The Essential Importance of Experimental Research for Advancing Chemical Engineering Thermodynamics

in Honor of the 60th Birthday of Prof. Dominique Richon

Kai Fischer
De:
John Prausnitz <prausnit@cchem.berkeley.edu>

Asunto:
Re: Your shoulder and Colloquium

Fecha:
Fri, 28 Aug 2009 17:19:27 -0700

A:
Dominique Richon <dominique.richon@mines-paristech.fr>

Cc:
"Luis A. Galicia-Luna" <lgalicial@ipn.mx>, Christophe COQUELET <christophe.coquelet@mines-paristech.fr>
The Essential Importance of Experimental Research for Advancing Chemical Engineering Thermodynamics

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Abstract
In chemical process design, we like to calculate required thermodynamic properties from correlations such as equations of state, excess Gibbs energy models and a variety of semi-empirical equations for vapor pressures, densities, surface tensions, etc. However, we sometimes forget that all of these relations depend on results from experimental measurements. Our correlations cannot exist without an experimental-data base.

To illustrate the essential importance of experimental data, some examples show new phase-behavior phenomena that cannot be predicted from theory or correlations. Further, while molecular simulation often provides a powerful tool, it too can fail to represent nature unless good experimental data are available to establish the all-important force field.

Experimental studies are especially important for quantitatively giving the physical properties of complex fluid mixtures that are often encountered in the chemical and related industries. For complex mixtures, we have few, if any, truly reliable theories. The required experimental studies are difficult; they demand much patience, ingenuity and painstaking attention to details. Fortunately, the laboratory for physical properties and phase behavior at the École des Mines is able to produce excellent experimental results due to its gifted director, Professor D. Richon. His laboratory is a jewel of French science.
"Models come and go, but good data are forever!"

(John M. Prausnitz)
Dear Friends of Professor Richon,

I regret that I cannot be with you on this happy occasion to celebrate Professor Richon's birthday. While in Spain earlier this summer, I fell and injured my right shoulder. I am now recovering from surgery; my surgeon says that I cannot do any traveling until mid-October.

However, my absence does not prevent me from extending congratulations to Dominique Richon or from extending greetings to all participants in this technical symposium.

It is a pleasure for me to indicate my admiration for Professor Richon's scientific and engineering achievements. His laboratory at Fontainebleau has produced a large collection of high-quality data concerning the physical properties of fluid mixtures, often at extreme conditions of temperature and pressure; while these data provide significant information toward advancing our understanding of condensed matter, they also serve the needs of industry. Especially the petroleum industry, toward design of processes that show improved energy efficiency and improved environmental protection. The extensive experimental work from Professor Richon's laboratory serves both science and engineering. For thermodynamic properties of mixtures, including phase equilibria, his laboratory is unique; there is no other laboratory in the world today that can match the high-quality productivity of Professor Richon and his coworkers.
# Large Collection of High Quality Data

<table>
<thead>
<tr>
<th>Properties</th>
<th>data sets</th>
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<th>articles</th>
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<td>Infinite dilution activity coefficients in solvent mixtures</td>
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<td>Solid liquid equilibrium data</td>
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<td>Densities of mixtures</td>
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<td>PVT data, VLLE data, refractive index</td>
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Articles Published by D. Richon

Publications per Year (Richon's CV)

Year

Relevance Index

Relevance of Richon’s Articles by Citation

Citations per Year per Article (Scopus)

Relevance Index

Year

Richon’s Top Five Articles by Citation

1) ROLSI sampler (2000) – 62 citations
2) Neural network modeling (2002) – 51 citations
3) New apparatus (1986) – 50 citations
5) New loading technique (1994) – 47 citations
Richon’s Important Achievements for an Experimentalist

- ROLSI sampler (direct gas chromatography)
- Dilutor – Technique (Inert gas stripping)
- PVT cell with sapphire tube (variable volume)
- Bubble point determination by densitometry
- Solubility measurement by calorimetry
- Rheology under pressure
- High pressure autoclaves for any purpose
Temperature and Pressure Ranges

- Maximum Pressure: 1000 bar
- Minimum Temperature: 95 K
- Maximum Temperature: 623 K
Rapid On-Line Sampler Injector (ROLSI)
Future Technologies

$\text{CO}_2$ capture and deposit

“Sulfur” capture and deposit

Process intensification by high pressure / high density

Biofuels

Reservoir processing

Syngas (Fischer-Topsch)
Experimental Strategies

Combination of phase equilibrium and PVTx data (Gibbs free energy) with:

Temperature gradients (enthalpies, heat capacities)

Pressure gradients (compressibility, speed of sound)

On-line analysis

In-situ analysis (speciation, solvation)

Transport properties

Reaction kinetics and equilibria

Visual observation of systems
Process Simulation

State of the art: Solution models and/or equations of state

Pure component properties

Binary interaction parameters

Key combinations of important components: always experimental data

Remaining mixtures: Parameter generalizations, estimations
SRK: General Mixing Rule

\[
\frac{a}{bRT} = \sum_i x_i \frac{a_i}{b_iRT} + \frac{A^E}{RT} \ln \left(\frac{u}{u + 1}\right)
\]

\[
\frac{G^E}{RT} = \ln(\varphi) - \sum_i x_i \ln(\varphi_i^*)
\]

\[
\frac{G^E}{RT} = \sum_i x_i \ln(\gamma_i)
\]
Heats of Mixing & LLE for Methyl Acetate + Water

HE hE/x-Chart

Methyl acetate mole fraction

H^E / J mol^-1

T = 298.15 K
VLE for $\text{H}_2\text{S} + \text{Benzene}$
NH₄Cl (solid) + NH₃ (supercritical)
$\text{NH}_3$ (supercritical) + $\text{CO}_2$ (supercritical)
Critical Point of Water + Hydrocarbon Mixture
Oxidation in Supercritical Water?
Thank you, Dominique

For your unique contributions in experimental thermodynamics.