

dependently, without cooperative links internationally, and that it has recently become an aggressive on-line marketer of chemical information, a competitor to all other on-line chemical information services, what opportunities remain? The answer is rather bleak. Clearly, no one, with the possible exception of the Russians, can afford to abstract and index the world's chemical literature anew. Therefore, there are only two choices—operate under license from CAS, which itself intends to operate a “superior” competing service, or develop an information system that does not depend upon the files of CAS. This is not very easy to do given the nature of chemical information and the files of CAS.

Perhaps some entrepreneurs will be able to carve out small areas, specialized files, that CAS does not dominate. We have examples of some successes such as ISI and DARC, some specialized services providing access to patent information or chemical data files. However, in each instance, we can probably expect CAS to develop competing products to maintain their worldwide market dominance.

The opportunities may appear bleak for alternative suppliers of secondary information, but is that bad? Is the user worldwide best served by the ACS-sponsored nonprofit service that seeks only to provide “... a single, comprehensive, online system that would be superior in its utility for scientists and engineers worldwide”?⁶

Is this a field where we do not need the pressure of competition to ensure innovation and reasonably priced services?

Only time will tell.

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ARTICLES

Vapor Pressure Data of Simple Organic Substances: Their Availability and Reliability[†]

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The literature and other sources of information were searched for vapor pressure data of organic substances. Some compilations were found and compared with the data recorded in the *Handbook of Chemistry and Physics*. Discrepancies were checked and, where possible, analyzed. The reliability of the recorded data has been discussed.

INTRODUCTION

The compilation of vapor pressure data for organic substances in the *Handbook of Chemistry and Physics* is taken from the paper of D. R. Stull.¹ It is reproduced in every edition up to the last one, the 63rd²—except for the 52nd, 53rd, and 54th editions, 1971–1974—as well as in the *American Institute of Physics Handbook*³ and in the *Chemical Engineers Handbook*.¹⁴ In addition, its data are cited in numerous other compilations.^{4,5} It is thus a most accessible and useful source of information and is probably used extensively in spite of its early publication in 1947. The vapor pressures of approximately 1200 organic substances are reported therein as a function of the temperature, within a pressure range of up to 1 atm. For 60.8% of these compounds, only single references sources are cited; 19.7%—that is, almost one-third of those single citations—date back beyond the year 1900; 14.8%—i.e., almost one-fourth of them—are actually one and the same—pre 1900—reference source.^{6,7} These facts by themselves need not necessarily reflect on the reliability of the data. It stands to reason, however, that confirmation from several independent

sources would enhance their reliability. In addition, it should be remembered that the experimental methods of measurement have undergone significant improvements in the last 80 years. Thus, the question arose whether there exist more recent, independent compilations that would verify these older data or, alternatively, whether one could obtain verification for specific compounds via the common literature or other sources.

AVAILABILITY OF DATA

In order to answer these questions, some seven simple organic compounds were chosen from Stull's compilation, the reference citation of which was this very same single—pre 1900—source.⁶ Four of these substances, methyl dichloroacetate, 1,2,3-trichloropropane, ethyl carbamate, and ethyl trichloroacetate, are commercially available, and inquiries were made as to whether the manufacturers had any vapor pressure data. The results were disappointing. Data could be obtained for only two—ethyl carbamate and 1,2,3-trichloropropane—of the four substances, and this was only from two of the four firms that were approached. One firm provided a couple of values for 1,2,3-trichloropropane. The other one did quote continuous values for 1,2,3-trichloropropane and ethyl carbamate, presumably from the literature, but these did not tally

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with the data that we found for these substances.

ACCESSIBILITY OF DATA

Manual perusal of the collective indices of *Chemical Abstracts* for vapor pressure data of the seven substances proved impractical. They were checked in the *Beilstein* up to and including the 4th *Ergaenzungswerk* (which covers the literature up to 1959), and some new references with pertinent data were found. The *Bulletin of Chemical Thermodynamics*¹⁵ was scanned for these compounds, and some new references with additional data were collected. More recent compilations^{4,5} did not provide additional data since many of them refer back to Stull's original paper.¹ Direct inquiries at various data centers were unsuccessful. **On-line searches** of the Chemical Abstracts Service data bases yielded more encouraging results and provided, in addition to the already retrieved data, further relevant references that may have been overlooked in the manual perusal. In addition, the on-line query after *specific* substances provided references to some *general*, previously unknown compilations.^{16,17} This capability is apparently based on the fact that the Registry Numbers by which we traced these substances were part of the machine-readable record of these compilations. Others,⁸ where this was apparently not the case, could not be retrieved via an on-line search for *specific* compounds. They were, however, retrieved by general descriptive index terms. In summing up, one can say that a manual search of the literature for vapor pressure data of *specific* organic compounds is difficult and no safeguards against oversights exist. The *Bulletin of Chemical Thermodynamics*¹⁵ should actually be the best available tool for tracing current references. However, we found it somewhat inconvenient to use because of its rather complex classification of compounds. A simple arrangement of organic substrates according to ascending brutto formula would probably be more practical. Tracing recent compilations—as such—seems even more difficult since *specific* compounds cannot be used here as search terms. Indeed, one of the major recent compilations⁸ was found only by chance through a very systematic perusal of the *Bulletin of Chemical Thermodynamics* could also have helped us retrieve it. In any case, an on-line search either alone or complimentary to the manual search is much to be preferred.

RELIABILITY OF DATA

Since in many cases the experimental conditions of the measurements are not reported in enough detail, it is admittedly difficult to judge the reliability of such data. When, however, vapor pressure data for certain substances are available from various different independent compilations, one can compare them and see if they coincide. If they do, one can then probably consider them reliable and correct. This, indeed, was done for vapor pressure data of *specific* substances from various compilations^{5,9} the one in the *Handbook of Chemistry and Physics* (Stull) (S)¹ and the one of Dykyj (D)⁸ being the most extensive ones. As a result, a certain number of discrepancies were, indeed, revealed. Some of these were easy to characterize. They amount to what may perhaps be called "editorial errors" such as "errors in nomenclature" or "errors in calculations".

Errors in Nomenclature. A set of values is given by Stull¹ for *tert*-butyl chloride. Such data are cited by Dykyj^{8a} quite properly under 2-chloro-2-methylpropane. His values, however, are entirely different and coincide with those quoted by Stull for isobutyl chloride. This is obviously a nomenclatural mix-up. Similarly, Stull gives data for 2,2,3-tribromobutane. Dykyj gives data for 2,3,3-tribromobutane. Both should be the same substance. The data sets, however, coincide only partially. *cis*-2-Bromo-2-butene and *trans*-2-bromo-2-butene

Table I. Vapor Pressure Data for 2-Nitrothiophene (2-NO₂C₄H₃S) Reported by Stull¹ (Column 2) and Dykyj^{8a} (Column 4) and Recalculated (Column 3)

P (mmHg)	t (°C)		
	Stull	recalc'd	Dykyj
10	92	92.17	92
20	108.2	107.8	107.9
40	125.8	124.84	124.9
60	137	135.53	135.6
100	151.5	149.85	149.9
200	174	170.96	171.0
400	199.6	194.3	194.3
760	224.5	218.2	218.2

are both reported by Stull and Dykyj. The values, however, are reversed; i.e., those reported by Stull for the *cis* compound are reported by Dykyj for the *trans* compound and vice versa.

Errors in Calculations. Very often vapor pressure data are given in the primary literature in the form of constants for an empirical equation that correlates the experimental values of the vapor pressure with the corresponding temperatures. The Antoine equation¹¹ is most widely used for this purpose:

$$\log P = A + B/(t + C) \quad (1)$$

where *A*, *B*, and *C* = constants, *t* = temperature (°C), and *P* = pressure (mmHg). Recalculating the actual values from such an equation may—and in fact often does—introduce errors. As an example, the values for 2-nitrothiophene are presented in Table I as reported by both Stull¹ (column 2) and Dykyj^{8a} (column 4). Both obtained the data from the paper of V. S. Babasinian and J. G. Jackson.¹⁰ In this paper, the vapor pressures were measured at temperatures different from those quoted in the compilations. The empirical equation (eq 2) that fits these measurements is given by the authors and

$$\log P = 8.334 - 2679.6/T \quad T (\text{K}) = t (^\circ\text{C}) + 273.2 \quad (2)$$

must have been used to obtain the values in the compilations. We recalculated them according to eq 2, and our values are given in column 3 of Table I. They provide an excellent fit with those in column 4, less so with those in column 2.

Methods of Verification. Pressure values calculated by means of the Antoine equation are usually in very good agreement with the experimental data.¹¹ The graphical representation of the equation as a plot of $\log P$ vs. $1/(t + C)$ gives a straight line. Deviations of experimental values from this straight line are therefore easy to discern. By substituting *T* for *t* + *C*, one obtains a more general equation (see eq 2), which is also used but is considered to be only applicable for a limited temperature range.^{11,12} We have obtained good results with this equation, and plots of $\log P$ vs. $1/T$ provided straight lines for the relevant ranges of temperatures. Figure 1 shows the results obtained for 2,4-dimethylpentan-3-one (see also Table IV) from five different sources, the two main compilations of Stull and Dykyj as well as three other primary sources. All represent straight lines, and all except one coincide and should thus be probably recognized as correct.

Discrepancies. The comparison of the two main compilations yielded quite a number of discrepancies. These are listed in Tables II–IV. Unfortunately, values in Tables II and III lacked additional complementary data for the sort of verification carried out in Figure 1. Those in Table II show differences that are by no means negligible but could probably still be accounted for within the limits of the experimental errors. Those in Table III show somewhat larger differences. In addition, they exhibit a definite trend as they rise from small differences of temperature at atmospheric pressure to significant ones at 10 mmHg. This could be explained by the fact that measurements at low pressure may be more difficult to carry out and entail a greater margin of error.

Table II. Vapor Pressure Data with Small Differences between the Compilations of Stull (S) and Dykyl (D)

P (mmHg)	t (°C)											
	acetic anhydride [(CH ₃ CO) ₂ O]		anisole (C ₆ H ₅ OCH ₃)		benzenethiol (C ₆ H ₅ SH)		diisopropyl ether [(CH ₃) ₂ CH] ₂ O		4-nitrotoluene (4-NO ₂ C ₆ H ₄ CH ₃)		valeric acid [CH ₃ (CH ₂) ₃ COOH]	
	D	S	D	S	D	S	D	S	D	S	D	S
10	31.20	36.0	42.6	42.2	52.3	56.0	-24.0	-27.4	99.7	100.5	82.8	79.8
20	47.26	48.3	55.5	55.8	67.8	69.7	-13.4	-16.7	115.6	117.7	95.1	93.1
40	60.64	62.1	69.8	70.7	80.8	84.2	-1.6	-4.5	133.2	136.0	108.7	107.8
60	69.16	70.8	78.92	80.1	90.4	93.9	5.9	3.4	144.3	147.9	117.4	116.6
100	80.73	82.2	91.32	93.0	103.4	106.6	16.2	13.7	159.4	163.0	129	128.3
200	98.14	100.0	110.00	112.3	123.1	125.8	31.7	30.0	181.8	186.7	146.4	146
400	117.87	119.8	131.21	133.8	145.5	146.7	49.5	48.2	207	212.5	165.8	165
760	138.62	139.6	153.58	155.5	169.1	168.0	68.3	67.5	237.3	238.3	186.0	184

Table III. Vapor Pressure Data with a Trend in the Differences between the Compilations of Stull (S) and Dykyl (D)

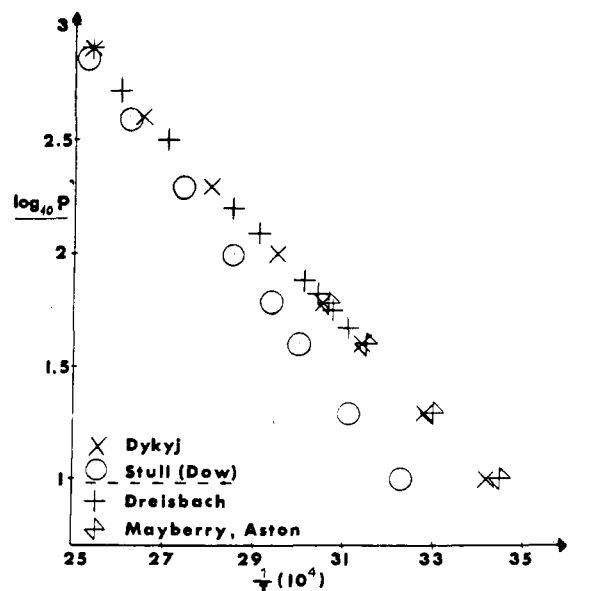
P (mmHg)	t (°C)							
	1,2-dibromobutane (BrCH ₂ CHBrCH ₂ CH ₃)		1,4-dibromobutane (BrCH ₂ CH ₂ CH ₂ CH ₂ Br)		2-methoxyphenol (2-CH ₃ OC ₆ H ₄ OH)		trichloroethylsilane (C ₂ H ₅ SiCl ₃)	
	D	S	D	S	D	S	D	S
10	55.8	46.1	79.2	72.4	85.9	92.0	-1.6	3.6
20	68.9	60.0	93.2	87.6	100	106.0	9.7	15.2
40	83.3	76.0	108.6	104	115.6	121.6	22.3	27.9
60	92.5	86.0	118.4	115.1	125.5	131.0	30.4	35.7
100	104.9	99.8	131.6	128.7	139	144.0	41.5	46.3
200	123.5	120.2	151.4	149.8	159.1	162.7	58.4	62.2
400	144.4	143.5	173.7	173.8	181.9	184.1	77.9	80.3
760	166.3	166.3	197.0	197.5	205.6	205.0	98.8	99.5

Table IV. Comparison of the Compilations of D. R. Stull (S) and J. Dykyl (D): Significant Differences in the Vapor Pressure/Temperature Values of Seven Organic Compounds

P (mmHg)	t (°C)													
	2-methyl-1-butene [CH ₃ CH ₂ C- (CH ₃)=CH ₂]		pentan-2-one (CH ₃ CH ₂ CH ₂ - COCH ₃)		pentan-3-one [(CH ₃ CH ₂) ₂ CO]		3-methyl- butan-2-one [(CH ₃) ₂ - CHCOCH ₃]		2,4-dimethyl- pentan-3-one [(CH ₃) ₂ CH] ₂ CO		fluoroethane (CH ₃ CH ₂ F)		1,2-ethane- diamine (NH ₂ CH ₂ - CH ₂ NH ₂)	
	D	S	D	S	D	S	D	S	D	S	D	S	D	S
10	-53.4	-64.3	3.2	17.9	3.3	17.2	-1.0	8.3	18.9	36.7	-103.28	-97.7	36.5	21.5
20	-43.7	-54.8	14.7	28.5	14.7	27.9	10.6	18.3	31.5	47.7	-95.7	-90.0	47.1	33.0
40	-32.87	-44.1	27.4	39.8	27.4	39.4	23.5	29.6	45.31	59.6	-87.28	-81.8	58.5	45.8
60	-25.96	-37.3	35.6	47.3	35.52	46.7	31.6	36.2	54.11	67.2	-81.9	-76.4	65.6	53.8
100	-16.54	-28.0	46.62	56.8	46.55	56.2	42.7	45.5	66.01	77.0	-74.58	-69.3	75.2	62.5
200	-2.308	-13.8	63.3	71.0	63.16	70.6	59.3	59.0	83.92	91.8	-63.54	-58.0	89.2	81.0
400	13.936	2.5	82.25	86.8	82.036	86.3	78.0	73.8	104.1	108.0	-50.98	-45.5	104.5	99.0
760	31.163	20.2	102.26	103.3	101.959	102.7	97.71	88.9	125.25	123.0	-37.7	-32.0	120.0	117.2

Finally, Table IV provides examples of rather larger differences. Luckily however, in this case enough additional data could be retrieved so that our graphical verification procedures could be used. Some of the discrepancies such as the one for fluoroethane have already been reported in the literature,¹⁸ and again extrapolation procedures seem to be at the heart of the problem.¹⁹ Similarly, the data for 1,2-diaminoethane have been reported to differ,²⁰ and the older data reported by D. R. Stull¹ from Hieber and Woerner²¹ are apparently verified. The data of Dykyl^{8a} obtained from Sivokova et al.²² are at variance. It is suggested²⁰ that the differences are due to the presence of water with which 1,2-diaminoethane forms an azeotropic mixture. Our graphical verifications confirm the results reported for fluoroethane¹⁸ and 1,2-diaminoethane.²⁰ The values of 2-methyl-1-butene reported by Dykyl^{8b} are based on measurements reported by Rossini et al.²³ and fit very well with the corresponding Antoine equation, reported by Scott et al.²⁴ for their measurements in a different temperature range. Stull's¹ data refer back to an old Russian source,²⁵ which we could not check.

The rest of the substances in Table IV are all ketones. The data reported by Stull for pentan-2-one and pentan-3-one are based on proprietary information²⁶ and on an old apparently

Figure 1. Values of log P against 1/T (×10⁻⁴) for 2,4-dimethyl-pentan-3-one.

incorrect source.²⁷ Those of Dykyj are presumably based on the data and the corresponding Antoine equations developed by Collerson et al.²⁸ These as well as additional data for pentan-2-one²⁹ and pentan-3-one,³⁰ as well as for both,¹³ all tend to confirm each other. The same holds true for 2,4-dimethylpentan-3-one (Figure 1) and 3-methylbutan-2-one.

CONCLUSIONS

The retrieval of much of the available data for vapor pressure of specific organic substances requires a variety of search efforts and strategies. In our hands, the computer-aided search gave the best results, but this is of course applicable only for computer-stored data. Once sufficient data have been collected, it is not difficult to evaluate them—by means of the Antoine or other empirical equation—in order to identify the correct reliable values.

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