Automated system for calculation thermophysical properties of important for power engineering substances

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Abstract. Data on thermodynamic and transport properties of gases and liquids are necessary for many branches of science and technology. Such data are required in different systems of independent variables and in a wide range of values of these variables for design and study of various plants. Reliable sources of information on the properties of substances and materials are data banks and automated information systems. Recently, a large number of automated systems have been created in the world that are designed to solve various applied problems. In this work is described the system that we developed, which is designed to calculate the values of the thermophysical properties of a number of substances important for power engineering.

1. Introduction

At last decades data banks (DB) and automated information systems (AIS) have been created to provide users with information about the properties of substances and materials. The TERMAL and IVTANTERMO banks developed at the JIHT RAS are rather known [1, 2]. They contain descriptions of about 80000 articles and information on the physical constants and thermodynamic properties of about 15000 substances. Among banks and systems from far abroad, the thermodynamic research center (TRC) database [3], the NIST Chemistry WebBook [4] and REFPROP [5] are widely known. The latest version of REFPROP system allows user to calculate the properties of 147 pure substances and mixtures with up to 20 components.

2. Description of the system developed at ONMU

The analysis of the advantages and some disadvantages of the above DB and AIS stimulated us to develop the AIS for calculating the thermophysical properties of important for power engineering substances: air and its components (nitrogen, oxygen, argon, helium, neon, krypton and xenon), carbon dioxide, water and water vapor, and as well a number of hydrocarbons and refrigerants. Despite the presence of powerful Russian and foreign data banks and systems, this development is relevant for a number of reasons. Databanks contain ready-made property tables, access to which is possible only when connected to the Internet. In our system which contains the equations of state and equations for calculating the transport properties of substances, the properties can be calculated off-line quickly and in unlimited quantities in a wide range of state parameters. The developed automated system also allows to include new equations into it for calculating the thermophysical properties of the studied substances.

Properties are calculated at two given independent variables for single-phase and two-phase regions and at one variable for calculating properties on saturation or melting curve. Two calculation options are provided: “Single” (at certain values of independent variables) and “Series” (at temperature or
pressure which change in a given interval with a specific step). The appearance of the window for choosing options for calculating thermophysical properties is shown on Figure 1.

![Figure 1. Window of selecting options for calculating thermophysical properties](image)

A set of thermophysical properties and their units of measurement (mass or molar for caloric properties, Celsius or Kelvin degrees for temperature) can be selected in accordance with the task. The operating window of the system is shown on Figure 2. It contains the main menu bar, operation panels, an information panel and the resulting table, which in the figure contains the values of the thermodynamic properties for carbon dioxide. The calculated properties can be saved as a text file or MS Excel spreadsheet. For comparison, Figure 3 shows the operating window of the system containing the values of the nitrogen properties.

![Figure 2. Working window with calculated values of carbon dioxide properties](image)
Figure 3. Working window with calculated values of nitrogen properties

The system provides calculations of compressibility coefficient, specific volume, density, enthalpy, internal energy, entropy, isochoric and isobaric heat capacities, speed of sound, adiabatic choke effect, adiabatic exponent, volume expansion coefficient, thermal pressure coefficient, saturation pressure, heat of vaporization, volatility, dynamic and kinematic viscosities, thermal conductivity, thermal diffusivity and Prandtl number. The values of the properties can be determined in the single-phase region, on the lines of phase equilibrium and in the two-phase region at temperatures from the triple point to 400 - 1500 K and pressures up to 70 - 100 MPa (for some substances, to higher or lower pressures). The window for selecting properties that are calculated, units of measurement and setting the number of significant digits is shown in Figure 4.

To calculate thermodynamic properties of substances, unified equations of state are used in polynomial and fundamental forms. In some cases, for greater reliability, two forms of the equation of state are offered, and the user is able to select any of them. To calculate transport properties, the dependences of viscosity and thermal conductivity on temperature and density are used. Equations of state in polynomial form are convenient for quick calculations of various properties. Despite the simplicity of form, these equations provide quite acceptable accuracy for calculating thermodynamic properties.

Fundamental equations provide higher accuracy in the critical region than polynomial ones. An advantage of these equations is the possibility of calculating all thermodynamic properties by differentiating the Helmholtz free energy from the reduced temperature and density. Both polynomial and fundamental equations of state allow to calculate the thermodynamic properties in the single-phase region and on the saturation curve, because the Maxwell rule was taken into account at compiling these equations.

The equations describe data on viscosity and thermal conductivity, data on ideal gas properties, and saturation and melting pressures have different forms for various substances. This circumstance was taken into account when creating a program for the system.
The equations of state used in the automated system make it possible to calculate the density of gas and liquid at pressures up to 10 MPa and temperatures up to 400 K with errors of ± 0.05%, and at higher values of these parameters with errors of ± 0.1%. The errors at calculating the enthalpy of gas and liquid do not exceed 0.5 and 1.5 kJ / kg, and for heat capacities – 0.5 and 2.0%. In critical region, the error can be 2–3 times larger than the maximum of indicated values. The literature sources from which equations for calculating the thermodynamic and transport properties of substances important for the power engineering were taken are given in Table 1. This table also shows the temperature intervals and the maximum values of density and pressure for each equation.

The coefficients of the equations of state and equations for transport properties are given for each substance. The critical point parameters and coefficients of equations for calculating the ideal gas functions, pressure values on the saturation and melting curves are also specified. For most substances the reliable equations of state that describe experimental data with high accuracy are used. These equations were used by their authors for calculating reference data tables.

At creating an automated system, much attention was paid to the compilation of an algorithm for calculating thermophysical properties using various combinations of independent variables, which can be both thermal and caloric properties. The calculations can be carried out with the following twelve combinations of independent variables: temperature - density (T - p), temperature - specific volume (T - v), temperature - pressure (T - p), temperature - enthalpy (T - h), temperature - entropy (T - s), temperature - degree of dryness (T - x), pressure - density (p - ρ), pressure - specific volume (p - v), pressure - enthalpy (p - h), pressure - entropy (p - s), pressure - degree of dryness (p - x), enthalpy - entropy (h - s).

Difficulties in calculating the thermophysical properties for various combinations of independent variables arise because the density and temperature in the equations of state have degrees above three and iterative methods must be used to determine these parameters.
Table 1. List of substances, sources of equations of state and parameter ranges

| Substances | Equations sources for thermodynamic properties | Equations sources for transport properties | temperature interval $\Delta T$, K | Max. density (kg/m$^3$) | Max. pressure (MPa) |
|------------|---------------------------------------------|------------------------------------------|-------------------------------|------------------------|---------------------|
| Argon      | [6]                                         |                                          | 84–700                       | 1830                   | 1000                |
|            | [7]                                         |                                          | 84–1200                      | 1830                   | 1000                |
|            | [8]                                         |                                          | 84–1300                      | 1500                   | 100                 |
| Neon       | [8]                                         |                                          | 25–1300                      | 1400                   | 100                 |
|            | [9]                                         |                                          | 25–700                       | 1248                   | 700                 |
| Krypton    | [8]                                         |                                          | 120–1300                     | 2570                   | 100                 |
|            | [10]                                        |                                          | 116–800                      | 2765                   | 300                 |
| Xenon      | [8]                                         |                                          | 161–1300                     | 3100                   | 100                 |
|            | [9]                                         |                                          | 161–800                      | 3361                   | 350                 |
| Helium     | [11]                                        |                                          | 2–1500                       | 300                    | 100                 |
|            | [12]                                        |                                          | 2–1000                       | 300                    | 100                 |
|            | [13]                                        |                                          | 2,2–1500                     | 307                    | 100                 |
| Hydrogen   | [9]                                         |                                          | 14–500                       | 76,9                   | 40                  |
| Nitrogen   | [14]                                        |                                          | 65–1500                      | 920                    | 100                 |
|            | [15]                                        |                                          | 63–1000                      | 1600                   | 2200                |
| Oxygen     | [17]                                        |                                          | 55–1500                      | 1350                   | 100                 |
|            | [18]                                        |                                          | 55–300                       | 1340                   | 80                  |
|            | [19]                                        |                                          | 70–500                       | 1340                   | 100                 |
| Air        | [20]                                        |                                          | 70–1500                      | 1020                   | 100                 |
|            | [21]                                        |                                          | 60–2000                      | 1650                   | 2000                |
|            | [22]                                        |                                          | 150–1000                     | 850                    | 100                 |
| Carbon dioxide | [23]                                  |                                          | 220–1300                     | 1300                   | 200                 |
|            | [24]                                        |                                          | 216–1100                     | 1450                   | 800                 |

To calculate the properties in two-phase region, as well as in the coordinates $T$ - $p$ and $T$ - $v$ at temperatures below the critical temperature one must first calculate properties on a saturation line. This is necessary to determine the phase state of substance. The necessary values of pressure (or temperature) and density of saturated vapor and liquid are calculated as a first approximation using auxiliary equations, and then by a unified equation of state, taking into account the Maxwell rule.

To calculate properties in the coordinates $T$ - $p$, $T$ - $h$, and $T$ - $s$, it is first necessary to determine the third parameter, which is used in the equation of state (and in the equations for transport properties), – the density. For density calculations iterative method of half division is used. The density in the $T$ - $h$ coordinates is determined on the basis that on many isotherms for one enthalpy there are two corresponding density values. After a certain number of iterations are carried out, the preset value of pressure, enthalpy, or entropy is consistent with the value calculated by the equation of state.

To determine the properties in the coordinates $p$ - $v$ and $p$ - $p$, the temperature is first calculated. It is iterated on a given isochore by the half division method. After that, all properties are calculated by the known algorithm in accordance with the phase state of the substance.

In the coordinates $p$ - $h$ and $p$ - $s$, for calculating the thermodynamic properties, it is necessary to determine the temperature and density. For their calculation, a double iterative cycle is used. First, temperature is determined by iterating on an isobar based on known thermodynamic relations. Then, for a given pressure, the density value is determined, which is necessary for calculating the caloric properties. When determining $T$ and $p$, iterative cycles are repeated until the errors in finding the density, enthalpy, and entropy reach the specified values.
When calculating the properties in the $h$ - $s$ coordinates, none of the three thermal parameters associated with the equation of state is specified. Therefore, the algorithm for calculating the thermophysical properties in these coordinates is based on a comparison of the specified and calculated enthalpy values on the isoentrope.

To ensure consistency of the values of thermodynamic properties, which are calculated in different coordinate systems, the following values of permissible errors are accepted: for pressure and density - 0.001%, for temperature - 0.0001 K, for enthalpy - 0.05 J / mol, and for entropy, 0.005 J / (mol ∙ K).

The developed system can also be used in a design of refrigeration and cryogenic plants. The accuracy of the calculations is ensured by using the well-known equations of state and equations for transport properties of each substance, as well as by setting small values of permissible errors in iterative cycles.

3. Conclusion
Automated systems that allow to determine quickly the properties of substances at various combinations of independent variables and replace property tables and state diagrams at calculations have significant advantages over conventional reference books. It is advisable to create specialized systems which combine property calculation programs and application programs for designing the energetic, cryogenic and refrigerating plants. The system developed by us can be used to create such specialized systems.

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