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Industrial Requirements for Thermodynamic and Transport Properties: 2020

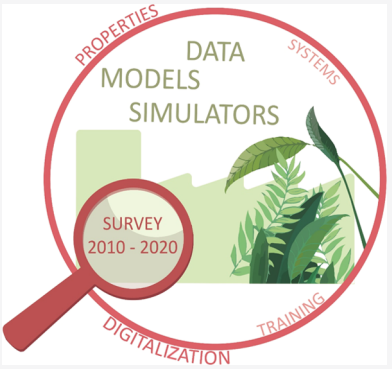
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Cite This: *Ind. Eng. Chem. Res.* 2021, 60, 4987−5013

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ABSTRACT: This paper reports the results of an investigation of industrial requirements for thermodynamic and transport properties carried out during the years 2019−2020. It is a follow-up of a similar investigation performed and published 10 years ago by the Working Party (WP) of Thermodynamics and Transport Properties of European Federation of Chemical Engineering (EFCE).[1] The main goal was to investigate the advances in this area over the past 10 years, to identify the limitations that still exist, and to propose future R&D directions that will address the industrial needs. An updated questionnaire, with two new categories, namely, digitalization and comparison to previous survey/changes over the past 10 years, was sent to a broad number of experts in companies with a diverse activity spectrum, in oil and gas, chemicals, pharmaceuticals/biotechnology, food, chemical/mechanical engineering, consultancy, and power generation, among others, and in software suppliers and contract research laboratories. Very comprehensive answers were received by 37 companies, mostly from Europe (operating globally), but answers were also provided by companies in the USA and Japan. The response rate was about 60%, compared to 47% in the year 2010. The paper is written in such a way that both the majority and minority points of view are presented, and although the discussion is focused on needs and challenges, the benefits of thermodynamics and success stories are also reported. The results of the survey are thematically structured and cover changes, challenges, and further needs for a number of areas of interest such as data, models, systems, properties, and computational aspects (molecular simulation, algorithms and standards, and digitalization). Education and collaboration are discussed and recommendations on the future research activities are also outlined. In addition, a few initiatives, books, and reviews published in the past decade are briefly discussed. It is a long paper and, to provide the reader with a more complete understanding of the survey, many (anonymous) quotations (indicated with "..." and italics) from the industrial colleagues who have participated in the survey are provided. To help disseminate the specific information of interest only to particular industrial sectors, the paper has been written in such a way that the individual sections can also be read independently of each other.



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1. INTRODUCTION

In numerous industrial applications that involve pure components and mixtures, knowledge of thermophysical properties is an essential pre-requisite for optimum design and operation. Not only is it necessary to better characterize compounds used in current industrial applications but also to be in a position to develop more optimal and purpose-specific chemicals by means of multiscale molecular approaches. In particular, data for thermodynamic (including also interfacial) and transport properties play a very important role in process and product design, optimization of processes, sustainable energy usage, and safety assessment in a number of diverse disciplines, such as environmental, chemical, and mechanical engineering, biotechnology, and materials science. This paper reports the results of a survey on industrial needs for thermodynamic and transport properties carried out during 2019−2020. It is a follow-up of a similar investigation published 10 years ago.[1] Both studies are results of initiatives taken by the Working Party (WP) of Thermodynamics and Transport Properties of the European Federation of Chemical Engineering (EFCE). Details of the survey are presented in Section 2 and we will return to it later in this introduction.

We start with a short summary of the state of the art in terms of recent investigations and reviews from petroleum, chemical, food, and pharmaceutical companies as well as software providers, as industrial and academic studies prior to and including 2010 were presented in our previous work.[1] To the best of our knowledge, only a few industrial reviews and books

Received: November 1, 2020
Revised: February 25, 2021
Accepted: February 25, 2021
Published: March 26, 2021



ACS Publications
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https://doi.org/10.1021/acs.iecr.0c05356
Ind. Eng. Chem. Res. 2021, 60, 4987−5013

have been published in the decade 2010−2020, as summarized below.

Following the publication of 2010 survey,[1] our WP launched a symposia series[2] on "Industrial Use of Thermodynamics (IUT)". So far, four symposia were held since 2012 and the fifth one is scheduled as an online event organized by IFP Energies Nouvelles in France in 2021 as part of the ESAT conference. More information on this is presented in Section 1.2.

During the past decade, a number of books have been published,[3−7] dealing with industrial aspects of use and applications of thermodynamics for process and product design as well as for biothermodynamics. Furthermore, Hendriks,[8] Piccione,[9] and Dohrn and co-workers[10,11] have published relevant industrial reviews: the first article focuses on the thermodynamic needs of the petroleum industry, and the second article is from the agrochemical/specialty chemicals point of view, while the two latter articles are recent reviews on high-pressure experimental data and methods to determine phase equilibria.

Finally, Gani and co-workers[12] and Uhlemann et al.[13] discussed in two seminal papers the role of thermodynamics in chemical engineering[12] and in product design and engineering.[13]

A number of more specialized reviews in selected areas of thermodynamic and transport properties have also been published during the past decade, dealing with association models,[14,15] transport properties,[16] viscosity,[17] computational aspects of equations of state,[18] molecular simulation with respect to clathrate hydrates and thermodynamic cycles such as organic Rankine cycle (ORC), heat pump cycles, and refrigeration cycles,[19,20] ionic liquids,[21] liquid biofuels for optimizing feedstock selection, processing, refining/blending, storage/transportation, and combustion,[22] CO_2 capture, transport and storage, and impact of uncertainties on thermophysical properties[23−26] as well as combination of thermodynamic models with artificial intelligence, machine learning, and computer-assisted quantitative structure−property relationships (QSPRs).[42,43] The reader is referred to the above-mentioned reviews for a more in-depth analysis of the literature in different specialized fields.

1.1. Industrial Needs of Thermodynamics as Seen in the PPEPPD Conference Series. One of the most well-known international conferences in applied thermodynamics is PPEPPD (Properties and Phase Equilibria for Product and Process Design), which commenced in 1977 and has been going ever since. In terms of attendance, the original target of these conferences was to have a balanced representation of academic and industrial colleagues. In his review of these conferences up to 2013, O'Connell[27] demonstrated how this balance was initially maintained, but the industrial participation declined significantly since 1989. In that year, there were 58 participants from industry out of 215 attendees compared to the 1980 conference with 101 industrials among 211 participants. The industrial numbers have decreased further from 53 out of 231 participants in 1998 and it was only 14% industrial participation in the 2013 conference.

The decline in industrial participation is not necessarily associated with the decline of interest or the decline of the importance of thermodynamics. External parameters and changes in company strategies as well as other parameters may have played a role.

In his book, O'Connell also gives a summary of some of the industrial focus in PPEPPD. Already in the first conference (1977), there was a talk by Krolikowski-Buck (Union Carbide) who presented an industrial view on the state of the art in phase equilibria, commenting on how new models were always being added in the in-house simulator, but none were ever deleted. At the same 1977 conference, Larson's industrial review[27] noted the absence of models for enthalpic properties and heat capacities, which made him "uneasy". He stressed that strategies for obtaining them are "urgently needed" and we cannot wait for 40 years that took to establish the good database for the petroleum industry.

In the 1980 conference, Nagel (BASF) mentioned that many successful models "allow us to cope with the majority of engineering tasks that confront us", but there are still several challenges, like electrolyte solutions over the entire range of conditions. In the same conference, van den Kraats (Shell) was unsatisfied with the performance of models like NRTL and UNIQUAC for LLE using VLE-based parameters as it creates problems for LLE-based separations, like LL extraction.

Almost 20 years later, in the proceedings published from the 1998 PPEPPD conference, de Swaan Arons states that "the success of thermodynamics in the oil, gas and petrochemical industry seems to have worked as a boomerang. There seems now to be a widespread belief in industry, that each equilibrium, every property, can be calculated or predicted, that the need for experiments has nearly vanished and if this need arises, well, then, computer simulations can take over the task." We will see later in this paper that even though more than 20 years has passed since the 1998 conference, this is not the case, as the industry itself will say. There is still a need for experiments!

1.2. Industrial Needs of Thermodynamics as Seen in the IUT Symposia. As a follow-up on the previous survey, the working party had decided to enhance interaction with industry by starting a symposium series called "IUT" for Industrial Use of Thermodynamics. Four such symposia have been held in the past decade, and each of them included a round-table discussion where industrial partners could freely express their concern regarding the state of their need. In each case, a summary of the discussion has been published in a peer-reviewed journal.

The first IUT in fact carried the name of "InMoTher" (industrial use of molecular thermodynamics) and was held in Lyon on 2012. It gave rise to a special issue of OGST (*Oil Gas Sci. Technol.-Rev.* IFP Energies nouvelles. **2013,** *68,* 187−215). The editorial in this issue (https://doi.org/10.2516/ogst/2013l20) presents some conclusions of the round-table discussion. Some interesting issues are pointed out, for example, the need to adapt the model selection to the process life cycle (screening various options or final design). The virtuous triangle is also defined, where a collective partnership between academia, software providers, and industrial end-users should be encouraged. Finally, the need to also focus on derivative and transport properties was brought up.

The second IUT meeting was part of the ESAT conference in Eindhoven in 2014. The minutes of the round table have been published in Chem. Eng. Res. Des. 92 (2014), p2795−2796. The need to know the fluid behavior in extreme conditions (high pressure and temperature but also high dilution or complex composition) was brought up, either using predictive tools or through adequate measurements. A concern was raised regarding closing labs and regarding the large variety of some models (SAFT): they can only be used in industrial applications if available with a proper parameterization.

https://doi.org/10.1021/acs.iecr.0c05356
Ind. Eng. Chem. Res. 2021, 60, 4987−5013

The next IUT meeting was held in conjunction with another EFCE working party at the Nice ECCE meeting in 2017 (Chem. Eng. Res. Des. 119 (2017), p183−187). In this round table, the difficulties for collaboration across disciplines were investigated. The first criterion for success is the acceptance of the differences (in vocabulary but also in objectives or priorities). The development of multiscale tools was also identified as an important asset.

The last IUT on this date was held in 2019 during the WCEC meeting in Barcelona on data. The focus here was on the link between experimental data and process modeling (Chem. Eng. Res. Des. 137 (2019), pA1−A8). The chain of responsibility from the lab all the way to the simulator end-user was brought up and, again, a thorough understanding of the various levels in the chain was found to be essential for a successful design.

Some common comments that came up in all cases are the importance of an adequate training, both at the degree level and also on the job, and the importance of communication across levels and the key position of the software providers in the transmission chain of innovations to industry.

1.3. The Philosophy behind the Survey and How This Paper Should be Read. Thirty-seven companies have answered the questionnaire used in this survey. Detailed information about the survey (questionnaire, statistics, profile of companies, etc.) is presented in Section 2. However, we believe that it is necessary to provide some information on the motivation and philosophy behind this survey and explain how the paper should be read or, in other words, what the paper is and what it is not.

The survey has been sent to a wide range of companies; about 60% have answered. For every company, the survey was sent to an expert in the area of thermodynamic and transport properties and it was up to them whether they would reply, considering only their own input or whether they would involve a broader number of experts in their companies. Some companies chose the first approach and others chose the second one, but in all cases, we have received from the companies very comprehensive answers on a rather detailed questionnaire. It was thus of paramount importance for us that the opinions of the participating companies are respected in full and that all voices are heard, recorded, and reported, not just the "majority views". As the reader of the paper will see, we use expressions like "the participating companies...", "some companies...", "few companies...", or "a single company..." state(s) depending on the situation. Moreover, whereas, in many cases, we have summarized the main points in our own words, it was clear that several companies expressed strongly held beliefs that we felt that those should be heard (anonymously of course) and, whenever we use statements in quotation marks "...", these are essentially the exact words as reported by the companies themselves.

Another aspect of a survey is how representative it is. Even though 37 is an acceptable number of responses, and very diverse companies (petroleum, chemical, material, food, biotechnology, and pharma sectors, consultancy, simulator vendors, etc.) took part, it still represents a small number. So, all results should be seen with this reservation in mind that we report the observations from 37 companies and not from 300 or 3000. While this cannot be changed, we do plan to present the results in international conferences and other forums, as well as local conferences organized by national chemical engineering societies, where a larger number of companies are present, and hopefully, in this way, to initiate more discussions and investigate the representative character of the current opinions in the years to come.

An additional aspect is that we hope that the results of this survey can be useful to academia, industry, and policymakers. The purpose is to present the "opinion of the industry", illustrate the importance of applied thermodynamics, and identify the aspects of thermodynamics, which are considered the most relevant for industry. Only sparingly do we comment, in the paper, on the views expressed but never with the intention to criticize. In a few selected places, we have added some comments with the purpose of providing some additional/updated information and, in a few cases, our own views. We are certain that both our academic and industrial colleagues (and, naturally, ourselves) will be tempted to comment on many of the expressed statements, for example, "we agree or disagree...", "why do you say this?", or "don't you know the answer here... we have better data... we have better models". We encourage academic and industrial colleagues to indeed ask these questions and get involved in the discussion. In this paper, however, it is the "voice of the industry" that we wish to be heard. For this reason, the personal views of the authors of the paper are limited to a minimum. Still, it is our intention to complement this survey with future opinion papers where more discussions will address all aspects of the survey (data, algorithms, models, etc.). Discussions have started on this within EFCE and we are in the process of preparing material for each targeted audience.

But how many voices does industry have? This brings us to the last issue to consider. As mentioned previously, with this number of diverse companies and interests, opinions do differ, sometimes considerably. However, there is quite a consensus on many topics. We have tried not to favor any specific modeling, theoretical, experimental, methodological, or other approaches, but to present the views as reported in order for the interested reader to consider all views, and decide how to proceed further, e.g., academics wishing to discuss and offer better or novel solutions or industrialists wishing to consider alternative solutions. The interested reader may conclude which of the mentioned approaches may deserve further study or attention in the future, indeed if any at all, or whether we should move in entirely new directions. We hope that this will rekindle the discussion among academic and industrial communities and lead to renewed interest in thermodynamics to face and resolve the challenges ahead.

As a final note, while this paper is mostly about needs and challenges, successes are also reported. As one of the companies states, "always there is lack of data and models about transport and interface properties. There are many limitations, as explained below. But we should not forget how much we can already do. e.g. for relatively simple systems one could perform a design of a distillation column from estimated vapor pressure curves and estimated activity coefficients with a reasonable chance of a successful design, certainly if the engineer builds in a bit of 'fat' in the design. Inclusion of uncertainty should improve the probability of success (by taking mitigating actions to reduce the estimated risk of failure)."

One of the questions asked in the survey was about "benefits of thermodynamics and success stories". We have seen that many of the participating companies were interested to report such stories, in some cases, even quantifying the benefits and, at other times, illustrating the benefits in qualitative terms. We have decided to summarize these answers in Table S1 (Supporting Information).

https://doi.org/10.1021/acs.iecr.0c05356
Ind. Eng. Chem. Res. 2021, 60, 4987−5013

Table 1. Profile of the Companies (See Question 1 in Table S2, Supporting Information)

type of activity	number of answers (yes or >4) (major part of business)[a]	number of answers (2 or 3) (minor part of business)[a]	type of activity	number of answers (yes or >4) (major part of business)[a]	number of answers (2 or 3) (minor part of business)[a]
exploration and production	9	1	pharma	10	6
refining	9	3	agrochemicals	6	2
bulk chemicals	10	6	mining	3	3
fine chemicals	10	5	chemical and mechanical engineering	13	5
specialty chemicals	12	5	recycling	7	4
natural gas	6	6	food	4	5
power	4	6	polymer	10	4
			consultancy (mostly software providers)	16	3

[a]The scale is from 1 to 5, with 1 indicating no importance and 5 indicating top importance.

The rest of the paper is structured as follows. The next section presents the survey, and Section 3 presents the answers on the "changes/challenges since 2010" as seen by the companies (for data, models, and systems including a special section on pharmaceuticals and education). Section 4 presents a broader view of the challenges seen by the companies divided into petrochemicals, process and product simulation, and pharma/biotechnology. The computational aspects discussed in Section 5 include the responses on the questions about molecular simulation, algorithms, and standards as well as digitalization. Section 6 presents the results of the survey for experimental data and models, possibly the two "major" topics of the survey. The discussion about models is extensive and contains several subsections (classical models, advanced models, electrolytes, transport property models, implementation in simulators, etc.). The final section summarizes all other comments the companies wished to share with us beyond the specific questions.

The paper's structure follows somewhat the survey results and, while merging some answers has been undertaken, there are some unavoidable repetitions. The advantage of this approach is that it permits several of the sections and subsections to be read independently of each other. This may be of interest to those who wish to pay extra attention to specific areas of own interest while spending less or no time on others.

2. QUESTIONNAIRE AND THE SURVEY: PROFILE OF THE PARTICIPATING COMPANIES

In 2019, the EFCE WP on Thermodynamics and Transport Properties concluded that the first survey, which is now 10 years old, led to many useful results and conclusions on the industrial needs and had influence on the directions taken by industry and academia. Therefore, it was concluded that it is worth investigating what has happened over the past decade. This led to the decision of a follow-up survey, aiming at a broader audience and also using an updated questionnaire.

The questionnaire prepared by the WP is shown in its complete form in Table S2 (Supporting Information), but the questions are summarized below.

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

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

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

Question 4. R&D in thermodynamic and transport properties.

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

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

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?

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

Question 9. Digitalization.

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

Many of the questions are identical/similar to those used 10 years ago, but new questions are also included (on digitalization, data, and comparisons to previous survey/changes over the past 10 years), raising the number of questions to 10 (from 7 in 2010).

Using this more comprehensive questionnaire, we received 37 answers mostly from European companies (many of them globally operating) but also from companies in the USA and Japan. The response rate was about 60% compared to 47% in 2010 (where 28 replies were received).

The profile of the companies is shown in Table 1, illustrating significant diversity. The profile table is compiled from the answers to question 1 (concerning the main businesses). A significant number of companies operate in several areas and this explains why the sum of the answers in Table 1 is far larger than the number of companies. More than 10 companies have indicated activities in bulk, fine, specialty chemicals, and pharmaceuticals, as well as polymers. Thirteen companies indicated direct interest in chemical/mechanical engineering and 16 companies have consultancy as the main or one of the main areas.

At this stage, we should emphasize that the selection of companies was mostly based on authors' networks and existing collaboration. Although the starting point was the list of companies who replied to the survey 10 years ago, more companies were contacted. We have contacted colleagues in companies in our network. In our opinion, this approach ensured that we get as many replies as possible. With our limited

https://doi.org/10.1021/acs.iecr.0c05356
Ind. Eng. Chem. Res. 2021, 60, 4987−5013

resources, it was not possible to reach out to all the companies that operate in this landscape. However, we would like to encourage companies, which would like to contribute to the ongoing discussions and have not been contacted within this survey to contact one of us in order for their opinions to be incorporated in a later survey or in the opinion papers that will follow this paper.

Based on the answers to question 4, Table 2 presents how the R&D in thermodynamic and transport properties is organized in the participating companies. It can be seen that 70% (23 out of the 33 companies who have answered to this question) have their own research labs, but only 32% (10/31) have a research subsidiary. The majority of the companies (12/24) have 2 or fewer senior experts who spend 50% or more of their time on tasks related to properties and 17/22 companies have 5 or fewer trained lab technicians.

Table 2. R&D Labs in Companies (See Question 4 in Table S2, Supporting Information)

topic	yes	no	comments
R&D labs	23	10	
research subsidiary	10	21	
subcontract research	11	9	partly: 12
			subcontract percentage
			0−10%: 15 companies
			10−30%: 4 companies
			30−50%: 3 companies
			>50: 8 companies

Interesting are also the results related to subcontracting research, as also shown in Table 2, with a somewhat divided picture, where 11 companies subcontract research and 9 companies say clearly that they do not. Twelve companies responded that they subcontract little or partly. These results are quantified based on the last subquestion of question 4, where 8/27 companies subcontract over 50%, whereas 56% (15/27) subcontract 10% or less.

Finally, it is relevant to report the results on question 6 on collaboration and sponsoring research work. A large number of companies (28/33) clearly mention that they participate in consortia with other companies, often led by universities or other corporations. Some of the consortia mentioned are UNIFAC Consortium (UNIFAC stands for UNIQUAC Functional-group Activity Coefficients), CERE (Center for Energy Resources Engineering), KT-Consortium, DIPPR (Design Institute for Physical Properties), University of Calgary, ISPT (Dutch Institute), Pharma Alliances (SbP, ADDoPT), EleTher (Electrolyte Thermodynamic Modeling Joint Industry Project), and EGAS (PhysProps taskforce in EGAS; European Group of AspenTech Software users). Some companies participate in several consortia. Thus, the remaining answers should be seen in the light of companies who are already engaged in several collaborations with universities and sometimes with other companies.

The areas of relevance to the participating companies are naturally within thermodynamic and transport property estimations and measurements. More specifically, they include also electrolyte thermodynamics, predictive models like group-contribution models and VTPR (volume-translated Peng−Robinson), (computer-aided) process modeling and optimization (as well as process intensification and continuous manufacturing), diverse thermophysical properties (e.g., vapor pressures, heats of vaporization, etc.), corrosion, reservoir simulation, CCUS (CO_2 capture, utilization, and storage), bio-based materials, and pharmaceuticals.

Some companies mention also that with increasing visibility or market, the expertise is an additional reason for participating in consortia as well as for influencing developments in software tools for process design.

In relation to the question "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?", a large number of companies (13) gave a negative answer, while 3 companies mentioned that they can consider this if relevant/suitable projects appear. A few companies mentioned that they tried a number of times to be a partner in a consortium of academics and industrialists; however, the proposals were never funded and questioned whether the importance of applied thermodynamics is always grasped by the policymakers and decision-makers.

Thirteen companies replied in clearly positive terms that they participate or have participated in multipartner projects (although four clearly mention local country projects, e.g., in the USA or France). The topics in these projects are quite diverse and include process development, physical property data modeling and engineering applications, CO_2, hydrates, energy and water resources, critical materials, bioprocessing, nanopore thermodynamics, and reservoir simulation.

In relation to the question "is your company willing to sponsor research work that is to be shared with the rest of the thermodynamic community?", the answers are again rather divided, with clear yes from 11 companies and clear no from 11 companies, while 3 reply possibly no and 5 reply yes/no depending on the area benefits, business value, and possible confidentiality conflicts (see later). The areas where the companies are willing to sponsor publicly available research include physical property modeling and measurements (including model developments), predictive models like UNIFAC, electrolytes, properties for solid mixtures (and polymorphism), crude oils and natural gas including reservoir fluid properties, software standards, and optimization of numerical routines, i.e., a very diverse range of topics. The predictive models and electrolytes are the areas most often mentioned.

As several companies replied negatively to this question and several of them rather emphatically so, it is relevant to analyze the reasons for this. For almost all companies, IPR (intellectual property right) considerations (12 answers) and cost considerations (9 answers) are the most important reasons for this. It is especially the former, which is considered the most serious problem. As one company expresses it, "most of our products are in very competitive areas, with huge production volumes and reduced margins". Any new data can make a difference. Process "owners" are particularly careful about any information sharing. Similar comments were expressed by other companies, as well especially within specialty chemicals.

Legal aspects are often cited. For instance, a company from the pharma sector mentions that "the resource (time & effort) required to set up a legal agreement for a Pharma alliance (expect time frames of 6-12 months) requires a high quality output to give us any return on investment. In some cases (projects < 1 year), the time required to set up an agreement can exceed the time for doing the work itself".

https://doi.org/10.1021/acs.iecr.0c05356
Ind. Eng. Chem. Res. 2021, 60, 4987−5013

There are, however, further issues. For some companies, physical properties are important in-house knowledge and such collaboration may compete with their own R&D activities.

In some cases, the lack of interest of the top management and difficulties to make them realize how thermodynamics could help in the daily work is cited. Furthermore, whether there is a business value in such collaborations is considered by some an issue. The property groups in several companies include a rather small number of experts with a very large scope of work that includes not just thermodynamics but also CFD (computational fluid dynamics), thermal engineering, mass transfer, and kinetics, among others.

The above-mentioned multiple interests combined with the associated cost can represent a significant problem in some industrial sectors, even the ones that are considered quite profitable. As one company in the pharma sector expresses it, "whilst Pharma companies on the whole may generate very significant profits, the engineering groups within those companies are not seeing many of those profits at our ends being invested. (At least that is the case for small molecules process engineering − this may well be different in the cell & gene and biopharm PE groups). Investment focuses more on the MedChem sections where new chemical entities are identified. As far as the budget of our Process Engineering department is concerned, money spent on capability/non-project related items are rare."

Within the pharmaceutical sectors, overlap with other industry sectors is limited due to different substances and processes used (leading to different models) and, thus, some companies in the pharma area focus on pharmaceutical alliances where greater synergies can be found and bilateral collaborations with universities rather than multilateral consortia with broad and diverse interests.

There exists a "natural" conflict in sharing the information as a result of the business case-driven attitude of industry: the business case drives the interest; hence, the desire to embark on a physical property study may, at the same time, be the restriction to share in order to maintain the competitive advantage.

Moreover, the decision in this kind of matters lays typically at the level of the budget holder and the appreciation of the need as perceived by the expert and his budget holder can be very different.

3. CHALLENGES OR CHANGES SINCE 2010 (PREVIOUS SURVEY)

Although less than half of the companies participated in the 2010 survey, almost all companies replied to question 2, whether they observe significant new challenges and/or changes, including improvements, in thermodynamic/transport properties over the past decade. All the participating companies were given a copy of the 2010 paper as well as a short summary of some opinions from the authors of the paper (shown in Table S3, Supporting Information).

The response to this question was rather extensive in both content and diversity and we provide below the most important comments divided into some characteristic categories.

3.1. Experimental Data and Methods. Both optimism and concerns are reported. Some consider that it is now (far) easier to find and access data than it was 10 years ago, but as the volume of data production has gone up, the quality of the data has, in some cases, diminished. Many participating companies state that there is clearly less investment in experimental measurements and increased use of molecular simulations, which require experimental verification. Many also mention that the number of experimental groups has declined. In our view, the companies are possibly referring to the measurements and groups in Europe and North America, as in Asia, the volume of measurements and experimental groups is not much different compared to 10 years ago.

There is an increased need for more measurements and development of new techniques, e.g., one company commented that the measurement techniques for the vapor pressure of high-molecular compounds of extremely low volatility (excluding polymers) have not evolved much (Knudsen, static, and headspace), but there is renewed interest from clients.

In addition, for certain classes of mixtures of importance to industry, there is still lack of data as some systems are not considered "exciting" enough to attract government funding. Governments assume that industry should fund property measurements that are always applied or chemicals that are too toxic to be handled in academic laboratories. Thus, while plenty of measurements have been made for vapor pressures and heats of vaporization, similar measurements are needed for more compounds and for a wider range of conditions including high-pressure and high-temperature phase equilibrium data of nonideal mixtures, data in dilute conditions, cryogenic conditions, and reactive multiphase systems.

Finally, NIST is praised for continuing the effort in collecting and publishing a large set of thermodynamic data, collaborating with commercial software companies such as AspenTech to make these data accessible to the process industry, and finally, for developing a standardized protocol for publishing data, called "Good Reporting Practice for Physical Property Measurements" as an IUPAC project.[28] Other organizations (Dechema and DDBST) offer similar services.

3.2. Models in General Including Standards and Implementation. The predictive models mentioned explicitly are UNIFAC (GC models in general), cubic equations of state especially in the form of the VTPR (PR using an EoS/G^E mixing rule), SAFT especially PC-SAFT, and COSMO-RS (see the books[3−6,41] for the references for these models). All of them are still considered important and highly useful in engineering practice, with VTPR and COSMO-RS appearing more well known and popular compared to 10 years ago. There is still interest in having a relatively few models, but the survey participants acknowledge that all four above-mentioned "model directions" (UNIFAC, EoS/G^E models like VTPR, SAFT, and COSMO-RS) have their role and applications. Models available in commercial simulators are used more these days and it is positive that VTPR is now available in simulators, as well as some high-precision equations of state, e.g., GERG2008. A number of companies say that implementation of PC-SAFT remains a challenge due to standardization issues and that its predictive ability should be further assessed. A comparison of models may be useful in some cases, especially in relation to their predictive ability and for "new" molecules. Benchmarking techniques, to identify promising new models, must be developed so that we are able to focus on good models for future applications. An effort by Jaubert and co-workers at Universite de Lorraine, France (EFCE WP TTP Meeting, 15th February 2019, Frankfurt am Main, Frankfurt), in establishing a database for model comparison may be useful in this direction,[40] as also mentioned by some of the companies.

In the case of polymers, electrolytes, and complex reactive systems, there are still many challenges for the available models

https://doi.org/10.1021/acs.iecr.0c05356
Ind. Eng. Chem. Res. 2021, 60, 4987−5013

(like polymer or electrolyte versions of NRTL), especially when no experimental data are available in the literature. These issues are discussed further in the paper (in Sections 4 and 6) based on the survey's comments.

3.3. Fluids and Mixtures: From Hydrocarbons and Inorganics to Polymers and Electrolytes. The companies interested in mixtures of hydrocarbons (sometimes in the presence of polar compounds) are overall satisfied with existing models and some mention that the requirement for accuracy is approximately unchanged compared to 2010. Request for new types of models has not been made strongly, except for GERG-2008 for gas applications and CPA approach (cubic + association) as an engineering tool for addition of aqueous components to reservoir models that can serve as an alternative to using cubic EoS with the Huron−Vidal mixing rule. Understanding and improving asphaltene modeling as well as the effect of capillary forces/properties in confinement and adsorption remain of significant importance.

Many companies mention that a much broader class of fluids and materials beyond hydrocarbons is of increased interest (including oxygenates, ionic systems/electrolytes, and complex polymers). For these systems, VLE, LLE, SLE, and adsorption are often important and, thus, phase behavior is more complex.

There is not a complete consensus among the participating companies, where we stand with the modeling of these more complex compounds in some cases. Some mention that we have improved our understanding of the behavior of mixtures containing oxygenates (present in renewable feedstocks that are replacing fossil fuels), while others consider this to remain challenging (including the decomposition and conversion products of the various bio-feedstocks).

An important issue, which is quite old but is still an important challenge, is the accurate prediction of ternary (and higher) phase equilibrium behavior based on binary data. It appears that current process simulators extensively apply thermodynamic models, which predict physical properties utilizing binary parameters as well as pure-component properties. "However, it is well-known that the approach has some limitations especially in application to mixtures containing supercritical fluid, polar components and non-polar components simultaneously. Currently some tentative cures are applied like the adjustment of binary parameters to make simulation match experimental data for ternary (or higher). A breakthrough in thermodynamic models for accurate and a priori prediction of ternary (and higher) phase equilibrium could have impact in petrochemical and chemical industries."

A large number of companies agree that modeling of electrolyte systems remains a major challenge, both from a fundamental point of view and from a more "practical" point of view (e.g., many parameters are not available for important systems in e-NRTL).

These are summarized in some of the statements from the participating companies:

> "Electrolytes are more prominent in processes, possibly due to the expansion of bioprocessing. The electrolyte models are more complex than the non-electrolyte ones, and much more difficult to use for practicing chemical engineers. One perceives a lack of standardization when it comes to using these models. There is a need for a critical review/comparison/evaluation on these models, similar to what has been done for non-electrolytic models, non-electrolytic predictive models, etc."

> "Lack of data to fit the parameters of the e-NRTL model, which is used systematically for electrolyte systems at our company. For our systems, measurements are difficult due to radioactivity and/or toxicity of some compounds."

Also, the survey participants indicate the need for higher accuracy puts more emphasis on minor impurities. Often these components cannot be isolated so that we can thermodynamically characterize them by experimental means; hence, accurate predictive models for multifunctional molecules become more important.

Finally, a number of companies see new and emerging challenges that require better data and models related to "novel" applications like:

- Electronics materials (lithium salts and rare earths).
- New hydrofluorocarbon refrigerants.
- Estimating properties of specialty chemicals and pharmaceutical active pharmaceutical ingredients (APIs), especially compounds containing halogens and group 1 and 2 metals.
- Improved knowledge of the chemical and physical basis of corrosion to enable more accurate prediction of corrosion potential and rates of corrosion.
- Increased application ranges challenge existing thermodynamic methods, e.g., heavier hydrocarbon feeds in hydrogen plants lead to issues with the dew point calculation.
- New areas related to sulfur thermodynamics.

3.4. Pharmaceuticals and Agrochemicals. As mentioned in the previous section, many surveyed companies focus on pharmaceuticals and other complex compounds, like agrochemicals. For a large number of these compounds, numerous challenges still exist, such as lack of experimental data and lack of estimation methods. In many applications, solids are involved and the properties of solid mixtures (including solubility prediction) are more difficult to predict. The science here is clearly less mature than for fluids. Some companies face new challenges in the development of new processes for bio-based products, which include weak electrolytes, solids, crystallization, and solubilities.

One company provided the following detailed comment: "TOP 200 medicines [https://njardarson.lab.arizona.edu/content/top-pharmaceuticals-poster]: vast majority still consists of "small molecules" (vs. cell & gene therapies and Biopharmaceuticals), however the so-called small molecules get increasingly large, complex & more multifunctional. An internal survey that we conducted >10 years ago showed that for the APIs from the current portfolio at the time, only one molecule could be incremented by UNIFAC. Similar evaluations for other group contribution methods such as g-SAFT, SAFT-gamma-Mie, Pharma Mod. UNIFAC that we conducted over the last 10 years showed even worse results - we found that none of our APIs could be fully incremented. With the inaccuracy of those models being strongly linked to the percentage of groups that cannot be described, with the percentage of groups within the molecules that cannot be described ranging from 20% at best up to 70%, and with the rate of group parameters being generated per year, we are pessimistic in how much predictive GC methods will become more applicable for dissolved compounds over the next 10−20 years."

It seems that several pharmaceutical companies have a similar issue. Here is what another company writes: "Our needs probably remain the same as from 10 years ago. Our processes

https://doi.org/10.1021/acs.iecr.0c05356
Ind. Eng. Chem. Res. 2021, 60, 4987−5013

usually consist of a bespoke complex molecule (either dissolved or in suspension) in a solvent system. Physical property information (NRTL interaction parameters and/or UNIFAC groups) is easily available for the solvents, but never available for the complex molecules. Group contribution methods do not generally provide sufficient coverage of the structures in question.

We would really like to model the solubility of complex structures including the formation of salts, hydrates and solvents, but I appreciate this is a hard problem."

3.5. Special Comments. Some companies see educational changes as something that is important and they have commented on both positive and negative developments, as they see them. In their own words, "the university curriculum includes a lot more programming, so the new starters are much more versatile in modelling. However, at the same time the experimental skills have decreased, partially due to a priority shift but also due to lack of laboratory space, so we find the time we spent in the past to train up starters in modelling, we are spending now in training starters laboratory skills."

"In-depth expertise in thermodynamics appears to be still strong in central and Southern Europe whilst this skill becomes more sparse in UK universities. (...). Therefore, many UK Process engineers lack experience, e.g. they do not recognize when a TXY or an activity coefficient plot "looks wrong". Students are (only) capable to generate activity coefficient models etc. using complex and costly software however they are overwhelmed when they would have to do so with that software not being available, e.g. if they had to do it in Excel or on a piece of paper. On the positive side, the absence of thermodynamic content during their curricula means that actually some of the new starters are very eager/curious to learn, as they would not be exposed to many thermodynamic contents during university however they are finding the contents hugely relevant for their work at our company."

Some companies stress the following uncertainty propagation issues: "the inclusion of model adequacy & parameter uncertainty in thermodynamics could potentially have a major impact on its application in various fields ranging from process to product design" and "the adoption of novel methods is hampered by a number of factors, such as clear proof of improvement over existing well-established methods, (lack of) parameterization, and lack of clarity about preferred version of novel method to be used".

Finally, some companies stress the importance of interfacial properties where more work is needed for both understanding and modeling as well as nonequilibrium thermodynamics, where a better understanding can lead to improvement in process efficiency. The use of CFD, and numerical simulation in general, as a tool for process development and troubleshooting has been also mentioned. In this case, there is a need for implementation of more general models and databanks compared to the relatively basic thermodynamics and material models currently used in customer projects.

In such a broad survey, we also meet more traditional voices, e.g., "no, the needs for thermodynamic calculations of common mixtures have not changed significantly over the last decade. The use of tabulated excess properties is essential, and these are typically found in literature. The alternative of applying a full-flung thermodynamic model (EoS) is not always appealing – as the model parameters present in the commercial simulator are only as sensible as the experimental data used for the estimation."

4. BROAD ANALYSIS OF THE INDUSTRIAL CHALLENGES

In addition to what was stated in Section 3, the companies have reported a number of limitations with respect to thermophysical properties (data and models), which we present here in some representative categories.

4.1. Related to the Application Area. *4.1.1. Upstream Petroleum-Related Applications.* For applications within reservoir simulation, gas processing, and enhanced oil recovery (EOR), which by many can be considered as some of the most mature areas of thermodynamic applications, it appears that there are still challenges, namely, lack of experimental data for MEG (monoethylene glycol) processes, H_2S scavengers (and associated chemical equilibria), and mercury and acid gas removal units. There is a need for high-pressure phase equilibrium, density, and enthalpy data as well as data on mineral reactivity (both on thermodynamic and kinetic basis) including metastable equilibria.

Asphaltene models, which rely on minimal data (i.e., most models are overtuned), are also important. Moreover, the surveyed participants also mentioned that accurate prediction of fluid-liquid phase equilibrium for mixtures including asphaltene and hydrogen is crucial, as in the petroleum industry, usage of heavy oil has been an important subject for a long time. It is stated that "recently Solvent de-asphalter (SDA) has been attracting attention by refineries especially in emerging countries, because low initial investment required. However, we don't have yet a reliable and established method to predict the equilibria at the extractor. Even though, a lot of "semi-empirical" approaches have been published, each method needs to be validated even when the type of the crude oil changes. A technical breakthrough for establishing definite, reliable and accurate prediction method could promote usage of SDA and eventually that of heavy oils."

Another important topic is the characterization of heavy oils. As one company writes that "if we persist with the approach of taking a simulated distillation (ASTM D2887 or similar) and characterizing the oil as a series of pseudo components (petro fractions), then we should use additional laboratory measurements and different estimation techniques for the prediction of the basic thermo-physical and transport properties of the pseudo components – techniques more appropriate for the higher naphthene and aromatic content of these oils.

Unfortunately, there are not a lot of measured thermophysical property data for the components with multiple naphthenic, aromatic and naphteno-aromatic ring structures that we know exist in heavy oils. Our previous work on property prediction based on molecular sub-groups and bonds shows promise and additional regression of sub-group and bond contributions from the body of existing measured data should be continued. We may be able to improve the reliability of solvent deasphalting equilibrium calculations by using the surrogate component approach."

Better understanding of phase behavior in porous media is also sought with questions whether properties can be measured for these systems and whether they can be related to models.

4.1.2. Downstream Processing. Another important topic related to the detailed design of gas processing units or petrochemical plants is the accurate prediction of density and compressibility (bulk modulus) for supercritical fluid and liquid mixture of hydrocarbons. This is important for hydrodynamic calculation including selecting and sizing of pumps, tubing, and

https://doi.org/10.1021/acs.iecr.0c05356
Ind. Eng. Chem. Res. 2021, 60, 4987–5013

plot planes. One company mentioned that "current methods have significant errors which force engineers to set a design margin. Increase in accuracy and reliability of prediction allows EPC firms to reduce the margin, so that the designs become competitive against those of their competitors."

Treatment of trace elements (mercury, sulfur compounds, arsenic, etc.) is important in improving the dehydration performance and needs better VLLE data and models. However, due to the safety implications of working with mercury, companies understand that the gaps in models and data for mercury speciation might be difficult to fill.

Moreover, more multicomponent data are needed to verify models (e.g., hydrate inhibitors, alkanolamines, reservoir fluids, etc.). It was mentioned that GPA (Gas Processors Association) does a great job with this, but the number of laboratories that can do this type of work is declining. Additionally, having plant data to verify simulation results would be very beneficial. Of course, we are talking about the performance of the integrated model, which depends on many assumptions, like steady-state operation, the models for the unit operations, and the certainty of the input variables like process conditions, and hence on many more parameters than just the physical property model. The latter should be ideally based on well-conditioned measurements and not tuned on plant data.

Finally, the requirements related to the maximum amount of impurities are increasing. The accurate thermodynamic models must be able to deal even with complex phase behavior (solids + hydrates). There is also a need for practical, industry-oriented models for surfactants and micellar systems. The same is true of corrosion inhibition used by various industries.

As mentioned in the survey, speed and robustness of calculations are important. Many of the publications, according to the companies, discuss how much improvement their method offers without providing details of the algorithm. These algorithms can be difficult to reproduce due to missing information and hidden coding shortcuts (both for reservoir simulation and for EOR).

Somewhat beyond just phase equilibria, the companies mention as challenges the transport properties of microstructured fluids and the development of (reasonably) fast and accurate reactive transport models. Some companies state that thermal and transport properties are connected to the volumetric behavior and, because the properties of petroleum fractions (cut) are not physically characterized, the volumetric behavior becomes less reliable.

For CCUS (CO_2 capture, utilization, and storage) applications, lack of experimental data including data on reactions among impurities in CO_2 environments, lack of data on reactions in storage environments (reactions with minerals), and insufficient understanding of corrosion in transportation are three of major issues mentioned in the survey. It is also noted that for specific technologies, the data needed are available, for example, for rate-based absorption. The high-pressure CO_2 modeling and the accuracy at the critical point are challenges as well as the lack of accurate models in process simulators.

4.1.3. Energy Storage and Transport. For energy storage and transport, it is felt that given the importance of thermodynamics for a robust techno-economic assessment of new technologies in the area, the field would benefit tremendously from standardization and guidelines on how to perform the thermodynamic part so that the conclusions are drawn on the same basis. Although such analyses require much more than thermodynamics, the latter can help understand how the concepts of entropy and exergy might be helpful. The role of these two thermodynamic quantities is not always entirely clear or appreciated.

Insufficient experimental data and models have been noted by the survey participants for the supply chain in the manufacture of lithium-ion (and other, more exploratory) batteries, including production of lithium, recycling of batteries, and production and recycling of rare-earth elements. Furthermore, it was noted that the physicochemical parameters of many carbohydrates are not sufficiently studied in the thermodynamic literature.

Finally, electrification leads to additional requirements with respect to new materials for electricity storage, i.e., batteries or chemicals (including H_2). Sophisticated property models are needed for these systems, not only for process design but also particularly for (product) design of those storage materials.

4.1.4. Pharma and Biotechnology. A significant number of companies within the pharmaceuticals and bio-business have responded to the questionnaire and this permitted to obtain some insight into the challenges they see with respect to thermodynamic and transport properties. The input we receive is that the use of thermodynamics in the pharma and bio-industries is still not as mature as it is in the (petro)chemical companies. In their own words, "we deal with complex multicomponent mixtures (including water, organic solvents, and dissolved solids including carbohydrates, dissolved gases especially in aqueous solutions of carbohydrates, ionic species, and macromolecules like proteins, enzymes, and catalysts)".

Particularly for the pharma business, it is noted that there are insufficient descriptions of solids, both theoretically and practically. This includes both polymorphism and bulk behavior, e.g., flowability. Moreover, there is insufficient incorporation of chemical properties/descriptors in thermo/property tools and crystallization modeling remains very difficult and requires parameterization, which is difficult to carry out. Several properties of solids and particles are mentioned (some beyond thermodynamics) like phase behavior of solids based on the crystal type, flowability, sticking, etc. Of interest is also to predict solubility in dynamic conditions (crystallization and precipitation).

Here is how the challenges are described in a more detailed form by one of the companies in the pharma/biotechnology sector: "Food and biological systems are generally multicomponent mixtures (including water, organic solvents, dissolved solids, dissolved gases, ionic species, and macromolecules). For building developmental models of such complex media (that can also contain living organisms), it is necessary to describe physical constraints, physiological reactions, their interactions and their responses to the environment. A robust modeling of any living system (microbial metabolism up any evolved living complex organism) must include chemical elements conservation principles, via stoichiometric approaches, and link this mass balance approach to energy conservation laws, i.e. to the first principle of thermodynamics and to the constraints imposed by the second law.

The characterization of the equilibrium properties of food and biological systems requires a deep understanding of the interactions between the molecules, especially the hydration of the species in the presence of several phases of different natures (liquid, gaseous and solid).

The limitations to apply thermodynamic modelling in the company are the lack of pharmaceuticals in the process simulator currently available in company, as well as the necessary

https://doi.org/10.1021/acs.iecr.0c05356
Ind. Eng. Chem. Res. 2021, 60, 4987−5013

experimental data needed for checking a potential candidate substance in a process simulator."

Moreover, the link to simulation is also commented on by survey participants: "We have no plant simulations for our new chemical entities (this sounds shocking to process engineers from other industry sectors than in the Pharmaceutical Industry). It is not part of the critical R&D deliverables to deliver a verified plant simulation. This may change in the future as more process simulators now include pharma-relevant operations, also more colleagues work in modelling, this may become a low hanging fruit to achieve implementation over the next 10 years."

Also, as a positive tone for the future, "I would expect the BioTech/BioPharm/C&G Therapy sectors to start getting more involved in modelling over the next 10 years. At this stage, I perceive them to be at a more basic level of getting a grip on their processes, with little empirical let alone predictive models being available or implemented. I expect that to increase with the increased knowledge of these processes and the need to scale-up processes to manufacturing scale."

4.2. Process Simulation Challenges. *4.2.1. Application Areas.* In terms of applications, a very large number of systems are mentioned, but we certainly see a big focus on data and modeling of electrolytes. Examples mentioned are as follows:

- The description of different phase equilibria of electrolyte solutions using a single set of binary interaction parameters.
- Combined prediction of phase and chemical equilibria and predictions in the absence of experimental data.
- Different hydrate forms of organic salts.
- Crystallization of electrolytes like Na_2CO_3 and $KHCO_3$ from mixed salt solution in concentrated conditions.
- Corrosion due to electrolytes in bioprocesses and polyelectrolytes.

Another important focus concerns complex compounds and mixtures, for example:

- Biological molecules, pharmaceuticals, and agrochemicals.
- Models for molecules with different functional groups close to each other like acid and hydroxyl groups.
- Polymer systems (like LDPE, low-density polyethylene, with comonomers).
- Combination of vapor-phase association and cubic EOS.
- Group contribution methods for molecules with heteroatoms.
- Handling of solids in unit operations, reactive systems, and mixed solvents (organic/aqueous).
- Solids in the gas phase like from the CO_2−amine (NH_3 or methylamines)−H_2O systems or in systems with amines and alcohols.

There is a need to populate the databases for chemical reaction rates (mentioned, strictly speaking, not within the thermodynamic area), including chemical equilibrium constants or Gibbs energy change of reaction, as well as provide predictive models for reaction kinetics. Good models for surface tension and transport properties (viscosity, diffusion, and thermal conductivity) are still needed, especially for polymer−solvent systems. It has been noted that models and data for high-pressure transport properties of mixtures comprising components different from hydrocarbons are not available.

Many companies rely more on the implementations made by software providers (of commercial simulators), leaving in some cases in-house simulators as a fall-back. It was noted that "flowsheeting is finally becoming more of a standard in the pharmaceutical industry. Software companies are paying a lot of attention to the need of the pharmaceutical industry as we are perceived as a growth market for them. Crystallization process modelling & process optimization in process simulators becoming more standard is something we see happening (it should be happening already to a much higher extent)."

4.2.2. Models. In terms of models, companies ideally wish for a single universal model for all/many applications, but there is understanding that this is possibly utopian. The second major wish is the need for predictive models validated on extensive experimental databases and not only on just a few available experimental data points. Equally important is the inclusion of uncertainty analysis in model calculations.

Ideally, one should aim to take advantage of all available data that include not only pure components and mixtures but encompass all available measured properties. Computational aspects of models (including speed) are also mentioned, especially if they are to be used in process simulators or CFD software. It is also relevant to have a priori prediction techniques with rigorous uncertainty analysis so that decisions can be made related to experimental design and process and product design based on quantifiable confidence levels.

Cubic EoS is the workhorse in many petroleum applications, especially for speed and simplicity reasons, but there are several issues that are unresolved, not only the treatment of glycols and electrolytes, as mentioned above, but also extrapolation to lower temperatures. Moreover, simultaneous correlation of critical transition (minimum miscibility pressure, MMP) and volumetric properties remain challenging with the usual cubic EoS. Here, some companies mentioned that PC-SAFT provides better compressibility but that the critical point correlation is a problem. In general, thermodynamic models for use in petroleum applications should deliver accurate and reliable results even very close to the critical point. Thus, a crucial aspect for novel models like PC-SAFT is the performance at the critical point as well as its ability to characterize oil and gas to facilitate their subsequent use in process simulations.

The several versions of SAFT have created confusion. It may indeed be true, as other companies indicate that "there has been a proliferation of many variants of essentially the same models (e.g. SAFT) with less than complete understanding of their relative advantages and disadvantages. In fact, one is often left with the suspicion that differences between these variants are due more to the quality of implementation (particularly regarding the estimation of the parameters and the solution of the phase equilibrium problems) than to differences in the underlying theory."

Other modeling challenges noted by the participants are numerous. For instance, for phase equilibrium calculations, inclusion of aqueous phases with electrolytes is still a challenge (sometimes not done consistently in some in-house software). Nonetheless, it is also stated that models like CPA and SRK/PR with Huron−Vidal mixing rules provide acceptable results in many situations, but sometimes, the predictability is poor and tuning may be needed for more complex systems.

4.2.3. Data and Parameterization. Several companies noted many additional challenges associated with process simulation linked, although not always directly, to the availability and quality of data and models. Many are related to the interfaces and other capabilities/limitations of process simulators as well as speed and reliability of calculations. We have chosen some of the

https://doi.org/10.1021/acs.iecr.0c05356
Ind. Eng. Chem. Res. 2021, 60, 4987−5013

more characteristic statements, which are cited here (more or less repeated by several companies):

> "Often properties for our specific molecules/mixtures have not been determined (or are not available in open literature) and therefore easy to access, affordable, and quick service providers are required to measure the missing properties. Maybe on EU level, more public money to partially fund the operations of the service providers are required? Not universities, but rather commercially operated service providers."

> "Process simulator contains a lot of options and parameters and probably so much that it becomes impossible to be sure to make the good choice. In the scientific literature there are few examples describing the general methodology applied for the parametrization of the model and the comparison between several options is never made."

There is often lack of data, as mentioned. "For the development of new processes we have potentially to deal with "new" components, "new" component mixtures, and "new" phase behaviour. The challenge is to characterize and parametrize the pure and binary model parameters from potentially scarce or no experimental data." Maybe, thermodynamic descriptors can help in some cases, e.g., for solvent screening/selection. Companies emphasize the need for computer-aided formulation design, being actually a huge opportunity, but comment that "the framework of CAPD (Computer-Aided Product Design) methods frequently is based on strict procedures, making use of databanks for data input, estimation methods for properties and non-fuzzy decisions on specifications. One could envision a better implementation of the methods by a more open 'architecture', e.g. by experimental provision of data instead of databanks, and/or inclusion of uncertainty considerations. For sure, validation of the developed methods is key, and unfortunately rather limited in literature."

"Physical properties for simulation (for design, optimization, debottlenecking) of separations based on difference in volatility like distillation, flashing, stripping etc., are rather well established. Yet, the simulation of purification to remove trace level of contaminants remains a challenge, due to inaccuracy of the thermodynamic models at near-infinite dilution as well as the inappropriateness of the unit operation models at those conditions.

The properties for other separation methods are far less established, even for extraction: accurate description of LLE is notoriously challenging for g^E models.

Another big challenge remains in the prediction of crystallization (melting) point of a given compound. Accuracy of the prediction of melting point and heat of fusion are even below the level required for a decent preliminary screening."

4.2.4. Simulation Platform. "Virtuous cycle by learning from previous studies and feedback from industrial plant is mandatory in the development and deployment of process simulation tools. Process engineering software that performs rigorous balanced mass and energy calculations for:

- Steady-state processes modeling.
- Modelling of equilibrium physicochemical properties in complex systems and non-equilibrium properties (including kinetic and transport properties)."

"Accuracy vs. complexity: simple-to-use robust platforms with sufficient accuracy are often preferred to high-complex high-accuracy platforms, as the latter is difficult to implement on a wide level.

Calculation speed, especially for rigorous equipment models, dynamic simulation, operator training systems, predictive maintenance models."

Several companies comment on the interface management of physical property data models in simulators being demanding; thus, only a small number of models can be applied in different simulation applications. There is thus a delay of research transfer to industry, including new innovative approaches. Moreover, complex physically based models are challenging for comprehensive flowsheet simulations and further efforts are needed in the appropriate implementation of, e.g., PC-SAFT, which is a model often explicitly mentioned.

However, there are also some positive developments. In some simulators (like gPROMS and Simulis), a generic environment has been developed within which different thermodynamic models can be plugged in by providing an expression for residual Helmholtz free energy, a feature that may facilitate a fairer comparison between different models.

4.3. Product Design Challenges. Intermolecular interaction information from databases and thermodynamic modeling should be transferred more effectively to the product design.

Some of the process simulation challenges mentioned above are also valid here, especially for complex and electrolytic mixtures as well as for large organic molecules with several functional groups. The range of systems of interest is, however, broader, as mentioned by the companies, including formulations (surface effects and emulsions), transport in polymers, e.g., of active ingredients or of plasticizers, predictions of solubility in food matrices, ionic liquids, etc.

Interfacial properties become increasingly important, as many phenomena are multiphase in emulsion and occur at interfaces or in confined spaces. Moreover, there is increasing industrial interest in the computation of more complex systems, such as those involving micelles.

Several companies also comment on the sometimes weak link between thermophysical and actual final product−performance properties, as stated below:

> "During a food process, environmental conditions may vary as a function of time or space in the food: for example, in many preservation techniques, temperature varies (cooling, cooking, pasteurization), pH goes down (acidification due to bacterial metabolism, fermentation), water activity (aw) decreases (drying process, addition of solutes) or redox potential (Eh) falls as food is reduced. As a consequence, phenomena of diffusion (water or solutes transfer) as well as heat transfer occurs in the product, indicating presence in a food of gradients of temperature, pH, water activity".

> "Though it is inspiring to see CAPD methods developing, they seem to fail in their widespread application due to a few general challenges:

- Product performance can typically not be expressed by a thermodynamic property, yet at best by a characteristic related to a thermodynamic property: e.g. open time of a paint related to evaporation rate, hence vapor pressure of the solvent. The models for the performance are typically non-existing. The product stability is also important, combination of thermodynamics and slow reactions.

https://doi.org/10.1021/acs.iecr.0c05356
Ind. Eng. Chem. Res. 2021, 60, 4987−5013

- Though CAPD methods could replace or accelerate part of the existing methods in product design, full replacement is not to be foreseen, certainly not in the near distinct future. There is a lack of connectivity between the existing methods and the novel approaches, which deteriorate the level of acceptance."

5. COMPUTATIONAL ASPECTS

5.1. The Role of Molecular Simulation (in General and as a Supplement of Experimental Data). Question 5 (see Table S2 in the Supporting Information) asked the participants to comment on data availability. Twenty-four companies have answered very emphatically that there is a lack of data, with eight companies opting for "yes/no" depending on the situation. Twenty companies measure some of their own data (often or sometimes), and nine companies answered that they do not perform any measurements.

We also asked the survey participants whether molecular simulation (MS) can be considered as an approach to supplement an experimental database when data are missing. The answer to this question is less clear. Five companies replied negatively on the usefulness of MS (some even emphatically so), while nine replied positively (some without justifying their answer). Most of the companies (18) replied yes/no (either directly or via an answer that can be interpreted as yes/no) and most companies justified their answer with additional statements. We will summarize the most important statements or "reservations" from the participating companies.

Several companies express a lack of knowledge on the full working capacity of MS, which clearly restricts the use of MS-based methods. This has led to many "negative" statements about the reliability of MS data and a lack of trust of such data in conditions outside the data range used to estimate the force field parameters. For these reasons, it is also stated that MS should be mainly used for "interpolation" and not "extrapolation" and can be used to supplement experimental data. A number of them suggest that in any database, it should be clearly indicated which data are from real measurements and which ones are from MS. This is rather important, as pointed out by one company: "already today a great deal of work is concerned with clarifying the origin of data and resisting the temptation to use easily accessible data without sensitivity analysis for the process application". Furthermore, the techniques used for the MS-generated data should be clearly presented and, if possible, with information on the associated uncertainties and expected limitations.

Some companies stress that one issue is that the regulatory bodies prefer experimental demonstration, and when modeling is concerned, there is greater acceptance for empirical/statistical models and less so for predictive models or molecular simulations.

Some companies emphasize that the usefulness of MS data depends on the systems of interest, indicating that for some systems, such data can be useful "but for many important complex (and often reactive) electrolyte systems, molecular simulation is not yet a practical option".

Most companies do not have experience with molecular simulation (this is a common denominator in many of the answers) but are hopeful that such techniques can be useful in the future even for difficult systems, e.g., radioactive and toxic compounds, for which molecular simulation may, in some cases, be the only choice for obtaining some data.

Another company states that "predictions should never replace observed data. If stored in a databank, the predicted 'pseudo-data' should be carefully and clearly flagged as such. Nonetheless, 'pseudo-data' can provide a useful alternative if true data cannot be obtained, e.g. due to reactions or extreme conditions and corrosion issues."

Another statement on the importance of MS for solvent screening reads as follows: "MS could be used for qualitative comparisons, for example in solvent screening. Also, for property estimation when only limits are important, for example in REACH registrations. An error of an order of magnitude can be acceptable if the results are 3 orders of magnitude below the limit. Also, in the generation of pseudo-experimental data which can then be used in traditional modelling." Other companies also mentioned the role of MS in helping in candidate selection and conceptual design.

Despite the aforementioned concerns, we can conclude that the situation with respect to usefulness of molecular simulation is significantly more positive compared to 10 years ago when the previous survey was carried out. The lack of appreciation in some cases is at least partially connected to education and information aspects on what is actually possible today, associated also with lack of information on the reliability of MS-generated data. We can conclude that with appropriate transfer of knowledge, specially focused on industrial applications and audience, accompanied by availability of excellent books,[39] reviews, and suitable software, molecular simulation may in the future become more accessible and more appreciated among industrial colleagues. In addition, the *Journal of Chemical and Engineering Data*, which is historically one of the premier journals in publishing high-quality experimental thermodynamic data, initiated in the mid-2010s the publication of highly accurate prediction of physical property values for real chemical systems using computational chemistry and molecular simulation methods.

5.2. Algorithms, Implementation, Speed, and Standards. *5.2.1. Algorithms.* In general terms, the participants were overall satisfied with the state of the art in the field of algorithms (e.g., for flash calculations and rate-based distillation), although calculation speed and robustness are often mentioned as areas that need improvements. Some companies mentioned that thermodynamic algorithms may be, in some cases, of lesser importance when convergence of a whole process simulation is considered.

Several companies mentioned a need for efficient combined chemical and multiphase (reactive) equilibrium algorithms, including electrolytes, an area where the literature appears sparse (although proprietary, unpublished algorithms exist). Another area is the need for flash algorithms that can handle the distribution changes of sulfur allotropes in the gas and liquid phases as well as for hydration phenomena where nonlinear constraints need to be solved for a set of multiequilibrium equations.

It is also stated that there have been many developments reported in the academic literature in the area of algorithms over the past 10 years or so, e.g., for the global solution of phase equilibrium problems that formally guarantee the correct identification of all phases in the system. It is, however, true, as reported by some companies, that some of these recent developments have not yet found their way in codes that can be used routinely by industry.

5.2.2. Speed. Opinions on algorithms and speed do vary. One company summarizes some of the challenges, as they see them:

https://doi.org/10.1021/acs.iecr.0c05356
Ind. Eng. Chem. Res. 2021, 60, 4987−5013

"As advanced users we make use of algorithms implemented in the commercial software tools. Challenges remain in multiphase flash (split) calculations, as well as improvements in data regression. Speed is important for large size flowsheet applications, dynamic simulations, and particularly real-time optimization applications. Inclusion of uncertainty in the output of the physical property models and the overarching models in which the output is used, is a rather unexplored territory beyond the typical computationally expensive Monte Carlo type of approach."

5.2.3. SAFT Implementation. The survey participants also noted the need to increase the speed of calculations for SAFT-type models as well as to improve the implementation of SAFT (in particular, PC-SAFT is mentioned) in commercial simulators like Aspen Plus.

On the aforementioned comment about the lower speed of SAFT models, there are also some opposite views. It has been mentioned that "by a combination of applied mathematics analysis, numerical methods and software engineering, it has been possible to achieve very significant improvements in the speed of sophisticated equations such as SAFT-γ Mie". It is concluded that "while these EoS will probably never be as fast as cubic EoS or simple activity coefficient models, it is now possible to use them to perform flowsheet simulations involving large tray-by-tray models of distillation columns and several dozens of species within acceptable CPU times".

5.2.4. Standards and Applications. The standardization of models and how they are used in applications (e.g., process simulations and product design) are of serious concern to the participating companies and can simplify processes and the transfer of models between colleagues and the various departments within the companies.

It was suggested that "the choice of standards should be a combined effort of academic and industrial scientists, taking into considerations the scientific adequacy of the model framework, the accessibility of training data (either from databanks or by dedicated measurements) and the obtainable uncertainty level. Not an easy task, but quite relevant! This is possibly something where EFCE-WP in Applied Thermodynamics can play a role in, together with its counterparts from other parts of the world." The recent work by Jaubert et al.[40] is a valuable contribution in this direction.

The participants commented that while standards are indeed needed, they are currently set by the main industry drivers, not standardization organizations.

Some comments regarding standards refer to the model development by universities with clear advice from industry:

> "Provide all necessary details required for implementing a new model.
>
> Improve reporting of models, including details on how these were/need to be parameterized and the sensibility of results with respect to changes in parameters. While evaluating model performance test not just pure components and binary mixture VLE, but also multi-component mixtures and LLE or VLLE.
>
> Also report results at supercritical conditions, where the extrapolation behaviour of the model can be assessed. Same for low temperature, close to the formation of solid phases."

5.3. Commercial Simulators. *5.3.1. Happiness: It Works Great!* Thermodynamics is of importance in many simulators and this is not always apparent until it becomes crucial. One company writes that "we have just changed to a new simulator, and although we are happy with the outcome, it became clear to everybody involved in the migration process that thermodynamics is of major importance in process simulation".

Several companies emphasize the need for training in the use of simulators, both in collaboration with a university (or as part of student education) and internally in the company.

As a general rule, models need to be implemented in commercial simulators if an industrial user is to use it. Hence, the presence of a variety of simulator tools, e.g., Simulis Thermodynamics, which can be used in any software used by chemical engineers, is a positive development.

5.3.2. Concerns: Parameterization and Uncertainty Propagation. Many companies rely, as mentioned, on commercial simulators. The presence of multiple versions of SAFT is again mentioned as a problem and the need for the community to converge to one to two widely accepted versions. Models like NRTL have parameters sometimes regressed on older data and are not always reliable. Furthermore, they may be regressed over a narrow temperature range, which limits their usage outside the range. Some GC models have several missing parameters and the tables must be filled in. Components present in ppm quantities are sometimes difficult to handle. Finally, uncertainty analysis is needed to quantitatively calculate the impact on flowsheet design and operation of thermo/transport property data. Most simulators provide a sensitivity analysis tool, which is a positive feature. It has been commented that to carry out uncertainty analysis and interpret the results, the simulator user needs to be an expert in Monte Carlo methods. What is needed are smart ways to perform the uncertainty analysis in a cost-efficient way and with proper diagnostic tools. Moreover, the uncertainty analysis should focus and be related to parameter uncertainty, rather than a result of simple variation in process variables.

In addition, transport properties need better prediction methods than what is available today, especially for viscosity. Not only are reliable data essential, but software should give warnings if no interaction parameters are available (and set to zero) or properties have been possibly wrongly estimated (although the latter may be difficult).

It is also suggested that special attention should be given to the uncertainty propagation and sensitivity analysis in process simulators: "Quantifying the uncertainty in physical properties is clearly recognized as being of paramount importance by scientists and technologists in the chemical industry. The design of chemical processes today invariably uses computer simulations, and many technologists have recognized the need to understand and evaluate the impact of uncertainties in property models on process design and plant operability."

5.3.3. Missing Properties/Predictive Methods. As many companies rely on commercial process simulator providers, it is thus a major concern to have the appropriate models available in these simulators so that they can be used. There are many suggestions to simulator vendors and a few characteristic ones are cited here on both current and future challenges (and capabilities):

> "Some process simulator features, like "estimate all missing properties", are too convenient for the users. The users should be "forced" to pay more attention to the property features of the model. There should be clear messages from the simulation program to the user on what purposes the physical properties are used so that

https://doi.org/10.1021/acs.iecr.0c05356
Ind. Eng. Chem. Res. 2021, 60, 4987−5013

> user can understand which properties are relevant for his/her case. Also, from which databanks the values were taken or which methods were used for their estimation. The simulator user should not be "interfered" by messages concerning properties that are not relevant for his/her case."
>
> "It is important to get more powerful thermodynamic models for biological and food systems in such tools. Quantum calculation tools like Turbomole also enable to have more structural information especially regarding conformers."
>
> "Here we face more and more new compounds, biological, such as amino acids, proteins, and weak electrolytes, salts beyond the common ones. We rely mostly on new measurements or estimation methods like Artist or ICAS. Efficient simulation tools can speed up product design, however the development of such tools require long term R&D studies that are time consuming in many industrial applications."

5.3.4. Standard Interfaces: CAPE-OPEN and Prodml. "Prodml is an important standard for reservoir fluid properties (measurements and models). This standard needs to be expanded for more measurements and models such as CPA, and solids. This should also be expanded to the literature, so readers can rapidly use/test published models and datasets."

The CAPE-OPEN framework is discussed by many companies. It is often mentioned as a very useful tool ("the use of CAPE OPEN to communicate between different software, and the possibility to use open-source algorithms (especially in Python) will be very interesting in the upcoming years") but also a tool with some problems ("many process simulators lack stability and speed when using CAPE-OPEN models").

Several companies call for improvement in the use of CAPE-OPEN tools in process simulators. One company comments also on educational aspects:

> "CAPE-OPEN is used within companies to connect various applications, but it is hardly used as a software standard for interoperability between companies. One reason is that CAPE-OPEN is not mentioned and introduced at university level to the students, who will carry the idea of interoperability into the companies. Any thermo package or unit model developed at a university should use CAPE-OPEN as default."
>
> "CAPE OPEN should be developed and followed. Systematic ways to report experimental data, like ThermoML, are also highly appreciated."

Nevertheless, CAPE-OPEN has not found a widespread use as one might have hoped or even expected. One company comments on this: "This may be a reflection of the fact that, whilst software considerations (e.g. interoperability) are indeed important, as far as industry is concerned they are secondary to being able to obtain accurate property predictions. And if a software code allows users to achieve the required accuracy, then they will use it irrespective of whether it is CAPE-OPEN compliant or not."

The low adoption rate of CAPE-OPEN may partially be attributed to the perceived benefits of such a standard by the commercial software providers, certainly if they consider the physical properties a crucial element of their software package and have heavily invested in the infrastructure thereof.

5.4. Digitalization. Question 9 on "Digitalization" was new in this survey, compared to 10 years ago, and was defined in a rather broad way. The aim was mostly to identify the new opportunities for property calculations—predictions seen by the participating companies using innovations related to the digitalization and associated technological advances in IT (big data, very powerful computations, and algorithms like machine learning (ML), artificial intelligence (AI), meta-modeling, and data mining).

Due to the rather broad definition (and maybe not complete consensus on all the aforementioned terms), it is thus not very surprising that rather diverse views have been received, both on current status and future trends. Still, most companies consider it important to address this question. The extensive discussion, which has taken several directions, is presented below and divided into some characteristic sections.

5.4.1. Some Rather Skeptical Views. According to some "'skeptical" companies, such "molecular or digital" concepts as an aid for property modeling have been mentioned before and it had been previously stated that they will be widely applied in 15 years. This answer was given 15 or 30 years ago or even before. Still, we continue to rely on experimental data, on experience from property data of similar compounds from databanks, and on models like COSMO-RS and UNIFAC and engineering feeling or previous expertise.

Some participants speculated on what is meant under the umbrella of "Digitalization" that is really new, especially as databanks of physical properties and computational models already exist. "Possibly the challenge is to retrieve and compile all data and the advanced algorithms like ML, AI could be useful to unravel complex systems and possibly build relationships. However, the power of the existing phenomena-based models is related to extrapolation, e.g. from binary systems to multi-component systems. Through the ever-increasing computational power complex and heavy calculations become more and more in reach, possibly enabling the use of those calculations in overarching models for flowsheeting etc."

A final concern is whether there are enough data for use of ML and related applications. This is an issue raised by many. One company mentions that "production data is not an option as it is run at set point. Therefore, it is unlikely that the production data will be the basis of any property calculations." Another company specifies that "big data, artificial Intelligence and machine learning are very interesting and can offer insight. However, access to NIST for real systems (reservoir fluids, multi-component systems) is important. Without the data there are no AI/ML opportunities. TDE is a great tool but out of the reach for most − quite expensive."

Moreover, it is often noted that AI/ML methods, while they can be useful (even towards developing a single model for all conditions/fluids), must be guided by physics (or fundamental understanding) rather than just be data-driven.

5.4.2. Modern Approach. These methods can be used for risk analysis and trend analysis, which turns down the need for accuracy from the simulation models involved.

The survey participants also mentioned that collaborations between thermodynamic and digitalization research groups are bound to happen, which is considered to be encouraging, and of relevance. They noted that some large companies do sponsor these types of projects but it will take time for these techniques to be accepted in industry, as is the case with most high-level, high-complexity models. Still, there is a feeling that these innovative efforts should continue.

https://doi.org/10.1021/acs.iecr.0c05356
Ind. Eng. Chem. Res. 2021, 60, 4987−5013

5.4.3. Specific Applications of Digitalization. Many companies are very positive on the use of ML/AI methods in facilitating thermodynamics (data and modeling) but also in unit operations. In some cases, they add some "critical concerns", but overall, there is much interest that digitalization can play an important role and, in many cases, detailed answers and several examples are mentioned. One company expresses the various potential uses as follows: "1) data scraping, comparison & reconciliation from published papers; 2) sanity check of proprietary databases by benchmarking; 3) meta analyses across many datasets; 4) better consolidation of company and university databases; 5) as a result, warnings for unlikely values from faulty measurements; 6) make more complicated methods available through simple interfaces; 7) make multiple predictions available at click of a button resulting in a window of values, with statistics; 8) integration of values from multiple sources resulting to more robust models. Note there is also a lot of hype in this area so understanding when to use big data techniques and when not is really important."

The following specific applications are often quoted by the participating companies:

- Development of new algorithms to find global minimum more robustly and quickly.
- Combination of experimental measurements and simulated values.
- Reduction of the effort to search physical property data publications starting from the identification of the measured property and the compounds that are included in a measurement. The data extraction would be the following step but may be less urgent issue because of the availability of well-defined databases.
- Automated prevalidation of experimental data based on thermodynamic criteria or similarity criteria derived from experimental and estimated data and an AI-based approach to validate publications of experimental data.
- Use of big data methods for data analysis and identification of trends that would allow better property estimations and the generation of pseudo-experimental data. This is already done, but now, it can be done in a faster manner and taking into account all the data available in large databanks.

The synergies between conventional "knowledge-based" models and deep learning approaches are mentioned several times by many of the companies, e.g.:

- Parameterization of "predictive models" using adequate "descriptors" (e.g., group contribution). Machine learning could be used to characterize parameters of equation of state as an example. It must be possible to mix a physical approach and machine learning.
- Use of a physical model generates pseudo-data that can "teach" a data-driven model to provide representative data much faster when called in a simulation environment.

5.4.4. Surrogate Models for Property Calculations/Product Design. For property calculation and prediction, QSPR/ML methods could open new possibilities, especially if validated data are applied and molecular descriptors are combined to physically reasonable functional terms or to thermodynamic fragments from reasonable model approximations. It is also recommended to consider artificial intelligence methods on property predictions for complex systems (e.g., crude oil characterization or improvement of product such as Carlsberg's Beer Fingerprinting Project).

Moreover, the survey contains responses where additive and solvent selection methods based on physical property and thermodynamic data criteria that are compiled from databases and estimation methods (GC and COSMO-RS) have a high economic impact on process and product design and the laborious work to compile nonthermodynamic properties could be enhanced by QSPR/ML methods.

5.4.5. Beyond Thermodynamics. Several companies mentioned the use of ML/AI methods also beyond thermodynamics, e.g., in process modeling and CFD. For example, to integrate molecular design and process design via superstructures to evaluate all possible combinations of processes in combination with solvents and azeotrope breakers.

Another company states that "the analysis of plant data can also allow adjustments in the process models, and the improvement of the thermodynamic properties which are in its base. Of course, this might be questionable from the scientific point of view, but it is perfectly valid when the goal is to have a "digital twin" of the plant, i.e., a model that describes the plant to the best detail."

The importance of the computational power increase in allowing thermodynamic models to be used in CFD is also noted, something that was previously generally considered to be too computationally heavy or too detailed for such calculations to be efficient. Digitalization allows us to gather crude engineering data and parameters in a reasonable time. As an example, it is mentioned that if ANSYS could incorporate more thermodynamics and material properties, then databanks into CFD would be profitable in several applications. That company concludes that "without these advances we could not use thermodynamics and advanced rheological properties in our routine simulations, commercial projects have very tight timetables".

5.4.6. As a Conclusion: Three Detailed Answers. We close this section with three of the detailed answers, which express some of the specific views on applications presented, illustrating also somewhat different views:

(1) "Very vague question!

The main thing I see is that the computational limitations which currently prevent wider use of molecular simulation techniques (of sufficient precision to be useful) will be overcome.

Also, it would be great to work towards understanding the limitations of the currently available and widely used thermodynamic models, and how we can enhance them by combining those with data-driven models. Thinking from the other side, if data-driven models are more computationally efficient and easier to be implemented, we should work towards shaping the rigorous thermodynamic models as consistency checking routines for the data-driven models."

(2) "Dealing with large quantities of data will become increasingly important in the following contexts:

i. Real-time data acquisition and use of data historian to obtain process intelligence.

ii. Use of thermodynamic models to make predictions based on information accumulated in data historians.

iii. I see the role of machine learning in making sense of big data and extracting useful information, which can be later used in thermodynamic/thermophysical property models; I do not see machine learning

https://doi.org/10.1021/acs.iecr.0c05356
Ind. Eng. Chem. Res. 2021, 60, 4987−5013

substituting physics-based models per se (although I am aware that there are opposing views)".

(3) "In the global context of thermodynamics and especially in process simulation, digitalization opens doors to many interesting deployments of existing models in the optimization of the performances of existing plants in actual industrial conditions. Thanks to cloud computing, we should be able to easily combine different complementary models through the use of appropriated algorithms and commercial software (if required). However, we are convinced that the open-source algorithms especially Python (that are natively suitable for multi-thread computing) open new insights in computational flexibility that are very interesting to deploy the next generation of thermodynamic models, especially for students and chemical engineers who will have to work in the so-called "Industry 4.0" companies. In fact, machine learning, AI, Meta-modelling and data mining algorithms can be very useful in the identification of optimum parameters in the simulation of complex systems like unit operations in chemical plants.

We must be aware that digitalization is only a transformation agent (enabling to use appropriate digital technologies to change or improve an existing business model and provide new revenue and value-producing opportunities)."

6. RESULTS ON MODELS AND DATA: WHAT SHOULD BE DONE TO ADDRESS THE LIMITATIONS AND CHALLENGES

6.1. Experimental Data. One of the topics, which attracted lengthy responses in the survey, is the experimental data (quality, availability and necessity for more measurements, databases, use in thermodynamic models, etc.). We present the most important conclusions roughly divided into the aforementioned categories.

6.1.1. Data Quality and Experimental Methods. The underlying theme in many of the replies was that on the one hand, there are many data on thermophysical properties produced and published and, on the other hand, measurements for important systems are still very much missing (see next section).

The plethora of published data is not considered always as a positive thing. There is some concern regarding the fact that many eminent labs have disappeared, and the measurements come from a limited number of laboratories placed in a few countries only. While we do not consider that in itself, it is a worrying factor (although it would be nice to rely on many labs/countries rather than few), many companies emphasized that the growth of published experimental data has enhanced the efforts for data validation, particularly the increase in the percentage of low-quality and erroneous data. More efforts are needed in this direction, especially the critical evaluation of the new measured data. There is also a need to report systematically the experimental errors and check the thermodynamic consistency of the finally reported values. Comparisons to existing data are needed and, overall, a guide to experimentalists for reporting data has been intensively requested by the participating companies. We are happy that we can report that a systematic effort led by NIST aims to provide such a guide.[28]

One particular area where data often need to be checked is at high pressures where the survey participants explicitly requested for the development of a reliable method to validate high-pressure VLE data. It is also stated that for competitive design, accurate predictions based on accurate data are essential. A company comments that "especially in research and development of new types of processes, EPC companies work with end-users to measure VLE data and determine parameter values of thermodynamic method. For validating the data at ambient pressure, methods based on Gibbs-Duhem are well-known. However, the methods are not applicable to high-pressure range as the gas phase has strong non-ideality. Currently we see only a few researches for the purpose. Well established and reliable methods will contribute to increasing accuracy of simulation and eventually increase the competitiveness of the users."

Another reported difficulty is that certain measurements are challenging and increasingly difficult due to safety regulations or particularly costly or very difficult in extreme conditions, e.g., lower concentration limits and very high or very low temperatures, thus resulting in either lack of data or data of low quality.

Another difficulty is the automation as one company comments that "a development of an automated platform for LLE or VLE (at p=1atm) would be interesting for us. We have routinely been using automated platforms for kinetic measurements and SLE, however there seem to be yet few options for LLE and VLE on the market, and the options that we looked at were of unsatisfying quality. This might be intrinsic to the problem being complex and altogether not amenable to automation. Automation is one of the areas of investment, so anybody working on this should be able to secure some support."

A final issue under this section is the education and the need of engineers to have a feeling of experimental data. One company summarized this problem as follows: "A constant need, with a worrying future. We saw a large decrease in experimental expertise in our company in the last years. Experts stay shorter times because they have other career expectations, and they move before becoming truly experts in experimental work. On the other hand, many methods are now commercially available and can be used without a true expertise. The problem is then a lack of expertise in the critical analysis of the results, resulting in an increase of erroneous data."

6.1.2. Lack of Data: A Serious Problem Mentioned Extensively. It was overwhelming to see a very large and very diverse need for measurements, expressing in various ways a dissatisfaction with the current practice as "there is still too few experimental data produced, especially beyond the limits that were already measured". The future demands for experimentalists are as follows: more automated apparatuses (faster data generation), improving the accuracy, and new measuring techniques/detectors/analytical methods to measure several physical properties consistently (e.g., phase equilibrium composition + densities + thermal properties in the same measurement).

While some companies stated that there is more emphasis on data for the oil and gas sector and trendy topics like DES (deep eutectic solvents) compared to areas like biotechnology where more pressing needs exist, the reality is somewhat more balanced when all answers are considered. However, one has to bear in mind that the gas and oil sector has long-standing funding arrangements with universities and internal capabilities that allowed for the data generation.

It appears that for all/most types of systems, there is lack of experimental data for a number of classes of systems that are

https://doi.org/10.1021/acs.iecr.0c05356
Ind. Eng. Chem. Res. 2021, 60, 4987−5013

important in industry but poorly investigated in the open literature. Moreover, the required needs for measurements include all types of phase equilibria (VLE, LLE, VLLE, SLE, and SLVE), density, thermal, surface and derivative properties, e.g., heat capacities, and transport properties like viscosity, diffusion coefficients, and thermal conductivity. Multicomponent system data are rare and these are important for model validation, especially multicomponent LLE. In addition, vapor pressure measurements of different organic compounds at very low pressures (<2 mbar) and dilute conditions are required, as well as measurements on reactive (multiphase) systems. Finally, salt effects are also important as well as high-pressure and high-temperature phase equilibrium data for many nonideal mixtures.

From the more classical areas (petroleum and chemical industries), lack of data was mentioned mainly for mixtures containing glycols, amines, mercury, and acid gases (H_2S and CO_2). The latter is of importance and is mentioned in many contexts, e.g., data for reactivity of minerals in CO_2 sequestration environments and reactions of impurities in CO_2 phases after CO_2 capture. A particularly problematic area appears to be the solubility of CO_2 in H_2O, which is a well-known system, but data do not agree (at least to the desired degree) with each other.

Other important systems mentioned are polar and/or reactive mixtures (H_2O−methyl formate, H_2O−CO_2−methylamines, multicomponent data, and formaldehyde with water and methanol and H_2O−acids).

There has been much discussion on data needs in other sectors, for instance, lack of high-quality data in the literature for the solubility of larger molecules in solvents. If the data do exist, then data measured by different laboratories show a large scatter. Furthermore, data on complex oxygenates are also lacking. For instance, measurements of boiling temperature in concentrated aqueous solutions of carbohydrates are very challenging and specific setups are required in this case. More data are needed for heavy molecules (MW > 150 g/mol), both VLE and SLE, for pharma-type molecules, e.g., fluorinated molecules and N-containing molecules. Also, data on solid properties include solid mixtures as well as biomolecules, bio-based chemicals, and bio-feedstock molecules.

One company is interested in specific systems containing fission products, with no data in the databanks; thus, the company only relies on internal databanks and is not aware of laboratories that are able to do measurements for such systems.

6.1.3. Improve Data Production? Finally, a note on the cost of measurements that some companies find to be expensive states that some industries tend to measure data according to "how much budget do I have for measurements?" rather than "what are the data I really need for my process?". One of the recommendations is to develop service centers for measuring the missing properties (cheaper and faster) and for increasing the capabilities to develop quickly missing analytics, e.g., identifying pertinent data. It was not entirely clear from the survey if the participants meant academic, governmental, or private labs; maybe, all of the above can be relevant in this context.

Moreover, some companies mention also "internal" challenges in the area of experimental data: "In industry, it is difficult to train new technicians on thermodynamic measurement protocols, as these demands often vary (unlike in a PhD environment), and often many months may pass before certain stills are remounted again. Here we should note that a significant portion of the compounds we produce are confidential so there will be no available data in the literature. We either measure some properties ourselves or rely on models that use the molecular structures to estimate the needed properties."

We believe that there might be an opportunity for developing improved predictive models if companies would be interested in sharing their data anonymously and for the sole purpose of developing predictive models.

6.1.4. Data Availability: Databases. The availability of collected and critically evaluated data in well-established databases was an important topic in the survey, as discussed by many companies. As an alternative (or supplement) of new measurements (often difficult, time-consuming, and expensive) or predictive models (often with unclear accuracy or not always appreciated by chemical engineers in industry), many companies praised many comprehensive, commercial databanks such as DDB, DIPPR, and NIST.

Several companies see, however, two serious problems. The first is that these databases are not easily accessible to small-to-medium enterprises, especially due to high cost (but also some other reasons, which include company strategy and/or usage). Due to cost, some companies purchase only specific datasets from these databanks.

Another problem is the existence of many (partially overlapping) databases. Associated with the cost issue mentioned, several companies expressed the wish to have a single or very few databases with critically evaluated data (or at least one database per field). A collaboration between databank providers is recommended. Some companies expressed the wish that their internal databases are better structured.

Molecular simulation or other pseudo-data should be clearly marked, if used in the databanks. Databases containing systematically presented multicomponent data are missing in many areas, e.g., for reservoir fluids—oil and gas.

Some companies proposed that the databanks can be further developed for use in machine learning approaches, which would be of special use, for instance, in the development of new chemicals.

6.1.5. Data and Model Validation. A large number of companies link the measurements with the development and validation of models, e.g., filling in the UNIFAC or other GC method tables including GC-based EoS like PSRK/VTPR. Many companies even recommend a model-based DoE (design of experiments) approach. By this, they mean that measurements should be conducted, and experimental data should be provided for systems and in conditions that are important or even optimal for the model work (estimation of parameters and/or validation of the predictive performance). Such GC-based methods supplemented with new measurements will be useful to cover a number of serious gaps identified by many companies in areas such as multifunctional chemicals including pharmaceuticals, large organic molecules, aqueous solutions of carbohydrates, and toxic/radioactive substances.

6.2. Models. *6.2.1. In General Terms.* The discussion about (thermodynamic) models was among the most "hot" topics of the survey with very many answers from the participating companies. We have structured the answers in some of the major categories, but we start with a section presenting some of the general statements, which illustrate some of overall sentiments.

First, on the usefulness of the models, "models are useful if 1) implemented in an available environment or 2) reported in a way that allows users to implement the model themselves. Otherwise, of little use to industry. A good example: SAFT models for most industrial users exist only in 'Aspen or Pro/II'. A

https://doi.org/10.1021/acs.iecr.0c05356
Ind. Eng. Chem. Res. 2021, 60, 4987−5013

model that only exists in a journal article does not provide much use to industry."

Opinions differ only superficially on whether a single model or multiple models are preferred.

Here are some of the pertinent comments:

> "There's no problem with many models so that the most appropriate model is selected for the problem at hand."
> "The promise to have a single EoS that is capable to deal with any component mixtures (from hydrocarbons to water to electrolytes to waxes to asphaltenes to polymers) seems still to be the holy grail, but it must also still fulfill the requirements of calculation speed, ease in parametrization, accuracy, practical applicability and behaving well mathematically. Clean up with the zoo of variants and sub-variants of equations of state and property models. Transform existing models with empirical parameters to models with theoretically based (and calculable) parameters with a physical meaning."

Next, there are concerns on model development, range of applicability, and recommendations:

> "Many model approaches need many parameters, hence a lot of data, but many model evaluations are too narrow. It is often a huge hurdle to have a new model implemented in commercial tools. The later should not stop basic research as that is where novelty comes from. Someday a worthy replacement for cubic EoS is there."
> "Unless the new model is able to replace (almost) all the current models for a given property, I suggest that greater efforts are directed towards the extension and harmonization of existing models. The models are particularly important to us as we usually need to simulate confidential molecules that are hence not available in external databanks. For us, equations estimating VLE data, V/L viscosity, latent heat of vaporization (all as a function of temperature) are the most important."
> "Demonstration of important effects, especially those that defy/demonstrate limits in conventional models is also very valuable. My honest opinion is that we should use GC as long as we need to, but eventually more rigorous calculations will be so accessible they will overtake GC."

6.2.2. Model Development and Demand for Validations. Before we address specific models, it is important to stress that for all models, companies have made extensive suggestions on how the models should be developed, with special emphasis on the parameter estimation process, as well as how the models should be validated.

It is often mentioned in the survey that the predictive models are required more than ever, including predictive models to obtain binary interaction parameters for mixtures that are difficult to measure. It is worth noting that gaps still exist even for the most popular models, even for the GC-based ones. For the multifunctional larger organic molecules, these problems are more extreme. For validation, the simultaneous description of different phase equilibria using a single set of binary interaction parameters is required: "simultaneous description of VLE and LLE with the same parameters and the same accuracy, correct extrapolation to infinite dilution, LLE in multicomponent systems, electrolyte systems, prediction of pure component properties (also of larger molecules), particularly normal boiling; viscosity, both group contribution methods and COSMO-RS models are needed; mixing rules for transport properties".

As could be expected (see also Sections 4 and 5.1), the generally applicable models are required to be able to calculate or predict phase behavior and other properties of, among others:

- Reactive mixtures (critical point and simultaneous physical and chemical equilibria).
- Acid gases, e.g., CO_2−H_2O−alkanolamines.
- Diverse aqueous systems (H_2O with acids, steam/water, H_2−H_2O, H_2O−CO, distribution of solutes between coexisting steam and water, and LLE where water and sulfuric acid are the liquid phases).
- Dew point/critical points of heavy hydrocarbon streams.

Many survey participants asked for guidelines for parameter regression, which would be a very welcome tool for practicing engineers.

One company writes that "the parametrization of models, especially physically based models (e.g. SAFT-type equations of state) is complex also due to the parameter degeneration. Global optimization and mathematical techniques cannot resolve the fundamental physical problem. The predictive power is therefore restricted for multicomponent systems, especially for liquid-liquid equilibria and gas solubilities. Therefore, demanding measurements in multicomponent mixtures are necessary. Physically based parameterization strategies should be developed and published."

Even for classical cubic EoS models, there is sometimes sizable intercorrelation of parameters and, thus, there should be focus on developing such model equations that reduce the correlation of the fitted model parameters. Two particular examples of highly correlated parameters that are quoted in the survey are as follows: (i) three parameters of the Twu function in the energy parameter of cubic EoS and (ii) the interaction parameters of the g^E models; we know that there are many more examples.

Another serious concern is the reliability of the models especially for extrapolations depending on how the parameters are regressed. Here is how one company discussed this issue: "Usually a data set is measured and then is fitted to one or several models. For models with a few parameters, fitting a curve that would provide reliable results when interpolating is usually not an issue even if the fitting is not done in a robust fashion. However, if extrapolated data is extracted from the model, one becomes uncertain about its reliability. Here, one should carefully select the equation itself and perform a more robust data fitting (multiple algorithms and starting points) and statistical analysis of the results (95% confidence intervals and prediction intervals). When this is done one would have a better idea about the reliability of the extrapolated data and if there is more work needed to validate it. There are instances in commercial software where the data fitting was done in "standard" ways that work fine for interpolation but caused significant errors with extrapolation."

6.2.3. Classical Models Are Still Here! Under "classical models", we consider the cubic EOS like Peng−Robinson and SRK with modifications and appropriate mixing rules including EoS/G^E ones (i.e., models like PSRK and especially VTPR) and the most well-known local composition models (UNIQUAC, NRTL, and modified UNIFAC (Do)) as well as a few specialized models like Flory−Huggins including modifications for polymers. They appear to be still widely used by very many companies. They are (sometimes) supplemented by the most advanced models (SAFT-type, CPA, and COSMO-RS; see discussion later), but these classical models are still highly useful in a large number of applications, as indicated in the survey.

https://doi.org/10.1021/acs.iecr.0c05356
Ind. Eng. Chem. Res. 2021, 60, 4987−5013

It is important to note that some of the aforementioned models (e.g., NRTL, UNIQUAC, and Flory−Huggins) are correlative, while others like UNIFAC, PSRK, and VTPR are predictive. Some of the predictive models are as recent as advanced SAFT-type approaches and are continuously improved by populating larger parameter matrices.

Here are characteristic statements on model choice, which illustrate the usefulness of these classical models:

> "Standard models for standard mixtures in standard processes are acceptable unless the accuracy of the available experimental data increases considerably. Models for extraordinary mixtures and/or extraordinary process conditions need to be improved for applicability, universality, and calculation speed. Thermodynamic models must be mathematically well-behaved (e.g. continuously differentiable up to third order) to be used in equation-oriented process modelling environments."
>
> "There are plenty of models that are able to estimate the different properties either from data sets or molecular structures. Each set of models are specific to either certain molecules, mixtures or operating conditions. For a non-expert, it is usually difficult to select the right model, which could cause faulty calculations. I believe that it would be beneficial to have a single algorithm that takes in all the available input (structure, measurements, mixture, process conditions) and selects the right equation itself and performs the calculation. In the hands of an expert, this algorithm might not be very useful. But, in the hands of the vast majority of users, it will save them plenty of time and reduces potential errors coming from wrong equation selection. To my knowledge, even the strongest process simulation and physical property estimation software on the market still ask that the user selects the equation him/her-self or does the calculation with several equations and lets the user decide which result is likely to be most accurate."
>
> "There is no need for more models; what is needed is a clear selection of dedicated well-parameterized models. The statement by Chen and Mathias and following still holds (in the review in 2010[1]): "...industry rarely updates or replaces its thermodynamic models with newer and better correlations unless a clear advantage is evident. It often takes a long time, of the order of 10 years or more, for a new model to be conceived, developed, validated, and accepted by the industry."
>
> i. In our company the mostly used frameworks concern the following: NRTL, UNIQUAC, UNIFAC-Dortmund, PSRK, VTPR, COSMO-RS.
>
> ii. Uncertainty should be part of the model output."

Especially for VTPR, where for companies, the choice between PSRK and VTPR still needs to be settled, some improvements are still needed for the parameters, but the model is now considered as one of the most successful ones for practical applications:

> "VTPR is gaining space. By the way, the offering of dedicated VTPR parameter matrix by UNIFAC Consortium could be an example of a future type of organizational structure between industry, academia and software providers to establish (pre-competitive) improvements in the area of applied thermodynamics."
>
> "There is a high need for reliable predictive models for both physical property and phase equilibrium modelling due to the fact that there are lot of early stage feasibility studies, which do not yet include experimenting the physical properties (economic evaluation is necessary first). The VTPR model, developed by UNIFAC consortium, seems very promising, but it is not yet as fully parametrized as other consortium models. Considering non-predictive models, in ideal case there would be one model that is well parametrized in commercial simulator. This is not the case yet."

The importance of continuing the parameterization of the VTPR model has been stated by several companies.

Indeed, for the VTPR model,[44−46] which differs from PSRK, we can confirm that there is strong support from industry to parameterize it and it is on-going in the UNIFAC consortium. The interesting point here is that the implementation of VTPR has been driven by industry and is incorporated in software tools. In our view, VTPR is superior to PSRK and the lack of parameters is addressed in the UNIFAC consortium. Consortium companies have, in fact, encouraged additional work on the parameter matrix. This is reflected in their survey answers.

6.2.4. SAFT, CPA, and COSMO-RS. Among the wide range of advanced models available, it is SAFT (especially PC-SAFT), CPA, and COSMO-RS that are mentioned explicitly by many companies. All three appear to be used in a number of applications, but there is a long way to go before they become standard tools, even for the companies that know the models well.

6.2.4.1. SAFT and CPA. One company writes that "we are somewhat conservative, and rely mainly on models such as NRTL or SRK. Attempts to introduce PC-SAFT or CPA were not able to convince some of the colleagues. It would be better to have a model of reference, for example a SAFT model, which could be better implemented in simulators. In a company standardization is important."

Although several applications of CPA and SAFT are mentioned, the usual provision is included that both models should be better documented and implemented in simulators and also that vapor phase association needs more attention. One company mentioned that the current implementation is not very good: "PC-SAFT slows down the Aspen Plus simulations so much that it cannot be used in practice yet."

It is also stated by some companies that progress has been made.

"SAFT models have allowed improvement in describing polar and associating mixtures", but "PC-SAFT has been greatly improved but the usability remains poor."

Many ask for a standardization of the SAFT approach and a consensus on which version of SAFT should be used. Despite the widespread use of PC-SAFT, the lack of consensus and many SAFT variants have created a confusion, which are factors that prohibit the wide applicability of the SAFT approach.

"Industry-wide models should be reasonably accurate but also general and easy to use. There is no point to have multiple versions of an accurate model (such as SAFT) that has only be tested for a few systems and requires a thermo expert to do the parametrization."

There are, however, also more positive voices on the SAFT development and, for example, there is now a version of SAFT (the SAFT-γ Mie equation of state) that contains an extensive group-contribution database with parameters for 150+ groups. Companies familiar with this model "believe that EoS-based group contributions are inherently more useful than activity

https://doi.org/10.1021/acs.iecr.0c05356
Ind. Eng. Chem. Res. 2021, 60, 4987−5013

coefficient models such as UNIFAC since they are applicable to both pure compounds and mixtures."

They comment that to be used for phase equilibria, approaches such as UNIFAC require an additional model for the vapor phase and knowledge of pure compound properties (i.e., vapor pressures) and therefore cannot be used alone to make predictions.

In view of this, they conclude that "we believe that it is more effective to invest the effort towards parameterization of EoS models such as SAFT-γ Mie. A key breakthrough would be to derive methods for determining at least some of these parameters from ab initio quantum mechanics calculations. This could significantly reduce the reliance on experimental data." Moreover, "because of their more fundamental theoretical basis, they allow better extrapolation, while activity coefficient models cannot describe gas phases (or critical regions), and cannot be used easily with gas molecules without a proper software implementation of Henry coefficients".

Progress has been made in some cases in the prediction of solid/liquid equilibria, "primarily arising from the better characterization of liquid-phase chemical potentials",[29,30] as stated, but "a big gap here is in the prediction of the pure component properties, e.g. formation or melting that are needed for the calculation of solid-phase chemical potentials". Some of the SAFT approaches have been applied successfully in the pharmaceutical industry, as recognized by few of the participating companies, but it is noted that "the main challenge is to grow the databank of functional groups to cover the heterocyclic groups that commonly appear in such molecules". Moreover, it has been stated that "a model for estimating solubility of bigger organic molecules with few to many functional groups in pure and mixed solvents (e.g., using PC-SAFT) would be also desirable".

Finally, an area where SAFT-based approaches can perform significantly better than cubic EoS (regardless of the mixing rules used) is the derivative properties, e.g., speed of sound. This has been only realized (or at least mentioned) by very few of the participating companies. One of them comments that "we have been having consistently good predictions of derivative and thermal properties with SAFT-γ Mie. The main requirement appears to be to include these classes of properties in the experimental data used for fitting the functional group parameters, complementing the usual phase equilibria and saturated liquid density data typically used for this purpose. Having said this, the derivative properties of water remain a challenge."

6.2.4.2. Cosmo. For COSMO-RS, there are diverse views among the participating companies in the survey. It is a well-known model in industry now and many want to see it be further developed by generating more COSMO profiles for a large number of components. We can add that to produce a COSMO file with Turbomole does not require a large effort, at least for the simpler molecules. Computing time is needed, but the input time for the user is limited to a few minutes and the process can be automated. However, for longer-chain, multifunctional compounds, the situation may be different. In such cases, there might be multiple conformers with similar (low) energies, or in other words, multiple conformers might have to be taken into account. The selection of the right conformer or set of conformers is critical to the quality of prediction. This selection can be a time-consuming effort for such complex molecules.

The survey participants also mentioned that:

i. "Group contribution models fail to describe the difference between conformers, while COSMO-RS models have the potential to do so even if many developments of specific phenomena like hydration or complexation must be handled efficiently in this kind of model."

ii. "COSMO-RS is taking its place as accepted and frequently applied model, maybe not directly in flowsheeting, but at least for generation of 'pseudo-data' for model parameterization."

iii. "Within the past 10 years we have started to use COSMO-RS to fill some of the gaps and complement experimental data."

Further comments include that "COSMO-RS sometimes outputs unreliable physical properties, which require additional work of parameter fitting" as well as the warning by a few companies not to use COSMO-RS to fill in the gaps in measurements, as "it fails on molecules with multi-functional groups and in case of proximity effects". It will be of interest to follow COSMO-RS also in the years to come. Within just a few years, it appears to have attracted almost as much attention as "classical" and SAFT-type models, which have existed for (much) longer.

Finally, some have requested the extension of the number of substances where a high-precision EOS can be applied.

6.2.4.3. Conclusions on Advanced Models. Let us close this section with a very interesting statement—wish from a company for a predictive model for diverse applications. Indeed, an area worth considering and comparing all approaches of this section against some of the classical models mentioned in the previous section is as follows: "A VLE & LLE model that we could use to describe Extractions as well as Distillations for the same system would be fantastic − but I believe this is widely known in the community. The question is whether an improved EoS could be the answer (which would result into more parameter fitting etc.) or whether we need to take a step back and look outside the box.

A predictive solubility model that requires molecular structure as the only input still remains to be highly desirable. I wonder how much effort it would be to either improve COSMO-RS or gather a body of NRTL-SAC/regressed UNIFAC parameters for a sufficiently large database to perhaps then be able to see how empirical model parameters correlate with molecular descriptors."

6.2.5. Electrolytes. Modeling the electrolytes dominated the discussion and, as one survey participant puts it succinctly, "understanding and description of electrolyte thermodynamics - the presence of ionic species affects the behavior of the phase equilibria - is a phenomenon that is observed in many applications."

There were a large number of requests that improved and, more importantly, predictive models are developed for electrolyte solutions. However, many companies also expressed concern that most existing models require large datasets or have no predictive power outside the experimental range (e.g., it is difficult to predict ternaries from binaries).

Thus, what is currently lacking are truly predictive models for electrolytes (with limited requirement for adjustable parameters and data regressions) at high concentrations, including speciation behavior. Indeed, the parameterization of electrolyte models is discussed extensively, and it is also noted that "the procedures should also comprise instruction to include uncertainty in the most effective way".

https://doi.org/10.1021/acs.iecr.0c05356
Ind. Eng. Chem. Res. 2021, 60, 4987−5013

Another aspect that needs improvement, according to the survey participants, is the fast and robust equilibrium calculation for dynamic simulation for mixtures with a large number of ionic components, as one company explains that "for competitive design and operation, dynamic simulation is being applied for investigating and optimizing operation procedures. The situation is the case with processes of inorganic substances such like those in metal mining, cement and ceramics productions of which dynamic simulation requires fast and robust equilibrium calculation of electrolytes. Currently, considerably lengthy computation time is required for rigorous calculation of electrolyte system, which contains plausibly large number of ionic species. Breakthrough for reducing the computation time by two orders of magnitudes brings huge benefit to the industries."

6.2.5.1. NRTL. Very few suggestions are provided on what electrolyte models to use, although several companies (which use Aspen Plus) discuss extensively e-NRTL, a model often used, but with serious limitations, e.g., a clear methodology to fit parameters is required.

Here are some characteristic statements from different companies:

> "We are users of AspenTech software (Aspen Plus for thermodynamic) and except with e-NRTL, there is no other model for electrolytes. The development of models (GC PPC SAFT) that could be used in Aspen Plus would be a major improvement. We are not fully satisfied with e-NRTL. Testing other models (SAFT for electrolyte) is under reflection."

> "There is need for improved electrolyte models. Also need to educate chemical engineers so that they will have improved understanding. The recently started projects, EleTher[31] and a project at DTU,[32] will most likely improve the status substantially."

> "Regarding electrolytic models, the focus should be on how to educate engineers to use them properly, rather than developing new ones. The e-NRTL of Aspen Plus is one of the older electrolyte models, but there still seems to be no standards when using it. There are a lot of different, and often divided, opinions on how to set up the model correctly and parametrize the parameters."

6.2.5.2. SAFT. As can be seen from the above (and previous sections), the majority of the comments from industry were on the extensive needs for electrolytes (covering a very wide range of systems, conditions, and applications) as well as the limitations of current models and the need to make improvements toward "predictive approaches". But there were not too many comments on what/how to improve except for the comments about improving e-NRTL. Only a single company noticed that "there have been some positive developments, including the inclusion of coulombic interaction terms in SAFT". Indeed, there are numerous such models today (electrolyte equations of state), but most likely, as they are not available in (most) commercial simulators, they have not received much attention from industry. However, these models require explicit contributions for the ionic interactions (taken often from the Debye−Hückel or MSA theories) and, sometimes, additional terms for the "solvation" or "ion−solvent" effects. The latter is sometimes taken from the so-called Born term, which has now become popular and received some acceptance in many e-EoSs.[33] While this may indeed be true, one of the comments received from a participating company was that the Born term remains fundamentally problematic (see, for example, Cobble and Murray[34]) and this leads to incorrect temperature dependence. While this is an old reference, a newer study[35] also points out that the Born term may not provide an adequate representation of ion−solvent interactions. One should keep in mind, as Thomsen[36] points out, that Born himself derived his term for single ions and the extension to mixtures of ions used in modern e-EoS (sometimes with concentration-dependent dielectric constants) requires further discussion. This is the only place in this paper where we touch upon this discussion on "thermodynamic fundamentals" as it appears that electrolyte thermodynamics is an area where the development of new models may require fundamental advancement. For example, on the role and importance of the Born term (in general of ion−solvent interactions) and the role of single ion activity coefficients, Vera and co-workers have presented extensive experimental values,[37,38] but as yet, they are not entirely accepted by the whole community. We hope that in the future, we will see "pragmatic" developments of electrolyte models with both the classical approach of activity coefficient models (like e-NRTL, extended UNIQUAC, and Pitzer) and the advanced e-EoS and we believe that this will provide industry with a larger number of potentially successful electrolyte models.

6.2.6. Transport Properties. The transport properties are still very important to the survey participants, although their comments are less lengthy than in this survey compared to the one 10 years ago. Some typical comments are summarized as follows: "there is insufficient progress in transport properties, especially in dense (often aqueous) systems" and "transport property (TP) models are still lacking in comparison to phase behaviour models. This is in part due to lack of measurements in this area (e.g. thermal conductivity and TP measurements for heavier − non-alkane systems)." Here, we would add that although, for dilute gases, kinetic theory provides a solid theoretical foundation, at higher densities, the underlying kinetic theory is incomplete. Hence, unlike thermodynamic models, the transport property models are, by necessity, less based on theoretical molecular description.

Especially modeling of mixture viscosity is a challenge, as mentioned by some: "interaction parameters can be fitted against experimental data, but would it be possible to develop predictive model that could be implemented to commercial simulator?"

The complexity of viscosity goes beyond the quest of fitting parameters and prediction. Many predictive models (GC-based) relate to Newtonian behavior. Yet, many fluids exhibit other rheological behavior. Hence, the first step in modeling viscosity should be to predict the kind of rheological behavior. Are there models that do this? Moreover, viscosity is very sensitive to temperature and/or density as one approaches the solidification line, resulting in large uncertainty in the predicted values.

Two particular areas where we lack reliable predictive models are the viscosity and thermal conductivity of block copolymer and of melted coal ashes.

Survey participants noted that "block copolymer is an important technique to light and strong polymer materials. Its physical properties are affected by the way of polymerization (-AAAA-BBBB- or -AB-AB-AB-AB-...). If accurate and reliable estimation methods are established for block copolymers, engineers may save time and cost for measuring the property which are needed every time when changing the product specification.

https://doi.org/10.1021/acs.iecr.0c05356
Ind. Eng. Chem. Res. 2021, 60, 4987−5013

Coal fired power plants are still one of the important power sources in the world. Highly efficient utilization of coals is being studied including Integrated Gasification Combined Cycle (IGCC) or ultra-supercritical steam system. However, in real situations, one of the most frequent causes of losses at power plants is clogging or slugging by ash, which occupies more than 10 wt% of coals. Currently good thermodynamic model has been reported which covers thermochemical properties and surface tension. However, there is not yet a reliable and established model for transport properties such as viscosity or thermal conductivity in the public domain."

6.3. The Role of Simulators and Interfaces. It is difficult to decouple the discussion on limitations and future prospects of developed models from the commercial process and other types of simulators where such models are used. Most companies rely on these simulators. The link between models and simulators is nicely illustrated in the following comment: "Model selection, development and maintenance remain confined within the scope of the process simulator used in the company. For example, if Aspen Plus is the simulator used by the company (or the client), one must select a model offered by the simulator. There is little room for originality, even if there is a call for it when there are no experimental data or parameters, predictive models are being used as a quick fix (or scapegoat...), without a real understanding of what they are, which predictive model to choose for what occasion, strengths and drawbacks of the selected predictive model."

Models are, of course, used for process optimization and in conjunction with general process or product models:

> "The real-time optimization of the process (from product design, process development, to plant performance optimization using computer aided process simulation tools) is the target. In this regard, predictive or well-parameterized thermodynamic models are the prerequisite for process simulators."
>
> "Thermodynamic models are never used as such, but as part of an overall model, e.g. for (conceptual) process or product design. This means the thermodynamic model needs to be accessible by the software tool that is used for the final objective."

Several simulators are relevant, depending on applications, mixture choice, and interest. Issues with model availability and compatibility in the various simulators need to be resolved for successful applications and the statements below illustrate some of the issues companies face:

> "We typically do not use ASPEN or any other process simulation software. So getting basic templates into CFD that are numerically stable is important, as sometimes we need to add the needed phenomena by ourselves."
>
> "The detailed models are not that important, we would need more thermodynamic models and material properties in commercial CFD platforms. Order of magnitude analysis and applicability is needed. We need information to know if the new design is better or worse and to assess which phenomena or properties are critical."

7. OTHER ASPECTS INCLUDING EDUCATION AND FUTURE TRENDS

The last question was an "open question", where participants had the possibility to comment on other relevant aspects or emphasize some of the previous points. Excluding direct repetitions, a number of important additional remarks have been made, and we present them here, often exactly as cited.

7.1. Peer-Review Process and Experimental Data. Many emphasized again their concerns on the lack or the quality of experimental data but also commented on the quality of the publications:

> "The quality of physical property related publications has deteriorated. The peer reviewing process seems not to work adequately anymore. Publications on experimental data often are incomplete so that an evaluation becomes elaborate and complex. Publications on modelling, which would be verifiable only with great effort, often are very selective and show noticeable omissions concerning the discussed systems or properties.
>
> In Academia in Europe much effort has been spent on molecular simulations with limited success while experimental know-how and measurements were left for Asian groups ... often with unprecise data. Nowadays it is difficult to say whose data are the most reliable, since the very good labs in Europe and North America are disappearing."
>
> "We would like to stress the importance of experimental measurements. The number of laboratories (industrial and academic) that can do accurate thermophysical measurements have significantly decreased over the past 10 years (laboratories are expensive to operate and maintain)."

7.2. Education. Chemical engineering education and the role of thermodynamics are discussed by many survey participants, often in a passionate way; hence, we decided to include some of the statements exactly as they were written to illustrate some of the characteristic industrial views:

"One more long-term thought is to run a study around the modernization of the basic chemical engineering thermodynamics curriculum that is taught in European universities, with the following targets:

- Future expert thermodynamic experts have a broader appreciation of the importance of their work, and how to best address requests both in industry and academia.
- Increase capability in basic skills around data science, molecular simulation, and the interface of thermodynamic modelling with other areas of modelling and simulation.
- Increase the presence of uncertainty analysis, and honest representation and explanation of errors and confidence intervals."

Some participants mentioned that nonequilibrium thermodynamics may be useful for improving the understanding of transfer phenomena, while some discussed the role exergy analysis may play: "Kinetics of phase separation and other phenomena will likely make fundamental Thermodynamic research of further relevance to industry. I believe this represents a gap between Industrial Operations and Academic Research. Those engaged in Industrial Operations will dismiss thermodynamic models and/or predictions due to the fact that that Operations tend to be characterized by transient, short residence-time kinetic phenomena, rather than true equilibrium. By measuring, reporting and modeling these transient effects, fundamental research can be more usefully aligned with the needs of industry."

Here is one of the most characteristic and extensive statements expressing some serious concerns about educational trends for thermodynamics. The particular industrial colleague

https://doi.org/10.1021/acs.iecr.0c05356
Ind. Eng. Chem. Res. 2021, 60, 4987−5013

with experiences and education from both UK and Germany comments on the shortening of studies and the fact that basic thermodynamics and associated models are often reduced or considered less critical. The colleague concludes the extensive analysis by stating that "I was part of a discussion in the Royal Academy of Engineering, where leaders from industry such as myself would analyse which skills are currently taught and where there is a gap to what industry needs hence where we need to make space in the curriculum. There has then however also be the notion that, with the curriculum being already compressed as it is, which topics should be shortened in order to create that space. Maths, also Thermodynamics, were some of the topics seen as not totally critical, e.g. as compared to design projects. I was raising the point that, another way of going about this would be to say, can we add topics while keeping the fundamentals. Both can be easily achieved if the study time was extended from 3−4 to 5−6 years as it used to be. Obviously, the impact on the student's budget would be very significant, however if tuition fees go, which has been proposed and is done in many European countries, this would no longer be an argument.

Again it comes back to the question whether we as an industry, and we as a society, are happy to compromise the level of knowledge from the student's population in the light of the big challenges that mankind is facing. If not, I believe we have to be prepared to do much more than what we do today, in order to allow more young motivated engineers access to high quality education, a combination of the quality of education & quantity of lectures they receive."

7.3. Relevance of Models and Link to Industry. The relevance of models for industry has been commented on by several participants. This is of concern to many and some characteristic statements are shown below:

> "Conferences focus too much on fancy systems (e.g. nano-stuff) or other completely irrelevant molecules (e.g. simple n-alkanes)."
>
> "Too much attention for molecular dynamics that can never be used in industry because they focus on simple and linear molecules and require too much computation time to serve in process design".
>
> "Gap between academics and industry is very large (exceptions are Denmark, Germany, Netherlands). We need more initiatives such as UNIFAC Consortium."
>
> "The abundance of different models is still a problem which hinders us from making the jump to the more complex models, such as SAFT."
>
> "I see two currents in our work, one more scientific where we try to describe the systems based on physics, and on thermodynamics. The other more pragmatic way is where we just try that the model matches the plant data as best as possible. This last tendency is keeping us from changing to more advanced models, because it often relies on simplistic models with empirical parameters to match the plant data. To counteract this tendency we need better description of the systems with electrolytes, solids, and complex associating systems. We also need a better implementation of these advanced thermodynamic models in commercial simulators."
>
> "Consider usability of models − my prejudice is that crystallization (and granulation) models sound good and understandable, but are very difficult to parametrize. The fundamental science of solids needs some work. Any tools to predict the behaviour of solids so as to process them better, predicting operating spaces, design spaces and the like, are hugely valuable".
>
> "In the modern age it becomes more and more important to make use of simple tools, see[9] for this."

7.4. Future Trends. One aspect, also mentioned earlier in the paper, is the combined use of artificial intelligence and thermodynamic/transport properties. This could be an alternative to the lack of data and the difficulties associated with using empirical, correlative models. Even if it does not allow for extrapolation, it could be a solution for problems, which only need interpolation of data or find correlation between properties: "We need to vulgarize a bit more at least the basic thermodynamic concepts and numerical methods in open-source software like python or R, this is a key way to increase the visibility of the thermodynamic community while making thermodynamic more attractive for students...

Statisticians have already performed this kind of exercise when introducing concepts of "Machine Learning" or "data Science". Since the thermodynamic community have structured databases (like DIPPR, NIST databases,...) which looks like "big data" that are mandatory in any hybrid modelling (combination of knowledge model and machine learning algorithms) can highly be helpful in the challenging development of "digital twins" of actual chemical and bio-chemical plants."

Another aspect is the climate change and sustainability, an issue that rather surprisingly did not feature much in the survey. One company, however, provided an extensive account of their thoughts (with some suggestions for possible future activities of the WP), concluding that "I think this topic (climate and sustainability) should be straight on top of the agenda everywhere. I certainly see that if I speak to the neighbours in the community I am living, this topic plays a very prominent role, and society is hoping for/demanding answers/recommendations/solutions from us in industry and academia. I would be interested what the position of the European Working Party is on this issue and what the plans are. Again, it may well be that here is a very vivid discussion already ongoing, and it is just me being ignorant − if so, great − if not, you may like to think whether you want to make this a more central part."

We can state, however, that this trend is changing and several companies have confirmed that sustainability (including significant reduction of field greenhouse gas footprint) is now becoming a core element in the companies' strategy. This is now the case for very many companies worldwide.

8. CONCLUDING REMARKS

One of the important messages that comes out of the present survey, as well as from the 2010 survey, is that there is an increased need for more measurements and development of new techniques for high-quality data, which are reliable and thermodynamically consistent with well-defined uncertainty limits. The same holds for a lack of data (VLE, LLE, VLLE, SLE, and adsorption) for high-molecular multifunctional and very complex compounds of extremely low volatility, including oxygenates, ionic systems/electrolytes, and complex polymers, but also with new emerging needs in novel applications connected with electronics and new hydrofluorocarbon refrigerants as well as in specialty chemicals, food industry, and pharmaceutical APIs. In the latter case, companies face new challenges in the development of new processes for bio-based products, which include weak electrolytes, solids, crystallization, solubilities, etc., and therefore, they are seeking new data as well

https://doi.org/10.1021/acs.iecr.0c05356
Ind. Eng. Chem. Res. 2021, 60, 4987−5013

as reliable models. The data are still lacking even for more mature applications in the oil recovery and gas processing, e.g., data for MEG processes, H_2S scavengers with associated chemical equilibria, mercury and acid gas removal, high-pressure phase equilibrium, and enthalpy data as well as data on mineral reactivity (both on thermodynamic and kinetic basis) including metastable equilibria and measurements of thermophysical properties for higher naphthene and aromatic content of heavy oils. What is new in the current survey is that there is also an interest in having more data on reactions and processes relevant to carbon capture and storage and a need for additional data in the production and recycling of lithium ion batteries and other rare earth elements.

Many companies expressed their concern about the quality of the data and the disappearance of the quality labs in general, especially in Europe. To assure good quality of the data, more efforts are needed to critically evaluate the new measured data, to report the experimental errors systematically, and to check for thermodynamic consistency of the finally reported values. A guide to experimentalists for reporting data that was requested by companies, and led by NIST, is being prepared and will soon be published. Comparison to existing data (data validation) at high pressures is explicitly requested to develop a reliable method. With an introduction of automation, many companies have a shortage on true experts in the field, especially in the critical analysis of the results, resulting in an increase in erroneous data.

A need for reliable models is another common feature that has not changed since the last survey. Among the models, the more predictive models such as UNIFAC (GC models in general), COSMO-RS, cubic EOS especially in the form of the PSRK/VTPR, and advanced EoS like CPA and PC-SAFT are of more interest to the industrial participants. It is suggested to have a relatively few models and to be well parameterized, but all "model directions" have their role and applications. Benchmarking techniques, to identify promising new models, need to be developed so that one can distinguish between the models and validate them for future applications. More effort should be given to the modeling of electrolyte systems, both from a fundamental point of view and from a more "practical" point of view, because of their complexity and very prominent role in bioprocessing. The e-NRTL model and other models mainly used for this purpose by industry are lacking of standardization and an increased need for a critical review/comparison/evaluation of these models is expressed. e-NRTL has serious limitations and needs a clear methodology to fit the parameters. Therefore, more predictive models are required for electrolytes with a limited number of adjustable parameters and data regression that cover a wide concentration range, including speciation behavior and uncertainty estimation. Some activities in this direction are initiated by two projects recently started (an ERC Advanced Grant and a joint industry project—both in electrolyte thermodynamics), partially under the auspices of the Working Party of Thermodynamics and Transport Properties of the European Federation of Chemical Engineering.

There is also an increasing interest in models for estimation of properties of specialty chemicals and pharmaceutical APIs, as well as for small molecules in cell and gene therapies. The use of thermodynamic models in the pharma and bio-related industries is still not as mature as it is in the petrochemical and chemical industry. This is mainly due to the lack of pharmaceutical descriptions in the process simulators, suitable predictive models not being available, the lack of necessary experimental data, and the fact that many pharmaceutical processes involve solids and associated operations, which are traditionally more difficult to model compared to processes involving only fluids.

Even in petroleum applications, the need for more accurate thermodynamic models, which deliver reliable results very close to the critical point, is still present. Novel models like PC-SAFT should be tested for their performance at the critical point but should also be able to describe oil and gas. Good models for interfacial and transport properties (viscosity, diffusion coefficients, and thermal conductivity) are lacking, partially due to the lack of measurements, especially for polymer−solvent systems and block copolymers. Predictive models for reaction kinetics are also mentioned, even though this is outside the scope of thermodynamics.

Complex molecular-based models, like PC-SAFT, have attracted a lot of attention and are mentioned very often in the survey. However, further efforts are needed toward appropriate implementation for comprehensive flowsheet simulations, as discussed by industrial participants. The parameterization of such models is complex and physically based parameterization strategies should be developed and published. The models should be better documented and implemented in simulators. It is suggested to invest more effort toward parameterization of EoS models such as SAFT-γ Mie due to an extensive group-contribution database and to derive methods for determining at least some of these parameters from *ab initio* quantum mechanics calculations, especially as SAFT-based approaches give better performance than cubic EoS in derivative properties, e.g., speed of sound.

It has been suggested that COSMO-RS, a well-accepted model over a number of years, is more suitable and should be used for generation of "pseudo-data" for model parameterization since it has the potential to distinguish between conformers rather than for process and product design.

Thermodynamic modeling should be used not only in process design but also more effectively in product design, including the formulations, where interfacial and transport properties are playing a very important role.

In contrast to the previous survey, where the participants were not very supportive of MS, the participants now see MS as a useful method for interpolation purposes and as being able to generate pseudo-experimental data that can supplement good experimental data. However, some survey participants felt that MS should only be used for making qualitative comparisons (e.g., in solvent screening or property estimation when only limits are important), but not to replace experimental data.

In our previous survey, the algorithm improvements were an area of interest. The results of this survey show that there have been many developments reported in the literature in the area of algorithms over the past 10 years, but not all were yet implemented in the simulators that are used by industry. The need for computational speed increase in commercial simulators for SAFT calculations is high up in the list and the challenges still remain in multiphase and/or reactive flash (split) calculations, as well as in data regression.

The issue of standardization and validation of models was highlighted in the previously published survey, and this issue still remains a serious concern to the surveyed companies. It has been suggested that the choice of standards should be a joint effort of academic and industrial undertaking. Model implementation in process simulators, especially for models such as SAFT, with multiple versions, leads to confusion. The attention should be given to the uncertainty propagation and sensitivity

https://doi.org/10.1021/acs.iecr.0c05356
Ind. Eng. Chem. Res. 2021, 60, 4987−5013

analysis in process simulators to understand and evaluate an impact of uncertainties in property models on process and product design and development. The CAPE-OPEN framework, to connect various applications, is also discussed and the consensus is that it should be developed further. As industry is mainly concerned with conceptual process/product design or plant performance optimization and rarely with thermodynamic models alone, the thermodynamic models need to be accessible by the appropriate software tool, e.g., by using CAPE-OPEN standards to assure accurate model implementation and sufficient parameterization. The companies that participated in this survey mentioned, as common platforms used by them, Aspen and gPROMS, while some companies are using an in-house simulator and/or CFD with an addition of the needed phenomena. Of course, there are many more software tools in the market, even though not extensively discussed in this survey.

The need for proper thermodynamic education is also a common theme with the previous survey. EFCE WP TTP has played a very important role during the mentioned years, organizing workshops on specific topics, which attracts industrial partners. The new generation of chemical engineers is more versatile in modeling but with limited experimental skills mainly due to the lack of laboratory experience. The lack of expertise in critical analysis, which was also noted in the survey, may result in an increased use of erroneous data and, consequently, wrong engineering calculations. Long-term modernization of the basic chemical engineering thermodynamics curriculum is suggested. However, there are areas where deeper understanding and education of engineers is needed. For instance, the concepts of entropy and exergy play an important part in technoeconomic assessment of new technologies in the area energy of energy storage and transport, while molecular simulations are increasingly used to generate useful data. The CAPE-OPEN framework as well as uncertainty analysis that includes confidence intervals should also be properly introduced at university level to the students.

An issue about digitalization is raised in this survey for the first time and very diverse views were received from industrial participants. There is a broad agreement that big databanks, combined with advanced algorithms like machine learning (ML), artificial intelligence (AI), and meta-modeling, to mention a few, should be used for very complex systems, risk and trend analysis, and generation of pseudo-experimental data in facilitating thermodynamics (data and modeling) and also in process modeling and CFD. For property calculation and prediction, QSPR (quantitative structure−property relationship)/ML methods are suggested, while ML, AI, meta-modeling, and data mining algorithms can be very useful in the identification of optimum parameters in the simulation of unit operations in chemical plants. Many participants are of the opinion that the synergy should be sought between conventional "knowledge-based" models and deep learning approaches and, therefore, these innovative efforts should continue in the future.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.0c05356.

Benefits from thermodynamics as seen from industry (examples provided by the participating companies), detailed questionnaire by EFCE WP on Thermodynamics and Transport Properties, and overview table "10 years after—what has happened" (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors wish to thank all the participating companies for their enthusiasm, active participation, and their detailed answers to the survey. Without them, this paper would have never been written. The authors wish to acknowledge Urška Linda Beuermann and Rok Dolinšek for the design of the graphical abstract. G.M.K. wishes to thank the European Research Council (ERC) for partial funding of this research under the European Union's Horizon 2020 research and innovation program (grant agreement no. 832460), the ERC Advanced Grant project "New Paradigm in Electrolyte Thermodynamics".

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