

# Establishing benchmarks for the Second Industrial Fluids Simulation Challenge<sup>☆</sup>

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## Abstract

This manuscript outlines the procedures used to establish benchmark property data for the Second Industrial Fluids Simulation Challenge. The process involved acquisition of some new data, evaluation of the literature data, and generation of recommended values with careful uncertainty estimates.

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## 1. Introduction

In order to judge the entries in the Second Fluid Properties Simulation Challenge [1], a benchmarking committee was established that was comprised of several of the authors of this paper (Friend, Frurip, and Olson). As in the first contest [2], the mandate of the committee was to determine best values for the physical property questions posed in the Challenge based on a thorough evaluation of the available literature and on new experimental measurements, as necessary. A key part of the activity was to determine robust uncertainty estimates for the benchmarks, as these also played a role in the evaluation of challenge entries.

In this paper, we outline the procedures used to establish the 40 benchmark property values required for the three problems of the second event. Complete descriptions of the benchmark procedures for all of the posed problems are found in this report. The results of new experimental measurements are included as part of the discussion. Additional

contributors to the project are listed in the acknowledgements of this paper. The interested reader is encouraged to consult a more detailed discussion of the various strategies used to obtain physical property data, and some reflections on the role of experiment in the continuing evolution of the property infrastructure. These issues were discussed in a paper published as part of the first Simulation Challenge [3].

## 2. Recommendations for Problem 1–1: acetone vapor pressure and heat of vaporization

### 2.1. Problem conditions and recommended values

Vapor pressure		
Problem conditions	330 K	375 K
Recommended values	(104.04 ± 0.3) kPa	(390.3 ± 1.0) kPa
Problem conditions	425 K	460 K
Recommended values	(1184 ± 6) kPa	(2225 ± 1) kPa
Heat of vaporization		
Problem conditions	330 K	375 K
Recommended values	(29.07 ± 0.15) kJ/mol	(25.92 ± 0.13) kJ/mol
Problem conditions	425 K	460 K
Recommended values	(21.4 ± 0.4) kJ/mol	(17.1 ± 0.4) kJ/mol

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## 2.2. Primary source of recommendation

The values indicated above were calculated from the equation of state of Lemmon and Span [4].

## 2.3. Justification for recommendation

The equation of state in Ref. [4] contains the current recommended formulation for the thermodynamic properties of acetone, based on an extensive evaluation of property data available in the literature. The formulation, in the form of a reduced Helmholtz energy correlation, was based on temperatures on the ITS-90 scale. The work of Lemmon and Span [4] considered PVT data, second virial coefficients, isobaric heat capacities, sound speeds, enthalpies, heats of vaporization, and saturation properties (including vapor pressures). Their work summarized the complete data set, and the full set of references is not provided here.

For the current benchmarking exercise, calculations based on the formulation of Ref. [4] were compared with experimental data, emphasizing the vapor pressure, enthalpy, heat of vaporization, and heat capacity data in the region of current interest. All available experimental data, including those incorporated in the NIST TRC Source database [5] and the AIChE DIPPR database [6], were considered.

## 2.4. Determination of uncertainty

The uncertainties of the formulation of Lemmon and Span were discussed in Ref. [4], and are based largely on comparisons with the experimental database. The total uncertainty given here includes that derived from experimental uncertainties, focusing on potential impurities in the sample. Because the main impurity in acetone samples is water, we have examined experimental information on acetone/water mixtures; this information indicates that a water impurity of up to 1% has little effect on vapor pressures, within the uncertainty range considered here. In particular, the estimated uncertainties in the formulation for acetone are 0.1% in the saturated liquid density between 280 and 310 K, 0.5% in density in the liquid phase below 380 K, and 1% in density elsewhere. The uncertainties in vapor pressure were estimated as 0.25% between 290 and 390 K, 0.5% from 270 to 290 K and 0.5% above 390 K. The uncertainties in heat capacities and speeds of sound, which are representative of derivative properties, have been estimated as 1%.

Multiple data sets, including heat capacities, sound speeds and single phase enthalpies, help to establish the uncertainties in the Helmholtz energy equation of state and the recommended values with uncertainties presented here. All thermodynamic properties can be calculated directly from the Helmholtz energy equation by taking various derivatives. Thus, the inclusion of such properties as the speed of sound and heat capacities in the determination and assessment of the equation of state impacts the uncertainty estimates.

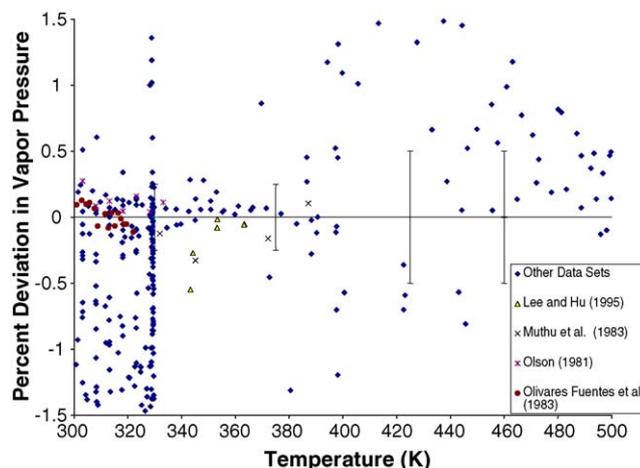


Fig. 1. Comparisons of vapor pressures calculated with the equation of state of Lemmon and Span [4] to experimental data [7–10]; points denoted “Other Data Sets” are cited in Ref. [4]. The benchmark points and their uncertainties are also shown.

Fig. 1 shows the deviation between the vapor pressure experimental data and vapor pressures calculated from the Helmholtz energy equation of state; this plot includes data from multiple sources, but excludes data outside the given temperature range and those with deviations of more than  $\pm 1.5\%$ . Fig. 2 shows the region between 325 and 335 K in closer detail. Between 280 and 330 K, many of the experimental vapor pressure points are represented by the equation of state to within 0.2% as shown in Fig. 1. The more recent data of Lee and Hu [7], Muthu et al. [8], Olivares Fuentes et al. [9] and Olson [10] indicate that the uncertainty in the equation is about 0.25% between 290 and 390 K. The scatter in the data above 400 K increases up to 2%, although at 50 K below the critical temperature, several data sets show

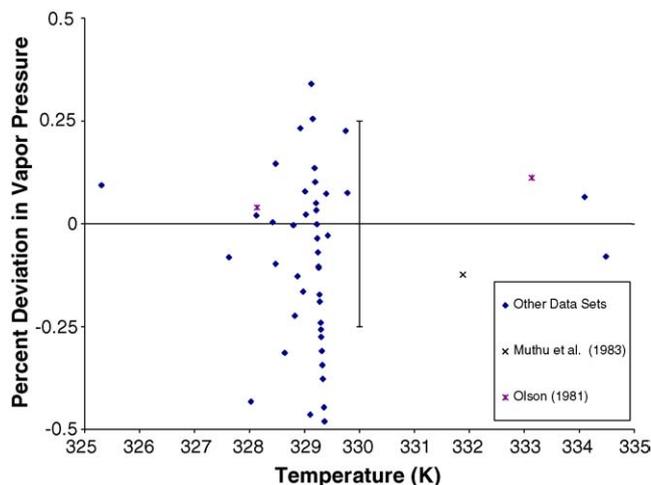


Fig. 2. Comparisons of vapor pressures calculated with the equation of state of Lemmon and Span [4] to experimental data in the range 325–335 K [8,10]; points denoted “Other Data Sets” are cited in Ref. [4]. The benchmark point at 330 K and its uncertainty are also shown.

consistent results and deviations from the equation of state are 0.75% (with agreement at 0.5% near the critical point).

On the saturation boundary, the equation of state agrees with the liquid phase isobaric heat capacities to within 1% from the triple point up to 310 K. There are isobaric heat capacities in the vapor phase above 330 K, and most are represented within 2%, with deviations of 0.2% from the data of Pennington and Kobe [11]. Deviations from the liquid phase speed of sound show a slight systematic offset in the equation, although most data points show deviations of less than 1%. The data cover a limited range from 250 to 325 K.

Fig. 3 compares calculated values of the heat of vaporization with experimental measurements. Comparisons between the data sets show good consistency (0.25%) for the data of Pennington and Kobe [11], Boublik and Aim [12], Collins et al. [13] and Yerlett and Wormald [14] between 300 and 400 K. Above 400 K, the equation shows deviations of about 2% from the data of Yerlett and Wormald. Additionally, the enthalpy data of Yerlett and Wormald show deviations of 1%, and it is quite likely that the uncertainty in the equation of state for heats of vaporization above 400 K is less than 2%. Because the uncertainty of heat of vaporization was not explicitly stated in Ref. [4], the uncertainty is estimated here to be 0.5% between 300 and 400 K and 2% above 400 K. Typically, uncertainties in energies, enthalpies and heats of vaporization are less than those for heat capacities, consistent with that given here below 400 K.

Calculations from a predictive extended corresponding states model [17], the DIPPR software [6], and from an automated data evaluation system, TDE, under development at NIST [18], were also considered. In all cases, the values selected here were consistent with all of these sources within their mutual uncertainties.

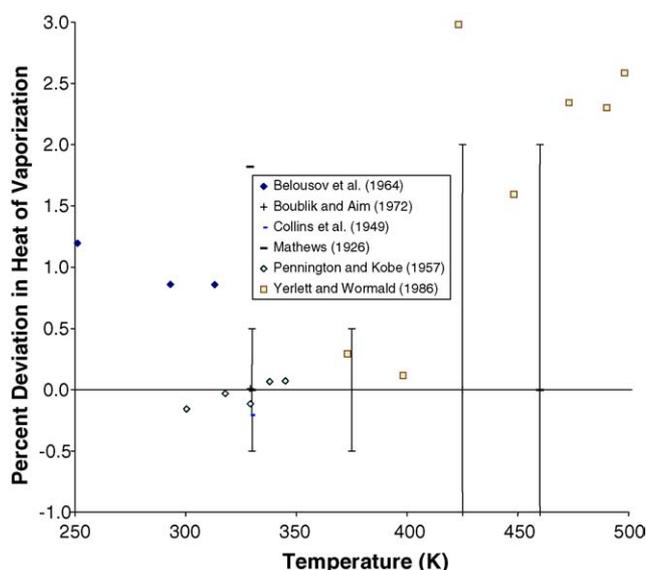


Fig. 3. Comparisons of heat of vaporizations calculated with the equation of state of Lemmon and Span [4] to experimental data [11–16]. The benchmark points and their uncertainties are also shown.

Yerlett and Wormald [14] reported that thermal decomposition was observed in acetone at around 420 K and that the total decomposition-related impurities reached 0.1 mole% at 473 K. Calculations from the equation of state will be less certain (as shown by the increased uncertainties given in the recommended values above) at higher temperatures (above 420 K), although the well-behaved functional form used for the equation of state will aid in extrapolating to higher temperatures with relatively small uncertainties (see Span and Wagner [19]).

### 3. Recommendations for Problem 1–2: vapor pressure and heat of vaporization of butyramide

#### 3.1. Problem conditions and recommended values

Vapor pressure		
Problem conditions	415 K	455 K
Recommended values	$(4.65 \pm 0.05)$ kPa	$(22.3 \pm 0.2)$ kPa
Problem conditions	490 K	520 K
Recommended values	$(67.7 \pm 0.7)$ kPa	$(151.6 \pm 3)$ kPa
Heat of vaporization		
Problem conditions	415 K	455 K
Recommended values	$(63.0 \pm 1.6)$ kJ/mol	$(59.3 \pm 1.2)$ kJ/mol
Problem conditions	490 K	520 K
Recommended values	$(56.2 \pm 1.2)$ kJ/mol	$(53.4 \pm 2.0)$ kJ/mol

#### 3.2. Primary source of recommendation

All eight values are derived directly from measurements performed for the simulation challenge at The Dow Chemical Company, Research and Development Department, Analytical Sciences and from experimental data reported in the scientific literature. Experimental details are given below.

#### 3.3. Justification for recommendation

Vapor pressures were derived from an Antoine vapor pressure equation fitted to laboratory data measured in a glass ebulliometer. Heats of vaporization were derived from a Clapeyron equation analysis of the vapor pressure data.

#### 3.4. Experimental details

##### 3.4.1. Materials

The butyramide was purchased from Fluka Chemicals (>98%, #19240 Lot #433980/140502)<sup>1</sup> and was used as received. A differential scanning calorimeter (DSC) analysis gave a melting onset temperature of 388.4 K compared to

<sup>1</sup> Certain commercial suppliers and instruments are identified in this manuscript in order to more clearly describe the experimental procedures. These citations do not indicate any endorsement by the National Institute of Standards and Technology, nor do they indicate that these have been established to be the best available for this or any other application.

Table 1  
Butyramide vapor pressure measurements

Ref. [23]		This work—1		This work—2		This work—3		This work—4	
<i>T</i> (K)	<i>p</i> (kPa)								
398.05	2.11	423.46	6.67	423.48	6.67	422.25	6.33	423.41	6.67
407.45	3.35	425.77	7.33	425.78	7.33	424.66	7.00	425.70	7.33
417.65	5.31	427.89	8.00	427.93	8.00	426.89	7.67	427.80	8.00
428.55	8.41	433.47	10.00	433.50	10.00	430.86	9.00	433.38	10.00
440.25	13.33	440.96	13.33	440.99	13.33	437.48	11.67	440.96	13.33
452.85	21.13			460.49	26.66	452.12	20.00	460.47	26.66
466.35	33.49			472.92	40.00	467.23	33.33	472.90	40.00
481.05	53.08			482.21	53.33	475.48	43.33	477.78	46.66
496.95	84.12					477.87	46.66		
503.75	101.32					480.09	50.00		

388.8 K in Ref. [20]. The melting point indicates that impurities likely to affect ebulliometric measurements are absent. Sample purity studies were not conducted at the conclusion of the measurements.

### 3.4.2. Apparatus

The vapor pressures were measured in a stirred-flask total-reflux ebulliometer [21]. The ebulliometer is constructed from a flask fused to a jacketed condenser, all constructed of glass. The flask is stirred using a spinning Teflon-coated magnet. The ebulliometer flask is immersed in an oil bath stirred with an air-driven impeller and controlled to  $\pm 0.01$  K by means of a proportional temperature controller. Pressures were measured and controlled with a recently calibrated Mentor Model PCS 400 manostat to  $\pm 13$  Pa. Temperatures were measured with a standard platinum resistance thermometer to  $\pm 0.01$  K. The PRT had been calibrated by comparison to a Burns Engineering standard platinum resistance thermometer traceable to NIST.

### 3.4.3. Procedure

The laboratory procedure is described in ASTM method E 1719, standard test method for vapor pressure of liquids by ebulliometry [22]. The vapor pressures were measured in quadruplicate using different specimens of the butyramide sample.

The measured data are given in Table 1. After the experiments were completed, additional data, also shown in Table 1, were discovered in the scientific literature [23]. An Antoine equation fitted to the combined data gives this equation,

$$\log_{10} p \text{ (kPa)} = 6.7719530 - \frac{1944.352}{T(\text{K}) - 96.506} \quad (1)$$

with an rms deviation of 1.1% in pressure. The data and the fitted equation are shown in Fig. 4.

The heats of vaporization were derived from the fitted Antoine equation by using ASTM method E 2071 Standard Practice for Calculating Heat of Vaporization or Sublimation from Vapor Pressure Data [24]. The critical temperature and pressure required for use of the Haggmacher method to estimate  $\Delta Z$  in ASTM method E 2071 were derived from

the butyramide normal boiling point (Equation (1)) using the Joback method [25].

### 3.5. Determination of uncertainty

As described in detail by Mandel [26], the evaluation of experimental measurements in the absence of exactly known reference values is a difficult and ill-defined process. In the absence (rarely achieved) of systematic errors, the uncertainty in the accuracy of experimental measurements is of the same order as the precision (rms error) of replicate experiments. Here, the rms error of a fit to both sets of data, those in Ref. [23] and the current measurements, is 1.1%. We judge that there is no a priori evidence to exclude either set of data from consideration.

The typical uncertainty of ebulliometric measurements, given by the Precision and Bias statement of ASTM E 1719 [22], which is based on an Interlaboratory Study (Round Robin), is  $\approx 0.5$ –3% in pressure.

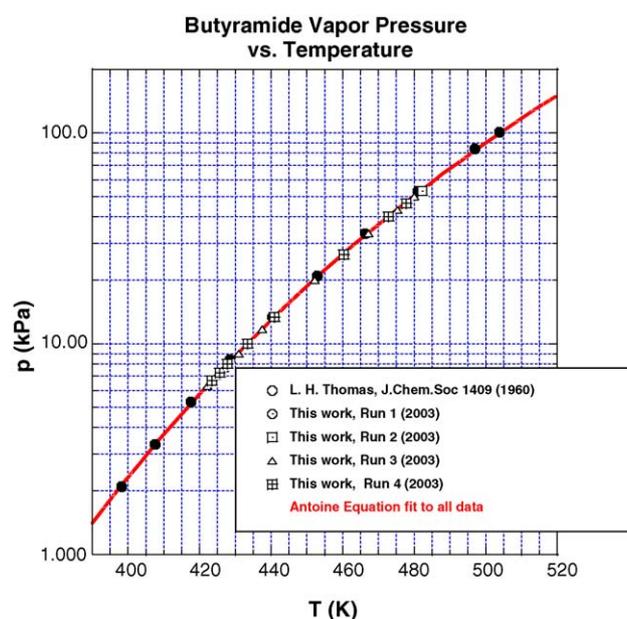


Fig. 4. The vapor pressure of butyramide as a function of temperature.

The uncertainties in the contest vapor pressure values for butyramide are larger than the rms fitting error uncertainties depending on the temperature. Although the use of the Antoine equation is considered robust from pressures of 1–200 kPa [25], the largest uncertainty for the contest state points was assigned to the value at 520 K because it represents a (modest) extension of the data above the experimental data temperatures.

The uncertainties in accuracy for the contest heat of vaporization values were estimated from the typical increase in uncertainty propagated from differentiation of vapor pressure data [25].

## 4. Recommendations for Problem 2: Henry's law constants of nitrogen, oxygen, methane and carbon dioxide in ethanol

### 4.1. Problem conditions and recommended values

Henry's law constant—nitrogen		
Problem conditions	323 K	373 K
Recommended values (mole fraction basis)	(253.6 ± 7.6) MPa	(221.3 ± 13.3) MPa
Henry's law constant—oxygen		
Problem conditions	323 K	373 K
Recommended values (mole fraction basis)	(174.8 ± 8.7) MPa	(159.9 ± 12.8) MPa
Henry's law constant—methane		
Problem conditions	323 K	373 K
Recommended values (mole fraction basis)	(81.5 ± 2.4) MPa	(83.4 ± 5.0) MPa
Henry's law constant—carbon dioxide		
Problem conditions	323 K	373 K
Recommended values (mole fraction basis)	(21.1 ± 1.1) MPa	(29.7 ± 3.3) MPa

### 4.2. Primary source of recommendation

All eight values are derived directly from gas solubility data measured for the simulation challenge at The Dow Chemical Company, Research and Development Department, Analytical Sciences. Experimental details are given below.

### 4.3. Justification for recommendation

Gas solubility data were in the dilute dissolved gas region from 0.0002 to 0.03 mole fraction gas. Henry's law constants were then determined from:

$$H_{i,\text{ethanol}}(T, p_{\text{ref}}) = \lim_{x_i \rightarrow 0} \frac{f_i}{x_i} \quad (2)$$

where component *i* is the gas (solute) and  $f_i$  is the fugacity of the gas. Fugacities were computed from the second

virial equation of state for methane and carbon dioxide and from the Hougen–Watson fugacity tables [27] for nitrogen and oxygen. The Henry's law constant (HLC) was then corrected to the reference pressure,  $P_{\text{sat}}$ , the saturation pressure of ethanol.

## 4.4. Experimental details

### 4.4.1. Materials

The ethanol was ACS reagent grade purchased from Aldrich (#45,983-6, 99.5%, <0.005% water) and used as received. Nitrogen was purchased from Airgas with a stated purity of 99.994%. The nitrogen/oxygen mixture was formulated from nitrogen and USP grade medical air, also from Airgas. Medical air is made by mixing USP purity nitrogen (99%) and USP purity oxygen (99%). Matheson research grade methane (99.99%) and carbon dioxide (99.995%) were used. These gas purities are well above the 99 mole% minimum usually required for gas solubility experiments [28].

### 4.4.2. Apparatus and procedure

Two apparatus were used to measure the gas solubility data: a saturation and sampling (analytical) method was used for nitrogen and oxygen [29], and a material balance on gas and liquid confined in a bomb of known volume (synthetic) method was used for methane and carbon dioxide [30]. The different techniques were used because of different materials compatibility and sample handling issues. Data for all four gases were corrected to the reference pressure using the Krichevsky–Kasarnovsky equation [30,31].

**4.4.2.1. Nitrogen and oxygen.** The gas solubilities were measured by sampling from a thermostatted stainless steel autoclave. This apparatus consisted of a 2 L autoclave in a temperature-controlled bath, a sample receiver, a gas buret, and a paramagnetic oxygen analyzer. A mixture of oxygen diluted in nitrogen was used to keep the concentration of oxygen in the apparatus below the flammability limit.

About 1000 cm<sup>3</sup> of ethanol were charged to the evacuated autoclave. The bath temperature was controlled to ±0.01 K with a proportional temperature controller using a recently calibrated Hart platinum resistance thermometer. The gas of interest (nitrogen or the nitrogen/oxygen mixture) was added to the autoclave to the desired pressure. Pressures were measured with a recently calibrated Heise pressure transducer (±0.7 MPa). After stirring, the entrained gas bubbles were allowed to leave the liquid phase and samples of the liquid were then slowly metered into a weighed bottle. The gas thereby flashed from the liquid was collected in the gas buret. A typical sample consisted of approximately 10 g of ethanol collected in the bottle, and 80 cm<sup>3</sup> of gas measured in the buret. The sample bottle was weighed with an accuracy of ±0.0002 g. The volume of gas was measured to ±0.2 cm<sup>3</sup>. Barometric pressure was measured with an accuracy of ±0.0013 MPa and the temperature of the gas buret was measured to ±0.1 K with a calibrated mercury

Table 2  
The solubility of nitrogen and oxygen in ethanol

Solubility of oxygen in ethanol			
Temperature (K)	Pressure (MPa)	O <sub>2</sub> in vapor (mole fraction)	O <sub>2</sub> in liquid (mole fraction)
323	3.496	0.00816	0.000148
323	5.219	0.00830	0.000223
323	6.909	0.00850	0.000298
373	3.489	0.00836	0.000171
373	5.116	0.00832	0.000241
373	6.929	0.00857	0.000329
Solubility of nitrogen in ethanol			
Temperature (K)	Pressure (MPa)	N <sub>2</sub> in vapor (mole fraction)	N <sub>2</sub> in liquid (mole fraction)
323	3.496	0.99159	0.01253
323	5.171	0.99432	0.01819
323	6.998	0.99580	0.02422
373	3.509	0.93639	0.01388
373	5.219	0.95722	0.02082
373	6.909	0.96766	0.02744

thermometer. Four or six replicates were collected at a given condition. After the amount of gas dissolved in ethanol had been measured, the composition of the gas was determined by a paramagnetic oxygen analyzer with a repeatability of  $\pm 2\%$  of the measured value. The measured data for oxygen and nitrogen are given in Table 2.

4.4.2.2. *Methane and carbon dioxide.* The gas solubilities were determined by measuring the mass of degassed ethanol charged to a metal sample holder of known volume, measuring the mass of gas added to the sample holder, and measuring the equilibrium pressure after shaking the sample holder and allowing it to equilibrate in a thermostat. The gas solubility was then computed from an iterative material balance on the amount of gas that remains in the vapor phase based on a simultaneous solution of the phase equilibrium equation and

Table 3  
The solubility of methane and carbon dioxide in ethanol

Solubility of methane in ethanol					
Temperature (K)	Pressure (MPa)	Total volume (cm <sup>3</sup> )	Mass of gas (g)	Mass of liquid (g)	CH <sub>4</sub> in liquid (mole fraction (derived))
323	2.320	337.557	3.180	163.641	0.02565
323	2.119	337.557	2.911	163.739	0.02363
323	2.337	340.120	3.346	158.742	0.02688
373	2.658	337.557	2.911	163.739	0.02702
Solubility of carbon dioxide in ethanol					
Temperature (K)	Pressure (MPa)	Total volume (cm <sup>3</sup> )	Mass of gas (g)	Mass of liquid (g)	CO <sub>2</sub> in liquid (mole fraction (derived))
323	0.4103	337.557	3.493	167.142	0.01703
323	0.4068	337.557	3.504	162.286	0.01739
323	0.4378	340.120	3.890	162.175	0.01931
373	0.7619	337.557	3.504	162.286	0.01701
373	0.7722	337.557	3.650	160.627	0.01789
373	0.7722	337.557	3.619	165.115	0.01753

Henry's Law Constants (mole fraction basis) in Ethanol vs Temperature

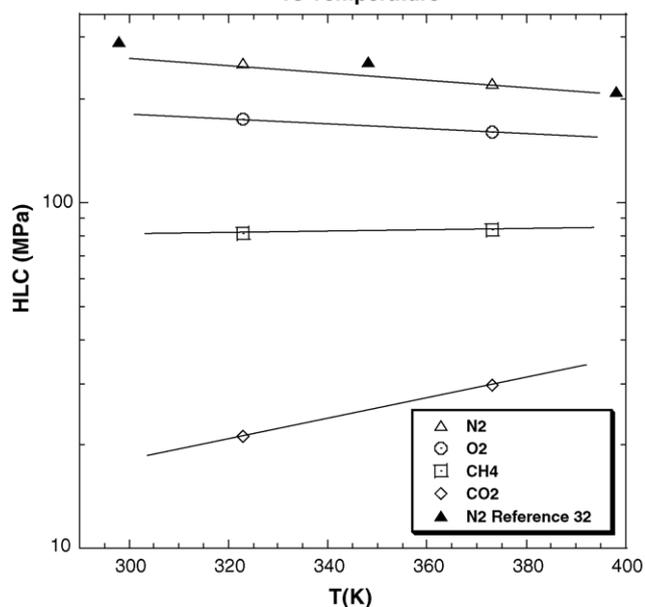


Fig. 5. Henry's law constants for various gases in ethanol.

a vapor phase equation of state (in this case, the second virial equation).

The gas solubility sample holder was a 350 cm<sup>3</sup> stainless steel sampling cylinder equipped with a Marsh Instrument Company Master Test (0.25%) bourdon gauge. The sample holder was equilibrated in a liquid thermostat to  $\pm 0.1$  K. The temperature of the thermostat was set with a recently calibrated mercury-in-glass thermometer. Masses of the liquid and gas additions were measured with 5 kg capacity Voland balance to  $\pm 1$  mg. The experimental procedure and the data reduction technique are described in detail elsewhere [30]. The experimental data for methane and carbon dioxide are given in Table 3.

The temperature dependence of the Henry's law constants for the four gases in ethanol is shown in Fig. 5. Also, shown in Fig. 5 are data for HLC of nitrogen in ethanol from a recent material balance experiment [32].

#### 4.5. Determination of uncertainty

As described in detail by Mandel [26], the evaluation of experimental measurements in the absence of exactly known reference values is a difficult and ill-defined process. In the absence (rarely achieved) of systematic errors, the uncertainty in the accuracy of experimental measurements is of the same order as the precision (rms error) of replicate experiments. Here, the rms error of replicates is 3–7% depending on the gas. The typical uncertainty of gas solubility measurements is 3–5% [28].

The uncertainties in accuracy of the contest Henry's law constants reported above are larger than the rms uncertainties in the experimental gas solubility data. These larger uncertainties are due the process of computing the HLC from equation (2) and correcting the HLC to the reference pressure.

### 5. Recommendations for Problem 3: the heat of mixing of *n*-butylamine and *n*-heptane, and of *n*-butylamine and water<sup>2</sup>

#### 5.1. Problem conditions and recommended values

The heat of mixing of <i>n</i> -butylamine and <i>n</i> -heptane at 298 K		
Problem conditions	0.2 Butylamine	0.4 Butylamine
Recommended values	(0.716 ± 0.046) kJ/mol	(1.11 ± 0.06) kJ/mol
Problem conditions	0.6 Butylamine	0.8 Butylamine
Recommended values	(1.08 ± 0.06) kJ/mol	(0.657 ± 0.045) kJ/mol
The heat of mixing of <i>n</i> -butylamine and <i>n</i> -heptane at 348 K		
Problem conditions	0.2 Butylamine	0.4 Butylamine
Recommended values	(0.631 ± 0.071) kJ/mol	(0.964 ± 0.099) kJ/mol
Problem conditions	0.6 Butylamine	0.8 Butylamine
Recommended values	(0.981 ± 0.100) kJ/mol	(0.666 ± 0.071) kJ/mol
The heat of mixing of <i>n</i> -butylamine and water at 298 K		
Problem conditions	0.2 Butylamine	0.4 Butylamine
Recommended values	(−2.21 ± 0.12) kJ/mol	(−3.21 ± 0.12) kJ/mol
Problem conditions	0.6 Butylamine	0.8 Butylamine
Recommended values	−3.10 ± 0.12) kJ/mol	(−2.00 ± 0.11) kJ/mol

<sup>2</sup> All concentrations are given as mole fractions.

(Continued)

The heat of mixing of <i>n</i> -butylamine and water at 348 K		
Problem conditions	0.2 Butylamine	0.4 Butylamine
Recommended values	(−2.18 ± 0.23) kJ/mol	(−3.12 ± 0.27) kJ/mol
Problem conditions	0.6 Butylamine	0.8 Butylamine
Recommended values	(−2.97 ± 0.26) kJ/mol	(−1.88 ± 0.21) kJ/mol

#### 5.2. Primary source of recommendation

All 16 values are derived directly from measurements performed for the simulation challenge at The Dow Chemical Company, Research and Development Department, Analytical Sciences and from experimental data reported in the scientific literature. Experimental details are given below.

#### 5.3. Justification for recommendation

Heats of mixing data at the state points were derived from Redlich–Kister equations fitted to laboratory data and literature data. The recommended values at 298 K are based on data measured in a differential heat conduction calorimeter as described below. The recommended values at 348 K were derived from the measured data at 298 K by use of temperature dependence derived from literature data.

#### 5.4. Experimental details

##### 5.4.1. Materials

The butylamine was purchased from Aldrich (>99%, #270512 Lot #09627EC) and was used as received. The heptane was also purchased from Aldrich (HPLC grade, >99%, #270512 Lot #12255HC) and was used as received. Water purified with a nanofiltration system was used.

##### 5.4.2. Apparatus

The heats of mixing were measured in a CSC 2-Drop Calorimeter model 2200 that uses an electrical resistance calibration for each run. The magnitude of the electrical calibration for each run was typically chosen to be close to the expected energy of the experiment.

##### 5.4.3. Procedure

In this calorimeter, one material was contained in a sealed glass vial (Teflon coated rubber septum and aluminum crimped cap, 2 mL total volume) and the other material was injected using a glass syringe after the electrical calibration. All compositions were calculated from the weights of the materials before and after the experiment. Typical sample sizes were 0.1–3 g and the vials (which always contained the amine) were stirred with a Teflon-coated magnet. The typical baseline noise of this calorimeter is 10 μW and the typical integrated signal size was approximately 2–20 J (exothermic

Table 4  
Butylamine + heptane heat of mixing measurements at 298 K

$x_{BA}$	$\Delta H_{\text{mix}}$ (kJ/mol)
0.000	0.000
0.102	0.409
0.206	0.725
0.401	1.106
0.403	1.106
0.580	1.110
0.612	1.071
0.756	0.768
1.000	0.000

and endothermic). As a check on the procedure, we ran a mixing experiment of methanol and water (approximately 50/50, v/v) and we were able to reproduce the literature data [33] to within 0.5%.

The 298 K heat of mixing data for butylamine + heptane are given in Table 4. These data were fitted with a three-parameter Redlich–Kister (RK) equation [31],

$$\Delta H_{\text{mix}} = x_1 x_2 (A + B(x_1 - x_2) + C(x_1 - x_2)^2) \quad (3)$$

as shown in Fig. 6. The data are less endothermic, but within the combined experimental errors of data reported by Letcher and Bayles [34]. The temperature dependence of the literature data [34] was used to calculate the heat of mixing at 348 K. The temperature dependence of the literature data was determined by fitting each of the RK parameters from the literature data to a linear equation, for example,

$$A_{\text{RK}} = \alpha + \beta T(K) \quad (4)$$

The 298 K heat of mixing data for butylamine + water are given in Table 5. These measured data and the 298 K literature

Table 5  
Butylamine + water heat of mixing measurements at 298 K

$x_{BA}$	$\Delta H_{\text{mix}}$ (kJ/mol)
0.000	0
0.219	-2.136
0.240	-2.323
0.246	-2.283
0.410	-3.271
0.438	-3.204
0.613	-3.335
0.808	-2.023
1.000	0

data of Dutta-Choudhury and Mathur [35] were fitted with a two-parameter RK equation, as shown in Fig. 7. The linear temperature dependence of the literature data [35,36] was used to calculate the heat of mixing at 348 K. The temperature dependence of the literature data was again determined by fitting the RK parameters from the literature data to linear equations.

Figs. 8 and 9 show the temperature dependence of the contest state points.

### 5.5. Determination of uncertainty

As described in detail by Mandel [26], the evaluation of experimental measurements in the absence of exactly known reference values is a difficult and ill-defined process. In the absence (rarely achieved) of systematic errors, the uncertainty in the accuracy of experimental measurements is of the same order as the precision (rms error) of replicate experiments. Here, the rms errors of Redlich–Kister equations fit to the two sets of data measured at 298 K are 2.0% for butylamine + heptane and 5.7% for butylamine + water.

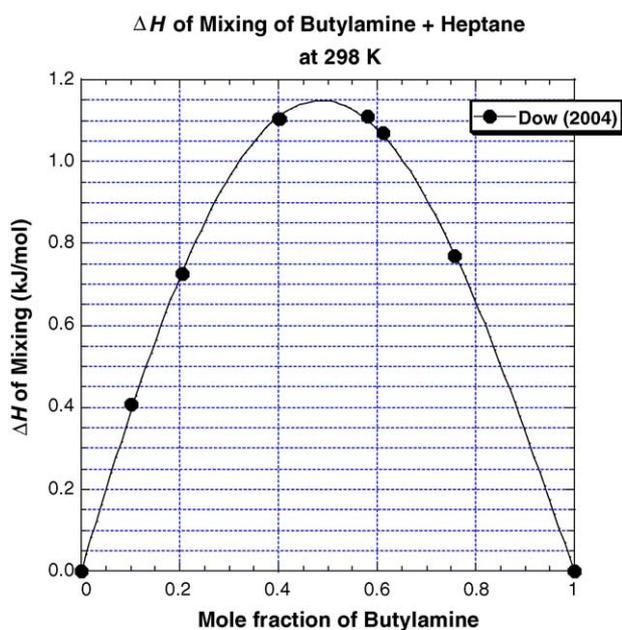


Fig. 6. Heat of mixing results for butylamine + heptane at 298 K.

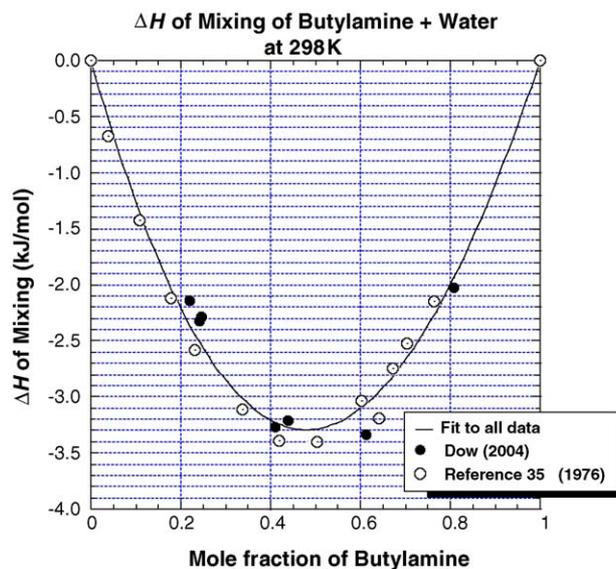


Fig. 7. Heat of mixing results for butylamine + water at 298 K.

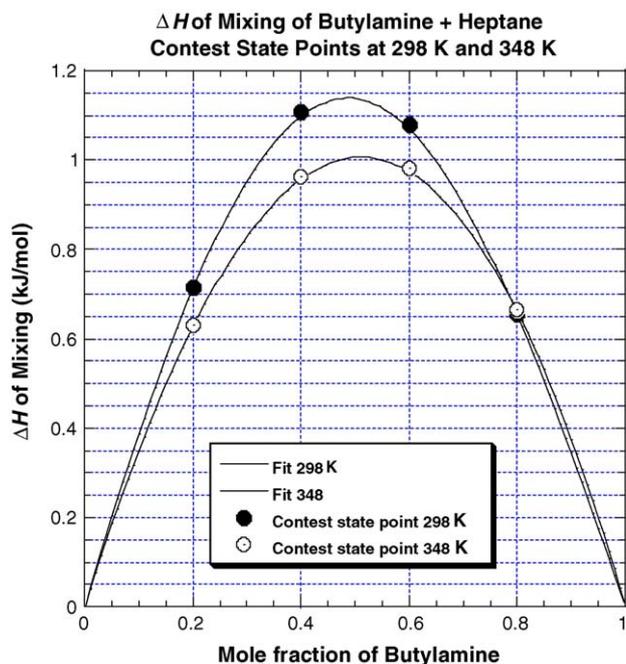


Fig. 8. Heat of mixing for butylamine + heptane, contest state points at 298 K and 348 K.

The uncertainty of calorimetric heat of mixing measurements varies from 0.5 to 2% for flow microcalorimeters to 5–10% for glass Dewar temperature-rise calorimeters. The uncertainties of the contest heat of mixing values are larger than the rms fitting errors because of systematic errors due to variability in sample size and mixing. In addition, the uncertainties at 348 K are larger because of the uncertainties in the linear temperature dependence equations.

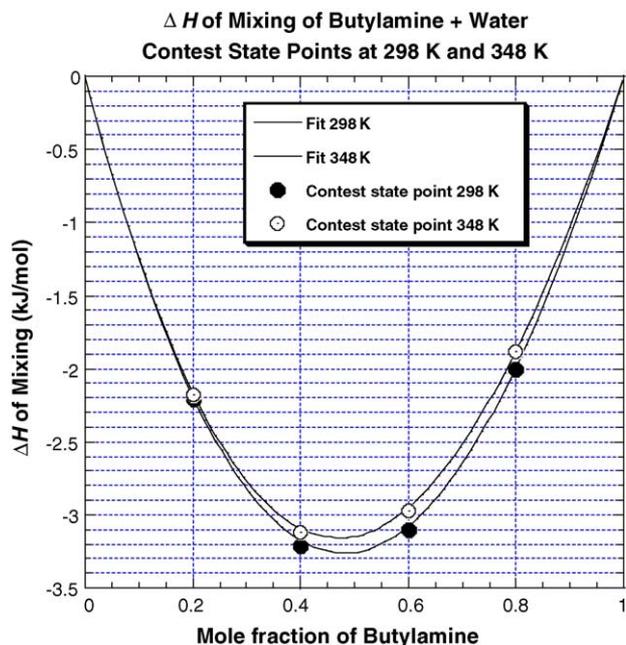


Fig. 9. Heat of mixing for butylamine + water, contest state points at 298 and 348 K.

## 6. Summary

As we noted in the first contest [3], simulation methods cannot be generally used unless and until robust validation procedures are established and practiced. The first and second fluid properties simulation challenges attempted to provide a double-blind evaluation of an assortment of techniques. We hope and assume that computer simulation techniques will continue to improve, as will theory and models for systems. As we move ahead toward future Simulation Challenges, experimental measurements will continue to provide the benchmark connection with physical reality.

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