Hybrid thermodynamic calculations

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Abstract. Dimensions of some physicochemical constants are discussed in relation to the mathematical methods used in power engineering calculations. It is shown that using contemporary software, numerical and symbolic methods can be combined in thermodynamic calculations, e.g., to calculate thermodynamic cycles, including binary cycles.

To explain the concept of “hybrid thermodynamic calculations” (more on p. 5 below) from an engineering standpoint, let’s begin with engineering thermodynamics rather than simply thermodynamics, specifically as it relates to power engineering.

A debate has been raging in this scientific discipline for more than a 100 years on whether some physicochemical constants are truly dimensionless [1]. In handbooks, for example, ionic product $K_w$ of water, the principal working medium and heat carrier in power engineering, is given without $(10^{-14})$ as well as with $(10^{-14} \text{ mol}^2/\text{l}^2)$ the units of measurement. The units are provided for purely practical reasons, to avoid calculation errors. The rationale for that is simple. The unit of l (liter) or, more precisely, $\text{dm}^3$ (for calculating concentrations a unit of volume is preferred over that of capacity) that is hidden in the unitless constant $K_w$ is not a basic SI unit. To follow the rules then, $K_w$ should be given as $10^{-8}$ or $10^{-8} \text{ mol}^2/\text{l}^2$ or $(\text{mmol}/\text{l})^2$. This often confuses engineers and leads to errors in calculations. In the formulations of the International Association for Properties of Water and Steam, the ionic product of water is dimensionless. Accordingly, it is dimensionless in the calculations found at the author’s site http://twt.mpei.ac.ru/MCS/Worksheets/WSP/KwTPo.xmcd [2].

In theoretical calculations the constant of the ionic product of water and other, similar constants are considered dimensionless. Ionic product of water is the product of the dimensionless activity of hydrogen cations $\text{H}^+$ and the dimensionless activity of hydroxyl anion $\text{OH}^-$. The activity here is the product of the dimensionless concentration and the dimensionless activity coefficient. However, concentration is a physical quantity with a dimension. It is a ratio of the amount of dissolved matter to the volume of solution. This contradiction is resolved by not using the real concentration, but instead using concentration divided by a standard concentration, usually equal to 1 mol/l, and called “reduced concentration”.

Calculation of ionic equilibrium is impossible without knowing the numeric values of dissociation constants. Here are some specific examples from power engineering.

1. Natural water treated before being added to steam boilers at power plants contains carbonic acid $\text{H}_2\text{CO}_3$ that dissociates to produce hydrogen cations $\text{H}^+$ and bicarbonate anions $\text{HCO}_3^-$,
which, in its turn, dissociate to produce more hydrogen cations and carbonate anions \( \text{CO}_3^{2-} \). The equilibrium in these reactions is determined by the constants \( K_1 \) and \( K_2 \), i.e., dissociation constants of carbonic acid in the first and second stages of dissociation, respectively.

2. Calcium carbonate \( \text{CaCO}_3 \), magnesium hydroxide \( \text{Mg(OH)}_2 \) and even calcium sulfate \( \text{CaSO}_4 \) can precipitate from water under certain conditions in heat exchangers, e.g., on tubes in turbine condensers. These processes can be evaluated and modeled providing we know the values of 3 constants: solubility products of calcium carbonate, magnesium hydroxide and calcium sulfate.

3. Different phosphates are added to water during its chemical treatment before feeding it to drum boilers. Phosphoric acid \( \text{H}_3\text{PO}_4 \) also dissociates to produce hydrogen cations \( \text{H}^+ \) and anions \( \text{H}_2\text{PO}_4^- \) (dihydrogen phosphate), \( \text{HPO}_4^{2-} \) (hydrogen phosphate) and \( \text{HPO}_3^{3-} \) (phosphate). Equilibrium in these reactions is determined by three constants: \( K_1 \), \( K_2 \) and \( K_3 \), i.e., dissociation constants of phosphoric acid in the first, second and third stages of dissociation, respectively.

4. Boric acid \( \text{H}_3\text{BO}_3 \) is sometimes added as a neutron scavenger to the cooling water in nuclear power plants to gradually adjust the reactivity of a reactor. As nuclear fuel in the reactor is depleted the concentration of boric acid in the cooling water is reduced to prevent termination of the nuclear fission chain reaction of uranium atoms. This weak acid dissociates in water. Knowing dissociation constants of boric acid is essential for the design and operation of a nuclear power plant.

How can we explain a habit of some power engineers working with quantities that have dimensions, such as mass, quantity of matter, volume, concentration, work, enthalpy, entropy (in power engineering calculations), etc. to use dimensionless constants derived from these quantities?!

Firstly but not mainly, it is easier to perform calculations with dimensionless quantities both, manually and with the help of calculators and computers, using unitless electronic tables or programming languages. These calculation devices operate with dimensionless numeric values of physical quantities expressed in appropriate units of measurement. Some dimension quantities have traditional units such as liters and gallons, grams and ounces, centimeters and inches, degrees Kelvin, Celsius, Rankine, Fahrenheit, etc. That impedes international collaboration of scientists. It is worth to mention that engineers had tried to get rid of the unit for such quintessentially physical quantity as density. In analytical chemistry handbooks, one can see an entry of \( d_{20} = 1.5 \) meaning that the density of a given solution is one of a half times that of pure water at 20°C. By the way, in the past, the temperature, which is a quintessentially physical quantity, was attempted to be made dimensionless by introducing the concept of a degree. Of course, Boltzmann had shown that it was not necessary, using instead the unit J/mol or just Joule (J). How to measure the temperature in these units is shown in figure 1. It is sufficient to multiply the values for temperature by the gas constant.

The Boltzmann constant can be used instead of the gas constant in the calculations shown in figure 1. Then the temperature will be in the units of energy, which is fully consistent with the Kinetic Molecular Theory of Matter. Of course, no one will switch now from customary degrees to “correct” Joules for measuring temperature. Also confusing is that the unit of temperature on “Boltzmann scale” is the same as the unit of specific enthalpy. There are many physical quantities with the same units of measurement. The authors have intentionally used an old and many times discussed example with “Boltzmann scale” (figure 1) to highlight the possibility of using “physical quantities” in calculation applications. Specific molar enthalpy and “Boltzmann temperature” are distinct physical quantities measured in the same units. Nowadays, calculation applications Mathcad and, in part, Maple can correctly process the
units of measurements, roughly speaking without adding meter to kilogram. However, they
do not distinguish different physical quantities with same units of measurement. An example
is in figure 1. Here is another example related to power engineering [3]. During calculation of
binary cycles, one should pay attention to the fact that enthalpy and entropy (again, in power
engineering calculations) of various working media are distinct physical quantities with same
units of measurement. Otherwise, this simplification could lead to the errors in calculations.
However, in this article we should be talking not about enthalpy and entropy but about their
deltas.

![Figure 1. Temperature on a “Boltzmann scale”](image)

Secondly but again not mainly, we could assume that the attempts to make physicochemical
quantities and related calculations dimensionless were linked to... the theory of similarity. There
was a desire to come up with physicochemical laws independent of the units of measurement.
Here is a classic example of the application of the theory of similarity in fluid dynamics. Water,
some other liquid or gas is flowing in a pipe. The flow, as it is well known, could be laminar or
turbulent. Where is the approximate boundary between these two types of flow? The theory
of similarity prescribes calculation of the dimensionless Reynolds number \( \text{Re} = \frac{d \cdot V}{\nu} \), where
\( d \) – pipe diameter, \( V \) – flow rate, and \( \nu \) – kinematic viscosity of the medium (dynamic viscosity
divided by the density of the medium). When this number is less than approximately 2,000, the
flow is laminar. If \( \text{Re} \) is greater than 2,000, the flow is turbulent. This is independent of the
specific diameter of the pipe, flow rate and viscosity of a liquid or gas. However, all the attempts
to establish analogous numbers for solutions of electrolytes ended in failure. For example, acids
could weak (carbonic and phosphoric acids) and strong (hydrochloric, sulfuric and nitric acids).
Where is the boundary between turbulent and laminar flows for solutions of these acids? There
is no solution based on a dimensionless number.

Thirdly and mainly, the preference to dimensionless quantities in engineering thermodynamics
has deeper roots. A diluted solution in this scientific discipline is expected to behave as ideal
gas according the Clapeyron–Medeleev equation \( p v = RT \). Calculation of work (enthalpy)
and entropy using this equation requires integration that involves a logarithm (see below) of
a quantity that must be dimensionless. If this quantity is not dimensionless, as in the case of
pressure, temperature or concentration, then they are made dimensionless, without considering
the fundamental issues, by introducing standard pressure, standard temperature, standard
(reduced – see above) concentration. For example, standard pressure is used as the lower limit
of the definite integral while working pressure – the upper limit. Logarithms, resulting from
integration, have arguments that have to be reduced to make them dimensionless. But is it
really necessary!?

Let’s solve a simple problem on a PC: pressure \( p_1 = 1 \) atm and temperature \( T_1 = 18^\circ \)C are
given for a diatomic ideal gas with specific isobaric heat capacity \( c_p = 7R/2 \). It is necessary to
calculate temperature \( T_2 \) and pressure \( p_2 \) of this gas adiabatically compressed by a factor of 7
\( (n – compression ratio) \). Thus, we will be calculating the first process of an ideal thermodynamic
cycle of a 4-stroke internal combustion engine. The second process of this cycle will be isochoric
(Otto cycle), isobaric (Diesel cycle) or mixed (Trinkler cycle) supply of heat. The third process of the cycle will be the movement of a piston (another adiabatic process), and the fourth – isobaric removal of the heat in engine exhaust. The entire cycle [4] can be calculated using methodology outlined below. Here we will calculate the first process only – compression of the air or fuel-air mixture.

The solution of this problem using Mathcad, a very popular application among the students, engineers and scientists [5], is shown in figure 2. Mathcad can handle with dimension quantities [6] and has a built-in basic physicochemical constants, e.g., the gas constant $R$. This makes physicochemical and thermodynamic calculations easier and faster and allows input and output of quantities having the units of measurement familiar to the users instead of the quantities requiring users to follow various rules that are not always practical.

Specific entropy of ideal gas $s_{12}$ is calculated using well-known formula with two integrals determined. It stays constant during compression of the gas and equals 69.27 J/(mol·K). Then, a system of two equations with two unknowns, $T_2$ and $p_2$, is solved with numeric results for the temperature and pressure of compressed gas with basic SI units of measurement (Kelvin and Pascal) and with customary units – centigrade and standard atmosphere. All the calculations, including integration, were numerical. However, in engineering thermodynamics, the absolute value of entropy or energy (Gibbs or Helmholtz) is meaningless in contrast to delta entropy or energy. In figure 2, we calculated gas entropy on a basis of the standard state $T_0 = 1$ K and $p_0 = 1$ Pa (see the first line in figure 2). Selecting another pair of basis points would not change the result. For water, these points could be the parameters of a triple point. This is analogous to mechanics. The value of the potential energy of a material point depends on the selected

\[
\begin{align*}
T_0 &= 1 \text{ K} \quad p_0 = 1 \text{ Pa} \\
T_1 &= 18 ^\circ \text{C} \quad p_1 = 1 \text{ atm} \\
v_1 &= \frac{R \cdot T_1}{p_1} = 0.023891 \text{ m}^3/\text{mol} \\
\frac{n}{v_1} &= 7 \quad \frac{v_2}{n} = 0.003413 \text{ m}^3/\text{mol} \\
s_{12} &= \int_{T_0}^{T_2} \frac{c_p}{T} \, dT - R \cdot \int_{p_0}^{p_2} \frac{1}{p} \, dp = 69.279 \text{ J/mol·K} \\
T_2 &= 500 \text{ K} \quad p_2 = 10 \text{ atm} \\
p_2 \cdot v_2 &= R \cdot T_2 \\
s_{12} &= \int_{T_0}^{T_2} \frac{c_p}{T} \, dT - R \cdot \int_{p_0}^{p_2} \frac{1}{p} \, dp \\
\begin{bmatrix}
T_2 \\
p_2
\end{bmatrix} &= \text{Find} \left( \begin{bmatrix}
T_2 \\
p_2
\end{bmatrix} \right) = \begin{bmatrix}
634.098 \text{ K} \quad 1.545 \times 10^8 \text{ Pa}
\end{bmatrix} \\
T_2 &= 360.948 ^\circ \text{C} \quad p_2 = 15.245 \text{ atm}
\end{align*}
\]

**Figure 2.** Numerical solution for compression of an ideal gas.

Specific entropy of ideal gas $s_{12}$ is calculated using well-known formula with two integrals determined. It stays constant during compression of the gas and equals 69.27 J/(mol·K). Then, a system of two equations with two unknowns, $T_2$ and $p_2$, is solved with numeric results for the temperature and pressure of compressed gas with basic SI units of measurement (Kelvin and Pascal) and with customary units – centigrade and standard atmosphere. All the calculations, including integration, were numerical. However, in engineering thermodynamics, the absolute value of entropy or energy (Gibbs or Helmholtz) is meaningless in contrast to delta entropy or energy. In figure 2, we calculated gas entropy on a basis of the standard state $T_0 = 1$ K and $p_0 = 1$ Pa (see the first line in figure 2). Selecting another pair of basis points would not change the result. For water, these points could be the parameters of a triple point. This is analogous to mechanics. The value of the potential energy of a material point depends on the selected
arbitrary zero point: floor level, ocean level or the center of the Earth. These values have no physical meaning, only the values of changes in the potential energy are meaningful.

In the figure 2 calculation, the second equation can be simplified – see figure 3. As a result, logarithms will contain dimension quantities, i.e., pressure and temperature. Here, it is useful to recall that the difference between algorithms of two quantities is an algorithm of their ratio; and the problem is solved because logarithm becomes that of dimensionless quantities. Thus, we can calculate the value of specific entropy at \( T_2 \) and \( p_2 \) and given standard values of \( T_0 \) and \( p_0 \). That is exactly what was done in the figure 2 calculation.

![Figure 3. Symbolic simplification of the formula for calculation of specific entropy.](image)

The belief that an algorithm cannot contain a dimension quantity became outdated due to development of modern computational methods.

What is the decimal (common) logarithm of 100 Pa? It is two plus logarithm ... of 1 Pa: \( \log(100 \text{ Pa}) = \log(100) + \log(\text{Pa}) = 2 + \log(\text{Pa}) \). That is it. It is some kind of a hybrid result with a value and a symbol! Further, instead of continuing this chain of transactions, we move forward. What is the decimal algorithm of pressure equal to 10 Pa? It is one plus the same logarithm of 1 Pa: \( \log(10 \text{ Pa}) = \log(10) + \log(\text{Pa}) = 1 + \log(\text{Pa}) \). What is the difference between these two logarithms, i.e., dimensionless ratio of the pressure of 100 Pa to the pressure of 10 Pa? The answer is 1: two plus logarithm of Pascal minus one and logarithm of same Pascal: \( 2 + \log(\text{Pa}) - 1 - \log(\text{Pa}) = 1 \). Logarithms of Pascal are reduced and 1 remains.

This notorious “logarithm of Pascal” is “present” in thermodynamic calculations of energy and entropy along with “logarithm of Kelvin”. These algorithms are eliminated in numeric calculations by introducing standard states as shown in figure 2. However, it is not necessary in ... hybrid calculations [7].

What is hybrid calculation? Figure 2 shows numeric calculation – Mathcad operates with numeric values for variables converted in SI units: degrees Kelvin rather than degrees centigrade, Pascals instead of atmospheres. Figure 3 shows analytic (symbolic) transformations wherein Mathcad operates with variables themselves rather than with their values. But these calculations can be combined! Figure 4 shows hybrid solution (Maple plus manual transformations by the authors) of our problem on gas compression. In this calculation, numeric computations are combined with symbolic transformations, wherein the units of measurement have no associated numerical values and the logarithms of dimension physical quantities are reduced and are not present in the final numeric results. This eliminates the necessity of determining the numerical value of entropy, which, we repeat, has no physical meaning. Moreover, these hypothetical values of energies and entropy lead to errors in calculation, for example, of binary thermodynamic cycle with two working media of different standard states.

Note that calculation in figure 4 shows a simplified “logarithmic” version of the original formula for specific entropy with two integrals. We should emphasize that this simplified version is not equivalent to the original because simplified formula can be obtained for the positive values of pressure and temperature only. The system of equations in figure 4 does not have hybrid solutions should it contain the formula for entropy with integrals.

Additional notice. To create figure 4, the authors combined the results from Maple and
Mathcad because it was not possible to transform the expressions for the variables $T_2$ and $p_2$ into numerical values (real values for the temperature and pressure of compressed ideal gas) in Maple. The function `evalf` (evaluation float, transforming the original value into a value with a floating decimal point) was extremely unstable. It produced either a value or an expression where the single variable $T_1$ was replaced by its numeric value, etc. New values were displayed after saving and opening of the file. This was a result of mixing numeric and symbolic calculations. The authors repeated transformation of the variables $T_2$ and $p_2$ in Mathcad to achieve stable calculation (see figure 5).

![Figure 4](image_url)  
**Figure 4.** Hybrid solution of a problem of ideal gas compression.

On the other hand, the authors were unable to reproduce Maple calculation shown in figure 4 on the Mathcad platform. Consequently, the authors had to use both applications.

At this point, as a compromise, certain thermal engineering calculations can be done without outputting the numeric values of enthalpy and entropy. Figure 6 shows calculation of adiabatic compression of air using cloud functions for thermodynamic properties of substances [3]. The initial parameters of air (pressure $p_1$ and temperature $t_1$) as well as the final pressure $p_2$ are given to calculate the temperature of compressed air $t_2$ and consumed specific energy.

![Figure 5](image_url)  
**Figure 5.** Calculation with logarithm of temperature in Mathcad.

A reference to the Mathcad file Gas.xmc in the calculation shown in figure 6 reveals the functions `wspgHGT`, `wspgSGPT`, `wspgTGPS` and `wspgVGPT` that return thermodynamic properties of air (Air) dependent on its parameters. Specific enthalpy $h$ and entropy $s$ are determined but cannot be shown in the calculation because they are hybrid quantities. Further calculations using these quantities are carried out without any problems and calculated quantities (temperature and specific energy or delta of specific enthalpies) are displayed as numeric values.
Conclusions
Modern applications can be used for hybrid thermodynamic calculations to eliminate the necessary calculation of hypothetical values of entropy and enthalpy. This makes engineering calculations simpler and reduces the number of certain errors, especially in calculations of binary thermodynamic cycles with working media having different standard state points.

It is not expected that power engineers will no longer use multiple tables containing values for enthalpy and entropy. But various thermodynamic constants provided in these tables will have their units of measurement.

Mathematical software should be developed that can support hybrid calculations described in this article. In the meantime, hybrid calculations can be done using a combination of different applications. In addition, a concept of “physical quantity” should be introduced in mathematical software.

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