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Concepts against mathematics: self-inconsistency in thermodynamic evaluations

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Abstract Various ways of thermodynamic evaluations can yield different results, contradicting to one another. Such a case is considered a paradox, with the attempts to solve it. This is because thermodynamics is thought to be the science established on solid conceptual ground, with accurate mathematical evaluations. Recently, we faced similar problem, when the relationship between heat capacity and pressure is described by two different equations, predicting opposite behavior. Both equations are free of evident errors. In searching for the reason of the discrepancy, we found out that it is common practice in thermodynamic evaluations to tune the mathematical operations in order to receive the necessary result. It is typical of empirical science, but inappropriate for the fundamental knowledge based on axiomatic background. Short historical survey on experimental data and theoretical concepts dealing with the relation between heat capacity and pressure proves that the thermodynamics is very flexible and effective tool for the solution of the problems in the field of relationships among *P*–*V*–*T* parameters and thermophysical properties of matter. One should not consider the solutions as the universal laws.

Keywords Air · Heat capacity · Ideal gas · Pressure · Thermodynamics

Introduction

Thermodynamics attracts especial attention because it is considered to govern all the processes in the Universe. Grate efforts were made to justify fundamental nature of basic thermodynamic concepts and to manage thermodynamic functions and variables according to rigorous mathematical operations. It is the thermodynamics that was announced to be reconstructed according to axiomatic approach, like geometry, algebra, and other mathematical branches [1, 2].

On the other hand, thermodynamics was created and developed as applied science. Thermodynamic concepts and methods were changed and improved many times and in different ways. Sometimes, new concept does not seem preferable as compared with old one, and the attempt to return to the previous concept is made. For instance, about one hundred years ago, the caloric theory was advocated by Callendar [3], the outstanding experimentalist. Recently, our Czech colleagues published the work on contemporary mathematical background of the caloric theory in order to revive it [4].

Usually, the struggle among ideas and concepts is the field of interests for specialists in history, philosophy, and logic of science [5]. They seem having very little to do with routine experiments and applied evaluations.

Recently, we faced practical task of the evaluation of calorimetric data under high pressure, which can be proceeded in two different ways. The results received differ from one another too much, predicting oppose, increasing and decreasing, changes in the heat capacity at elevated

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pressures. Both results were derived from thermodynamic considerations and seem to be free of evident errors. They cannot be correct both. At least one of them must be wrong. In searching for the error in the thermodynamic evaluations in these two ways, we found out that the reason of the discrepancy is in the fundamental background of thermodynamics. This result is the main subject of the current work.

The problem we faced is as follows. It is well known that the heat capacity changes with pressure according to equation

$$\frac{\mathrm{d}C_\mathrm{P}}{\mathrm{d}P} = -T\frac{\mathrm{d}^2V}{\mathrm{d}T^2} = -TV\left(\alpha^2 + \frac{\mathrm{d}\alpha}{\mathrm{d}T}\right), \tag{1}$$

where C_P is the isobaric heat capacity, P is the pressure, T is the temperature, V is the molar volume, and α is the coefficient of thermal expansion. If applied to the ideal gas ($PV = RT$), Eq. 1 predicts no changes in its heat capacity.

$$\frac{\mathrm{d}C_\mathrm{P}}{\mathrm{d}P} = 0 \tag{2}$$

Unfortunately, it was established at least 70 years ago that the heat capacity of gases increases with pressure, and the effect increases with decreasing temperature [6]. Thermodynamics failed to explain these experimental results.

Recently, we have showed that the increase in the heat capacity can be explained with rather simple equation that can be derived from simple thermodynamic considerations

$$\frac{\mathrm{d}C_\mathrm{P}}{\mathrm{d}P} = \frac{\mathrm{d}V}{\mathrm{d}T} = \alpha V. \tag{3}$$

The equation explains why the heat capacity of gases increases with pressure and why the effect increases with decreasing temperature [7].

New equation brings up two new questions. First, it seems very strange that two different results with opposite predictions and both correct were derived from the same concepts and with the same rules for mathematical operations, within the single scientific system. Second, it is very strange that simple Eq. 3 was received for the first time in the beginning of XXI century, not in the middle of XIX or early XX, when the increase in the heat capacity of gases was certainly established. Equation 3 was received in [7] after the consideration of cyclic process with changes in temperature and pressure. Such a way is not typical of contemporary thermodynamics. Pure mathematical procedures of the differentiation of thermodynamic functions with respect to temperature and pressure are widely used today instead.

We will show in this work that

1. Equation 3 can be readily received after conventional differentiation.
2. It is considered a priori in thermodynamics that the heat capacity of gases does not depend on pressure. This is the main reason why Eq. 3 was not received so far.
3. Thermodynamics is not a rigorous mathematical science. Thermodynamic evaluations are corrected for the concepts in order to receive the desired result.

Mathematics and considerations in thermodynamics

How to derive Eq. 3

Let us consider the equality

$$\frac{\partial}{\partial P}\frac{\partial H}{\partial T} = \frac{\partial}{\partial T}\frac{\partial H}{\partial P}, \tag{4}$$

where H is the enthalpy, and P and T are the pressure and temperature, respectively. On the left side, the evaluation starts with

$$\frac{\partial H}{\partial T} = C_\mathrm{P} \tag{5}$$

and then

$$\frac{\partial}{\partial P}\frac{\partial H}{\partial T} = \frac{\partial C_\mathrm{P}}{\partial P}. \tag{6}$$

On the right side, the evaluation starts with

$$\frac{\partial H}{\partial P} = V, \tag{7}$$

and then

$$\frac{\partial}{\partial T}\frac{\partial H}{\partial P} = \frac{\partial V}{\partial T}. \tag{8}$$

Thus, Eq. 3 is readily derived from Eq. 4:

$$\frac{\partial C_\mathrm{P}}{\partial P} = \frac{\partial V}{\partial T} \tag{9}$$

When applied to the ideal gas, Eq. 9 predicts that its heat capacity is proportional to the logarithm of pressure, and the effect increases with decreasing temperature [7].

How not to derive Eq. 3

Equation 4 can be treated in another way, and Eq. 3 will not be derived from it. This approach was described in the monograph by Guggenheim [8]. Eq. 201 of the monograph is

$$\frac{\partial}{\partial P}\frac{\partial H}{\partial T} = \frac{\partial}{\partial T}\frac{\partial H}{\partial P} = 0. \tag{10}$$

Equations 5 and 7 are used in other evaluations throughout the monograph, but they are not applied to the ideal gas and Eq. 10.

It is evident that the distinction between two ways of calculations, (4)–(9) and (10), are not in the mathematics. Before the discussion of Eq. 10 (number 201 in the monograph), Guggenheim explained that the enthalpy (H) and internal energy (E) of the ideal gas do not depend on pressure and volume, only on temperature. It is the concept of the ideal gas, he wrote in his monograph (text between Eqs. 197 and 198).

In other words, Guggenheim states that Eq. 7 must not be applied to ideal gas. Other result is used instead:

$$\frac{\partial H}{\partial P} = 0. \tag{11}$$

The situation is very strange. On the one hand, Eq. 7 is a rigorous thermodynamic result. It is correct for all thermodynamic phases and under all conditions. On the other hand, Eq. 7 is not applicable to the ideal gas. Nobody states that the ideal gas does not possess mass and volume or it cannot be characterized with pressure or temperature. Nevertheless, the derivative of its enthalpy with respect to pressure is zero (Eq. 11), not the volume (Eq. 7). And its volume does not equal to zero. Mathematical notation of this strange situation is:

$$\frac{\partial H}{\partial P} = V, \quad \frac{\partial H}{\partial P} = 0, \quad V \neq 0. \tag{12}$$

It means that the mathematical operation of the differentiation is not universal in thermodynamic evaluations. We do not know to what extent this situation is common in thermodynamics and how many similar examples there are in thermodynamics. This is very dangerous property. Starting our evaluations from different points and choosing different ways, we can finish with different results. In fact, this is the main reason for the difference between two equations for the relationship between heat capacity and pressure. Equation 1 was derived starting from entropy and then the Gibbs function, and Eq. 3 was derived starting from enthalpy.

The danger of non-universality of mathematical operations is in its prejudice. Mathematics does not govern the truth or falsity of the derived equation. Right or wrong expression is deduced not after mathematical transformation, but after the conceptual analysis of the object considered. Guggenheim states that the derivative of the enthalpy of the ideal gas with respect to pressure is zero, but someone else may state that the derivative is equal to the volume, and not equal to zero. This is the real case. Stracher and Guy [9] stated that the enthalpy of the ideal gas depends not only on temperature, but also on pressure and volume. This point of view [10–12] met considerable opposition [13].

Here, two opposite points of view are shared by different scientists. In the search for the truth, the main goal of discussions is to clarify who is right and who is wrong. The search does not deal with mathematics. The calculations are above suspicion. The search is focused on the concepts. The more scientists share the concept, the more correct it is. The truth or falsity of the equation is defined by means of voting. Stracher and Guy are in the minority and, hence, they are wrong.

The Gibbs' paradox is another example of discrepant thermodynamic results. Two ways for the evaluation of the entropy for the mixing of two gases yield two results, which differ from one another by R ln2 [14]. Again, the reason of the discrepancy is not in the mathematics. The literature on the Gibbs' paradox is large in number (see, for example, http://www.mdpi.org/lin/entropy/gibbs-paradox.htm). The paradox is discussed by many scientists, from schoolteachers to Nobel Prize winners, for many years, about one and a half centuries. What is the reason for such a vivid interest? What is the problem under solution? In disengaging from mathematical evaluations (we know that they are above suspicion), one can conclude that the problem is in two correct but different results for one phenomenon. It is inappropriate for objective and reliable science to produce several different results without the decision of which one is wrong or right. Unfortunately, for the Gibbs' paradox, the truth cannot be find by means of voting. There is no conflict between different scientists or scientific communities here, because both results were received by one man, J. W. Gibbs, and he did not identify himself which one is correct.

The main goal of the works on the Gibbs' paradox is to explain that here we face the particular case when two different results are correct both. Such an explanation is necessary for scientific community and for individual scientists in order to be sure in the truth of thermodynamics, to accept this particular case of ambiguity in thermodynamic results. Scientific progress changes the meaning of concepts, the set of models and explanations of phenomena. It is necessary to update the solutions to the Gibbs' paradox from time to time, making the process permanent. In particular, the solutions to the Gibbs' paradox reflect the progress in the concept of entropy: (1) classical thermodynamic entropy by Clausius (starting from 1865); (2) classical statistical entropy by Boltzmann (1877); (3) quantum entropy by Sackur, Tetrode, and Plank (1910s); (4) information entropy by Nyquist and Shennon (starting from 1920s); (5) operational entropy by Brillouin, Born, and Jaynes [15]. All these stages are marked with the works that describe the solution to the Gibbs' paradox via their particular concepts of entropy. Thus, the progress in the solution of the Gibbs' paradox is never ending, until the thermodynamic results are considered to be always unambiguous and of universal nature.

There is an alternative point of view that the results of thermodynamic evaluations and thermodynamics itself are empirical by nature and approximate in values. It is appropriate mention here that, according to Maxwell, the second law of thermodynamics, dealing with the entropy, cannot be an absolute law of nature and has only a statistical certainty [16]. To support his idea, Maxwell invented the Maxwell's demon, also considered now as a paradox [17].

As for the relation between mathematics and concepts in thermodynamics, the example of the derivative of the enthalpy with respect to pressure for the ideal gas shows that the mathematical operations in thermodynamic evaluations are meaning-dependent, not objective. We discussed here two examples of discrepancies in thermodynamic evaluations. The first one is considered as the matter of controversy between proponents and opponents. The second one is considered as paradox, because there are no opponents and proponents. Below, we will examine another example of unconventional mathematical transformations in thermodynamics, without a conflict between concepts and mathematics.

Mathematical origins of internal inconsistency in thermodynamic evaluations

Let us consider transformations

$$C_V\mathrm{d}T - P\mathrm{d}V + \mathrm{d}(PV) = C_V\mathrm{d}T - P\mathrm{d}V + P\mathrm{d}V + V\mathrm{d}P = C_V\mathrm{d}T + V\mathrm{d}P. \tag{13}$$

They are correct in mathematics and thermodynamics. The left expression is equal to the middle and to the right ones. The next example shows the set of wrong equations:

$$C_V\mathrm{d}T + V\mathrm{d}P = C_P\mathrm{d}T + V\mathrm{d}P; \rightarrow C_V\mathrm{d}T = C_P\mathrm{d}T; \rightarrow C_V = C_P. \tag{14}$$

Everyone who is familiar with thermodynamics knows that

$$C_V \neq C_P. \tag{15}$$

All three equations in (14) are wrong in thermodynamic sense, not in mathematics. Let us now change the form of the starting expression in Eq. 14

$$\begin{aligned} &C_V\mathrm{d}T + V\mathrm{d}P = T\mathrm{d}S + V\mathrm{d}P;\\ &T\mathrm{d}S + V\mathrm{d}P = C_P\mathrm{d}T + V\mathrm{d}P. \end{aligned} \tag{16}$$

Now, it is quite another matter. Everyone who is familiar with thermodynamics will recognize the fragment of the transformation from internal energy to enthalpy. The complete transformation is as follows:

$$\mathrm{d}E = C_V\mathrm{d}T - P\mathrm{d}V = T\mathrm{d}S - P\mathrm{d}V; \tag{17}$$

$$\mathrm{d}E + \mathrm{d}(PV) = T\mathrm{d}S - P\mathrm{d}V + \mathrm{d}(PV) = C_V\mathrm{d}T + V\mathrm{d}P = T\mathrm{d}S + V\mathrm{d}P; \tag{18}$$

$$\mathrm{d}E + \mathrm{d}(PV) = \mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P = C_P\mathrm{d}T + V\mathrm{d}P. \tag{19}$$

We avoid writing C_V and C_P together in a single line. It is common practice. Sometimes, the indexes V and P for heat capacity are omitted in the transformation from E to H, writing just C instead of C_V and C_P (see, for example, [8]). We write them here, making evident the transformation of C_V into C_P. There is a special equation for the transition from isochoric to isobaric heat capacity

$$C_P = C_V + T\frac{\mathrm{d}P}{\mathrm{d}T}\cdot\frac{\mathrm{d}V}{\mathrm{d}T}, \tag{20}$$

but it is not used here. The transition is accomplished through intermediate term $T\mathrm{d}S$, like it was made in Eq. 16. This transformation leads to the conflict:

$$C_V\mathrm{d}T = T\mathrm{d}S;\ T\mathrm{d}S = C_P\mathrm{d}T;\ C_V\mathrm{d}T \neq C_P\mathrm{d}T. \tag{21}$$

We face non-transitive mathematical operation (equality) in thermodynamic evaluations and we may expect the discrepancy in the results of evaluations that operate with isochoric and isobaric heat capacities. Two examples of the discrepancies of this kind are described in Appendix. Again, one may consider them new paradoxes or search for the errors in the procedure of how they were derived. This way is for those, who consider thermodynamic evaluations rigorous and strictly self-consistent. We consider thermodynamic evaluations approximate and examine how this peculiarity can affect the effect of pressure on the heat capacity of gases. Let us apply Eq. 3, identical with Eq. 9,

$$\frac{\mathrm{d}C_P}{\mathrm{d}P} = \frac{\mathrm{d}V}{\mathrm{d}T} = \alpha V$$

to the ideal gas with

$$V = \frac{RT}{P} \text{ and } \alpha = \frac{1}{T}. \tag{22}$$

We receive

$$\frac{\mathrm{d}C_P}{\mathrm{d}P} = \frac{R}{P} \tag{23}$$

and

$$C_P(P,T) = C_P(P_0,T) + R\ln\frac{P}{P_0}. \tag{24}$$

As

$$C_P = C_V + R, \tag{25}$$

then

$$C_V(P,T) = C_V(P_0,T) + R\ln\frac{P}{P_0}. \tag{26}$$

On the other hand, from Eq. 25 we also have

$$\frac{\mathrm{d}C_P}{\mathrm{d}P} = \frac{\mathrm{d}C_V}{\mathrm{d}P} = \alpha V. \tag{27}$$

Substituting

$$V = \text{const}, \text{ and } \alpha = \frac{1}{T}, \tag{28}$$

we have

$$\frac{dC_V}{dP} = \alpha V = \frac{\text{const}}{T} \tag{29}$$

and

$$C_V(P,T) = C_V(P_0,T) + \frac{\text{const}}{T}(P - P_0). \tag{30}$$

Equation 30 differs evidently from Eq. 26. It is because we used different ways to derive these two equations for C_V and the different ways with non-transitive operations may lead to different results. It is interesting that both equations are useful in their own way for the explanation of experimental results on C_V of air under pressure. Equation 26 predicts the increase proportional to the logarithm of pressure, and Eq. 30 predicts that the effect of pressure increases with decreasing temperature.

Thus, we saw that the mathematical operations in thermodynamic evaluations differ from conventional arithmetical ones. The difference is in the non-transitivity of equality. This peculiarity of mathematical operations in thermodynamics leads to the ambiguity of the results derived from thermodynamic relationships. This is not the oversight, but deliberate approach. In choosing between conventional mathematical operations and heat-related concepts, thermodynamics prefers the latter. Pure mathematical deductions are considered "rather of the nature of playing with symbols than of reasoning by consecutive steps" (P. G. Tait about L. Boltzmann's deductions [18]). Such a peculiarity in relation between concepts and mathematics is, in its turn, the result of reasoning by consecutive steps. Let us examine the progress in the pressure—heat capacity relation starting from the first quantitative data.

Short historical survey of the effects of pressure on heat capacity

Caloric theory: $dC_P/dP < 0$ (for air)

In the beginning of XIX century, heat was a fluid substance, caloric, which cannot appear or disappear. Heating of a gas after compression was considered the manifestation of the decrease in its heat capacity. Indeed, the temperature is proportional to the amount of caloric and inversely proportional to the heat capacity. In compressing the gas, we do not change the amount of caloric, and temperature increases only because of the decrease in the heat capacity. Direct experimental test of the theory was rather difficult task. In 1813, Delaroche et Bérard have carried out the measurements of air and found out that its heat capacity decreases by 3.3% when pressure increases from 760 to 1000 mmHg. This result agrees with caloric theory and the authors were proud of it:

> Everyone knows that when air is compressed heat is disengaged. This phenomenon has long been explained by the change supposed to take place in its specific heat; but the explanation was founded upon mere supposition, without any direct proof. The experiments, which we have carried out, seem to us sufficient to remove all doubts upon this subject. (cited from [5])

This result of Delaroche et Bérard was used in "Réflexions sur la puissance motrice du feu" by Carnot [19]. Carnot applied logarithm function for the approximation of experimental data and calculated that the heat capacity of air decreases nearly six times when pressure increases from 1 to 1024 atm. For higher pressures, he discussed the further decrease in the heat capacity of air and even negative values of heat capacity. Here is the origins of the problem of negative heat capacity under ultra-high pressure [20]. To calculate the heat capacity of air as a function of volume and pressure, Carnot used equations

$$C_P = A + B\ln V \tag{31}$$

and

$$C_P = A' - B'\ln P, \tag{32}$$

where A, B, A', and B' are the coefficients. Logarithmic heat capacities in the Carnot's work were a subject of discussions [21]. Such a functional relation was considered wrong and based on "rather poor" data available to Carnot. In fact, the logarithm is derived from the equation of state for the ideal gas. Later, similar functional relation was derived for contemporary data on heat capacity, but with opposite sign, "+" instead of "−" (see below).

Thus, good agreement between theory (Eqs. 31 and 32 by Carnot) and experiment (Delaroche et Bérard) was in the caloric theory.

Heat as a kind of energy: $dC_P/dP = 0$ (for air)

New thermodynamics was created in the middle of XIX century. Formula "heat = caloric" was substituted with a new one: "heat = energy". Now, the heating of air under compression is the result of transformation of the work into the internal energy of air. The greater the work, the greater the increase in temperature. Heating is proportional to the work, with the constant of proportionality equal to the heat capacity. In preparing his "Dynamical Theory of Heat", Lord Kelvin used the results of the Regnault's experiments on accurate measurements of heat capacity of air. These values were necessary for the analysis of the heat engine. The C_P/C_V ratio is used in the calculation of adiabatic processes in the Carnot cycle. This ratio was temperature-dependent according to Poisson, but constant according to Clapeyron. Regnault found out that the heat capacity of air is constant within the limits of ±0.2% in the temperature range from −30 to +225 °C and at pressures ranging from 1 to 10 atm. This information was reported in the postscript to the article reprinted in the collected works by Lord Kelvin [22, 23]. As compared with Delaroche and Bérard, the Regnault's results show 10 times less effect over 8 times greater pressure interval, total about two order units less.

The effect of pressure on the heat capacity of condensed phases was not measured directly, but derived from reasoning as follows. Increase in pressure leads to the compression of a substance. The difference in the heat capacity of substances with identical composition but different densities may shed light on the changes in the heat capacity under pressure. For most substances, density of liquid phase is less than that of a solid, and the heat capacity of liquid phase is greater than that of a solid. Thus, one may conclude that the increase in pressure increases the density and decreases the heat capacity. Another example is the polymorphs of carbon. Density is decreases in a row of "diamond > graphite > charcoal" and the heat capacity increases: "diamond < graphite < charcoal" [24].

Finally, the main idea about the pressure effect on the heat capacity was that $\frac{dC_P}{dP} < 0$ for solids and liquids, but $\frac{dC_P}{dP} = 0$ for gases. Equation 1

$$\frac{dC_P}{dP} = -TV\left(\alpha^2 + \frac{d\alpha}{dT}\right)$$

fits this concept exactly. Again, we see good agreement between theory and experiment. We do not know who was the first to receive Eq. 1 because we failed to find this information in the literature.

Contemporary experimental data: $dC_P/dP > 0$ (for air)

Progress in the high-pressure experiments in the beginning of XX century made it possible to measure heat capacity of gases at pressures 100 times higher than it was made by Regnault. By 1940, it was known with certainty that the heat capacity increases with pressure and the effect increases with decreasing temperature [6]. At the same time, there were no thermodynamic explanations for this fact. The heat capacity of gases was still considered independent of pressure in the theory.

Equation 3 was received only in 2009 and found to fit the experimental data on air [25] well. In combining Eqs. 26 and 30, one can use approximate equation:

$$C_P = A + \frac{B}{T}\ln P, \tag{33}$$

where A and B are the coefficients, for the approximation of experimental data on the heat capacity of air under high pressure.

Short historic survey on the theory–experiment relationship for the pressure effect on the heat capacity reveals very interesting evolution. At the first step, i.e., in caloric time, the experiment met the theory and detected decreasing heat capacity at increasing pressure as it was necessary for the theory. At the second step, when the theory was indifferent to the changes in the heat capacity with respect to the changes in pressure, experiment did not found effect of pressure on the heat capacity. Nowadays, when the experiment revealed certainly the increase in the heat capacity with pressure, theory can meet the experimental data, but with the loss in its universality. It is very painful step.

Conclusions

Thermodynamics was developed on the empirical background of facts about the relationship between energy (work) and heat (caloric, then energy). Thermodynamics in its current conditions is very useful and effective in the field where it was originated. It provides us with the tool to predict the direction of thermal processes and calculate their efficacy.

Thermodynamics is not rigorous mathematical branch. Its mathematical tools were created after generalization of empirical data and then developed to update and consolidate various concepts that change permanently, together with the scientific progress. Pure mathematical calculations in thermodynamics are considered wrong ("playing with symbols"). The correction of mathematical operation in order to receive the necessary result ("reasoning by consecutive steps") is considered the right way instead. As there are different considerations for the same problem, it is normal that the different ways of thermodynamic evaluations can lead to different results. In considering thermodynamics the science with rigorous mathematics and universal laws, we interpret the differences as paradoxes. In considering thermodynamics the empirical branch of science, we have to test the theoretical results against experimental data, like in other empirical branches.

Appendix

Deriving paradoxes from the C_P–C_V relationship

We will start with the conventional equation for the relationship between C_P and C_V

$$C_P = C_V + T\frac{dP}{dT} \cdot \frac{dV}{dT} \tag{34}$$

and then, after conventional transformations, receive something completely different. Let us apply Eq. (34) to the ideal gas ($PV = RT$) with

$$\frac{dP}{dT} = \frac{R}{V} \tag{35}$$

and

$$\frac{dV}{dT} = \frac{R}{P}: \tag{36}$$

$$C_P = C_V + T\frac{R}{V} \cdot \frac{R}{P} = C_V + R. \tag{37}$$

Thus, we receive another conventional result

$$C_P = C_V + R. \tag{38}$$

Let us multiply both sides of Eq. (38) by dT ($dT \neq 0$):

$$C_P dT = C_V dT + R dT. \tag{39}$$

Then

$$R dT = d(RT), \tag{40}$$

$$d(PV) = d(RT). \tag{41}$$

Now Eq. (39) is transformed into

$$C_P dT = C_V dT + d(PV). \tag{42}$$

Here, we receive the first paradox if divide both sides in Eq. (42) by dT ($dT \neq 0$):

$$C_P = C_V + V\frac{dP}{dT} + P\frac{dV}{dT} = C_V + 2R. \tag{43}$$

Equation (43) differs evidently from Eq. (37). The second paradox we receive when use Eq. (42) in the transformation from the internal energy to enthalpy (see Eqs. (17)–(19))

$$dE = C_V dT - P dV; \tag{44}$$

$$dE + d(PV) = C_V dT + d(PV) - P dV; \tag{45}$$

$$\begin{aligned} dE + d(PV) = dH &= [C_V dT + d(PV)] - P dV \\ &= C_P dT - P dV. \end{aligned} \tag{46}$$

Thus, we received

$$dH = C_P dT - P dV, \tag{47}$$

completely different from conventional

$$dH = C_P dT + V dP. \tag{48}$$

Thus, we proceeded with conventional (in mathematical sense) thermodynamic transformations of conventional thermodynamic equations and received two contradicting results: the first for the C_P–C_V relationship, (37) against (43); and the second for the differential of enthalpy, (47) against (48). Equation (42) plays a major part in these two paradoxes. It is used in textbooks for the explanation of thermodynamic properties of the ideal gas (see, for example, [26] p. 32).

References

1. Caratheodory C. Untersuchungen über die Grundlagen der Thermodynamik. Math Ann. 1909;67:355–86.
2. Antoniou IE. Caratheodory and the foundations of thermodynamics and statistical physics. Found Phys. 2002;32:627–41.
3. Callendar HL. The caloric theory of heat and Carnot's principle. Proc Phys Soc Lond. 1911;23:153–89.
4. Mareš JJ, Hubík P, Šesták J, Špička V, Krištofik J, Stávek J. Phenomenological approach to the caloric theory of heat. Thermochim Acta. 2008;474:16–24.
5. Lavenda BH. A new perspective on thermodynamics. New York, Dordrecht, Heidelberg, London: Springer; 2010.
6. Bridgman PW. Recent work in the field of high pressures. Rev Mod Phys. 1946;18:1–93.
7. Drebushchak VA. Heat capacity increases with pressure. J Therm Anal Calorim. 2009;95:313–7.
8. Guggenheim EA. Modern thermodynamics by the methods of Willard Gibbs. London: Methuen & Co Ltd.; 1933. (Russian edition of 1941).
9. Stracher GB, Guy AG. The internal energy of PV = RT gas: A univariable or miltivariable function. Math Geol. 1998;30:251–8.
10. Guy AG. The 7th major disproof of the ideal-gas concept. JOM. 1995;47(9):3–4.
11. Guy AG. The seventh major disproof of the 'ideal-gas' concept (vol 47, pg 4, 1995). JOM. 1996;48(4):4.
12. Guy AG. More on ideal gas. JOM. 1997;49(6):4–5.
13. Trumble KP, Gaskell DR. More on the ideal gas law. JOM. 1997;49(1):3.
14. Gibbs JW. The collected works. Vol. 1. Thermodynamics. New York, London, Toronto: Longmans, Green and Co.; 1928.
15. Haitun SD. The history of the Gibbs paradox. Moscow: Nauka; 1986 (in Russian).
16. Brush SG. The development of the kinetic theory of gases, VIII. Randomness and irreversibility. Arch Hist Exact Sci. 1974;12:1–88.
17. Fink JK. Physical chemistry in depth. Berlin, Heidelberg: Springer-Verlag; 2009. p. 295.
18. Brush SG. Foundations of statistical mechanics 1845–1915. Arch Hist Exact Sci. 1967;4:145–83.
19. Carnot NLS. Réflexions sur la puissance motrice du feu. Paris (1824). English translation: Sadi Carnot. Reflections on the motive power of fire. Dover ed. 1960.
20. Brosh E, Makov G, Shneck RZ. Application of CALPHAD to high pressures. CALPHAD. 2007;31:173–85.
21. Lervig PH. On the structure of Carnot's theory of heat. Arch Hist Exact Sci. 1972;9:222–39.
22. Thomson W. Note (A) on the mechanical action of heat, and (B) the specific heat of air. Camb Dublin Math J. 1853.
23. Thomson W. Mathematical and physical papers. Vol. 1. Cambridge; 1882.
24. Miller WA. Elements of chemistry theoretical and practical. Part 1. chemical physics. 4th ed. London: Longmans, Greenm, Reader, and Dyer; 1867.
25. Magee JW. Molar heat capacity at constant volume for air from 67 to 300 K at pressures to 35 MPa. Int J Thermophys. 1994;15:849–61.
26. Bransom SH. Applied thermodynamics. London: D. Van Nostrand Company, LTD.; 1961.