

The Imperial College Thermophysical Properties Data Centre¹

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The IUPAC Thermodynamic Tables Project Centre in London has at its disposal considerable expertise on the production and utilization of high-accuracy equations of state which represent the thermodynamic properties of substances. For some years they have been content to propagate this information by the traditional method of book production, but the increasing use of the computer in industry for process design has shown that an additional method was needed. The setting up of the IUPAC Transport Properties Project Centre, also at Imperial College, whose products would also be in demand by industry, afforded the occasion for a new look at the problem. The solution has been to set up the Imperial College Thermophysical Properties Data Centre, which embraces the two IUPAC Project Centres, and for it to establish a link with the existing Physical Properties Data Service of the Institution of Chemical Engineers, thus providing for the dissemination of the available information without involving the Centres in problems such as those of marketing and advertising. This paper outlines the activities of the Centres and discusses the problems in bringing their products to the attention of industry in suitable form.

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1. INTRODUCTION

In recent years there has been an increasing demand from industry for data on the thermophysical properties of materials for use in process design. This paper reviews one attempt to meet these demands which now includes

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both a United Kingdom effort and an international activity. It is intended that the review should serve as a guide to future efforts elsewhere in the world in the same direction. The guidance may be derived partly from the problems involved in such work, which can be identified only with hindsight, and partly from the success which the project to be described now enjoys.

2. THE BACKGROUND

When the IUPAC Thermodynamic Tables Project began in 1965, participants were faced with two major problems. One was purely scientific: How were the experimental data to be combined so as to produce accurate and usable equations of state? At the time, there were units operating at many levels and the role of the IUPAC Project was to provide a platform for those working at the highest level, such as those at the NBS in Boulder, at Texas A&M University, at the van der Waals' Laboratory in Amsterdam, at the Moscow Engineering Institute, and at the Odessa Institute of Marine Engineers. The second problem, which was the concern of the Project Centre, was that of propaganda: How was it to convince the world of the importance of the work of such people as those?

Well before this project was set up the electrical power industry had found that as the scale of their operations increased, it was no longer possible to work with small relative errors in the properties of steam, and steps had to be taken to improve the absolute accuracy. It was the late Professor Newitt who saw that other industries would face the same problem as their scale of operations increased, and so it proved. However, it was necessary to be able to prepare the data before industry had realized that it was going to need them. Fortunately, the Centre's plans received sufficient support to survive this difficult period. The liquid air industry, the users of LNG and of ethylene, did discover the need for thermodynamic properties that were both reliable and consistent, and other industries—such as the space industry and the nuclear power industry—found that there was a paramount need for the highest possible accuracy in thermodynamic properties.

Many studies made in the United States have confirmed this need for accuracy in plant design, and the introduction of CAD with more powerful computers has enabled the designer to make use of such data as a routine matter. The most stringent requirements have arisen in the nuclear engineering field, with the extension of the Quality Assurance scheme to data: it is no longer sufficient to specify the data used, but in addition, it is necessary to demonstrate its quality. We have been told that in the U.K. the IUPAC books are considered to do this so well that they are held up as

a model of how such assurance of quality should be demonstrated for all data.

In fact, having for so long sought to prove the need for our products, the Centre is now faced with the problems of success (all of which arise from the demands of our users), which have led to a reorganization and expansion of the work at Imperial College into the Imperial College Thermophysical Properties Data Centre. The expanded Centre has incorporated the transport properties of fluids into its activities and again acts as the IUPAC Project Centre for this study.

3. CURRENT DEVELOPMENTS

The expansion of the Centre combined with the developments in the utilization of thermophysical property data in process design has resulted in a rather different environment in which the Centre must act and in a number of new problems.

3.1. The Fluids to be Studied

The first problem is to decide what fluids should be studied in future. In the past, there were a dozen or so substances which had to be studied such as the components of air, LNG, carbon dioxide, ethylene, helium, and so on. These were all characterized by a wealth of experimental data, covering a wide range of parameters and a variety of properties, so that once a suitable equation of state was found there were ample data both to fix the surface with accuracy and to demonstrate that this had been done. Now it is time to turn to fluids such as the alcohols and the simpler aromatics, fluids for which there typically exist limited studies of a high accuracy, broader studies of a low accuracy, and no data at all in some key parts of the thermodynamic surface. Existing techniques of surface fitting assume virtually complete coverage of the surface.

The way forward is not clear: Goodwin at the NBS, Boulder, relies on using an equation of state which, because of its form, must produce a thermodynamically plausible surface, the experimental data determining the scale and location of the surface, as he has demonstrated for benzene [1]. The Thermophysical Properties Data Centre is examining modifications of the corresponding-states principle to improve its accuracy, so that predictions can be made to provide a guide to the shape of the surface, the experimental data again fixing the final surface. A first example of this is found in the study of chlorine [2, 3] and it will undoubtedly be improved and used again. Another possibility, when the molecule is amenable to theoretical study, is to use theory to help fix the surface, and this the Ther-

mophysical Properties Data Centre is trying to do in a study of sulfurhexafluoride. A further approach is to use some equation which has been found by experience to fit several substances and hope that they will prove to give a plausible surface when fitted to other substances. This is being done by Younglove [4] at the NBS, Boulder, using the Stewart and Jacobsen equation and for a very wide range of fluids by Bender and Polt using Bender's equation.

A side effect of this technique is that it provides a set of equations similar in form for those who approach mixture calculations via coefficient-combining rules, which, as Stewart [5] of CATS at Idaho has found, work well for air and its components. The problems are not confined to handling the available data: CATS, wishing to study the halomethanes, found that the first step needed was to compile a meticulous set of data maps for each of the fluids before the extent of the study could be appreciated [6].

All the above refers to a wide-ranging analytic equation which does not include the critical region. For the substances the Centre are contemplating now there is a dearth of data for this region, except for measurements of the critical point itself, which were often made in apparatuses not specifically designed for such measurements. The problem of predicting nearcritical behavior from no data at all is one we have not yet examined. Some time ago Sengers and Levelt Sengers [7] of the NBS at Gaithersburg did examine how far such predictions could be made using the principle of universality: whether their methods would work on more complicated substances and whether they could predict the parameters for the Wegner correction terms are not certain. Perhaps it would be best to say that at the moment we are hoping for a lead from the experts in this field.

3.2. The Properties to be Studied

The second problem is to decide what properties should be studied. Although a complete equation of state will provide a self-consistent set of all the equilibrium thermodynamic properties, the process designer also needs transport properties if he/she is to be able to handle mass and energy transfer problems. At present, these are not measured to the same accuracy or over the same range of parameters as thermodynamic properties, but there is the same need for review and for correlations to provide the best sets of values. The IUPAC Commission on Thermodynamics has been aware of this for some time and finally inaugurated a Sub-Committee on Transport Properties by the simple expedient of asking Professor Kestin to formulate and implement a program. We now have a busy and vigorous project under way, making studies in its own right and also supplementing the work of the Thermodynamic Tables Project. It is necessary for workers

in transport properties to advance simultaneously on three fronts: to advance theoretical knowledge of transport properties, to increase greatly the amount of experimental data, and to make the reviews and correlations which will make their work available in a form suitable for users. It was at all times clear that, if it was to succeed, this project, like the Thermodynamic Tables Project, would need an active project center, and the U.K. Department of Trade and Industry recognized this and offered to finance one at Imperial College.

3.3. Dissemination of Information

The third problem is how best to report the results of our studies. For thermodynamic properties the traditional answer has been as books containing tables. One of the Project Centre's innovations was to include in the books a discussion of the available data and equations with a demonstration of how we were led to our final tables, but basically our books are in a direct line from the first steam tables of Mollier in 1906 [8]. Such books still have an important part to play, but more and more our results are needed on computers. It is possible to write complete computer programs from the information given in the IUPAC books, but this is inefficient, especially at the debugging stage, where problems due to the different behavior of computers may be mistaken for errors in programming. The results of the work on transport properties are not even suitable for issue as a book. They study groups of fluids over restricted ranges and would be much more suitable as scientific papers, from which in later years books could be compiled.

The answer is for the Thermophysical Properties Data Centre to issue its own programs rewritten so as to be suitable for users, including whatever is known on the transport properties, and which should be capable of amendment as needed. This answer leads to another problem: Who is to market, install, service, and update such equations? Certainly the Centre has neither the expertise nor the number of staff that would be needed to do this properly, and since we were contemplating a commercial service, it had to be done properly or not at all.

We were fortunate to find the ideal solution: a unit which had all the necessary marketing skills and a data base to which our product was a welcome addition.

This unit is the Physical Properties Data Service (PPDS) of the Institution of Chemical Engineers, which maintains a data bank (also called PPDS). The principal contents of this were data on several hundred substances which can be accessed remotely either for the data or for estimations based on calculation routines, which also form part of the data

base, using what method seems most accurate. PPDS also includes several subsidiary packages, such as VLE data and estimators, so another package giving high-accuracy properties of pure fluids was an obvious extension to its facilities. The data bank as a whole is designed to be "user-friendly" and can be installed on a wide variety of computers. To convert our equations into a package capable of meeting these constraints, given also a specified amount of memory and the requirement for reasonable response times was not a trivial task. Probably the most frustrating requirement was that the package should run on a wide variety of computers; Marjorie de Reuck, who was responsible for this work, was unhappy to find that, again and again, elegant programming had to be replaced by most elaborate routines if the result was to be intelligible to the full range of computers.

The major contents of the package are equations giving the Helmholtz free energy as a function of density and temperature, from which any thermodynamic property can be calculated if it is recognized by the "front end" of the PPDS. At present this is not every property, but PPDS monitors its customers' needs and can expand the properties available without further work from the Project Centre. There are at present about 20 substances in the package which include all the IUPAC equations [9] and others of high quality. Equations for the transport properties are being added as rapidly as possible, substance by substance. These equations are inevitably of a lower accuracy, but they meet our requirement that they be as accurate as possible.

4. FINANCE AND ORGANIZATION

When this activity was merely a concept it was put to the U.K. Department of Trade and Industry, which agreed to finance this work also, separately from the work of the Project Centres. Thus we had, under the same roof, two Project Centres and a programming project. Our solution was to incorporate them all into one body, the Imperial College Thermophysical Properties Data Centre. It has a staff of nine, some of whom are part-time, and it does not try to divide its personnel into three watertight compartments, but rather splits up its work schedule into three. The system is working well, and in particular, there is no pressure from our sponsors to concentrate on our data-bank work at the expense of our international duties.

5. THE FUTURE

The greatest need of the Imperial College Centre at present is for experimental data. The head of the Centre, Dr. Wakeham, has a laboratory for the study of transport properties, so the Transport Properties Centre can lead by example, but the Thermodynamic Tables Centre must, as

usual, rely on the response of experimental institutes to its suggestions. Our own immediate suggestions are the simpler alcohols and aromatics and hydrocarbons from the pentanes upward, the sulfuroxides, and most of the halomethanes and haloethanes, but this is by no means an exclusive list.

One reason why there are few data on many of the substances of interest is that they are toxic, carcinogenic, and highly inflammable or explosive and may decompose or associate or in other ways become indeterminate, and are thus liable to require complicated laboratory precautions with little assurance of reward. Dr. Angus has suggested several times, but without success, that there should be a special fund available to pay the extra costs of handling noxious materials over and above the costs necessary to study, say, nitrogen. It seems that such a fund could have an important influence in the planning of experimenters.

It might be useful to say a few words about what is meant by "more experimental data." The easiest way is to show what a correlator ideally would like to be given. The amount of work necessary makes it uneconomic to prepare a correlation for a range of less than, say, 0 to $5P_c$ and T_1 to $2(T_c - T_1)$. Within those ranges, we would like to have the following.

Triple Point. Pressure, temperature, and liquid density measurements.

Critical Point. Pressure, temperature, and density measurements.

Saturation Curve. Vapor pressure measurements from P_1 pressure to P_c , initially at 5 K intervals, decreasing as dP/dT increases.

Saturated vapor density measurements to be attempted.

Enthalpy of evaporation measurements from T_1 to T_c initially at 20 K intervals, decreasing as $d\Delta H/dT$ increases negatively.

Melting Curve. Pressure, temperature, and, if practicable, liquid density measurements to $5P_c$ at 0.1 K intervals.

Gas Phase. About 300 measurements of $P\rho T$ from T_1 (or T_σ) to $2(T_c - T_1)$ and from P_1 (or P_σ) to P_c and about 200 similar measurements in the same temperature range from P_c to $5P_c$, the intervals being decided by the behavior of $(\partial P/\partial \rho)_T$ and $(\partial P/\partial T)_\rho$.

In the low-pressure region, measurements of the speed of sound, most numerous near the saturation curve.

In the high-pressure region, measurements of C_p sufficiently numerous to define the shape of the maxima.

Liquid Phase. About 500 measurements of $P\rho T$ from T_1 (or T_σ) to $2(T_c - T_1)$ and from P_1 (or P_σ) to $5P_c$, the intervals being decided by the behavior of $(\partial P/\partial \rho)_T$ and $(\partial P/\partial T)_\rho$.

About 100 measurements of C_v close to the saturation curve and in the region where $(\partial^2 P/\partial T^2)_v = 0$.

Special attention should be given to a region hitherto ignored by experimenters: that extending from P_t to about $0.1 P_c$. Data in this region have a major effect on the final behavior of the equation of state, and even a few data are important, if measured accurately. The possible advantage of ΔH measurements over density measurements should be explored.

Critical Region. $P\rho T$ measurements in both gas and liquid phases from $0.9 T_c$ to $1.3 T_c$ and from $0.3 \rho_c$ to $1.5 \rho_c$ at intervals sufficiently close to define the surface.

Second Virial Coefficient. $(\partial H/\partial P)_T$ measurements from atmospheric pressure to as low as is needed to define the zero pressure limit, at temperatures from T_t to $2(T_c - T_t)$ intervals depending on the magnitude of dB/dT . Direct measurements of B in static equipment may be affected by adsorption.

Other Properties. Measurements of the speed of sound and C_p in the liquid region are valuable either as checks on the equation of state or for direct use in constructing the equation. Measurements of C_v in the gas phase and of $(\partial T/\partial P)_H$ in any region have little influence on the behavior of the equation of state.

It may be mentioned that one of those requirements, the measurement of PVT in the liquid phase, is being met by a group at the University of the Ruhr, Bochum, under Professor Kohler [10], which is directed specifically to measurements on hitherto unexplored fluids.

Finally, it may be apparent that no mention has been made of work on mixtures at the enlarged Centre. This topic has been suggested, and the answer has been that if we were to tackle mixtures, we should be just another group among many, and our expertise on pure fluids would be lost. In any case, success in dealing with mixtures depends on an accurate knowledge of the pure fluid components, so to continue our present work would make a greater contribution to mixtures than to work on them directly.

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