Industrial Requirements for Thermodynamic and Transport Properties – 2020

Supporting Information

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Table S1. Benefits from Thermodynamics as seen from industry – their own examples

Question 7: Can you provide examples of achievements in Thermodynamic R&D where you can give an estimate of potential business or avoided risk?

Benefit: Examples and estimated potential business or avoided risk (kEUR) or in qualitative terms

Case description	**Benefits**
Experimental methods and data	
Measurement of very low vapor pressures, below 1 Pa	Around 300 k€ saved in the registration of substances, with around 50 substances over the last years.
We developed an apparatus that allowed the measurement of phase equilibria from low (a few mbar) to moderate (up to 10 bar) pressures with in-situ sampling and without disturbing equilibria.	The apparatus allowed us to deal with measurements in the 2 – 4 bar range, which previously had been difficult with the equipment available at our facilities. Several business potentials had previously targeted this pressure range specifically.
Development of a new surface PVT laboratory equipment and microfluidic technologies.	rapid and accurate measurements with smaller sample sizes
Accurate measurement of the temperature dependency of the density of a mixture organics+water.	> 1000 k€/yr
Modeling	
Entrainer selection using COSMO-RS for extractive distillation (instead of crystallization + distillation)	1000 kEUR/a
-Digitalization in operation (online thermodynamic tools) - Improved calculations of dehydration processes (CPA – EoS) - Acid gas removal (CO_2 removal and injection)	

Trace by-products behavior modeling in order to meet process guarantees (f.ex. DME, organic acids, formates, amines, etc)	HSSE aspects f.ex. corrosion or catalyst poisoning
Modeling of sulfur allotropes	Benefit of not using commercial, black box software Package
Development of thermodynamic models for new processes related to biomass conversion. These developments are generally performed in two main steps : - Using predictive approach for preliminary work - adjusting a more conventional model for process development.	
<u>Water activity tool</u> I identified an error in an internal activity calculation tool that has been used for >10 years. The error in the calculation of the activity calculations using the Wilson model was never spotted – I identified the error and designed a new calculation tool as well as an improved workflow so that this error can be avoided in future by carrying out a rigorous validation process up front. On my part, this work took me less than 2 days incl. documentation – whilst the impact in terms of quality or business risk is very significant. The water activity tool has been routinely used by a particular business unit to inform version selection. The error did not pose a quality risk as such because the version is experimentally validated, however the error in the calculation tool would result in significant delays in development time, as experimental studies could likely be wrongly designed, which would then have to be repeated at a later point in time. It goes to show what someone with only very rudimentary understanding of thermodynamic models (such as Wilson) can achieve – it turns out that this is a rare skill.	
Determination and modeling of high-pressure phase equilibria including the solubility of gas in polymers. Low pressure measurements of equilibria in systems with low concentration monomers.	New concept and redesign of the downstream process, with changes in the selected unit operations
New model parameters were developed for existing predictive techniques for properties such as the normal boiling point and vapor pressures, using proprietary data from clients and supplemented with our own measurements.	These in-house models are still being used today to deal with new compounds proposed by the client, and updated regularly
Downhole Fluid Analysis – determine fluid properties of reservoir fluids insitu.	Understanding the reservoir early in the exploration phase (better sampling locations

	determined), ascertaining fluid gradients in the reservoir.
Thermodynamics and Processes	
Minerals enrichment, improvement of Gas-Liquid-Solid chemical reactor performance	50 kEUR/year, better yield and less waste
<u>Design of a membrane-distillation hybrid process for solvent recovery</u> This was to re-use a high-cost solvent in a high-throughput project. Previously, the accumulation of solvent posed a capacity issue on manufacturing site as well as a cost issue. Thermodynamic understanding strongly contributed to baseline the current process and show its inherent limitations, as well as informing us in the solution, which was a hybrid membrane-distillation process. Payback time was 1/2 year.	~ £2M per annum
Simulation of a separation section of a process revealed a risk of accumulation of a side product into the process when ramping up the capacity of the process. The observation urged for better quality VLE data.	
Optimization of a batch reaction, by knowing the solubility of the monomer in the reacting solution	500 kEUR/a
Paper industry. Chemical additive preparation in a mixing tank (viscous polymer mixing / foaming)	20 kEUR/year, better product less waste
<u>Design of a continuous liquid-liquid extraction process</u> The process was previously using a batch extraction process, as it is common in the pharmaceutical industry, with a continuous extraction column. The proposed process was highly preferable as it showed very high selectivity regarding the removal of critical impurities from the product stream, which could have otherwise led to batch failures.	
Diverse - corrosion	
Prevention of corrosion in refinery overheads due to the formation of corrosive amine hydrochlorides – thermodynamic simulation makes it possible to avoid conditions that may lead to failure	Proactively scheduling inspections in order to avoid costly shutdowns or, even worse, equipment failures, saves refiners millions of dollars
Prediction of mineral scaling in oil and gas production, with emphasis on high-pressure, high-temperature production environments and on systems that involve glycols and methanol. The mineral scales include various sparingly soluble carbonates, sulfates, and sulfides. Thermodynamics plays a key part here	Prevention of mineral scaling is essential for flow assurance in oil and gas production. Formation of scales can cause tremendous damage to

because of a need to predict solubilities in multicomponent systems	production facilities and stop production.
Prediction of corrosivity in HF alkylation. The problem is primarily thermodynamic because of the need to predict the water and acid-soluble oil content in the acid-rich phase (corrosivity increases rapidly with water content)	Corrosion can cause catastrophic damage in alkylation units, which can be very costly. To prevent damage, simulation can help schedule proactive corrosion testing.
Prediction (and exp. verification) of a hydrate formation at low pressure of a poisonous substance	Lifes saved: 18 months later 4 people died in plant of competitor who was not aware of the risk of hydrate formation
Team member in task force for root cause analysis in production processes	Avoided lost sales of high value products (millions of €)

Table S2. Questionnaire by EFCE WP on Thermodynamics and Transport Properties

Please read this first

Who we are ?

We represent the task group Industrial Perspectives, which is part of the Working Party (WP) on Thermodynamics and Transport Properties which started in 2007 as one of the WP's of the European Federation of Chemical Engineers (EFCE).

What do we (the Working Party) do ?

Our task is to review for EFCE the current situation in industry with respect to thermodynamics and transport properties, identify limitations in currently used approaches, and provide specific recommendations on R & D work that needs to be initiated by industry and academia in this area.

Why ?

A main role of the WP is to support to the European oil, petrochemical, chemical, materials, pharmaceutical and process industry with the necessary up-to-date information related to physical property experimental methods and theoretical / computational models. For this purpose a survey on the industrial needs for thermodynamic and transport properties was carried out 10 years ago and the article summarizing the results is attached. The authors now feel that 10 years after the article a new survey is necessary. A summary of some developments, compiled by the authors, over the last 10 years is also attached.

What do we ask from you ?

You have been identified as an expert in the field, working inside or in close collaboration with industry. Your ideas and opinions will be valuable. For this reason we drafted a simple questionnaire. We hope you will find time to provide your responses which will be very valuable for our research.

Guidelines

All questions are to be considered in relation to thermophysical properties (thermodynamics and transport properties) of chemical systems in the solid, liquid or gas phase. Please consider all questions that are relevant to you and fill in the fields where applicable. (If you need more space or extra lines for your input, please feel free to create those).

Question 1. Your company's business: What are the main businesses of your company?

Please put Yes or No or use a scale of importance (1: no importance, 5: top importance)

- Exploration and production
- Refining
- Bulk chemicals
- Fine chemicals
- Specialty chemicals
- Natural gas
- Power generation
- Pharmaceuticals/Bioprocessing
- Agrochemicals
- Mining
- Chemical/Mechanical Engineering
- Recycling
- Food
- Polymers
- Consultancy, engineering and process development services
- Other (please specify)

Question 2. Comparison to the previous survey (10 years go)

Please put Yes or No to this question and add comments if relevant

- Do you observe significant new challenges and/or considerable changes - improvements in the thermodynamic and transport properties (needs, measurements, calculations) in your company during the last 10 years (since the previous survey)?

Question 3. Limitations in thermodynamics and transport properties: What do you consider as the limitations in thermodynamics and transport properties in addressing your company's challenges?

- In general
- Products – Product Design
- Processes – Process Simulation
- Data measurements and Databanks
- Models incl. both model frameworks and model parameterization
- Process simulation
- Reservoir simulation
- CO2 capture, transportation and storage
- Enhanced oil recovery
- Gas processing
- Energy storage and transport

Question 5. Data: How is the data acquired in your company?

Please put Yes or No or use a scale of importance (1: no importance, 5: top importance)

- Do you feel that there is a lack of data?
- Do you measure your own data?
- Do you think molecular simulation or other predictive models can help in completing the database?

Question 6. Collaboration: Consortia or other collaborative work in thermodynamics and transport properties.

Please put Yes or No or use a scale of importance (1: no importance, 5: top importance).

- Do you participate in consortia?
- If so, in which areas?
- Do you participate in multi-partner projects such as Horizon 2020 in Europe or other similar projects in other parts of the world e.g. NSF and if so, in which areas?
- Is your company willing to sponsor research work that is to be shared with the rest of the thermodynamic community?
- If so, in which areas?
- If not, what are the main reasons for this (e.g. cost, IP & other competitive considerations, lack of interest, trust, etc.)?

Question 7. Benefit: Can you provide examples of achievements in Thermodynamic R&D where you can give an estimate of potential business or avoided risk

Estimated potential business or avoided risk (kEUR) or in qualitative terms

- add as many examples as you wish

Question 8. Areas: What are your ideas and opinions concerning the development in the following areas?

Suggestions:

Try to be concrete, so refer explicitly to elements such as components (CO2, sulfur), models (SAFT), phenomena (gas hydrates), experimental quantities (SLE, speed of sound), standards (CAPE OPEN), algorithms (multiphase flash, speed improvement), conditions (T>500K), applications (heavy oil, reinjection of H2S), procedures (characterization of well fluids), and so on wherever this is possible.

Look at competing or complementary approaches, such as Group Contribution methods versus COSMO-RS. Is there a need for both? Do we have a preference?

Look at the need for standardization versus flexibility. For example, do we want yet another equation of state or should we devote all effort to extending the traditional ones now present in most process simulation programs? And if the latter holds true, which ones would we single out in this stage?

- Physical Data
- Phenomena
- Conditions and environments
- Models
- Algorithms
- Measurements
- Procedures
- Implementation
- Applications
- Process simulation
- Product design
- Standards
- Add your own item(s)

Question 9. Digitalization: Do you see new opportunities for property calculations / predictions using innovations related to the digitalization – big data?

Please consider the term "digitalization" as you understand it including but not limited to electronic commercial or other type of databanks, models availability in program libraries and commercial simulators, development, purchase and use of computational chemistry/molecular simulation tools.

You may also consider technological advances in IT that may be used to advance model-based innovation & engineering, either individually or in combination with each other, like:

Data (Bigger volume, Wider range, Higher quality, More accessible); Computation (More power, Lower cost, More flexibility) and Algorithms (Machine Learning, Artificial Intelligence, Meta-modelling, Data Mining).

- Add you comment here

Question 10. Other thoughts: Do you have any other thoughts on thermodynamics and transport properties that could be relevant to us?

- Add you comment here

Table S3. 10 years after – what has happened. This table, without the right column, was provided to the companies together with the questionnaire and summarizes some of the views of the authors prior to the start of the survey. The right column summarizes the conclusions from the present study.

Suggestion 2010	**Status 2019 as seen by the authors before the survey**	**Result of survey 2020**
Electrolytes – better models needed, need to arrive to same level as non-electrolytes	Many new e-EoS since 2010 Born term appears accepted We are far from the target!	Major challenge (for many important system e-NRTL parameters are not available). Lack of data is also an issue. "There needs to be a critical review/comparison/evaluation on these models, similar to what has been done for non-electrolytic models, non-electrolytic predictive models, etc" Predictive models are needed.
Many classical systems (ammonia, Hg, S, water/CO2, inorganic acids,…) need to be addressed	OK with modelling Not many new measurements	There is a need to develop techniques to measure low vapour pressures of high molar mass molecules. Measurements for more components (including toxic ones) in wider range of conditions.
Phase equilibria **and** other properties (heat of mixing, Cp, derivative properties,…) should be considered with models	Significant work on some derivative properties with many SAFT-type models shows we have challenges Very little with thermal properties has been published	
Transport properties should be addressed much more, better models and theories needed, combined with thermodynamics, field to arrive to same level as equilibrium thermodynamics	Low Pressure gases – major advances made. Now able to calculate all transport properties of selected gases & gas mixtures (incl. Natural gas) to within 1-2%. High pressure & liquids the situation is still unsatisfactory, lots of new 'theories' & models have been proposed, but hardly any tested against a critical set of data.	Interfacial properties are important in some applications. Predictive models for viscosity

	Molecular simulation is used today to predict a broad range of transport and interfacial properties.	
New work on algorithms needed	Not much since Michelsen	Satisfaction on flash calculations and rate-based distillation, but speed and robustness need improvements. Needs on efficient combined chemical and multiphase (reactive) equilibrium algorithms, including electrolytes. Sulfur allotropes and hydration phenomena.
Standards are very important	CAPE-OPEN has not progressed much, interest from operating companies has decreased	
High quality data needed, there are few qualified labs	Still fewer data, most measurements in Asia Trends is worse than 2010, many experiment labs are closing	Data accessibility improved. Quality of the data and many labs closing are major concerns. Service provider having also public funding could be a solution?
Fewer models, towards a unique model?	UNIFAC still very much used No SAFT model is clearly widely accepted vs. Others (maybe PC-SAFT more than others)	Ideally one universal model, but this is possibly utopian. Interest to have relatively few models. Naturally, models available in the commercial simulators are used more.
SAFT – UNIFAC- COSMO-RS all need to be continuously developed	This is indeed happening Significant part of UNIFAC-Dortmund table is available only for UNIFAC consortium	COSMO-RS more well-known and popular compared to 10 years ago.
Better GC models UNIFAC requests: fill the gaps, more oxygenated compounds, comparison with COSMO-RS	More UNIFAC parameters and variations have appeared. No radical changes Increased development of SAFT-based GC models	VTPR more well-known and popular compared to 10 years ago. Multifunctional (pharma & agricultural) components are problematic.
SAFT: Better speed, application to oil, polymers, electrolytes, standards, manage complex	Speed: the same Standards: the same More work on oil and polymers Also electrolytes, but no consensus Still far too many versions and sub-versions and polar, q- versions, etc.	Standardization is an issue. Predictive capabilities should be studied. More attention to the accuracy close to the critical point. Speed should be improved in some simulators.

Need for better education of engineers	An excellent book by Jean-Charles de Hemptinne and co-workers specifically for engineers [3]	Electrolytes, experimental techniques, thermodynamics (depends on the country). Programming and modelling skills are better nowadays. Laboratory skills are worse. Number of courses teaching thermodynamics varies between countries. Training to use simulators.
More effort to make Molecular Simulation known and accepted by industry (not widely used today)	Several editors have decided to increase the journal coverage of molecular simulation (https://pubs.acs.org/doi/pdf/10.1021/acs.jced.5b01054) There are a lot of very successful companies in molecular simulation with success in oil & gas, chemical, pharma industry, etc: Examples: Accelrys, Materials Design, Scienomics, etc. Lots of companies use molecular simulation data as ”pseudo-experimental” data to fit EoS parameters. Computing time is not an issue anymore!	MS considered more useful than 10 years ago. Several companies express lack of knowledge on the full working capacity of MS. MS is considered good for interpolation (not for extrapolation). Experimental verification should be always done. Qualitative screening like solvent screening.
Complicated (multifunctional, hyper-branched, ...) molecules	Some work has been done but far from sufficient (using SAFT, GCA, CPA)	Asphaltene modelling is important. The crude oils are becoming increasingly heavier. Predictive model for SDA needed. Modelling of surfactants and micellar systems.