

FACING SOME PROBLEMS WITH ENTROPY

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ABSTRACT. This article is a short summary of the problems resulting with respect to the working fluid used in building low temperature thermal engines. It has been shown by experience that the relationship or interrelationship of the properties of materials in thermostatics discloses erroneous results in particular as far as heat capacity is concerned when exploiting low thermal heat in the supercritical state, ie in the range beyond the critical point. The discussion of these problems leads to a critical assessment of these interrelationships of the properties of materials. A new method of analysis is being proposed by which one arrives at a presentation of the complete profile of the working fluid starting from thermal measurements.

Considerable efforts have been invested for some time to find out how the large amounts of energy due to waste heat can be exploited technically by machines in converting said energy into an electrical current or in generating turning moment. The attempts at finding a solution comprise the use of low-boiling liquids such as Frigen or Freon in multistage turbines; other attempts take recourse to pure fluids and to the design of cyclic processes using high pressure without phase transition. GERENA Co. with seat in Berlin is developing a piston engine containing a working fluid with which the cyclic process is entirely run in the supercritical range.

The following ideas have been determinative in this decision:

- All fluids have in this state their relative highest coefficient of expansion with the consequence that considerable work in volume can be performed even at small differences in temperature.
- Moreover, the thermal capacities C_p and C_v vary in this state as a rule by at least one order of magnitude. This has determinative consequences for the design of the cyclic process which can be run, in principle, in a manner so that along those sections of the process where heat is taken up, the thermal capacity is on the average

large, while at those sections where heat has to be given off, such thermal capacity is small. The greater the difference in thermal capacity and the more divergent the temperature differences in heating and cooling, the more advantageous is its effect on efficiency.

These arguments are rendered relative on account of the supposition that the maximum efficiency η attainable at given temperatures T_1 and T_2 is delimited and defined by the formula

$$\eta \leq \frac{T_2 - T_1}{T_1} \quad (1)$$

The meaning of this supposition would be very sobering if it were not based on an assumption made with respect to entropy which results, in certain cases, in considerable discrepancies when giving an account of material properties. The discrepancies arise for instance when, in the vicinity of the critical point, the thermal capacity C_v is provided from thermal data such as the real gas factor $Z(T,V)$. It should be remembered in this connection that C_v has, in general, a maximum along the isothermal line at variable volumes, which maximum increases the more, the more the critical point is approached. It is almost commonplace when Abdulgatov and Alibekov point out that the equation of state calculated from P-V-T data for C_v "cannot describe quantitatively the sharp anomalous growth of C_v and other thermodynamic functions near the critical point" (Abdulgatov et al., 1982, p.135) (cf. also figures (I) and (II)).

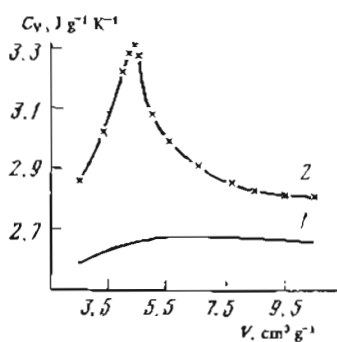


Figure (I). Comparison of the specific heats C_v of n-heptane at 543 K calculated from the thermal Benedict-Webb-Rubin equation (curve 1) with experimental data (curve 2).

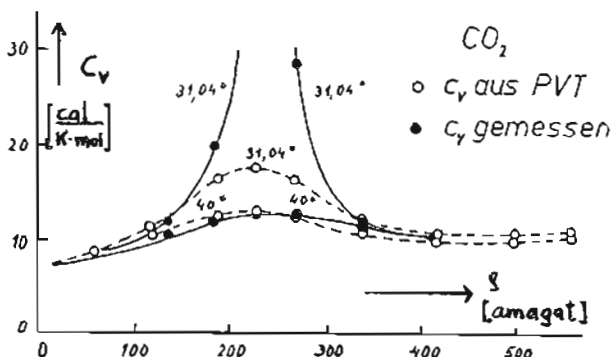


Figure (II). C_v for carbon dioxide in proximity to the critical point.

References

- Fig.(I): cf. Abdulgatov et al., 1982, p.804
 Fig.(II): cf. Benzler, 1954, p.60

To be sure, the problem of giving a due presentation of C_p and C_v from P-V-T data is in no way trivial. Material properties relations as we know them are expressed by the formulae:

$$C_v = C_v^0 + \int \left\{ \frac{\partial^2 p}{\partial T^2} \right\}_v dv \tag{2}$$

$$C_p = C_v + T \left\{ \frac{\partial p}{\partial T} \right\}_v \left\{ \frac{\partial V}{\partial T} \right\}_p \tag{3}$$

In order to be able to represent C_v it is necessary to take recourse to an equation of state $P(V,T)$ which is sufficiently precise so that the requirements for precise presentation may be satisfied even after carrying out two partial derivations and one integration. Either the thermal equations of state used cannot live up to this requirement in certain cases or, however, the material properties relations (2) and (3) are (among others) principally not adequate.

Prior to entering into a discussion of the consequences to be derived from both of these possibilities, we would like that close attention be paid to two figures both of which relate to the rare gas argon. Figure (III) illustrates the field of state in which investigations carried out by Shah and Thodos give a "very good" representation of the thermal behaviour of argon by way of Van der Waals equation of state (cf. Landolt-Börnstein, II.1, 1967, p.298). This range of state corresponds by the relation $T > 150^\circ$ Kelvin and $p < 48$ atm. The reason why we refer to this figure is the following: if the P-V-T data can be approximated "very well" by the equation of state mentioned above, then - with equal certitude - the formulation for thermal capacity C_v holds: C_v is in the field of state a pure function of temperature, ie it is, in particular, independent of pressure. This follows directly from equation (2), for in this instance.

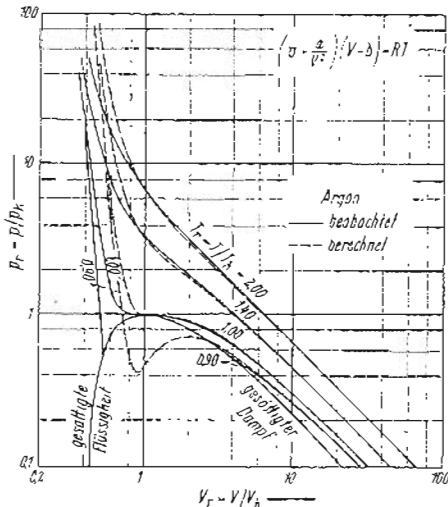


Figure (III). Comparison of the P-V Data for argon with those calculated by way of the Van der Waals equation.

$$\left. \frac{\partial^2 p}{\partial T^2} \right|_V = 0 \quad (4)$$

and hence C_v is a pure function of temperature.

For this field of state Michels et al. (cf. Landolt-Börnstein, II.4, 1967, p.702; Michels et al., 1958, p.769ff.) calculate now thermal capacities which are everything else but independent of pressure (cf. figure (IV)).

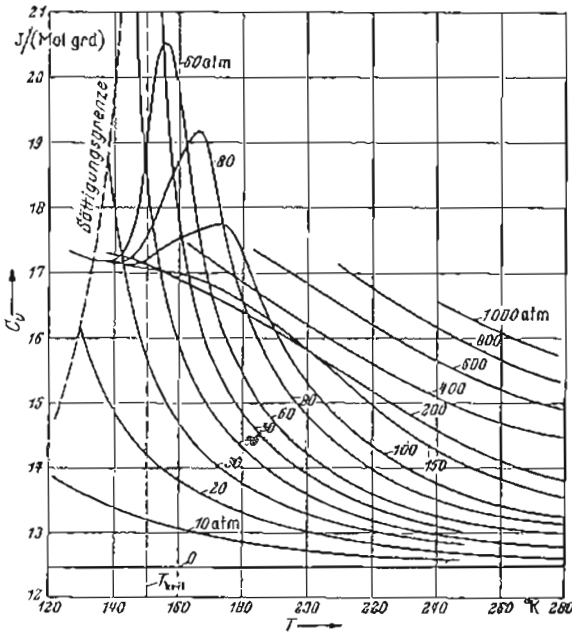


Figure (IV). C_v as calculated for argon.

They base their calculations, in general, on the same material properties relations as Shah and Thodos do also. This example shows, hence, that the material properties relations are in their formulation as partial differential equations in and by themselves problematical, to start with, on account of setting, evidently, the highest requirements for the precision of the approximation of measured P-V-T data.

These circumstances motivated us, in the end, to develop a new method for the complete representation of the material properties while using exclusively P-V-T data which we want to present in the final section of our article.

If, to be sure, the known material properties relations are insufficient in certain circumstances, then it is necessary to look for the reason herefor in an inadequate axiomatization in thermostatics. Since solely two relevant propositions are made on the mathematical level of thermostatics, it turns out that at least one of these must be false. These propositions relate to the existence of total differentials whereby "internal energy" and "entropy" are addressed. Because the material properties relations mentioned are immediately retraceable to the total differential of entropy we must discuss it here.

There is but one reason or argument for the definition of the entropy differential dS as

$$dS = \frac{\delta Q}{T} \quad (5)$$

This argument is supplied by an assumption of a contradiction, viz. the assumption of material specific integrating denominators for the thermal differential dQ which would result in material specific efficiency factors in one and the same Carnot process. Under such conditions one could convert heat completely into work by means of two oppositely operating ideal Carnot engines. This conclusion is deemed, for reasons whatsoever, to be unacceptable. The sole integrating denominator which does not lead to a contradiction with respect to the argument that there is no aggregate which converts heat in a cyclic process entirely into work is given by absolute temperature T . It must be kept in mind that the emphasis in this presentation of arguments is placed on the impossibility of carrying out a thought experiment and not - in any case not directly - on the verifiability of the definition of entropy by way of measurements.

Under these circumstances it will become clear that the contradictions cited will not immediately entice one to rethink the definition of entropy but rather to investigate other sources of error.

We will discuss below the feasibility as to whether a less "trenchant" definition of entropy may not lead to a more adequate representation of material properties. Let us start with a theory immanent criticism of the mathematical version of the second law of thermodynamics.

$$1. \text{ First law: } dU = \delta Q + \sum \delta W_i = \delta Q + \sum X_i dx_i \quad (6)$$

$$2. \text{ Second law: } dS = \frac{1}{T} dU - \frac{1}{T} \sum X_i dx_i \quad (7)$$

Let us first turn to the version of the first law. The differentials of different forms of energy designated by dW_i may be specified thus:

$$\delta W_1 = -pdV \quad \text{mechanical volumetric work} \quad (8)$$

$$\delta W_2 = HdM \quad \text{magnetic work} \quad (9)$$

For the continued discussion the fact is determinative that - from the phenomenological point of view - the elements of each dyad X_i, x_i is associated with a material specific equation of state:

$$\begin{array}{l} p, V - \text{"thermal"} \text{ equation of state } p(V, T), \text{ e.g. } p = RT/V \\ H, M - \text{"magnetic"} \text{ equation of state } M(H, T), \text{ e.g. } M = CH/T \end{array}$$

Thus, for any form of energy there is **always** a particular equation of state and without its knowledge the information as to substance would be incomplete. Apparently, however, this does not apply to the heat differential δQ . There is here, to be sure, also factorization into an intensive and an extensive variable, for $\delta Q = TdS$, yet there is supposed to be no distinct material specific connection between T and S . The sole connection is established by the defining equation (5) where no material characteristics are found but where only the characteristic of process δQ is encountered.

There are no reasons for explaining this particularity which would only be removed in part by the general definition:

$$dS = \delta Q/v \text{ with } v = v(T, V) \quad (10)$$

In part, to be sure, because the quantities "entropy" and "integrating denominator" cannot be directly determined as are the other extensive and intensive variables via measurement of mass, length and time. They would be separately incapable of measurement and could be determined quantitatively as product by taking the mechanical heat equivalent as basis. This latter being the essential expression of the first law is also the basis of the method of representation for $v(T, V)$ to be discussed below.

Precisely for the reason that the quantities v and S cannot be measured directly, the conclusions resulting from generalisation of the definition of entropy are for this very reason of great importance. This will become apparent when the generalized material properties relation (12) is being compared with the standard relation (11):

$$\left. \frac{\partial U}{\partial V} \right|_T = T \left. \frac{\partial p}{\partial T} \right|_V - p \quad (11)$$

$$\left. \frac{\partial v}{\partial T} \right|_V \left. \frac{\partial U}{\partial V} \right|_T - \left. \frac{\partial v}{\partial V} \right|_T \left. \frac{\partial U}{\partial T} \right|_V = v \left. \frac{\partial p}{\partial T} \right|_V - p \left. \frac{\partial v}{\partial T} \right|_V \quad (12)$$

With respect to the relation between the functions of state $U(T, V)$ and $p(T, V)$ another function of state plays a part in (12), which turns out to be the integrating denominator of the heat differential.

Why, may one ask, should the information from U and p not suffice to provide for a relation such as (11)? The answer: the function of state U represents merely the prerequisite so that the sum of exchanges of energy of the system in all possible forms between any two states is, independent of the course followed, supposed to be the same at all times. The existence of U signifies, hence, a restriction as to the possible changes of physical quantities and represents, in this sense, no material properties such as e.g. $p(T,V)$. The so-called 'caloric function of state' U is, in the end, merely the warrant for the constancy of the mechanical heat equivalent. The caloric function of state proper is $\nu(T,V)$, the physical meaning and importance of which need be elucidated. Phenomenologically, nothing more can be said than that it is brought into play because the thermal function of state and the existence of a constant mechanical heat equivalent alone do not yet suffice in order to characterize all possible material properties.

In terms of statistical physics we obtain a more profound insight with respect to the function ν . To this purpose we sketch the "bridging" of statistical to phenomenological entropy. In both, entropy S and internal energy U are defined; they are found in a relation of mutually identical structure. Thus, respectively:

$$\left. \frac{\partial S}{\partial U} \right|_{\nu} = \frac{1}{\nu} \quad (13)$$

$$\left. \frac{\partial S}{\partial U} \right|_{\nu} = k \beta \quad (14)$$

The β from equation (14) constitutes a Lagrange parameter which is brought into play by giving due concern to the constraint of constant total energy U also when there are fluctuations within the system. The customary identification $\beta = 1/kT$ is due to equating (13) with (14) with the supposition of $\nu \equiv T$. In terms of statistical physics there is, presently, no intelligible reason why β is supposed to be essentially identical with absolute temperature. To the contrary, an investigation of the consequences of this one-sided determination allows for the conclusion which we drew already with respect to the integrating denominator of the heat differential: β must be constructed generally to be a material specific function not only of temperature T but also of other physical quantities.

In statistical mechanics we obtain by way of the relation

$$\bar{E}_{\text{kin}} = 3N \int \frac{m}{2} v^2 \cdot \exp(-\beta \frac{m}{2} v^2) dv \cdot \{ \int \exp(-\beta \frac{m}{2} v^2) dv \}^{-1} \quad (15)$$

the expression

$$\overline{E}_{\text{kin}} = \frac{3N}{2\beta} \quad (16)$$

for the mean kinetic energy for N particles. On the other hand, there is the virial theorem:

$$\overline{E}_{\text{kin}} = \frac{1}{2} \sum_{i=1}^N \underline{K}_i \cdot \underline{r}_i = \frac{3N}{2\beta} \quad (17)$$

wherein \underline{K}_i stands for the total force exerted by the respectively $(N-1)$ other particles of the total. If, now, β is identified as $1/kT$, two situations or conditions have been determined at one and the same time.

1. For any empirical temperature T there is precisely one form of energy distribution. Hence, it is precluded in principle that the same temperature - being a macroscopic measured quantity or variable - can be provoked by another distribution of energy or velocities at another mean velocity. This is, physically speaking, a nonsensical requirement. It would mean, to be sure, that an ideal and a real gas would have to have the same energy distribution at same temperatures although the kinetic energy for the real gas has a complicated relationship to potential distribution (cf. (17)). An example demonstrating the opposite may be presented thus: when an ideal gas, i.e. an extraordinarily rarefied gas, is subjected to isothermal compression, interaction sets in, of which attraction comes first. On the average an increasingly greater amount of the gas particles will stay in the range of attraction of the potentials of other particles. These are, then, all particles none of which will have zero velocity because they would otherwise not be able to leave the range of attraction. It follows from this that the maximum of the distribution towards higher velocities is shifted with the distribution curve flattening out on the whole (for an example calculated in extenso cf. Blöss, 1985, p.43ff.).
2. This problem may be discussed also from the point of view as to which forms or types of interaction potentials are still possible at all under such conditions. We assert that in case of $\beta = 1/kT$ on the right side of the equation (17) there is, but for the natural constant k and particle number N , only one macroscopic quantity to be found, ie temperature T . In other words, the distribution of loci of the interacting particles must always proceed so that the sum of material specific terms on the left side of equation (17) becomes material unspecific. These terms of the sum comprise explicit material constants because the total forces \underline{K}_i can be generally ascribed to potentials the configuration of which varies from one fluid to another, and this should, in principle, find expres-

sion also on the right side of equation (17). From this it suggests itself, just as expressed under item 1, that a more general function be assumed than - of all things - the Boltzmann's factor $1/kT$.

What has been said can also be applied and translated to other forms of energy. Looking at the rotational spectra of molecules which provide indirect information regarding the population densities of the rotational energy levels, we find that such population densities of rotational energy levels E_j are shown to be governed, to the present day, by the Boltzmann's factor. Yet, it is precisely the rotation of macromolecules from which it becomes intelligible that not only temperature affects the population of the levels available but also that it is affected by the density and pressure, respectively, within the fluid. What may rotate unimpeded in the rarefied state does so no longer, to be sure, at the same empirical temperatures in the compressed state, and it would be premature to hold only the change of the Hamiltonians responsible for changes in population densities (cf. Blöss, 1983, p.32ff.).

Thinking about what governs, properly speaking, the population density of the rotational energy levels or quantum states has led us, when we were starting our investigations, to take a close and extensive look at rotational band spectra. We have found that gas mixtures are particularly interesting in this respect. We based our investigation on the following: if a gas - the rotational spectra of which can be represented when taking as basis the model of the rigid rotator - subjected to isothermal compression give an indication of a shift of the absorption maximum while simultaneously retaining its spacing of absorption peaks, then the population densities need be governed by something more than just temperature. The maximum of absorption is obtained from the formula

$$j_m = \sqrt{\left(\frac{2I}{\beta \hbar^2}\right)} - \frac{1}{2} \quad (18)$$

wherein j_m is the quantum number of the associated quantum state. It is apparent from equation (18) that it is first the assumption that β were a more general function than $1/kT$ which will lead one to expect under isothermal compression that there is a shift in the maximum. Inspecting figure (V) will reveal corresponding conditions. The lower series of spectra has been taken with a HCl-Ar mixture. Here, the partial pressure of the buffer gas argon was raised isothermally while holding the partial pressure of HCl constant. It is evident from this that, when increasing the pressure from 9 to 169 amagat, the absorption maximum will shift particularly on the right branch towards the right.

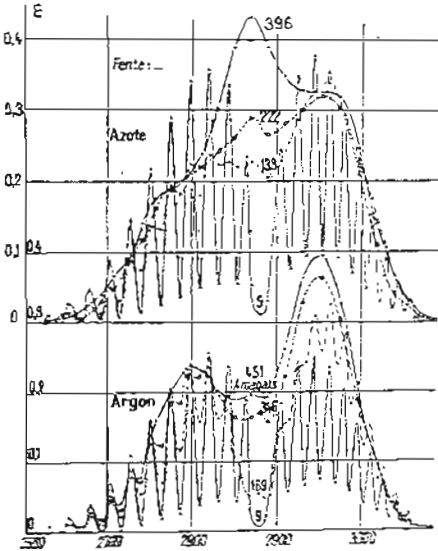


Figure (V). Rotational vibration band of HCl (gas) in the mixture with argon (gas), respectively, taken at 300° Kelvin at various partial pressures of both buffer gases (cf. Coulon, 1954, p.642).

This revelation constitutes, of course, but a qualitative indication to the effect that the Lagrange parameter must be "more" than just $1/kT$. Yet, we are confirmed in our suspicion that instead of the known material relations in certain ranges of state and, especially, in the very high pressure ranges generalized material relations must be used.

These findings have led us to develop a method of measurement and evaluation which we present here and which can present direct evidence as to whether entropy must in general be defined as

$$dS = \frac{\delta Q}{v(T, V)} \quad (19)$$

or not.

In our reflections we set out from the requirement of doing without genuine caloric measurements so as not to render the measurements needlessly expensive in cost and labor from the start. Thus, a method of evaluation and analysis had to be found so as to glean from thermal measurements sufficient information data in order to be able to answer the question as to the character of the integrating denominator and in order to calculate cyclic processes with regard to efficiency. On account of the fact that in this manner no complete data are, principally, available we had to find a way of bridging this data deficit. Contrary to the standard method wherein the differential material properties relations are used resulting from the existence of the total differential with the assumption $v \equiv T$, our method uses the integral version of the first law in the following form:

$$\oint dU = \oint dQ + \oint dW \equiv 0 \quad (20)$$

Moreover, we start from the mere understanding of the existence of an integrating denominator for $\oint Q$; yet, there are no presuppositions taken as to its nature or character. This method will then furnish the function v by way of an iteration algorithm.

The method is based on measuring the isothermal and isentropic lines*. Its presentation in the p - V diagram furnishes a continuous region unfolding or spreading from adjacent Carnot processes with associated areas. In the case of $v \equiv T$ a corresponding rectangular process in the T - S diagram may be associated with each of the Carnot processes in the p - V diagram. This becomes readily evident, for the isentropic and isothermal lines in the T - S diagram are, respectively, genuine horizontal and vertical lines. Evidence going counter to the assumption of $v \equiv T$ can be examined with relative ease. With the temperature scale in the T - S diagram being fixed, transferring one Carnot process from the p - V to the T - S diagram will automatically generate the correct spacing of the corresponding isentropes when presupposing area identity in keeping with equation (20). All other Carnot processes located between both of these isentropic lines must produce, upon areal transfer, always the same spacing for both isentropic lines. If this is the case it is justified to postulate $v \equiv T$. If, however, the Carnot processes between two respective isentropic lines produce when transferred divergent isentropic line spacing, then this supposition is in error (cf. figure (VI)).

In this latter case one can only proceed with the assumption that the isotherms are not genuinely horizontals but rather curved trajectories the course of which can be obtained iteratively from the requirement of equation (20). These iterative methods provide a matrix \underline{H}

$$\underline{H} := \begin{pmatrix} h_{11} & h_{12} \\ 0 & h_{22} \end{pmatrix} \quad (21)$$

which distorts the isotherms T' and effects a parallel shifting of the isentropes S' in the figure

$$\begin{pmatrix} T' \\ S' \end{pmatrix} = \begin{pmatrix} h_{11} & h_{12} \\ 0 & h_{22} \end{pmatrix} \begin{pmatrix} v \\ \sigma \end{pmatrix} \quad (22)$$

so that the prescription regarding representation

* Reasons of patent protection prevent us from entering into a deeper discussion of the method of measurement.

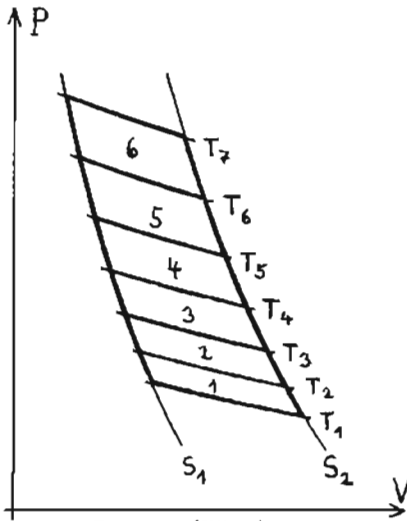


Figure (VI.1)

Figure (VI). The figure (VI.1) shows six Carnot processes unfolded or spreading out by two isentrops and seven isotherms. Transferring it into the T-S diagram (VI.2) would lead to divergent spacings of the isentrops S_1 and S_2 . In the figure (VI.3) the isotherms are distorted and the isentrops are shifted in such a manner that sameness of area is retained between VI.1 and VI.3.

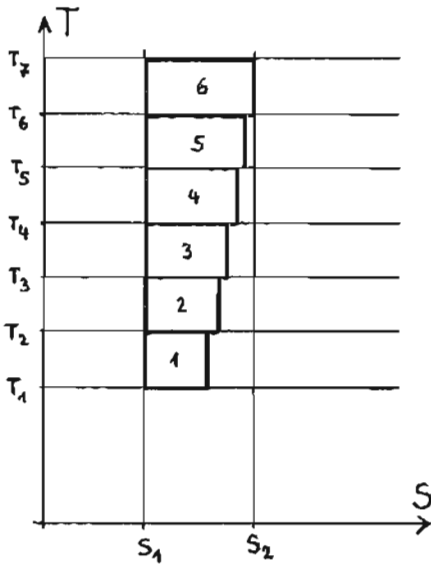


Figure (VI.2)

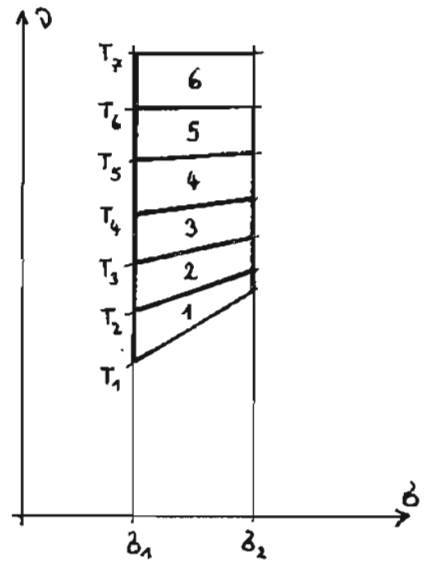


Figure (VI.3)

$$|\oint p dV| = |\oint v d\sigma| \quad (23)$$

is, once again, fulfilled for all cyclic processes. The course of isobars and isochores in the figure may be represented in a similar manner. The "true" course is obtained by comparing isobar/isochor-isentropic cyclic processes, the loci of isentrops being already fixed by way of the prior iterative process. Having arrived here, the thermal capacities are obtained by:

$$C_v = v \left. \frac{\partial \sigma}{\partial T} \right|_v \quad (24)$$

$$C_p = v \left. \frac{\partial \sigma}{\partial T} \right|_p \quad (25)$$

We like to emphasize that the representation of the figure requires at no time simple or multiple partial derivations of compensation curves, but merely comparing the areas enclosed thereby. The iterative method itself is, in principle, no source of error since it is applied for such an extent in time until still existing differences of contents of mutually associated areas have been brought down to zero. In addition to these advantages there is another one to bear fruit. Whereas the use of differentially formulated material properties relations will only uncover local incommensurabilities, this method aims, from the start, at global congruency. It is thus possible to discover discrepancies remaining undetected within the capacity of resolution in the local field of investigations; such small local errors may add up, globally speaking, to not unimportant errors.

GERENA Co. of Berlin will finance, over the next two years, a research program based on this method and aimed at solving the problems for the design and construction of a thermal engine for exploiting low temperature heat. It would be to advantage if interested institutions were to cooperate in this venture.

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