

## Reference books and data banks on the thermodynamic properties of individual substances

Lev V. Gurvich

THERMOCENTER of the USSR Ac. of Sci., IVTAN, Izhorskaya 13/19, Moscow, USSR 127412

**Abstract** - Data on the thermodynamic properties of substances published in the reference books or stored in the computer memory should satisfy two requirements - the recommended data should be reliable within the frame of the modern knowledge and these data should be given for a comprehensive set of elements and their compounds. Taken into consideration these requirements some reference books and two data banks are compared and discussed.

During the last decades the methods of thermodynamics have been finding more and more applications in the investigation of various processes and creation of new technologies. The development of new methods of providing mankind with energy, the choice of the optimum paths of utilization of the raw material resources and reprocessing of industrial wastes, the precautionary measures for preventing environmental pollution and forecasting the after-effects of accidents, including those in nuclear power stations, could not have been achieved without a preliminary analysis based on thermodynamic investigations. All that makes essential a further study of the thermodynamic properties of individual substances and the accumulation of available data, their critical analysis, processing and systemization in a form acceptable to scientists and engineers working in various branches of science and technology. The collection of the available data concerning the thermodynamic properties of substances after analysis, processing and selection of the recommended values must be issued in the form of periodically updated and easily accessible reference books or stored in data centers in computer memories from whence these data could be obtained via communication lines or on magnetic carriers.

Reference data on the thermodynamic properties of substances, published in print or stored in databases, should satisfy the following requirements:

1. The recommended data should be selected as the result of critical analysis of all data published in the literature, using correct methods of processing the primary information and the calculation of the thermodynamic properties.
2. The recommended values of the thermodynamic properties should represent a system of mutually consistent quantities, including consistency of the thermochemical data and the thermal functions.
3. The recommended values should be based on fundamental constants, key thermochemical values, and atomic weights recommended by appropriate international organizations.
4. For all recommended values, an estimate of their reliability should be given.
5. Brief texts should be available devoted to the evaluation and calculation of the recommended quantities and an estimate of their uncertainties.
6. Bibliography of all papers used in the preparation of the reference data should be available.
7. The values of the recommended properties should be given for a wide and logically chosen set of substances.

The existing reference books could be divided into two types: the so called critical reference books and compilation, secondary and even tertiary handbooks. Critical reference books, the number of which in the world literature is extremely limited, are based on a critical analysis of primary literature and independent calculations of the recommended values of the thermodynamic properties. They have to satisfy most of the requirements formulated above. The first such publications were "The International Critical Tables" and the reference book by Bichowsky and Rossini.

Compilation handbooks form the main part of the reference literature on thermodynamic properties of substances. They are based not on an analysis of original papers and independent calculations, but wholly or to a considerable extent on the reproduction of data from other reference publications, frequently from several of them, or they use uncritically data published in periodicals. In these reference books there is no internal consistency of the recommended values and inconsistent values are given frequently.

In this review we propose to restrict the discussion to reference books and data banks dealing with such properties as heat capacity, heat content, entropy, and free energy function as well as enthalpy of formation, enthalpy of phase transitions, dissociation energy, ionization potential, and electronic affinity of inorganic and simple organic substances.

The critical reference publications on the thermodynamic properties of substances could be divided into two types, according to their content. Reference books, in which the properties of substances at 298.15 K and the phase transition temperatures are presented, belong to the one type. Those containing the thermodynamic properties over a wide range of temperatures belong to the other one. The best known reference books of the first type are those prepared in the National Bureau of Standards of the USA and in the Academy of Sciences of the USSR.

The book "The NBS Tables on Chemical Thermodynamics" (ref. 1) contains data on thermodynamic properties at 298.15 K for about 9000 substances in the solid, liquid, gaseous states, and aqueous solutions as well. During the preparation of this book the authors have thoroughly analyzed all the primary literature and also developed the method allowing to obtain, with the help of a computer, the system of internally consistent values of thermodynamic properties for all compounds of the chosen element. The method, based on creating a catalog of the investigated chemical reactions, is a program for the solution of the redetermined system of the corresponding linear equations, enabling one to determine the required thermochemical quantities and their uncertainties.

Unfortunately, this reference book does not include data on phase transitions and polymorphous transformations, in contrast to its well-known previous edition "The NBS Circular 500". The bibliography is also missing. At present, the reaction catalogs for all elements are being consequently prepared in the Chemical Thermodynamics Data Center of NBS. The catalogs are supposed to be published together with the bibliography. The catalogs for elements from oxygen through nitrogen (standard thermochemical order), alkali metals and lanthanum have been prepared and will be published in the next future. Catalogs on rare earth elements are envisaged next.

The reference publication "Thermal Constants of Substances" (ref. 2), prepared under the direction of Academician V.P.Glushko in IVTAN and VINITI with the participation of many Soviet scientists, is the most complete publication of this type. In its coverage of substances (more than 25,000) and properties, it considerably exceeds other similar publications, and during its preparation all the requirements formulated above were satisfied, except for the third and fifth. At present, the Hemisphere Publishing Corporation is completing the preparation of an English version of this book.

While preparing these two books during the last 10 years, the authors from NBS and IVTAN have been working in permanent contact, exchanging bibliographies and literature data and reviewing the most questionable ones. This has assisted in raising the level of both publications and eliminating some errors. These two books are based on different sets of key thermochemical values. Thus the recommended values in these publications, strictly speaking, are incompatible although in the majority of cases they are close to one another.

The reference books "Thermodynamic Properties of Individual Substances" and "The JANAF Thermochemical Tables", prepared in the USSR and the USA, are critical reference publications of the second type. Both of them include the results of long term projects. Being destined first to assist investigations of rocket-space technology, they both soon have developed beyond this framework, providing specialists from different branches of science and engineering with necessary information. Rates of their development during the period of more than 20 years are shown in Table 1.

During the preparation of all the three editions of the reference book "TPIS" (ref. 3, 4, 5) attention was paid to the development of methods of calculations of the thermal functions of gases, methods of processing primary experimental data and semi-empirical methods of estimating constants, necessary for the evaluation and calculation of thermodynamic properties.

TABLE 1. Increase of information presented in the TPIS and JANAF.

Number of	TPIS			JANAF		
	1st Ed 1956	2nd Ed 1962	3rd Ed 1978-82	1st Ed 1965	2nd Ed 1971	3rd Ed 1985
Elements	21	31	50	23	29	47
Substances						
total	206	336	1100	560	750	1050
in gaseous state	178	335	1060	460	625	905
in condensed state	29	45	278	220	275	400

At the same time, a complex of measurements of molecular, thermochemical and thermodynamic constants was organized, required for calculations of the thermodynamic properties of substances in a wide temperature range. Many laboratories in the USSR have participated in these experimental investigations for more than 30 years.

Already in the 1956 edition, for the first time in the literature, the total internal consistency of all recommended values was achieved, including the consistency of thermochemical quantities and thermal functions. In the 1962 edition for the first time the uncertainties of all recommended values, including the tables of thermal functions, were estimated. In fact, this edition satisfied all the requirements formulated above. However, only a small set of compounds of 31 elements was considered in it.

During the preparation of the third edition in 4 volumes (ref. 5) a number of methods and programs were advanced. This was necessitated, in particular, by the inclusion of compounds of d- and f-elements in this edition. These methods allowed us to increase the accuracy of calculations of the thermal functions of gases, as well as to estimate correctly the reliability of the calculated quantities, even when the data on the molecular constants were absent. In Table 2 the values of entropy of UO(g), calculated in TPIS (ref.5) using estimated molecular constants as well as calculated by Pedley and Marshall (ref. 16) using their own estimation, are compared with those calculated in IVTANTERMO data bank using the results of UO spectrum investigations in the Thermocenter of the USSR Academy of Sciences in 1985-87. One can see in the Table that the values of S (UO,g), calculated in TPIS in the absence of the experimental data agree fairly well with the new calculations within the whole temperature range.

TABLE 2. The entropy of UO(g) in J/K.mol

T/K	TPIS 1982	Pedley 1983	IVTANTERMO 1987
298	248.8 +/- 4	260.6	252.0 +/- 0.1
1000	308.1	302.4	304.6 +/- 0.3
2000	343.3	328.0	336.0 +/- 1.5
3000	362.9 +/- 8	343.1	356.3 +/- 1.8
4000	376.5	353.9	372.8 +/- 2
5000	387.1	-	386.9 +/- 3
6000	396.0 +/- 12	-	399.1 +/- 4

At present, the preparation of the fifth volume of this reference book is being completed. The volume includes about 300 compounds of six more elements (Mn, Fe, Co, Ni, Cu, Zn), as well as additional compounds of Ge, Sn, Pb, Ti, Cr and 40-50 updated tables from volumes 1 and 2. The renewal of all materials of previous editions is the peculiarity of TPIS. Now the Hemisphere Publishing Corporation is preparing the publication of the book "Thermodynamic Properties of Individual Substances" in English. The English edition will be modified and updated translation as thermodynamic properties for many substances are recalculated using experimental data published in 1978-87. It will contain data for 56 elements and more than 1300 compounds. We hope that the last volume of the English edition will be published very soon after the publication of the fifth volume of the Russian edition.

The reference book "The JANAF Thermochemical Tables" is the development of a number of projects carried out in the USA starting in the middle of the fifties. In the second edition of JANAF Tables (ref. 7) the number of considered substances, especially in the condensed state, significantly exceeded all other reference books of that time. Although, strictly speaking, the data recommended in the two last editions were not internally consistent, there were no significant internal contradictions between them. Unfortunately, an estimate of the reliability of tabulated thermodynamic data is absent, in fact, in all three editions of the JANAF Tables. For calculating the thermal functions of gases in the JANAF Tables, approximate methods and different approaches were used in many cases. The thermal functions of diatomic gases were calculated by the method of Mayer and Goeppert-Mayer. As a result errors appeared at low temperatures in calculated values of a free energy function and enthalpy content of many gases which molecules have a multiplet ground state, and at elevated temperatures in the calculated values of entropy, heat capacity and heat content of gases which have dissociation energies below 250 kJ/mol. Some inconsistency exists as a result of different approaches in the calculation of electronic partition functions of monatomic, diatomic and polyatomic gases. In the course of preparation of the second and third editions some tables were adopted from previous editions. Thus, in the last edition the tables of properties calculated in 1962-75 remained for some substances, though they are based on wrong data.

Due to the large amount of data in both books (TPIS and JANAF), the probability of accidental errors in analysis and calculations is quite high, especially taking into account that the whole procedure for preparing the tables was not completely automatic and computerized.

As a result in TPIS (ref. 5), for example, the thermal functions of O<sub>2</sub>(g) below and above 6000K disagree: one set of molecular constants was adopted for methyl alcohol in the text, while the calculations were done using another, less accurate, set of constants. In the last edition of the JANAF Tables (ref. 8) during the recalculations of the titanium dichloride thermal functions from calories to joules the enthalpy of fusion was kept in the old units. It is difficult to understand the source of errors in the calculated thermal functions of gaseous monatomic zirconium over the whole temperature range, though they were correct in the previous edition of JANAF, see Table 3.

TABLE 3. The entropy of Zr(g) in J/mol.K

T/K	TPIS 1962	JANAF 1971	TPIS 1982	JANAF 1985
298.15	181.238	181.230	181.233	183.027
1000	213.762	213.752	213.756	212.895

An important part of THERMODATA is the complex of software providing via communication lines the information stored in the databases as well as ensuring various thermodynamic calculations. The latter varies from calculations of thermodynamic parameters for some chemical reactions to calculations of phase diagrams for multicomponent systems. Though the main THERMODATA's original task was to satisfy demands of metallurgical industry of Western Europe, today THERMODATA has accumulated data enabling solution of various problems to be achieved.

The computerized system "IVTANTERMO" (ref. 14, 15) contains numerical data on the thermodynamic properties of individual substances within a wide temperature range. The data are interconsistent within the framework of the basic laws of thermodynamics and the reliability of all the recommended values is estimated. The recommended values are calculated using constants chosen as a result of critical analyzing and processing of all primary data from the literature. The corresponding processing and calculations are performed using a set of methods and programs created during the preparation of the reference book TPIS (ref. 4, 5) and were developed later by its authors.

The IVTANTERMO system consists of a set of databases and programs. IVTANTERMO presently performs the following functions:

- storage and processing of primary numerical data to obtain constants required for the calculation of thermodynamic properties in a wide temperature range;
- calculation of the thermodynamic properties of individual substances in the solid, liquid and gaseous states;
- assessment of the reliability of the primary data and recommended values;
- supplying the users with requested data.

Information from IVTANTERMO may be obtained on magnetic tapes for a subsequent input of data to the user's computer (on floppy-discs for PC compatible with IBM PC AT, since 1989) or via telecommunication channels in an interactive mode.

The information on the magnetic carriers consists of the database and the program system. These utilities enable us to obtain a catalog of substances, tables of thermodynamic properties and equations approximating thermal functions of substances in the wide temperature range as well as to calculate the thermodynamic parameters of any reaction, the composition and properties of arbitrary multielement systems.

The IVTANTERMO database is regularly expanded and updated by including chemical elements and substances not considered before as well as by correcting the accumulated data. The rate of development of IVTANTERMO is shown in Table 4.

One can see (the same holds for THERMODATA) that the rate of development of computerized systems is higher than that of the preparation of critical reference books, such as TPIS and JANAF. However, they have one shortcoming. Users get the numerical data from the database as from the "black box", practically without any accompanying information. THERMODATA notes only that the data are adopted from JANAF or any other source, or are calculated by THERMODATA. IVTANTERMO postulated that all its recommendations are based on a critical analysis and the calculations carried out by the experts of THERMOCENTER.

TABLE 4. The increase in information presented in the IVTANTERMO Database

Number of	1983	1985	1987	1990
Elements	56	61	78	85
Substances:				
total	1350	1650	1950	2300
in gaseous state	1300	1600	1900	2200
in condensed state	350	425	530	600

In contrast to the reference books JANAF and TPIS, the numerical data in THERMODATA and IVTANTERMO are not accompanied by a text describing the analysis and calculations. Information about the constants used in the calculations of thermodynamic properties is also absent.

A complete bibliography of papers dealing with the investigations of properties of a given substance can be received from THERMODATA separately, but as far as it is known, without any indication what information was used in the evaluation procedure. Thermocenter will supply the tables of thermodynamic properties accumulated in IVTANTERMO bases with brief texts, values of the constants used in the calculations and bibliography, but not before 1991.

It is obvious that the number of substances presented in the databanks of THERMODATA and IVTANTERMO is insufficient to satisfy scientists and engineers today, especially if we take into account that both databanks contain information mainly on the same substances. This is why it is desirable to have an international program for creating computerized data system on thermodynamic properties of the individual substances. Such project may allow to divide the work among many persons and to speed the task of producing a comprehensive and reliable data system using the experience accumulated by CODATA TG on CTT and such databanks as THERMODATA, IVTANTERMO, and databank at Texas University.

## REFERENCES

1. D.D. Wagman, W. Evans et al., The NBS Tables of Chemical Thermodynamic Properties, J. Ph. Chem. Ref. Data, Suppl. 2 (1982).
2. V.A. Medvedev, G.A. Bergman et al., The Thermal Constants of Substances, in 10 parts, Eds. V.P. Glushko et al., VINITI (1965-82).
3. L.V. Gurvich, V.S. Yungman et al., Thermodynamic Properties of the Components of Combustion's Products, in 3 volumes, Ed. V.P. Glushko, USSR Ac. of Sci, M. (1956)
4. L.V. Gurvich, G.A. Khachkuruzov et al., Thermodynamic Properties of Individual Substances, in 2 volumes, Ed. V.P. Glushko, USSR Ac. of Sci., M. (1962).
5. L.V. Gurvich, I.V. Veitz et al., Thermodynamic Properties of Individual Substances, in 4 volumes, Eds. V.P. Glushko et al., Nauka, M. (1978-82).
6. D.R. Stull et al., The JANAF Thermochemical Tables, PB-168370 (1965).
7. D.R. Stull, H. Prohet, The JANAF Thermochemical Tables, 2nd Ed., NSRDS-NBS-37, W. (1971).
8. M.W. Chase, C.A. Davies et al., The JANAF Thermochemical Tables, 3rd Ed., J. Ph. Chem. Ref. Data, v. 14, Suppl. 1 (1985).
9. The Chemical Thermodynamics of Actinide Elements and Compounds, Eds. E.L. Oetting et al., IAEA, Vienna (1976).
10. CODATA Thermodynamic Tables. A Prototype Set of Tables, Eds. D. Garvin et al., Hemisphere Publ. Co., W., N.-Y., L. (1987).
11. H. Yokokawa, S. Yamauchi, S. Fujeda, Computer Handling and Dissemination of Data, Proc. of the Tenth CODATA Conf., Ottawa, Canada, Ed. Ph. S. Glaeser, pp. 257-261, North-Holland, Am., N.-Y., Ox., To. (1987).
12. B. Cheynet, THERMODATA, On-line Integral Information System.
13. I. Ansara, B. Sundman, Computer Handling and Dissemination of Data, Proc. of the Tenth CODATA Conf., Ottawa, Canada, Ed. Ph. S. Glaeser, pp. 154-158, North-Holland, Am., N.-Y., Ox., To. (1987).
14. L.V. Gurvich, Vestnik AN SSSR, No. 3, pp. 54-63 (1983).
15. L.V. Gurvich, Computer Handling and Dissemination of Data, Proc. of the Tenth CODATA Conf., Ottawa, Canada, Ed. Ph. S. Glaeser, pp. 252-256, North-Holland, Am., N.-Y., Ox., To. (1987).
16. J.B. Pedley, E. M. Marshall, J. Ph. Chem. Ref. Data, No. 4, pp. 967-1032 (1983).