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On the physical interpretation of the mathematics of thermodynamics [1]

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Abstract — The use of mathematical relations is discussed with the idea of enhancing the teaching–learning process in thermodynamics. It is emphasized that the physical interpretation of mathematical relations is of importance in explaining thermodynamic phenomena, showing how thermodynamic tables are made, the physical interpretation of thermodynamic diagrams, the design of experiments, and research in fields that require thermodynamics, particularly for quantities that involve nonmeasurable thermodynamic properties. It is believed that the appropriate use of these relationships contributes to the clear understanding of thermodynamic concepts, processes and systems. © 2000 Éditions scientifiques et médicales Elsevier SAS

thermodynamics / relations / phenomena / tables / diagrams / experiments / research

Nomenclature

c	speed of sound	$\mathrm{m \cdot s^{-1}}$
c_p	specific heat at constant pressure	$\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$
c_v	specific heat at constant volume	$\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$
h	specific enthalpy	$\mathrm{kJ \cdot kg^{-1}}$
k	ratio of specific heats, c_p/c_v	
p	pressure	kPa
s	specific entropy	$\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$
T	temperature	K
$\mathbf{V}$	flow velocity	$\mathrm{m \cdot s^{-1}}$
v	specific volume	$\mathrm{m^3 \cdot kg^{-1}}$
X	any other thermodynamic property	

Greek symbols

ρ	density	$\mathrm{kg \cdot m^{-3}}$

1. INTRODUCTION

In almost all books of *Thermodynamics*, there is a chapter on the “Thermodynamic relations for simple compressible substances” [1], “Thermodynamic property relations” [2], or “Thermodynamics of a simple compressible substance” [3]. This is included, it seems, as an afterthought without following through the physical interpretation of the results. The reasons why certain processes result in given relations, or why the slopes of lines have the form that they do on certain thermodynamic diagrams can easily be explained by simple physical interpretation of the mathematical analysis of thermodynamics. Often, the Maxwell equations are obtained as a consequence of mathematical reasoning rather than the physical value of such relations. It is never discussed, however, how thermodynamic experiments can be designed, how thermodynamic assumptions must be satisfied, and how the results may be used.

Research in thermal hydraulics requires the analyses to include various thermodynamic properties and relations [6]. If these are of the nonmeasurable type, then the numerical integration of these relations lead to different results due to the accumulation of errors. Nevertheless, fundamental thermodynamics teaches us that the choice of these parameters are arbitrary as long as they are inde-

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pendent [1–3]. It is indeed easy, but interesting, to show that the end result is the same, as it should be, and a simple analysis does prove it very elegantly [7]. In one of the examples given below, this is proven. As a matter of fact, similar concepts were used to clarify the numerical difficulties of two-phase flow situations that commonly arise in nuclear thermal hydraulics as well as two-phase correlations that are used for design [8].

There are different ways to solve for or discuss these useful relations. Here the method of Jacobians [4] is used. This is a personal preference and other methods may be used equally successfully depending on one's choice. The method is not discussed here; rather it is used to show the results of some thermodynamic situations of interest.

1.1. Example 1

In this example, the slope of a constant volume line in the superheated region of the Mollier diagram will be investigated. The result will be applied to an ideal gas, since steam at elevated temperatures acts as one, and its functional form, in general, will be determined.

The quantity that is to be investigated is $(\partial h/\partial s)_v$ since the h–s diagram is the Mollier diagram. As a first step, this relation is written in terms of Jacobians as

$$\left(\frac{\partial h}{\partial s}\right)_v = \frac{[h,v]}{[s,v]} \tag{1}$$

Then, the terms that involve u, h, g and f, specific internal energy, enthalpy, the Gibbs and Helmholtz potentials, respectively, are eliminated by using equations of the form

$$\mathrm{d}h = T\,\mathrm{d}s + v\,\mathrm{d}p \tag{2}$$

written in the form of Jacobians as

$$[h,X] = T[s,X] + v[p,X] \tag{3}$$

where X is any other thermodynamic property. Thus in this case,

$$[h,v] = T[s,v] + v[p,v] \tag{4}$$

Since in a cycle, from the first law,

$$[T,s] = [p,v] \tag{5}$$

and since the definition of the specific heat at constant volume is

$$\frac{c_v}{T} = \frac{[s,v]}{[T,v]} \tag{6}$$

then the combination of equations (1), (4), (5) and (6) gives

$$\left(\frac{\partial h}{\partial s}\right)_v = T\left\{1 + \frac{v}{c_v}\left(\frac{\partial p}{\partial T}\right)_v\right\} \tag{7}$$

This result shows that the constant volume line on the Mollier diagram is that of temperature along with a correction term. For an ideal gas,

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{c_p - c_v}{v} \tag{8}$$

which upon substitution into (7) gives

$$\left(\frac{\partial h}{\partial s}\right)_v = kT \tag{9}$$

This, therefore, shows that the slope of the constant volume line of an ideal gas on the Mollier diagram follows that of the temperature increased by the factor of the ratio of specific heats. For a given situation, the validity of the ideal gas assumption must be investigated before equation (9) can be used. Equation (7), however, is the generalized result and is applicable to steam at any state.

Other slopes on the Mollier diagram can also be investigated to better explain and clarify the physical interpretation of the diagram. Similarly, other diagrams can be investigated. The undergraduate and graduate students find this approach very useful and learn on their own the mathematics of the Jacobians in its mathematical context since the physical significance can be better understood.

1.2. Example 2

The relation between the pressure, p, and temperature, T, in a reversible adiabatic process is useful in solving many important and interesting problems. The application of the result to a special case of an ideal gas with constant specific heats is also very useful in solving many problems of significance. Therefore, the relation that is to be investigated can be written as $(\partial p/\partial T)_s$ which becomes in terms of Jacobians

$$\left(\frac{\partial p}{\partial T}\right)_s = \frac{[p,s]}{[T,s]} \tag{10}$$

With the use of equation (5) and the definition of specific heat at constant pressure,

$$\frac{c_p}{T} = \frac{[s,p]}{[T,p]} \tag{11}$$

equation (10) reduces to

$$\left(\frac{\partial p}{\partial T}\right)_s = \frac{c_p}{T}\left(\frac{\partial T}{\partial v}\right)_p \tag{12}$$

For the case of an ideal gas,

$$\left(\frac{\partial T}{\partial v}\right)_p = \frac{p}{c_p - c_v} \tag{13}$$

Upon substitution into equation (12),

$$\left(\frac{\partial p}{\partial T}\right)_s = \frac{p}{T}\,\frac{k}{k-1} \tag{14}$$

For the case of an isentropic process, which is the case of interest, then

$$\frac{\mathrm{d}p/p}{\mathrm{d}T/T} = \frac{k}{k-1} \tag{15}$$

results in a relation given as

$$T = p^{(k-1)/k} \tag{16}$$

which is valid for an isentropic process of an ideal gas with constant specific heats. Equation (16) is not only well known but also used extensively. Similar results between p and v, and T and v can also be obtained following through a similar procedure.

1.3. Example 3

Maxwell relations can be found from the Jacobians themselves and need not be introduced separately. Indeed, the relations are only yet another way of expressing the integrability condition of a property. Thus for a cyclic process in a simple system, the area in a p–v diagram, representing reversible net work out, will transform to the same area in a T–s diagram, representing reversible net heat in, as in equation (5). In mathematical representation,

$$\frac{\partial(p, v)}{\partial(T, s)} = 1 \tag{17}$$

For example,

$$\left(\frac{\partial s}{\partial p}\right)_T = \left\{\frac{\partial(s, T)}{\partial(p, T)}\right\}$$

which when multiplied by equation (17) becomes

$$\begin{aligned}\left(\frac{\partial s}{\partial p}\right)_T &= \left\{\frac{\partial(s, T)}{\partial(p, T)}\right\}\left\{\frac{\partial(p, v)}{\partial(T, s)}\right\}\\ &= \left\{\frac{\partial(s, T)}{\partial(T, s)}\right\}\left\{\frac{\partial(p, v)}{\partial(p, T)}\right\}\end{aligned}$$

reducing to the well known Maxwell relation

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \tag{18}$$

It seems to be desirable to introduce Maxwell relations this way since it refers to the fundamental law by which energy and its Legendre transformations are indeed properties or potential functions subject to Maxwell relations [5].

1.4. Example 4

As an example of design of experiments, consider the measurement of the speed of sound, which is defined as

$$c^2 = \left(\frac{\partial p}{\partial \rho}\right)_s \tag{19}$$

where ρ is the density of the medium and is equal to the inverse of the specific volume. In view of the fact that the entropy is a nonmeasurable quantity, it must be eliminated in favor of those that are measurable. Using equations (6) and (11), the speed of sound becomes

$$c^2 = -k\left(\frac{\partial p}{\partial \rho}\right)_T \tag{20}$$

which now is totally measurable. Therefore, an isothermal experiment must be designed in which the variation in pressure with respect to density must be measured.

Although it is a well known fact that the choice of thermodynamic properties that characterize a physical situation is arbitrary as long as those properties are independent, one finds in the literature situations where this fact is overlooked in some thermal hydraulics research [6–8].

Assuming that the variables are $\mathbf{V}$, p, and h, where $\mathbf{V}$ is the flow velocity, the speed of sound reduces to [6]

$$c^2 = \frac{1}{(\partial\rho/\partial p)_h + (1/\rho)(\partial\rho/\partial h)_p} \tag{21}$$

The first term is obtained as

$$\left(\frac{\partial \rho}{\partial p}\right)_h = -(\rho^2)\left(\frac{\partial v}{\partial p}\right)_h = -(\rho^2)\frac{[h, v]}{[h, p]} \tag{22}$$

With the use of equations (4), (6) and (11), it can be shown that equation (22) reduces to

$$\left(\frac{\partial \rho}{\partial p}\right)_h = -(\rho^2)\left\{\frac{1}{k}\left(\frac{\partial v}{\partial p}\right)_T - \frac{1}{\rho c_p}\left(\frac{\partial v}{\partial T}\right)_p\right\} \tag{23}$$

From equations (4) and (11), it follows that the second term of equation (23) can be expressed as

$$\frac{1}{\rho}\left(\frac{\partial \rho}{\partial h}\right)_p = -\frac{\rho}{c_p}\left(\frac{\partial v}{\partial T}\right)_p \tag{24}$$

When equations (21), (23) and (24) are combined, equation (20) is obtained.

Assuming the variables are $\mathbf{V}$, ρ, and p, the speed of sound reduces to [6]

$$c^2 = \frac{-\rho(\partial h/\partial \rho)_p}{\rho(\partial h/\partial p)_\rho - 1} \tag{25}$$

The numerator is the inverse of equation (24). Since

$$\left(\frac{\partial T}{\partial p}\right)_\rho \left(\frac{\partial p}{\partial \rho}\right)_T \left(\frac{\partial \rho}{\partial T}\right)_p = -1 \tag{26}$$

the denominator of equation (25) can be written as

$$\rho\left(\frac{\partial h}{\partial p}\right)_\rho - 1 = \rho\,\frac{[h,\rho]}{[p,\rho]} - 1 = c_v \rho\left(\frac{\partial T}{\partial p}\right)_\rho \tag{27}$$

where equations (4) and (6) are used. When equations (24), (25) and (27) are combined, equation (20) is obtained.

Assuming the variables as $\mathbf{V}$, p, and T, the speed of sound reduces to [6]

$$c^2 = \left\{\left[-\frac{(\partial \rho/\partial T)_p}{\rho c_p}\right]\left[\rho\left(\frac{\partial h}{\partial p}\right)_T - 1\right] + \left(\frac{\partial \rho}{\partial p}\right)_T\right\}^{-1} \tag{28}$$

The only term to analyze is $[\rho(\partial h/\partial p)_T - 1]$ which simplifies to

$$\left[\rho\left(\frac{\partial h}{\partial p}\right)_T - 1\right] = -(T\rho)\left(\frac{\partial v}{\partial T}\right)_p \tag{29}$$

where equations (4) and (17) are used. From the identity [3]

$$(c_p - c_v) = T\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_v \tag{30}$$

and the equations (28) and (29), equation (20) follows.

It is, therefore, obvious that no matter what properties are chosen, the final result is unique because of the fundamental concepts of thermodynamics [7]. However, if the results in [6] were not reduced in this fashion, they would have to be evaluated numerically. Since the series representation of enthalpy, entropy and other nonmeasurable terms are not similar, the numerical solutions of equations (21), (25) and (28) will give different results. The justification for it was attempted [6]. It is now proven that that attempt is really a communication that has absolutely no thermodynamic basis [7].

It is, therefore, seen that the method of Jacobians is indeed a very powerful one to simplify the various mathematical relations encountered in the study of thermodynamics and gives them physical significance. It is this physical significance that further increases the appreciation that the students have for thermodynamic reasoning and, as a result, they can better relate, understand and learn thermodynamics [10–12] and makes the teaching of the subject more pleasurable.

Other experiments can also be designed using the techniques and methodologies developed above and in the literature. In the past, along with the speed of sound, experiments have been designed for the Joule–Thomson coefficient and the Clausius–Clapeyron equation with great success and enthusiasm.

2. CONCLUDING REMARKS

It is indeed obvious that the applications of these techniques are very meaningful and give even further insight to why and how things happen. When the student is taught these methodologies, the learning should improve. If the mathematical topics are approached in this fashion, the thermodynamic concepts and equations make more sense [9].

These concepts and methodologies have been used for undergraduates, and graduate students, with extreme success in the United States, Belgium, the Netherlands, Italy and Turkey. The students have been able to relate to thermodynamics better once they see and understand the reasons behind the natural happenings.

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