benefit will be derived when all three

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\*Paper based on a presentation at the 20<sup>th</sup> International Conference on Chemical Thermodynamics (ICCT 20), 3–8 August 2008, Warsaw, Poland. Other presentations are published in this issue, pp. 1719–1959.

methods are employed to complement each other [3]. This paper focuses on the experimental method of knowledge acquisition and studies the two critical roles experimental data have served in chemical process technology: (1) by providing the definitive quantitative basis to evaluate competing processes, to optimize designs, and ultimately to guarantee plant performance; and (2) by guiding the form and structure of applied-thermodynamics correlations. The first role of experimental data is well recognized since accurate thermodynamic correlations used in practice are usually semi-empirical models with adjustable parameters that are fitted to experimental data [4], thus the correlation accuracy is directly dependent on the range and accuracy of the underlying data. The second role of data is less appreciated and accepted since it is the author's perception that many, if not most, applied thermodynamicists feel that theory conceives the form of the model and the role of data is merely to test the validity of the concept and then determine the adjustable parameters.

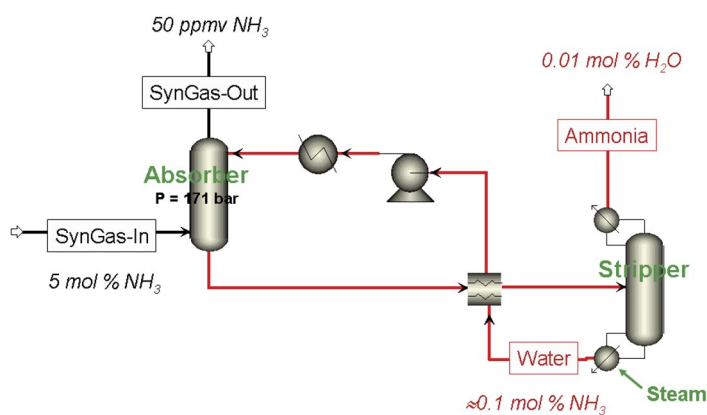
The first part of this paper presents two typical applications of applied thermodynamics in the chemical process industry to identify the value derived and also to comment on the available and needed data. The second part of the paper examines the historical role of experimental data in guiding the development of thermodynamic theories and correlations over the past two centuries by reviewing the evolution of key concepts and correlations. Older models and correlations have been emphasized since we have the benefit of the perspective of time to draw conclusions on their development and historical impact.

## APPLIED THERMODYNAMICS IN THE CHEMICAL PROCESS INDUSTRY

Many papers have been written on the deployment of applied thermodynamics in the chemical process industry [5]. Mathias [6] has presented some of these applications and provides four case studies. Two additional cases are presented here to identify the successes and development needs.

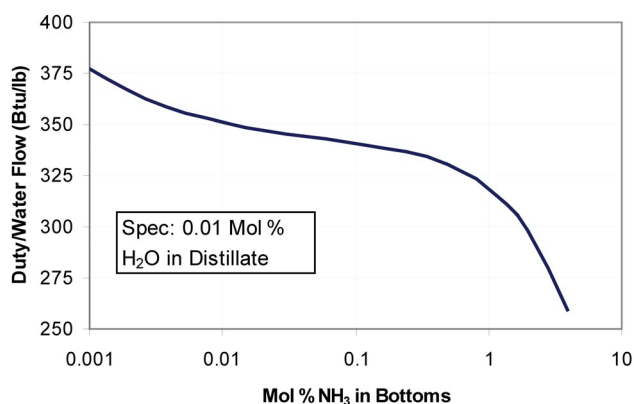
### Ammonia recovery from syngas

Ammonia is recovered from the purge synthesis-gas (syngas) stream in an ammonia plant by using water as a solvent. The composition of a typical purge stream is 67 mol %  $H_2$ , 22 mol %  $N_2$ , 6 mol % Ar, and 5 mol %  $NH_3$ . The process flow diagram, which is shown in Fig. 1, is a common absorber-stripper arrangement [7] where the lean (regenerated) solvent is used to absorb the more soluble component (ammonia), and the ammonia is produced as the distillate in the stripper where the solvent is regenerated. Process schemes analogous to Fig. 1 are in use for other absorber-stripper applications, including processes to recover  $CO_2$  from combustion flue gas in order to mitigate global warming [8,9].

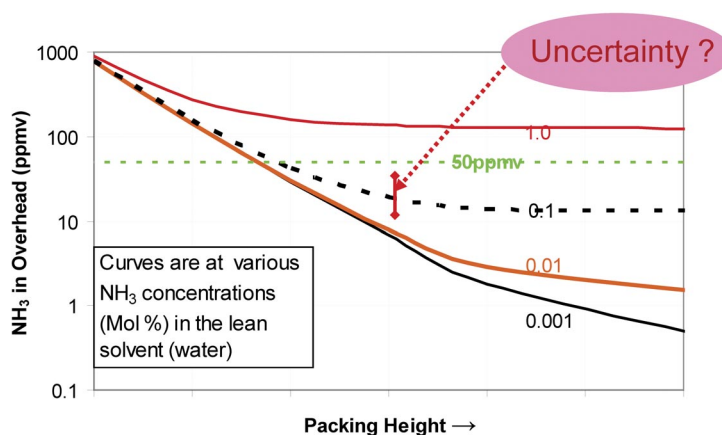


**Fig. 1** Process flow diagram for ammonia recovery from purge gas in an ammonia plant. Ammonia is absorbed in water in the absorber, while the stripper regenerates the solvent and produces ammonia as the distillate.

The design target of the ammonia-recovery process is to reduce the ammonia concentration in the exiting syngas from the feed concentration of 5 mol % down to 50 ppmv, and the design engineer must achieve this target while minimizing the capital costs (e.g., height and diameter of the absorber) and operating costs (e.g., consumption of heating steam in the stripper). Commercial software available today can accurately model the process shown in Fig. 1 using rigorous rate-based models [10], and typical results obtained using the RateSep model from Aspen Technology, Inc. are presented in Figs. 2 and 3 [11]. Figure 2 indicates how much the heat rate can be reduced if a higher ammonia concentration can be tolerated in the regenerated solvent, while Fig. 3 shows how much the ammonia concentration can be reduced in the exiting syngas stream as the absorber height is increased at various levels of residual ammonia in the regenerated solvent.



**Fig. 2** Stripper heat duty (duty per unit mass of ammonia in the distillate) required to achieve various concentrations of ammonia in the lean solvent produced in the stripper.



**Fig. 3** Concentration of ammonia in the absorber overhead as a function of packing height. The various curves correspond to various residual concentrations of ammonia in the lean solvent. The target ammonia concentration in the overhead (50 ppmv) is also shown.

Process modeling results like those shown in Figs. 2 and 3 give the design engineer insight and quantitative results needed to design an effective and efficient absorption system. The concentration of ammonia in the lean solvent needs to be about 0.1 mol % or less, otherwise the concentration of ammonia in the exiting syngas will not achieve the target of 50 ppmv even with an absorber of infinite

height. It is probably not necessary to reduce the lean solvent ammonia concentration much below 0.1 mol % since the reduction in absorber height will be small. Results similar to those presented here enable the design engineer to evaluate the benefits of other process variables, for example, the effect of varying the solvent circulation rate and the possible advantage of introducing intercooling in the absorber.

An important issue the design engineer must deal with is the uncertainty of the simulation results, shown schematically in Fig. 3. The uncertainty of the simulation results is directly related to the uncertainty of the thermodynamic and transport-property models. The thermodynamic model used here is a combination of the nonrandom two-liquid (NRTL) [12] model for solution nonideality and the Redlich–Kwong [13] equation of state for the vapor phase, which is expected to be accurate for this system [4]. Figures 4 and 5 show that the model provides good agreement with data for vapor–liquid equilibrium [14] and heat of mixing [15]. In general, experimental data for thermodynamic properties of common systems like  $\text{NH}_3\text{--H}_2\text{O}$  are well covered in the technical literature, but transport properties are

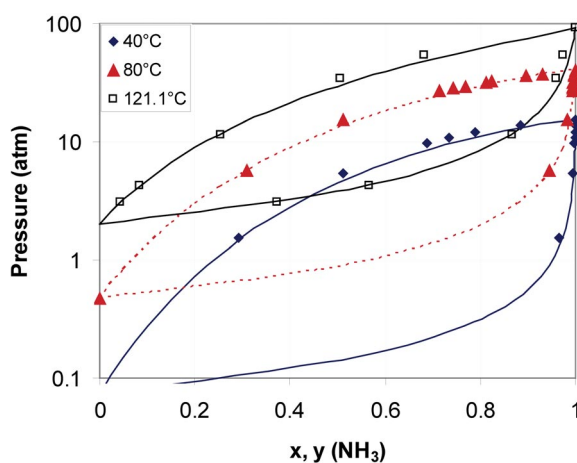


Fig. 4 Comparison between model and data [14] for vapor–liquid equilibrium in the ammonia–water system.

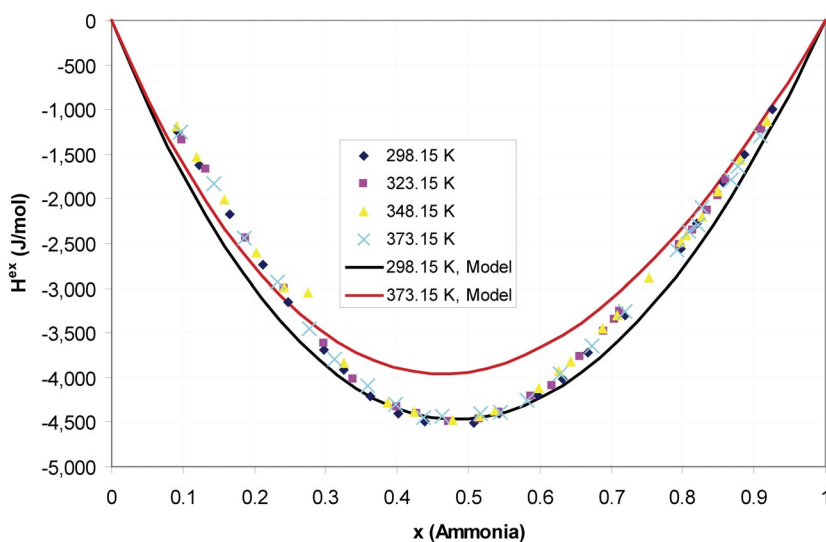


Fig. 5 Comparison between model and data [15] for heat of mixing in the ammonia–water system.

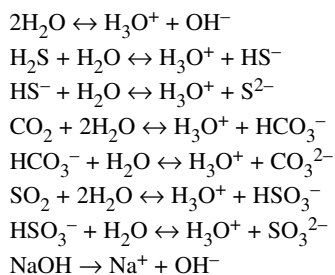
less available and validated mainly because they were considered to be of secondary importance before the emergence of rate-based distillation. Hence, much of the uncertainty alluded to in Fig. 3 most likely results from inaccuracies in the transport properties (mass-transfer coefficients, viscosity, and thermal conductivity) and these inaccuracies need to be analyzed.

### Caustic guard system for SO<sub>2</sub> capture

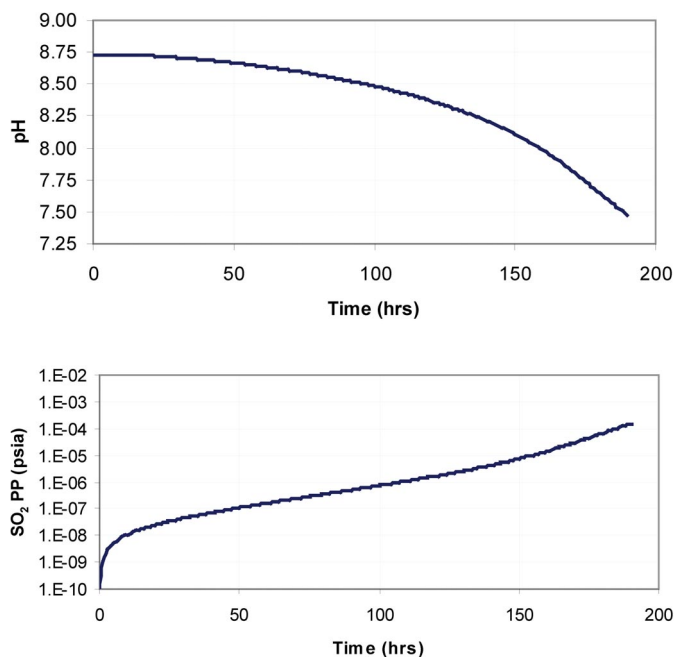
In gasification plants, H<sub>2</sub>S and CO<sub>2</sub> are separated from tail-gas streams using a chemical solvent such as methyldiethanolamine (MDEA) [16]. The process diagram of the MDEA system is similar to Fig. 1. SO<sub>2</sub> must be removed upstream of the absorption system since it poisons the chemical solvent [16]. Referring to Fig. 1, an essential feature of a properly working absorption-stripping system is that the absorption of the dissolved components can be reversed in the stripper. This desired reversibility will not occur for strongly absorbed acidic components like SO<sub>2</sub>, and hence SO<sub>2</sub> must be removed upstream of the absorption system, typically by catalytic hydrogenation to H<sub>2</sub>S. A guard tank with circulating caustic (usually 20 wt %) is usually included in the design in case the hydrogenation reactor is malfunctioning. This case analyzes the design and operation of the caustic guard system.

Design of the guard system requires prediction of SO<sub>2</sub> breakthrough times and the pH at which caustic should be replenished, and the calculation here is done by first equilibrating the system with H<sub>2</sub>S and CO<sub>2</sub>, and then adding a certain concentration (say, 30–50 ppm) of SO<sub>2</sub> to the feed gas. Mather [17] has summarized the basis and structure of models for electrolyte systems. The chemistry model, which is a practical representation of the ionization reactions that occur in the system, is presented in Table 1. NaOH is a strong base and is assumed to be completely dissociated. H<sub>2</sub>S, CO<sub>2</sub>, and SO<sub>2</sub> are acids, in order of increasing strength. In the absence of SO<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>S will partially dissociate in caustic solutions, with CO<sub>2</sub> being more dissociated than H<sub>2</sub>S. As SO<sub>2</sub> is added to the gas stream, the dissociation reactions of CO<sub>2</sub> and H<sub>2</sub>S will be reversed to some extent.

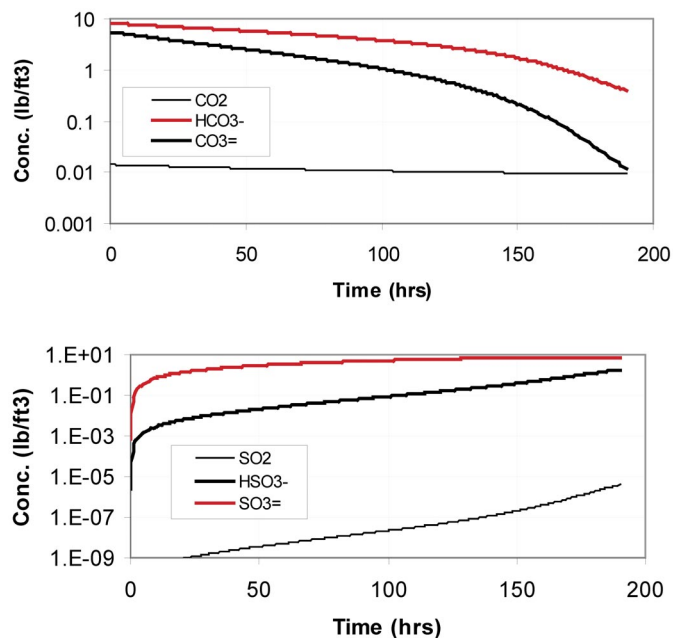
**Table 1** Chemistry model for the NaOH–SO<sub>2</sub>–CO<sub>2</sub>–H<sub>2</sub>S system.



The calculations presented here were performed using the electrolyte NRTL model [18] available in Aspen Properties®; other equivalent models are available from research groups and in commercial software [17]. Typical results, which are shown in Fig. 6, indicate that the system pH at equilibrium with CO<sub>2</sub> and H<sub>2</sub>S is about 8.75. As SO<sub>2</sub> is introduced into the feed tail gas, the pH decreases and the SO<sub>2</sub> partial pressure in the effluent vapor stream from the caustic guard tank rises. The design engineer is able to estimate the breakthrough time and also the pH at which the caustic must be replenished. Figure 7 presents the changes in concentration of CO<sub>2</sub>- and SO<sub>2</sub>-related species with time after SO<sub>2</sub> is introduced into the gas stream. The concentration of molecular CO<sub>2</sub> remains approximately constant since its gas-phase concentration (partial pressure) is constant. The concentration of CO<sub>2</sub>-related anions decreases as SO<sub>2</sub> is absorbed and forms HSO<sub>3</sub><sup>-</sup> and SO<sub>3</sub><sup>2-</sup>. The concentration of dissolved molecular SO<sub>2</sub> increases slowly with time and parallels the increase in SO<sub>2</sub> partial pressure. These results help the



**Fig. 6** pH and SO<sub>2</sub> partial changes with time as SO<sub>2</sub> is introduced into the gas stream feeding the caustic guard system.



**Fig. 7** Concentration changes with time of CO<sub>2</sub>- and SO<sub>2</sub>-related species as SO<sub>2</sub> is introduced into the gas stream feeding the caustic guard system.

design engineer to understand the process chemistry and to develop an effective and optimum process design.

### Applied thermodynamics in the chemical process industry: Overview

The two case studies presented here illustrate the value applied thermodynamics provides to the chemical process industry. Additional cases have been given by Mathias [6]. The contribution of applied thermodynamics follows from the accuracy and range of the property correlations and the available commercial software. In turn, the accuracy of the correlations is based upon theory and experimental data. The roles of experimental data are to guide the structure of the engineering correlations and to establish their accuracy through optimization of adjustable parameters. The former role of experimental data is not well accepted and appreciated, and is the subject of the next section of this paper.

### HISTORICAL CONTRIBUTION OF EXPERIMENTAL DATA TO THEORETICAL CONCEPTS AND CORRELATION DEVELOPMENT

Experimental data have played an important role in revealing theoretical concepts and determining the structure of thermodynamic models over the past 200 years. Table 2 summarizes the representative cases discussed in this paper. Older models and correlations have been emphasized since we have the benefit of the perspective of time to draw conclusions on their development and historical impact.

**Table 2** Some contributions of experimental data to theoretical concepts and correlation development in applied thermodynamics.

Year	Researcher and contribution
1803	Henry (Henry's law)
1842	Kopp (group-contribution methods)
1878	Raoult as physicochemist
1907	Berthelot (second virial coefficient)
1923	McLeod-Sudgen (surface tension)
1940	Othmer (relative properties or "property leapfrog")
1949	Redlich-Kwong (cubic equations of state)
1949	van Krevelen (electrolytes)
1955	Pitzer (acentric factor)
2003	Span-Wagner (equations of state)

#### 1803—Henry (Henry's law)

Henry's law is used in a variety of situations in chemical and environmental science and engineering [19], and even today is an important tool of applied thermodynamics [20]. In its simplest form, Henry's law states that the solubility of a gas in a liquid is proportional to the partial pressure of the gas.

$$Py_i = Hx_i \quad (1)$$

Equation 1, which is the model proposed by Henry in 1803, is the simplest statement of Henry's law, and corrections are usually applied [4], but even the simple form of eq. 1 is sufficiently accurate for many applications [19].

Henry's law is one of the first thermodynamic correlations and was directly suggested by Henry's experimental measurements [21,22]. Henry's own words best explain his experimental results and critical thinking.

1. "...water takes up, of gas condensed by one, two or more additional atmospheres, a quantity which, ordinarily compressed, would equal to twice, thrice, &c. the volume absorbed under the common pressure of the atmosphere."
2. "By frequent repetition of the experiments, I obtained results differing a little from the general principle stated above; but, for all practical purposes, I apprehend, the law has been announced with sufficient accuracy."
3. "For, the theory which Mr. Dalton has suggested to me on this subject, and which appears to be confirmed by my experiments, is, that the absorption of gases by water is purely a mechanical effect, and that its amount is exactly proportional to the density of the gas, considered abstractly from any other gas with which it may accidentally be mixed. Conformably to this theory if the gas contain  $1/2$ ,  $1/10$  or any other proportion, of foreign gas, the quantity absorbed by water will be  $1/2$ ,  $1/10$  &c. short of the maximum."

Statement 1 presents Henry's law for the limiting case where the vapor phase is pure ( $y_i = 1$ ). Statement 2 reflects Henry's analysis whether the departures he observed from the proposed law are due to failure of the law or small inaccuracies in his measurements, and he concluded that the proposed law is valid. Finally, Statement 3 presents the law for mixed gases ( $y_i < 1$ ). The work of Henry has a special place in the development of thermodynamics since it was proposed at the beginning of the era of modern chemistry, and yet remains a valid tool of scientific application today [20].

### 1842—Kopp (group-contribution methods)

Kopp [23] is the father of group-contribution methods since he recognized that the molar volumes of organic molecules are, to a reasonable approximation, additive functions of effective volumes of their constitutive elements or groups. In a series of papers, Le Blas [24] built upon the ideas of Kopp and elucidated the effect of constitution on the molar volumes of families of compounds. The Le Blas paper referenced here studied ring compounds, but it should be noted that Le Blas analyzed a wide variety of organic compounds, and his work served as the basis for the estimation of the molar volumes of organic compounds for many decades [25]. Today, group-contribution methods are a valued and essential part of chemical process technology [26], but it should be recognized the concept of additivity arose from the experimental data, and the accuracy of group-contribution correlations are dependent upon the accuracy and range of the available experimental data.

### 1878—Raoult as physicochemist

Raoult's distinguished scientific career may be divided into three distinct periods: physical, chemical, and physicochemical [27]. While all three periods are remarkable and distinguished, it is the third period that is especially relevant to the thermodynamics community. Raoult's law is the cornerstone of solution thermodynamics because it defines the ideal solution, and thus introduces and defines solution nonideality [28]. It is useful and insightful to study Raoult's approach to physicochemical research.

Raoult's research work was based upon the conviction that scientific laws are revealed by careful experimentation. In the words of van't Hoff [27]: "Raoult stood at once foremost, in the position of great advantage belonging to the man who relies on fact in the first instance and is eager for generalization, absolutely independent in his opinions, and open to every achievement on his way." Van't Hoff reported an incident that revealed his high regard for Raoult as an experimentalist [29]. Raoult's thermometer was made by the celebrated Baudin of Paris, but apparently the latter did not approve of the type of thermometer specified by Raoult for his particular work. Happening to be in Paris, van't Hoff paid a visit to Baudin and asked him to supply him with an exact replica of Raoult's thermometer. Baudin strongly advised him against this remarking, "The thermometer which M. Raoult uses is 'ante-



diluvian'!” To which van't Hoff responded, “Nevertheless with this ‘antediluvian’ thermometer the world was conquered.”

From 1878 to the end of his life (1901), Raoult studied lowering of freezing point, lowering of vapor pressure, and rise of boiling point. For lowering of vapor pressure, Raoult found

$$\frac{f - f'}{fP} \frac{M}{M_1} = K \quad (2)$$

where

- $f$  = vapor pressure of solvent
- $f'$  = vapor pressure with solute
- $P$  = grams of solute in 100 grams of solvent
- $M$  = molecular weight of solute
- $M_1$  = molecular weight of solvent
- $K$  = universal constant equal to 0.0105

If the liquid mixture followed Raoult's law as we use it today,  $K$  would be exactly equal to 0.01. According to Raoult, for associating liquids (e.g., acetic acid and formic acid), eq. 2 must be modified to

$$\frac{f - f'}{fP} \frac{M}{M_1} \left( \frac{d}{d_1} \right) = K \quad (3)$$

where  $d$  is the vapor density calculated from the ideal-gas model and  $d_1$  is the observed vapor density. Raoult's experiments gave him the correct notion of the effects of association, although today we may question the assumption that the effects of association in the vapor and liquid phases are quantitatively equivalent.

Raoult found that the molecular depression of salts, strong acids, and strong bases can be calculated by a summation of numbers related to their radicals (ions), and wrote: “These facts show that, contrary to what I thought until now, the general law freezing does not apply to the salts dissolved in water. They tend to show that it applies to radicals constituting the salts, almost as if these radicals were simply mixtures in dissolutions.” Raoult's experiments taught him that dissolved salts and strong acids and bases dissociate almost completely into ions.

Van't Hoff [27] summarized the scientific approach and contribution of Raoult: “Activity, patience, tenacity to an extreme degree in pursuing an aim, having an eye as much for detail as for the vaster and vaster horizons, absolute independence of mind, power of criticizing or of admitting without passion the views of others as well as his own, and of testing both with the same calm conviction that the last word must rest with experiment; this is what we read in every page and what the whole chemical world may know.” One hundred and twenty-five years after Raoult's first work as a physicochemist, his contributions are relevant and his scientific approach that emphasized careful experimentation is valid and applicable.

### 1907—Berthelot (second virial coefficient)

Berthelot developed a method, based upon the second virial coefficient, to calculate very accurate departures from the ideal-gas equation of state at near-ambient conditions so that molecular weights could be calculated from vapor-phase mass-density measurements [30–32]. At that time it was of scientific interest to compare and evaluate molecular weights determined by chemical methods with those from physicochemical methods (i.e., densities). For further details on Berthelot's work on the second virial coefficient, see the paper by Mathias [33].

The molecular weight of a substance can be calculated from its experimental vapor-phase mass density as follows:

$$MW = \rho_{mass}(T_0, P_0) Z(T_0, P_0) \frac{RT_0}{P_0} \quad (4)$$

where  $\rho_{mass}$  is the mass density,  $Z$  is the compressibility factor, and  $R$  is the gas constant. Equation 4 is, of course, an exact equation at any temperature/pressure pair, but is typically applied at “normal” conditions of  $T_0 = 273.15$  K and  $P_0 = 1$  atm. In the late 1800s and early 1900s, it was expected that  $\rho_{mass}(T_0, P_0)$  could be measured to an accuracy of about 1/10000 or 0.01 % and hence  $Z$  needs to be established to better accuracy to enable estimation of MW to an equivalent accuracy of 0.01 %.

Berthelot concluded that the virial equation of state truncated after the second term is sufficiently accurate to estimate  $Z$  at normal conditions.

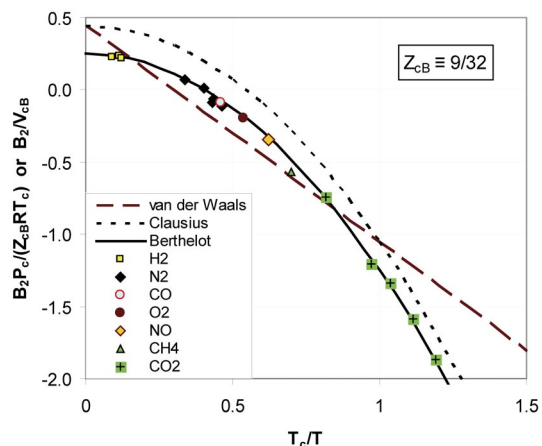
$$Z \equiv \frac{P}{\rho RT} \approx 1 + \frac{PB_2}{RT} \quad (5)$$

Further, based upon data for the second virial coefficient  $B_2$ , Berthelot proposed the first generalized two-parameter correlation for  $B_2$ .

$$\frac{B_2 P_c}{RT_c} = \frac{9}{128} - \frac{54/128}{T_R^2} \quad (6)$$

where  $T_c$  is the critical temperature,  $P_c$  is the critical pressure, and  $T_R (=T/T_c)$  is the reduced temperature.

Berthelot’s correlation, which is compared to experimental data in Fig. 8, is a fine example of using experimental data to guide the structure of thermodynamic correlations. Through comparison with experimental data, he concluded that the temperature dependence of  $B_2$  from the van der Waals (vdW) equation is too weak and hence he adopted the model of Clausius, who postulated that “ $a$ ” varies inversely with temperature; Berthelot called this model the “modified vdW” equation (Fig. 8). Berthelot further concluded that the modified vdW model gave a second virial coefficient that was biased high and this was because the critical compressibility from the vdW equation ( $Z_c = 3/8$ ) is too high. He reviewed the experimental critical compressibilities of the molecules he had studied, and concluded that a better value of the “universal” critical compressibility is  $Z_c = 9/32 \approx 0.281$ . Figure 8 shows that Berthelot’s model provides excellent agreement with experimental data for the components and temperature range of interest.



**Fig. 8** Comparison between experimental data and generalized models for the second virial coefficient evaluated and developed by Berthelot.

Berthelot's model achieved its intended purpose since it enabled an accuracy of about 0.01 % for molecular-weight estimation by the physicochemical method [33]. More importantly, Berthelot's work served as guidance for later scientists to solve additional problems, mostly outside the originally envisioned scope. Developers of corresponding-states models need to pick two of the three critical properties ( $T_c$ ,  $P_c$ ,  $V_c$ ) to use in the model formulation. Most scientists and engineers follow the lead of Berthelot and use  $T_c$  and  $P_c$ . Rowlinson and coworkers [34,35] used the notion that the Berthelot model "is generally regarded as providing a satisfactory empirical approximation to an equation of state for vapors at pressures below 1 atm," to infer two distinct classes of behavior. The measured second virial coefficients of Class I or nonpolar substances (e.g., ethane, *n*-hexane, chloroform, cyclohexane) are in agreement with the Berthelot equation, while those of Class II or polar substances (e.g., acetone, acetonitrile, methanol) are considerably lower (more negative) than the Berthelot predictions. Figure 9 demonstrates that the Berthelot model provides a good prediction of the second virial coefficient of cyclohexane, but a poor prediction of the second virial coefficient of methanol. Armed with this insight, Rowlinson [35] developed a model of the intermolecular potential that included dipolar forces to interpret and fit the second-virial-coefficient data for strongly polar substances such as water, methanol, and acetone. Pitzer and Curl [36] started with the Berthelot equation as a base two-parameter corresponding-states model and developed the first three-parameter corresponding-states model, with the acentric factor ( $\omega$ ) in addition to  $T_c$  and  $P_c$ , for the second virial coefficients of "normal" (nonpolar) fluids.

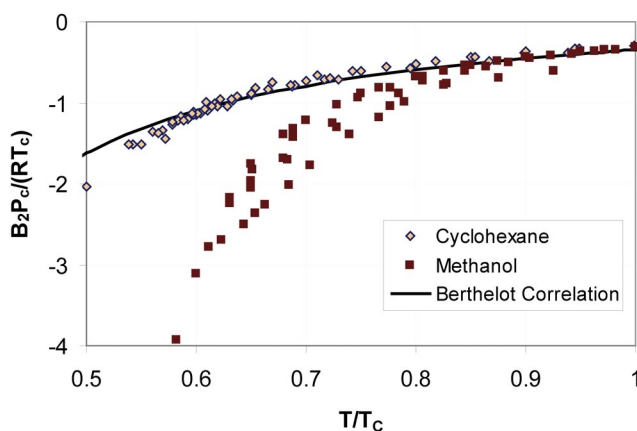


Fig. 9 Prediction of the second virial coefficients of cyclohexane and methanol by the Berthelot model.

### 1923—Macleod–Sudgen (surface tension)

Macleod [37] proposed a simple and accurate correlation for the surface tension of pure liquids based entirely on the pattern of the experimental data

$$\sigma = K(\rho_L - \rho_V)^4 \quad (7)$$

where  $\sigma$  is the surface tension of the saturated pure component,  $\rho_L$  and  $\rho_V$  are the molar densities of the saturated liquid and vapor, respectively, and  $K$  is a component-dependent constant that is independent of temperature. Sudgen [38] established the accuracy of the Macleod empirical equation and proposed the concept of a parachor  $P$  that he speculated has molecular significance.

$$P = \frac{\sigma^{1/4}}{\rho_L - \rho_V} = \sum_i P_i \quad (8)$$

The last part of eq. 8 implies that  $P$  is an additive property that can be predicted as the sum of the contributions of the groups composing the molecule. Sudgen's concept of the parachor generated great interest and spawned many research projects. Quale [39] considered the parachor as a highly promising indicator of molecular structure and published an extensive list of parachors. But the parachor does not seem to justify its role as an indicator of molecular structure when rigorously tested. Exner's study [40] suggests that the additivity of the parachor derives mostly from the additivity of the molar volume, and the parachor is a poorer additive property than the molar volume.

The significance of the parachor is in doubt, and the analysis presented here is a cautionary note that accuracy of empirical correlations may not imply an underlying theoretical basis.

#### 1940—Othmer (relative properties or “property leapfrog”)

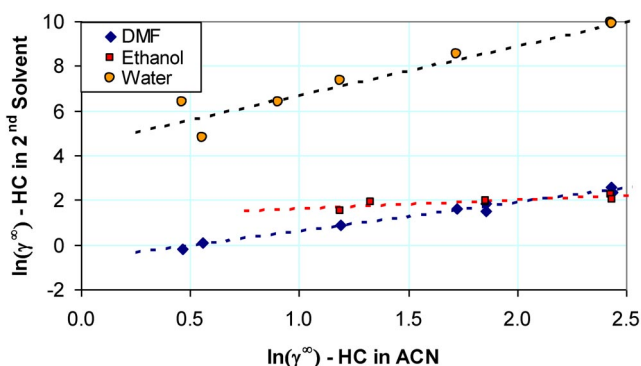
Othmer [41] proposed a methodology to correlate and estimate the vapor pressure of liquids, solids, and solutions by plotting the logarithm of the desired vapor pressure against the logarithm of the vapor pressure of a reference substance at the same temperature. A linear relationship is usually obtained, and this enables the development of a useful correlation or estimation method. Othmer [41] studied many systems and concluded that his method provides an effective tool to correlate and estimate vapor-pressure data. The broad application of Othmer's idea may provide a way to develop new correlations.

Greenshields and Rossini [42] divide property-estimation methods into three categories: (1) total-property group-contribution methods; (2) homologous-series methods and (3) isomeric-variation methods in which the isomeric increment in the value of a property is correlated rather than the total value of a property for each isomer. Estimation methods today predominantly use the “total-property” approach, and thus do not make the best use of the available data. For example, it is well known that correlations to predict the critical temperature are substantially improved if the normal boiling point is used as an input [4]. We here provide an example illustrating how the application of the Othmer idea (designated as relative properties or “property leapfrog”) may be used to develop improved estimation methods.

Mathias, Elliott, and Klamt [43] studied the estimation of solution nonideality related to the extractive-distillation processes that recover 1,3-butadiene from steam-cracker hydrocarbons. The effectiveness of *n*-dimethylformamide (DMF) and acetonitrile (ACN) as extractive solvents were explored in order to study the effectiveness of various predictive methods, including group contribution (UNIFAC [26]), quantum mechanical (COSMO-RS [44]), and molecular simulation. Here, the role of the data alone as an estimation tool is emphasized. Table 3 presents experimental data for the infinite-dilution activity coefficients of hydrocarbons in DMF and ACN at 40 °C, which has been chosen as a representative value since it is typical of temperatures encountered in extraction-distillation columns. Only the infinite-dilution activity coefficients have been reported here since at plant conditions the solubility of the hydrocarbons in the liquid phase is relatively low. The results in Table 3 demonstrate that the data fall into the pattern expected from “thermodynamic intuition.” The infinite-dilution activity coefficients decrease as the degree of unsaturation of the hydrocarbon increases, i.e., the activity coefficients progressively decrease as the hydrocarbon class goes from paraffin to olefin to diolefins to triple bond to olefin plus triple bond. This, of course, is the reason why DMF and ACN are chosen as extractive solvents, but the fact that the activity coefficients fall into the expected pattern provides confidence in the experimental data and offers capability to fill in data gaps. Figure 10, which is based upon the Othmer method, illustrates the relationship among the infinite-dilution activity coefficients of hydrocarbons in DMF and ACN, and also in ethanol and water. Clearly, the data itself—without any theoretical model—reveals a simple, clear pattern that helps to evaluate the consistency of the various data sources and also to fill in gaps in the data as needed.

**Table 3** Activity coefficients at infinite dilution of hydrocarbons in DMF and ACN at 40 °C.

Compound	$\gamma^\infty$ in DMF	$\gamma^\infty$ in ACN	Class of hydrocarbon
Vinyl acetylene	0.84	1.78	Olefin and triple bond
Methyl acetylene	1.09	1.95	Triple bond
1-Butyne		2.98	
1,3-Butadiene	2.38	3.73	Diolefin
1,2-Butadiene	2.80		
c-Butene	4.51	7.44	Olefin
1-Butene	4.97	7.22	
Isobutene	5.21		
<i>t</i> -Butene	6.46		
<i>n</i> -Butane	10.4	10.36	Paraffin
Isobutane	13.5	12.18	

**Fig. 10** Correlation between hydrocarbon infinite-dilution activity coefficients in DMF, ethanol, and water and those in ACN. All activity coefficients are at 40 °C. The dashed lines are best-fit straight lines.

### 1949—Redlich–Kwong (cubic equations of state)

Equations of state based upon the vdW equation (often referred to as “cubic equations of state”) have proved to be extremely useful to chemical process technology because they enable an accurate and reliable correlation of thermodynamic properties (densities, fugacities for phase equilibria, and thermodynamic properties like enthalpy and entropy), while requiring only a small number of adjustable parameters and few experimental data [45,46]. The performance of vdW equations of state is far better than may be expected from their weak theoretical basis, and this is mainly because semi-empirical approximations have been made to improve model accuracy and these modifications have been guided by the experimental data. Redlich and Kwong [47] proposed the first vdW modification that was used for industrial applications. Their model was developed to meet two important boundary conditions: the temperature dependence was modified to describe the second virial coefficient and the functional form was changed to follow the observation that the high-pressure molar volume is  $\frac{1}{4}$  the critical volume. Subsequent modifications, for example, improved the correlation of the vapor pressure [48], liquid density [49], nonideal multicomponent mixtures [50], and even extended the model to polymer solutions [46]. Further details on these improvements are available in review papers [45,46], but the point to be noted here is that the patterns of the experimental data have had a strong influence in guiding the model improvements.

### 1949—van Krevelen (electrolyte systems)

Modeling of electrolyte systems such as the caustic guard system for SO<sub>2</sub> capture discussed in this paper are done on a routine basis in the chemical process industry thanks to the availability of a rigorous modeling framework, fundamental data, and sophisticated software [17]. The models used today are based upon correct speciation and a thermodynamically consistent model for solution nonideality [1,51]. The first model to describe the vapor–liquid equilibria in electrolyte systems was developed by Van Krevelen et al. [52]. This model is largely empirical and designed to capture the dominant behavior of the NH<sub>3</sub>–CO<sub>2</sub>–H<sub>2</sub>S sour-water system, which is that the simultaneous presence of a weak base (NH<sub>3</sub>) and weak acids (CO<sub>2</sub> and H<sub>2</sub>S) in aqueous solution result in the formation of ionic species that are nonvolatile. Van Krevelen et al. [52] based their model on reaction–equilibrium coefficients for the ionization reactions and Henry’s law coefficients. The equilibrium constants were empirically adjusted and the Henry’s law “constants” were made concentration dependent. The value of the 1949 work of Van Krevelen et al., which was clearly guided by the experimental data, is that it provided the first useful model for the design of electrolyte systems and effectively paved the way for the more theoretically rigorous models that are used today.

### 1955—Pitzer (acentric factor)

Pitzer’s acentric factor  $\omega$  provides a powerful way to estimate the properties of systems containing non-polar substances [4]. Three-parameter correlations, based upon the  $T_c$ ,  $P_c$ , and  $\omega$ , are widely used in the gas-processing and petroleum-refining industries. Pitzer [53] reviewed the ideas and general point of view that led him to propose the acentric factor in 1955 [54]. He theoretically showed that the fluid properties of chain molecules (e.g., propane and *n*-pentane) and globular molecules (neopentane) departed from those of simple, spherical molecules (e.g., Ar, CH<sub>4</sub>), because the pair potential operates between each part of the chain or globular molecule, which causes the attractive term to become steeper. He needed an experimental basis for the parameter  $\omega$ , and chose the reduced vapor pressure at a reduced temperature of 0.7

$$\omega \equiv -\log P_R - 1.0 \quad (9)$$

with  $P_R (=P^{\text{sat}}/P_c)$  the reduced vapor pressure at  $T_R = 0.7$ . It was the choice of the experimental basis of  $\omega$  that most determined the successful adoption of the acentric factor in thermodynamic correlations. As noted by Prausnitz [55], who compared Pitzer’s acentric factor to other similar proposals: “Pitzer’s proposal is, perhaps, the most useful because his third parameter is calculated from experimental data, which tend to be accurate as well as accessible.”

### 2003—Span–Wagner (equations of state)

Reference equations of state provide the very high accuracy needed for certain scientific and industrial applications. For example, Wagner and Pr $\ddot{u}$ ß [56] developed the reference equation of state for the properties of water and steam, which enables highly accurate and reliable modeling of thermal power cycles. A key feature in the development of reference equations of state is that the optimization procedure is presented with a bank of many terms, and chooses the optimum subset of terms for the substance under consideration. In other words, the experimental data determine the optimum functional form of the reference equation of state.

The development of reference equations of state requires very large and reliable and comprehensive data sets, which may not be available for all substances of scientific and industrial interest. “Equations of state for technical applications” are less accurate than reference equations of state, but also require less data for the parameter optimization. The desired feature of technical equations of state is that the model remains numerically stable even though restricted data sets are used in the parameter

optimization. Span and Wagner [57–59] solved the problem by creating a new kind of algorithm that considers data sets for different substances simultaneously and thus developed functional forms that work reliably for groups of substances, like nonpolar [58] fluids and polar [59] fluids. Here again, the experimental data established the optimum functional form of the equation of state, this time for each of the two classes of fluids.

### **Historical contribution of data to theoretical concepts and correlation development: Summary and conclusions**

The case studies presented in this section demonstrate that experimental data have played a key role in revealing theoretical concepts and determining the structure of thermodynamic models. That, of course, is the focus of the present paper. But the cases also indicate the contribution of and the need for the other two methods of knowledge acquisition: theory and simulation. While Henry and Raoult did indeed make seminal contributions to models for phase equilibria, the highly accurate and widely applicable models available today would not have been possible without the enhancements from theory and, increasingly, simulation [4]. Group-contribution methods based upon the simple additivity assumption of Kopp are still used today, but they have been improved by theory, and simulation is expected to make strong contributions in the near future [44,60]. Study of the contribution of Berthelot shows that data and theory are quite complementary. Rigorous testing of the parachor [40] warns us that quantitative success of an empirical correlation does not necessarily mean that it has a theoretical basis. Estimation methods based upon the “property leapfrog” idea of Othmer are empirically successful, but are also improved by the application of theory and simulation [43]. Redlich and Kwong demonstrated the power of semi-empirical approximations, but recent advances in theory have extended the range and improved the predictive power of equations of state [61]. Theory has enabled considerable advances in the modeling of electrolyte systems [17], and the models available today are far more accurate and reliable than the first crude approximation proposed by Van Krevelen et al. [52]. Perhaps theory will guide extensions to the three-parameter corresponding-states framework of Pitzer, a development that has remained elusive. Span and Wagner [57] concluded that terms based upon theory (specifically, hard-sphere and square-well terms) did not improve the performance of technical equations of state, but this does not mean that theory inherently cannot improve these models. Experimental data are very important to developing thermodynamic models, but it is clearly advantageous to utilize all three methods of knowledge acquisition.

## **CONCLUSIONS**

Experimental data have played a strong role in chemical process technology by guiding the structure of thermodynamic models and by providing the definitive quantitative basis to develop correlations of high accuracy. Theory and simulation will make increasingly important contributions to chemical process technology in the future, but the valuable and important role of experimental data will continue. In 1882, Heike Kamerlingh Onnes gave an inaugural speech entitled “Through measurement to knowledge” on the occasion of his appointment as Professor of Experimental Physics at the University of Leiden [3]. One hundred and twenty five years later, the importance given to the role of experimental data by Prof. Kamerlingh Onnes is still relevant and valid.

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