

SMath and CoolProp: thermophysical properties of liquids and gases: trust but verify

The article presents the results of numerical experiments with the free software package of CoolProp functions that return the thermophysical properties of liquids, gases and their mixtures. The features of working with this package within the freely distributed mathematical program SMath are described. The features of the use of units of measurement in such calculations are discussed.

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An old Polish film, "Gangsters and Philanthropists", has the following plot. A man is fired from his job in a chemical laboratory because, through negligence, he created a small workplace explosion. The poor fellow enters a restaurant and, out of grief, orders himself a glass of vodka and an appetizer—a herring with bread (see Figure 1). Sadly, the chemist mechanically pulls out a hydrometer from the breast pocket of his jacket and begins to stir the vodka with it. The staff thinks he an auditor who checks the strength of the drink (whether vodka is diluted with water), and gives him a bribe. Our unemployed chemist guesses what's what and begins to do the same in other restaurants in Warsaw.



Fig. 1

Frame from the film "Gangsters and Philanthropists"

A hydrometer is one of the handy measuring instruments of analytical chemists. No wonder it ended up in the pocket of our chemist. The device is a glass float with an immersion scale. With a hydrometer, you can measure the density of a solution, then use it to determine its concentration. Older car owners will immediately remember lead batteries filled with sulfuric acid solution. Its concentration had to be periodically checked with a special hydrometer and, if necessary, have distilled water¹ added, which evaporated over time, which required a new check. If the hydrometer scale is marked in degrees (percentage) of alcoholic beverages, then it will be called a thermometer, sorry, alcoholometer. The thermometer is a completely different measuring instrument.

Let's evaluate the thermophysical parameters of vodka in SMath using the CoolProp package of functions loaded to it. This will be an instructive computational experiment. The mathematical program SMath can be freely downloaded in a couple of minutes from the site www.smath.com, and then, again, in a couple of minutes, it can be equipped with functions that return the thermophysical properties of liquids, gases, and their mixtures. This is done through the command chain Tools/Options/Additions/Gallery Online/CoolProp Wrapper. How to work in the SMath environment is described in the tutorial <http://twt.mpei.ac.ru/ochkov/EC-SMath.pdf>. Information about the CoolProp package can be found at www.coolprop.org. The address ending org means that this is a non-profit organization. Names of sites with programs that need to be purchased for money², usually end in com—a commercial site. The paid version of CoolProp is called RefProp. It can be obtained from the site <https://www.nist.gov/srd/refprop>, owned by the National Institute of Standards and Technology (NIST—USA). Cool and Ref are the beginnings of the English words Coolant (cooler) and Refrigerant (refrigerant). Prop is the beginning of the word Property—property. The term Cool turned out to be successful also because in youth slang this English word has the meaning—cool! But the computer translator produced more than three dozen translations of the word Cool into Russian. Let's see how CoolProp turned out to be cool in relation to vodka.

So, as they say now, let's create a digital twin of the situation recorded in Figure 1.

Figure 2 shows how temperature and pressure values are entered into the calculation, at which the thermophysical parameters of water and anhydrous ethyl alcohol will be determined further.

Figures 2 and 3 show the call in SMath of two functions from the CoolProp package—the CoolProp_get_fluid_param_string function with two arguments and the CoolProp_Props function with six arguments. The first function returned is the chemical formula, and the second returned the density ("D"), the molar mass ("M"), the boiling point at atmospheric pressure ("T"), the boiling pressure (vapor pressure) at normal temperature ("P"), viscosity ("V"—viscosity), mass specific heat ("Cpmass") and thermal conductivity ("conductivity"). A complete list of parameters and substances can be found on the above website www.coolprop.org. The unit entered as the fifth argument of the CoolProp_Props function when calculating the boiling temperature and pressure on the saturation line indicates that we are dealing with dry saturated steam. If the unit is replaced by zero, then it will be a liquid on the saturation line. Instead of one, you can put any number in the range from zero to one. This will not affect the boiling temperature and pressure, which cannot be said when determining other parameters—specific enthalpy, for example.

¹At that time, the author was a post-graduate student at the Department of Water and Fuel Technology of the Moscow Power Engineering Institute, which supplied distilled water to motorists throughout the institute.

² An anecdote from the future times of easing sanctions.

– *Now Photoshop can be bought again on the developer's website.*

- *What!? Buy?!*

$$T := 20 \text{ } ^\circ\text{C} \quad p := 1 \text{ атм}$$

$$\text{CoolProp_get_fluid_param_string}(\text{"H2O"; "formula"}) = \text{"H}_{2}\text{O}_{1}\text{"}$$

$$\rho_{\text{H2O}} := \text{CoolProp_Props}(\text{"D"; "P"; } p; \text{"T"; } T; \text{"H2O"}) = 0,9982 \frac{\text{г}}{\text{см}^3}$$

$$\text{CoolProp_Props}(\text{"M"; "P"; } p; \text{"T"; } T; \text{"H2O"}) = 18,02 \frac{\text{г}}{\text{моль}}$$

$$\text{CoolProp_Props}(\text{"T"; "P"; } p; \text{"Q"; } 1; \text{"H2O"}) = 100 \text{ } ^\circ\text{C}$$

$$\text{CoolProp_Props}(\text{"P"; "T"; } T; \text{"Q"; } 1; \text{"H2O"}) = 17,55 \text{ мм рт.ст.}$$

$$\text{CoolProp_Props}(\text{"V"; "P"; } p; \text{"T"; } T; \text{"H2O"}) = 1,002 \frac{\text{л}}{\text{кг}}$$

$$\text{CoolProp_Props}(\text{"Cpmass"; "P"; } p; \text{"T"; } T; \text{"H2O"}) = 0,9993 \frac{\text{ккал}}{\text{г К}}$$

$$\text{CoolProp_Props}(\text{"conductivity"; "P"; } p; \text{"T"; } T; \text{"H2O"}) = 598 \frac{\text{Вт мм}}{\text{м}^2 \text{ К}}$$

Fig. 2

Thermophysical properties of water under normal conditions

If we collect the values of density, viscosity and specific isobaric heat capacity of water under normal conditions, then we get three units³. In the article to which the link is made, unusual, but more correct, in the opinion of the author, are the units of viscosity and thermal conductivity used in the calculation in Figures 2 and 3. And God himself ordered the heat capacity of water to be measured in calories, not joules! A calorie is the energy that needs to be transferred to a gram of water in order to raise its temperature by one kelvin—one degree Celsius under normal conditions and constant pressure. Everything is simple and clear. Joules are used to measure mechanical work.⁴ The way the units of measurement are built into the SMATH package, is flexible in that it allows you to enter into the calculation and print out the values of physical quantities with the units that are more familiar to the user. In the bowels of the computer, everything is stored in SI units. Imitating Kozma Prutkov, one can say this. If you see a record of 1 atm in the calculation, then do not believe it. In this cell, sorry, this calculation does not store the physical atmosphere, but the pascal. This is very unusual for those who are used to doing calculations manually using a calculator or in the environments of "dimensionless" spreadsheets and programming languages.⁵

By the way, with a "light movement of the hand"—by clicking on a pair of commands from the SMATH package, you can in one fell swoop translate the Russian names of the units of measurement involved in our calculations into English (international). Along the way, you can replace the commas that separate the integer and fractional parts of numbers with a dot (the international

³ Ochkov V.F., Orlov K.A. Digital twin of water // Energy: economics, technology, ecology. No. 10, 2021, pp. 18-22 (<http://www.twt.mpei.ac.ru/ochkov/Ochkov-3water.pdf>)

⁴ The author proposes to celebrate the day of heat engineering on April 19 of each year. Following the example for a mathematician March 14.

⁵ Очков В.Ф. Физические и экономические величины в Mathcad и Maple. М.: Финансы и статистика, 2002 (<http://www.twt.mpei.ac.ru/ochkov/Fis-Eco-Units-Mathcad-Maple.pdf>)

standard for writing decimal fractions). This facilitates the international exchange of information, in particular, the exchange of calculation results.

Figure 3 almost repeats Figure 2. Only the word H2O (water) has been replaced by the word Ethanol (ethyl alcohol).

```
CoolProp_get_fluid_param_string("Ethanol"; "formula") = "C_{2}H_{6}O_{1}"

ρC2H5OH := CoolProp_Props("D"; "P"; p; "T"; T; "Ethanol") = 0,7894  $\frac{\text{Г}}{\text{CM}^3}$ 

CoolProp_Props("M"; "P"; p; "T"; T; "Ethanol") = 46,07  $\frac{\text{Г}}{\text{МОЛЬ}}$ 

CoolProp_Props("T"; "P"; p; "Q"; 1; "Ethanol") = 78,42 °C

CoolProp_Props("P"; "T"; T; "Q"; 1; "Ethanol") = 44,07 мм рт.ст.

CoolProp_Props("V"; "P"; p; "T"; T; "Ethanol") = 1,194  $\frac{\text{H MM}}{\frac{\text{M}}{\text{C}} \text{ M}^2}$ 

CoolProp_Props("Cpmass"; "P"; p; "T"; T; "Ethanol") = 0,5723  $\frac{\text{кал}}{\text{Г K}}$ 

CoolProp_Props("conductivity"; "P"; p; "T"; T; "Ethanol") = 164,5  $\frac{\text{Вт MM}}{\text{M}^2 \text{ K}}$ 
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Fig. 3

Thermophysical properties of anhydrous ethyl alcohol

Figure 4 shows the calculation of the parameters of vodka obtained by mixing 40 ml of ethyl alcohol and 60 ml of water⁶. After such an operation, the temperature of the solution will rise slightly, but the calculations will be carried out for the given 20 degrees Celsius, since everything will return to a stable temperature state in a short time.

The masses of the components (m) of the finished mixture (31.58 g⁷ alcohol and 59.89 g of water), as well as the mass fractions of alcohol (0.3452) and water (0.6548), which form the Vodka variable involved in calculating the properties of this alcoholic beverage.

⁶ In perestroika times, the famous Royal alcohol was sold, which was diluted with water. How can one not recall the classic Bulgakov's: "- Doctor Bormental, I beg you, leave the caviar alone! And if you want to follow good advice, pour not English, but ordinary Russian vodka.

- Newly blessed? he inquired.

"God be with you, my dear," the owner replied. - It's alcohol. Darya Petrovna makes excellent vodka herself."

⁷ In restaurants in Russia, as a rule, they never order strong alcoholic drinks in milliliters, they always mention grams here, meaning not units of mass, but units of volume, capacity: "Another hundred grams per staff and we disperse!". But in our calculations, such a default will not work: grams are grams, and milliliters are milliliters. And they never mix in a physico-chemical, rather than philological sense.

$$m_{C_2H_5OH} := 40 \text{ мл} \cdot \rho_{C_2H_5OH} = 31,58 \text{ г} \quad m_{H_2O} := 60 \text{ мл} \cdot \rho_{H_2O} = 59,89 \text{ г}$$

$$m_{\text{Водка}} := m_{C_2H_5OH} + m_{H_2O} = 91,47 \text{ г}$$

$$\frac{m_{C_2H_5OH}}{m_{\text{Водка}}} = 0,3452 \quad \frac{m_{H_2O}}{m_{\text{Водка}}} = 0,6548 \quad 0,3456 + 0,6544 = 1$$

$\text{Водка} := \text{"Ethanol}[0.3456] \& \text{Water}[0.6544] \text{"}$

$$\rho_{\text{Водка}} := \text{CoolProp_Props}(\text{"D"; "P"; p; "T"; T; Водка}) = 0,8508 \frac{\text{г}}{\text{см}^3}$$

$$V_{\text{Водка}} := \frac{m_{\text{Водка}}}{\rho_{\text{Водка}}} = 107,5 \text{ мл}$$

Fig. 4

Calculation of the volume of vodka

Venichka Erofeev in his immortal poem "Moscow-Petushki" wrote that "... no one in Russia knows why Pushkin died—but the fact that when mixing 40 ml of alcohol and 60 ml of water comes out less than 100 ml of vodka—everyone knows"⁸. And in our calculation it turned out the opposite—vodka turned out to be a little more than 100 ml! This, of course, is very successful from the point of view of some drunkard diluting hawthorn alcohol infusion with water. You definitely need to put a hydrometer or something else into the vial of this infusion and make sure that there is ethyl alcohol, and not methyl alcohol. The CoolProp package, by the way, shows that at our 20 degrees Celsius, the density of ethyl alcohol is 0.7894 g/cm³, and that of methyl alcohol is 0.7913 g/cm³. The difference is small and is within the measurement error. Uncertainties of measurements, as they began to say now. So it is better not to drink what is not intended for drinking!

But we digress!

What's the matter here!?! Where is the mistake! You can also recall here the doctoral dissertation of D.I. Mendeleev "On the combination of alcohol with water", which has acquired many myths.

If you make a request on the Internet using the key "Density of aqueous solutions of ethanol", then a lot of information will be displayed, including the table shown in Figure 5. Someone kindly scanned it from the book of Rabinovich V.A. and Khavin Z.Ya. "Brief Chemical Reference" (3rd ed., St. Petersburg, Chemistry, 1991) and posted on the Internet. You can also find other such tables from other paper directories there, compare them and make sure that they practically coincide. Yes, quite dubious information is often published on the Internet, which always needs to be checked and double-checked. But even in paper reference books that have undergone strict review and editing, alas, there are errors and typos (misspellings). So the table in Figure 5 indicates that density is measured in g/cm instead of the correct g/cm³. In our calculations, such a mistake will be immediately noticed—the SMath program will add the missing units of length squared to the answer. It turns out an unusual unit of density—a gram divided by a centimeter and a square meter. This will immediately catch your eye, and the error will be corrected.

⁸ Yerofeev is a little different: "... no one in Russia knows why Pushkin died, but how polish is cleaned—everyone knows." Due to its high alcohol content, this technical liquid can be used as a surrogate alcoholic beverage. So our reinterpretation of Erofeev did not knock us out of the topic of the story.

Таблица 6-6

Плотность водных растворов этилового спирта в зависимости от температуры, г/см

Весовой процент спирта	Температура, °C				Весовой процент спирта	Температура, °C			
	10	15	20	40		10	15	20	40
0	0,99973	0,99913	0,99823	0,99225	52	0,91723	0,91333	0,90936	0,89288
4	0,99218	0,99195	0,99103	0,98485	56	0,90831	0,90433	0,90031	0,88335
8	0,98660	0,98584	0,98478	0,97808	60	0,89927	0,89523	0,89113	0,87417
12	0,98145	0,98041	0,97910	0,97150	64	0,89006	0,88597	0,88183	0,86466
16	0,97692	0,97552	0,97387	0,96512	68	0,88074	0,87660	0,87241	0,85507
20	0,97252	0,97068	0,96864	0,95856	72	0,87127	0,86710	0,86287	0,84540
24	0,96787	0,96558	0,96312	0,95168	76	0,86168	0,85747	0,85322	0,83564
28	0,96268	0,95996	0,95710	0,94438	80	0,85197	0,84772	0,84344	0,82578
32	0,95655	0,95357	0,95038	0,93662	84	0,84203	0,83777	0,83348	0,81576
36	0,94986	0,94650	0,94306	0,92843	88	0,83181	0,82754	0,82323	0,80552
40	0,94238	0,93882	0,93518	0,91992	92	0,82114	0,81688	0,81257	0,79491
44	0,93433	0,93062	0,92685	0,91108	96	0,80991	0,80566	0,80138	0,78388
48	0,92593	0,92211	0,91823	0,90207	100	0,79784	0,79360	0,78934	0,77203

Fig. 5

Table of density of aqueous solutions of ethyl alcohol

At the beginning of the article, the Institute of Standards and Technology NIST was mentioned. The author, during a previous visit to this scientific organization in the city of Boulder, Colorado, saw the following sight there. In the computer class, young people sat working in pairs at the monitors, whispering and clattering the keyboard keys. The author was surprised and asked his American colleagues: "What, you also do not have enough computer technology, and you have to plant two people at one computer ?!" But the author was told that they were students working part-time at NIST. They enter information into the computer, similar to the one shown in Figure 5. The first student dictates numbers from a paper book or magazine, and the second one enters them into the computer. At the same time, the first student additionally controls the correctness of the input, alternately glancing either at the reference book or at the computer monitor. NIST tried to scan such tables and digitize them automatically. But the poor quality of the printed original and the imperfection of automatic readers⁹ led to the fact that in the final digitized table there were many typos that had to be identified and corrected manually. It was easier and more reliable to immediately hire students, giving them the opportunity to earn extra money at the same time. Education in US universities is paid and quite high—students have to turn around.

During a practical lesson, the author instructed his students to do such work on a computer using the "cheek to cheek" technology—compare Figures 5 and 6.

Figure 6 shows the contents of the matrix M with a "head" that stores the temperature, and a "side" that stores the weight percentage of alcohol. This, of course, is not a weight, but a mass percentage. But in the "good old days" these two physical quantities were often confused. And now we measure the weight of a person in kilograms, and not in the more correct newtons. Weight, after all, is a force, not a mass! But the exclamation: "I weigh 1000 Newtons not 102 kilograms!" among other things, smacks of megalomania!

⁹ Programs that translate scanned texts into digital format.

"n/t"	10	15	20	40
0	0.99973	0.99913	0.99823	0.99225
4	0.99218	0.99105	0.99103	0.98485
8	0.9866	0.98584	0.98478	0.97808
12	0.98145	0.98041	0.9791	0.9715
16	0.97692	0.97552	0.97387	0.96512
20	0.97252	0.97068	0.96864	0.95856
24	0.96787	0.96558	0.96312	0.95168
28	0.96268	0.95996	0.9571	0.94438
32	0.95655	0.95357	0.95038	0.93662
36	0.94986	0.9465	0.94306	0.92843
40	0.94238	0.93882	0.93518	0.91992
44	0.93433	0.93262	0.92685	0.91108
48	0.92593	0.92211	0.91823	0.90207
52	0.91723	0.91333	0.90936	0.89288
56	0.90831	0.90433	0.90031	0.88335
60	0.89927	0.89523	0.89113	0.87417
64	0.89006	0.88597	0.88183	0.86466
68	0.88074	0.8766	0.87241	0.85507
72	0.87127	0.8671	0.86287	0.8454
76	0.86168	0.85747	0.85322	0.83564
80	0.85197	0.84772	0.84344	0.82578
84	0.84203	0.83777	0.83348	0.81576
88	0.83181	0.82754	0.82323	0.80552
92	0.82114	0.81688	0.81257	0.79491
96	0.80991	0.80566	0.80138	0.78388
100	0.79784	0.7936	0.78934	0.77203

Fig. 6
The digital twin of the paper table shown in Figure 5

The matrix M is further used in the author's program¹⁰ with double spline interpolation shown in Figure 7.

¹⁰ Thermotechnical studies with Excel, Mathcad and the Internet / Ed. ed. V.F. Ochkova. Publishing house BHV-Petersburg. 2014. - 336 p. (latest edition <http://tw.mpei.ac.ru/ochkov/Therm-Studies.pdf>)

$$\rho_{Vodka}(n, T) := \left\{ \begin{array}{l} x := 100 \cdot n \\ t := \frac{T}{K} - 273.15 \\ X := \text{submatrix}(M, 2, \text{rows}(M), 1, 1) \\ Y := \text{submatrix}(M, 1, 1, 2, \text{cols}(M))^T \\ Z := \text{submatrix}(M, 2, \text{rows}(M), 2, \text{cols}(M)) \\ \text{for } i \in [1.. \text{cols}(Z)] \\ \quad Zv_i := \text{lspline}(X, \text{col}(Z, i), x) \\ \text{lspline}(Y, Zv, t) \frac{\text{g}}{\text{cm}^3} \end{array} \right.$$

$$\rho_{Vodka}(0; 10 \text{ }^\circ\text{C}) = 0,99973 \frac{\text{T}}{\text{CM}^3} \quad \rho_{Vodka}(0; 40 \text{ }^\circ\text{C}) = 0,99225 \frac{\text{T}}{\text{CM}^3}$$

$$\rho_{Vodka}(1; 10 \text{ }^\circ\text{C}) = 0,79784 \frac{\text{T}}{\text{CM}^3} \quad \rho_{Vodka}(1; 40 \text{ }^\circ\text{C}) = 0,77203 \frac{\text{T}}{\text{CM}^3}$$

Fig. 7

Table data double spline interpolation program

In the program, firstly, the arguments are processed: the mass fraction is converted into a mass percentage ($x = 100n$), and the temperature is converted to degrees Celsius ($t = T/K - 273.15$): everything is in accordance with the sidebar and the header of the original table. On the last line, a unit of measurement is added to the calculated dimensionless density. These are the standard rules for working with empirical formulas¹¹. The bottom of Figure 7 shows the test calls to the ρ_{Vodka} function with the "corner" argument values.

In the program in Figure 7, the submatrix function built into SMath is called three times, which removes from the matrix M the side vector X with discrete values of the mass fraction, the top vector Y with discrete values of temperature, and the matrix Z with discrete density values (the kernel of the matrix M). The vector Zv , formed in the loop with the *for* parameter, is an additional row of the Z matrix, which stores four discrete values of density at discrete values of temperature and at a given value of the mass fraction ranging from zero to one. The work uses the built-in SMath function *lspline* with three arguments, which interpolates with cubic splines when a polynomial curve of the third degree is drawn through four points.

The built-in functions *rows* and *cols* take one argument and return the number of rows and columns of a matrix. The two-argument built-in functions *row* and *col* return the specified row or column of a matrix. When creating the vector Y , a transposition (power of T) was carried out: a matrix with one row turned into a regular vector—a matrix with one column.

In our problem, cubic spline interpolation (*lspline*) can be replaced by piecewise linear interpolation (*linterp*), for which line segments are drawn between points. Figure 8 shows the differences in the

¹¹ Ochkov V.F., Orlov K.A. Units of measurement in three types of formulas: in physical, empirical and ... pseudo-empirical // World of Measurements No. 1-2, 2021 (<http://tw.t.mpei.ac.ru/ochkov/Pseudo.pdf>)

operation of these two functions—the blue curve is piecewise linear interpolation, the red curve is spline interpolation. Green dots are discrete data that were interpolated.

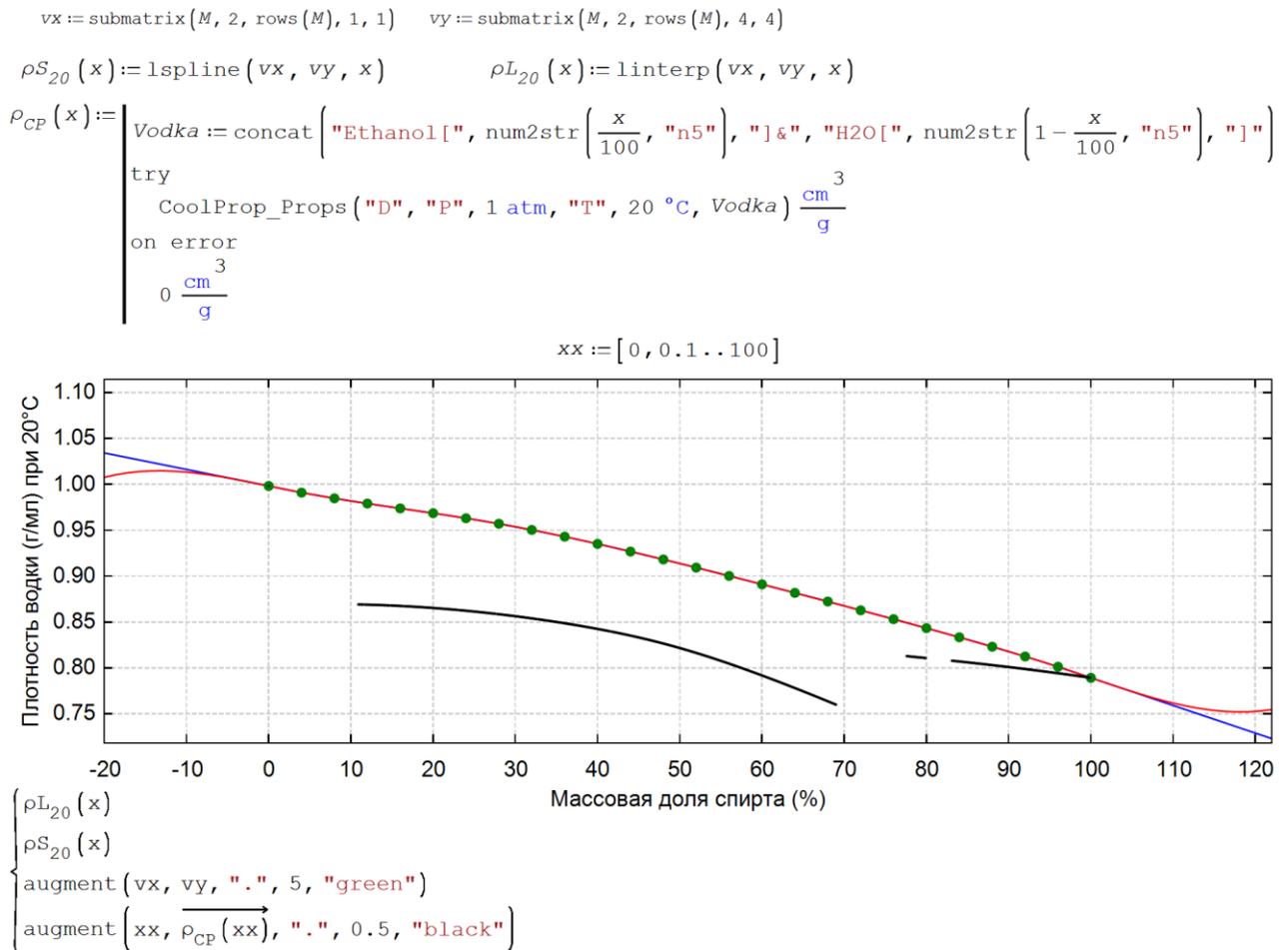
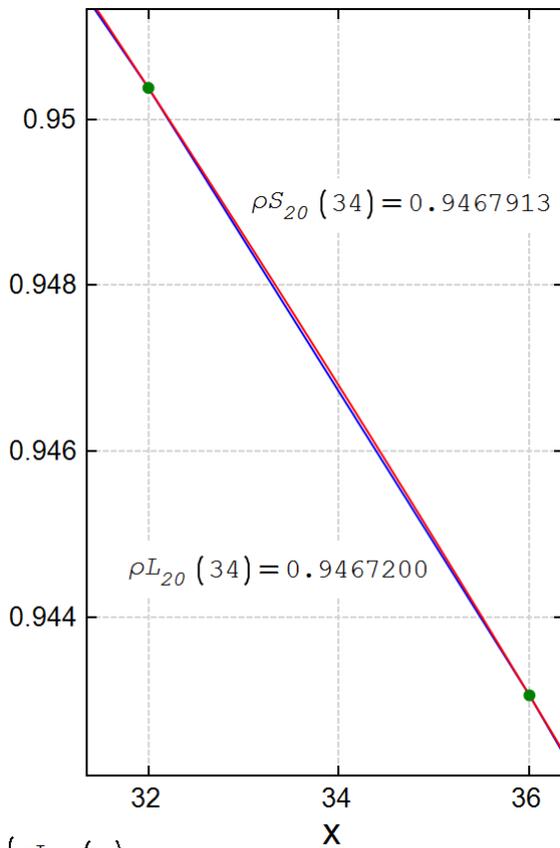


Fig. 8

20°C isotherm: linear and spline interpolation

Inside the points (interpolation), the blue (function ρ_{L20}) and red (ρ_{S20}) curves almost coincided. They essentially disperse in different directions outside the green dots (an extrapolation, which in this problem, has no physical meaning).

Figure 9 shows how the curves of the two types of interpolation scale up near two points where you can see a slight difference. But these two types of interpolation differ from each other not only quantitatively (see Figure 9), but also qualitatively. The fact is that the first derivative of piecewise linear interpolation is a set of columns, and the second derivative is generally equal to zero. This is bad for the implementation of various numerical methods—the search for zeros, maxima, etc. Interpolation by splines doesn't suffer from such a disadvantage..



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{ ρL20(x)
{ ρS20(x)
{ augment(vx, vy, ".", 5, "green")

```

Fig. 9

Linear interpolation curves (blue) and spline interpolation

Additionally, the graph in Figure 8 shows the curve, or rather individual pieces of the vodka density curve, calculated according to the CoolProp package. The black curve is an erroneous density value, and the breaks in it are unsuccessful attempts (try) to call the ρ_{CP} function, when not a number, but an error message is issued.

Conclusion. CoolProp's ethanol-water mixing tools are no good. Most likely, the same picture will be observed when working with other mixtures of liquids. For example, water and methyl alcohol. And the point here, apparently, is that these tools are designed to work only with gases. And vodka is far from gas.

The rejection of the built-in function of the CoolProp package and the transition to a "home-grown" function named ρ_{Vodka} gave the correct result for calculating the volume of vodka (96.71 ml)—see Figure 10. In the collapsed area (a line with a plus sign on the left) is the function shown in Figure 7 and based on the matrix from Figure 6.

$$P := 1 \text{ aTM} \quad T := 20 \text{ }^\circ\text{C}$$

$$V_{C2H5OH} := 40 \text{ MJL} \quad m_{C2H5OH} := V_{C2H5OH} \cdot \rho_{C2H5OH} = 31,58 \text{ T}$$

$$V_{H2O} := 100 \text{ MJL} - V_{C2H5OH} = 60 \text{ MJL} \quad m_{H2O} := V_{H2O} \cdot \rho_{H2O} = 59,89 \text{ T}$$

$$m_{Vodka} := m_{C2H5OH} + m_{H2O} = 91,47 \text{ T} \quad n_{C2H5OH} := \frac{m_{C2H5OH}}{m_{Vodka}} = 0,3452$$

□

$$\rho_{Vodka} \left(n_{C2H5OH}; T \right) = 0,9458 \frac{\text{T}}{\text{CM}^3} \quad V_{Vodka} := \frac{m_{Vodka}}{\rho_{Vodka} \left(n_{C2H5OH}; T \right)} = 96,71 \text{ MJL}$$

Fig. 10

Correct calculation of the volume of vodka

Figure 11 solves the inverse problem: given the density of vodka (0.95 g/cm³)—find the mass fraction. The solve function built into SMath is used, which returns the root of the equation in the given range of the unknown from zero to one (bisection method).

$$n_{C2H5OH} := \text{solve} \left(\rho_{Vodka} \left(n_{C2H5OH}; T \right) = 0,95 \frac{\text{T}}{\text{CM}^3}; n_{C2H5OH}; 0; 1 \right) = 0,3221$$

Fig. 11

Calculation of the mass fraction of alcohol in diluted vodka with a density of 0.95 g/cm³

The solution of the inverse problem (Figure 11) is, by the way, an important topic in determining the thermophysical parameters of water and steam. The International Association for the Properties of this Main Working Fluid and Coolant in the Energy Industry (www.iapws.org) has released two formulations—a 1995 and 1997 formulation. The first formulation, codenamed IAPWS-95, takes temperature and density as arguments. This was not very convenient for practical purposes, when not density, but pressure is measured. Therefore, a second formulation was released, codenamed IAPWS-IF97, with temperature and pressure arguments. It had to go to great lengths to do so. In particular, the formulation area was divided into separate zones, for each of which analytical equations were written. And these zones often do not mesh exactly with each other. If at that time there existed a simple and exact function for solving inverse problems, similar to the one shown in Figure 11, there would most likely not be a bifurcation of the IAPWS formulations. There would be one formulation with initial data (arguments) temperature and density and recommendations for a numerical rather than analytical solution of the inverse problem—finding the thermophysical parameters of water and water vapor from pressure and temperature, and not from temperature and density.

Our numerical experiment with vodka suggests that the methods of working with mixtures can only give an acceptable answer with gases, which, with a certain degree of convention, can be considered ideal, but not with liquids.

The example of mixing ethyl alcohol with water, as the reader may understand, is not entirely appropriate in the educational literature. But ethyl alcohol is used not only in the alcoholic beverage industry, but also in thermal power engineering.

Imagine such a power supply scheme for a small house (cottage).

The house has a hot water boiler, which burns gas and heats the water supplied to the radiators for heating the premises of the house. The slightly cooled water is then returned to the boiler for heating.

The flue gas of this boiler contains low-grade heat, which is partially recovered in an ORC (Organic Rankine Cycle) plant with an organic Rankine Cycle, ORC. The ORC technology differs from the traditional thermodynamic cycle from a standard steam turbine in that it does not use water and water vapor as a working fluid, but organic substances with a low boiling point—with ethyl alcohol, for example. Figures 2 and 3 show that at atmospheric pressure, water boils at 100 degrees Celsius and ethanol at 78.42. From the site <http://www.twt.mpei.ac.ru/TTHB/Rankin-Ethanol.zip> you can download the SMATH-calculation of such an installation, where liquid ethanol is heated to the boiling point in an "alcohol" boiler, then evaporates and enters the turbine in the form of saturated steam, the generator of which generates electrical energy for the house. Wet ethanol vapor from the turbine enters the condenser, again turning into a liquid, which is pumped back to the boiler. The cycle closes.

Imagine that such gas is supplied not by mains, but by liquefied gas, which is transported by car and poured into a special tank dug into the ground near the house. Or they bring it up and distribute it in special cylinders, which can often be seen in non-gasified settlements. In dachas, for example, where the heating can be a stove, and the gas stove in the kitchen runs on such imported gas.

The transition state from liquid to gas is a two-phase medium. We "burned ourselves" on a mixture of ethanol and water—let's "blow" on propane-butane and solve just such a problem.

A new empty 27-liter (variable V) cylinder for storing liquefied petroleum gas (LPG or LCG) was placed on a balance and its mass was fixed at 14.5 kg (m_1 —see the beginning of Figure 12). Then this cylinder was filled with liquefied gas so that the mass of the cylinder became equal to 25 kg.

Determine the volumes and masses of the liquid and gaseous parts in the cylinder, if the temperature of the cylinder and the gas in it has become equal to the ambient temperature of 20 °C (T). The mass fraction of propane is 60% (variable Propane), and butane 40 (variable Butane). This ratio is summer and winter. The fact is that propane is much more expensive than butane and is saved. But in winter, the proportion of propane has to be increased so that the pressure in the cylinder remains high enough and the gas itself, without an additional pump (turbine), enters the burners of boilers and stoves. Or into car cylinders, many of which run on CNG. Proportion 60/40 winter. In summer, you can reduce the proportion of propane to 40 percent.

$$V := 27 \text{ L} \quad m_1 := 14.5 \text{ kg} \quad m_2 := 25 \text{ kg} \quad T := 20 \text{ }^\circ\text{C} \quad (1)$$

$$m_{\text{Air}} := V \cdot \text{CoolProp_Props}(\text{"D"}, \text{"T"}, T, \text{"P"}, 1 \text{ atm}, \text{"Air"}) = 32.52 \text{ g} \quad (2)$$

$$m_1 := m_1 - m_{\text{Air}} = 14.47 \text{ kg} \quad m := m_2 - m_1 = 10.53 \text{ kg} \quad (3)$$

$$\text{Propane} := 60 \% \quad \text{Butane} := 100 \% - \text{Propane} = 40 \% \quad (4)$$

$$\text{Propane} := \text{num2str}(\text{Propane}, \text{"n5"}) = \text{"0.6"} \quad (5)$$

$$\text{Butane} := \text{num2str}(\text{Butane}, \text{"n5"}) = \text{"0.4"} \quad (6)$$

$$\text{Смесь} := \text{concat}(\text{"Propane"}, \text{"["}, \text{Propane}, \text{"}&\text{Butane["}, \text{Butane}, \text{"]"} \quad (7)$$

$$\text{Смесь} = \text{"Propane[0.6]&Butane[0.4]"} \quad (8)$$

$$\text{CoolProp_Props}(\text{"P"}, \text{"T"}, T, \text{"Q"}, 0, \text{"Butane"}) = 2.049 \text{ atm} \quad (9)$$

$$p := \text{CoolProp_Props}(\text{"P"}, \text{"T"}, T, \text{"Q"}, 0, \text{Смесь}) = 5.615 \text{ atm} \quad (10)$$

$$\text{CoolProp_Props}(\text{"P"}, \text{"T"}, T, \text{"Q"}, 0, \text{"Propane"}) = 8.255 \text{ atm} \quad (11)$$

$$\rho_G := \text{CoolProp_Props}(\text{"D"}, \text{"T"}, T, \text{"Q"}, 1, \text{Смесь}) = 8.624 \frac{\text{kg}}{\text{m}^3} \quad (12)$$

$$\rho_L := \text{CoolProp_Props}(\text{"D"}, \text{"T"}, T, \text{"Q"}, 0, \text{Смесь}) = 536.7 \frac{\text{kg}}{\text{m}^3} \quad (13)$$

$$Q := \text{solve}\left(\frac{Q \cdot m}{\rho_G} + \frac{(1-Q) \cdot m}{\rho_L} = V, Q, 0, 1\right) = 6.137 \% \quad (14)$$

$$m_G := m \cdot Q = 64.64 \text{ g} \quad m_L := m \cdot (1-Q) = 10.47 \text{ kg} \quad (15)$$

$$V_G := \frac{m_G}{\rho_G} = 7.495 \text{ L} \quad V_L := \frac{m_L}{\rho_L} = 19.51 \text{ L} \quad (16)$$

Fig. 12
Calculation of a mixture of propane and butane

Figure 12 shows the input of the initial data (item 1), the calculation of the mass of air in an empty cylinder (2) and the mass of the cylinder m with air pumped out of it (3). The air in an empty cylinder doesn't have to be taken into account, but why not do so if it is so easy to do on a computer. In paragraph 4, the mass fractions of propane and butane in the mixture are set, which are then converted from numbers to strings (items 5 and 6), which then form the string variable Mix (items 7 and 8). The built-in SMATH functions `num2str` (converting a number to a string) and `concat` (string addition, including square brackets and the & sign) are used. Further (items 9, 10 and 11) saturation pressures (elasticity) of pure butane (item 9), a mixture of 60/40 (item 10) and pure propane (item 11) are calculated. It can be seen that the elasticity of propane is higher. Therefore, it is more in the winter mixture. The unit of pressure is the physical atmosphere (760 mm of mercury), and not megapascals, so that you can immediately see how much the pressure in the cylinder exceeds atmospheric pressure. The pressure obtained in the calculation is, of course, absolute, and not relative, which would be indicated by a pressure gauge mounted on a cylinder. To the reading of the manometer, you must also add the value of atmospheric pressure read from the barometer.

In items 12 and 13, the gas and liquid densities of the propane-butane mixture in our cylinder are calculated. Next, the material balance equation is solved (14), which determines the mass fraction Q of the gas in the cylinder (displayed in ppm) and the mass of gas and liquid (15).

If the temperature is made equal, not to 20, but to minus 25 ° C, then propane will boil at 2.008 atm, and butane at 0.3544 atm, that is, at a pressure less than atmospheric. Therefore, the proportion of butane in the winter mixture is reduced by diluting it with more expensive propane.

Here, of course, it is necessary, as in the case of the ethanol mixture, to check whether the correct density values are given by the functions in Figure 12. On the Internet, where data from paper reference books are translated, there are many similar tables. We suggest the reader do this interesting work with elements of a computational experiment on their own. The result of this work can be a graph similar to the one shown in Figure 8. Will the curves of tabular data match the calculated data for propane-butane?! This did not happen in the case of a mixture of ethanol and water.

Note that NIST, which was mentioned in the article, began its work with such a task. The pipes carry natural gas or gas obtained from coal gasification. The parameters of such gas are different at the ends of the pipeline. How can the buyer of gas settle with its seller?! This problem cannot be solved without knowledge of the thermophysical properties of the gas. This is what NIST has been doing since its inception in 1901. This is why NIST belongs to the US Department of Commerce and not to any other agency.

Conclusion.

Calculation programs require additional verification and certification. If not in general, then on the individual most important components. Unverified components should be temporarily blocked.

The literature is scattered around the footnotes of this article.