

“Secrets” of High Pressure Phase Equilibrium Experiment

KUI 26/2005
Received September 5, 2005
Accepted October 3, 2005

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Communication problems between authors, editors and potential readers are surveyed and described in connection with determination of vapour-liquid equilibrium at high pressures. However, those and similar problems may also be encountered in other research fields which deal with experimental work.

Keywords: *Vapour-liquid equilibrium, high pressure, comprehensibility, disinformation*

At first, I must say that in this paper no secrets will be discovered. However, there are “secrets” present in almost every paper, particularly in those describing a sophisticated experimental technique and procedure. Such a “secret” can be defined as missing, latent or in written papers incommunicable information.

The investigated papers were published in relevant journals such as *Fluid Phase Equilibria*, *Journal of Chemical Engineering Data*, *Journal of Chemical Thermodynamics*, etc. Of course, this does not imply any charge against any journal; the vast amount of papers is excellent and it is obvious that a search for the mentioned “secrets” is beyond the referee’s duty. These core papers have served as a springboard because they refer to earlier published communications in other journals, so extending the source spectrum. I am not taking into account good looking (but not first class) publications which can occasionally be found anywhere. No reference is given since distribution of “secrets” is not uniform and depends on time, journal, author, the problem, and its complexity. I dare say that papers without “secrets” do not exist.

I am not going to discuss the quantity and quality of information provided by the author, which by the way is not usually sufficient for repeating, reproduction, and thus verification of the experiment. I do not want to blame reviewers, because first of all the authors are responsible for foggy formulations. There should not be any doubt about what has to be cited, what just not omitted and what can be inferred or deduced. One feels that some information is still lacking and that such absence represents the main source of secrets.

In any case, this is a difficult problem to fight. On the one hand the paper should not be too long, on the other a very brief and simplified description could testify either to the author’s disparagement of the reader or to overestimation of the reader as someone capable of understanding all ideas (often available only between the lines). The high pressure vapour-liquid experimental technique is so complicated that it makes it hardly possible to find a golden middle path of the extent of information. Nevertheless, the average result is more likely worse than better.

There seems to be an ethical problem, too: the author may feel (and this feeling may not be far from reality) that his equipment is the sole one in the world able to solve a group of particular problems. Therefore, he should not simply put his cards on the table and show all the experimental tricks elaborated and subsequently invested into the experimenter/operator, so forming his know-how and routine. (No fear – such tricks are entirely indescribable.) On the other side it is impossible to publish every move of the experimental procedure (each step is extremely important, of course!) or journals would be flooded with superfluous information. Reference to previous work does not improve the situation much: in a chain of citations the details are rather dissolved than clarified.

The way to understand completely the work on a high pressure apparatus for the measurement of vapour-liquid equilibrium is to go and see the equipment *in natura* or even better to operate it for as long as possible. This is the only way to disclose unpublishable secrets. However, such a “reading of a paper” is costly, time consuming and generally not feasible.

There are three kinds of secrets. The first one concerns important information which is kept back in fact and knowingly neglected by the author. This is a real imperfection and should be noticed by the reviewer. The second kind is the most frequent: usually some parts of the equipment or procedure are mentioned briefly and left to the reader’s imagination. This is exemplified by a simple statement that there is “a pressure measurement part and a composition analysis part of the apparatus” with no further detail. Sometimes the description is so simple that it would be better to drop it altogether.

Since the author is familiar with his equipment, every particular of it is a matter of course for him as for an everyday experimenter. As a rule, he does not admit this advantage to himself and lets the unknowing reader “stew in his own juice”. The statement “the cell was magnetically stirred” opens the door to various speculations: mixing can be radial, axial, manual, diverse with respect to the construction of the stirrer or the whole equipment, and also vigorous, intermittent etc. This is admittedly a trifle; many trifles could

be mentioned but there is the last straw that broke the camel's back.

The procedure of phase sampling for analysis is another story. The description neglects important know-how, as to diameter and length of tubing, homogenization of sample (i.e. reproducibility of analysis), heating of lines, type and size of valves. Similarly, the amount of sample withdrawn (and consequently its effect on equilibrium pressure) is often not given.

Further, various procedures can be applied to degassing that lead to different results. Despite the importance of degassing, it is considered as a marginal problem. Therefore, it is described briefly, resulting rather in an obfuscation than an explanation. For example, a statement like “freeze-pump-thaw method” is superficial (e. g. the temperature differences used can affect the quality of the product). On the other hand, in some cases an effect of gas traces removal is not as significant as an error caused by impurities in the gas mixture (e.g. 0.1 % of nitrogen in carbon dioxide yields 2 bar difference in pressure at critical conditions).

Less important information is usually exaggerated at the cost of more substantial details. I have found a paper written probably by a salesman in fittings: it gave the specification of every single fitting piece (including the manufacturers) which was incomparable with the reduced description of the remaining parts.

It has already been mentioned above that tracing back to cited papers is unsuccessful, too. There is a series of papers and in each of them the apparatus described in a previous article is used (“it was essentially the same, with small changes and improvements, newly designed parts”, etc.). In fact, the equipment designed in the original paper differs greatly from the one used in the most recent communication. This step-by-step (over decades) development of apparatus is invisible to the author who cannot notice the daily differential changes. It brings problems to a reader not acquainted with the evolution of the equipment. Another dead end occurs when a very original work is published in a strange, commonly unavailable journal, in a research report or as a conference contribution. It is often said that “the equipment is discussed in detail elsewhere” with reference to a dissertation. However true this may be, such a source can be reached usually only by direct contact with the author.

The third type of secret is the most difficult to depict, since it can hardly be expressed in writing. Months and years of experience, the experimenter's skill and practice are hidden behind the words. The communication of experimental tricks to a scientific readership is practically impossible and, in any case, at the cost of further overshadowing the main features of the work.

Look at the plain sentence “the cell was carefully flushed”. In fact, the art of flushing is irrelevant and does not concern the merits i.e. measurement of vapour-liquid equilibrium. Everybody can imagine several methods of flushing the cell, but each of them requires many exact and more or less indescribable operations consisting of many single steps. “...Filled with carefully degassed material...” – many more steps are necessary to fill out this statement. “A sample is drawn for analysis...” – how simple is a content of these words, but how many experiments and modifications of

equipment had to be done in advance. “Increment of the second component was added to the cell...” – is anybody able even to admit how difficult it is, moreover, if the absolute amount is to be determined? “The sample was fed so as to maintain the liquid level in the glass window position...” – it sounds easy but Nature is always against it. “Lines and manometers were heated to avoid condensation...” – it looks so obvious, nevertheless, how should a manometer be heated so as to easily avoid its failure due to temperature effect. It is clear to everybody that the whole apparatus must be pressure tight. However, no one describes the thorny path to it, etc.

The above comments represent only a small fraction of what could have been said. Besides, a lot of trouble, inconvenience and difficulty is simply not mentioned at all; we cannot avoid it nor is there any serious reason to speak of it.

A list of similar secrets could be very long. Revealing these (never mentioned) secrets in practice is difficult. The amount of them can be mathematically expressed by means of a multiplier of the really effective work so evaluating the total amount of work input. It can be estimated from 2 to 10 for equipment already in operation but it is much higher for newly built apparatuses. Therefore, some serious 50 to 90 % (I would say 95 to 98 %) of experimental work consists of incommunicable secrets.

Concluding, it must be said that no proof of the nonfeasibility of easy experimental studies was presented here. I wanted to state that the secrets of experimental work at high pressure are not invincible but only hard to overcome since they are hard to gain from the literature. I would not wish to discourage potential or real experiment-fans; I would stress: the better the mutual contacts, the better the information, the quicker the achievement. I have to point out that despite the permanently shrinking family of experimenters, their work cannot be replaced with computers (this is a steady-state process – look round about!). However, as long as the *Homo Experimentator* exists (for definition and illustration see¹), the rediscovery of experimental secrets will inevitably take place.

It is worth to remind of the comment² of my colleague and the Honorary President of the Czech Society of Chemical Engineering, Dr. Tomáš Mišek, who has acquired long and painful experience on both sides of the publication barrier since he belongs to both family of readers and family of reviewers. In all three relevant branches, each one representing the point of view of different party the confrontation of common expectation and sad reality can be expressed as follows (see table).

After many years of the same and own experience, I may strongly confirm the above confrontation. At present, the only change consists in reading on-line journals comfortably seated in a chair instead of a “tiring” walk to library.

References Literatura

1. H. Knapp, *Fluid Phase Equilib.* **29**, (1986), 1–21.
2. T. Mišek, private communication (1991).

Expectation Očekivanja	Reality Stvarnost
<i>The author</i> strives in service to mankind to inform the world community concisely and completely of her/his scientific achievements	<i>The author</i> urgently needs some precisely given number of publications in the prescribed media
<i>The publisher/editor</i> guarantees the excellent quality, formal perfection and most up-to-date technical aims of her/his Journal	<i>The publisher/editor</i> must collect and edit enough pages for this damned Journal every month
<i>The potential readers</i> are perpetually longing for knowledge, diligently reading all Journals in their special field and make lucrative use of the information gained	<i>The potential readers</i> do not read Journals at all and are happy (80% of them); they look through the Journals in the library and read an article or two if in a good mood (15%); they try in vain to make some use of an article in their field of real interest which is full of secrets, mistakes and disinformation (5%). Fortunately, all ten possible authors in special field of a reader are her/his good friends with whom she/he meets and discusses the topic regularly

SAŽETAK

"Tajne" određivanja fazne ravnoteže pod visokim tlakovima

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Razmatrani su i opisani problemi komunikacije između autora, izdavača i potencijalnih čitatelja na primjeru eksperimentalnog određivanja fazne ravnoteže kapljevine-para pod visokim tlakovima. Takovi i slični problemi susreću se i u ostalim područjima koja zahtijevaju eksperimentalni rad.

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*Prispjelo 5. rujna 2005.
Prihvaćeno 3. listopada 2005.*