

CERTAIN FEATURES OF APPLYING GENERALIZED ANALYSIS
IN THERMODYNAMICS

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The possibility is examined of obtaining thermodynamic relationships of a different kind for an ideal (perfect) gas and equilibrium radiation on the basis of applying generalized analysis.

Generalized analysis is utilized comparatively rarely in thermodynamics. The exception is the division devoted to studying specific forms of the equation of state, i.e., the problem about its substance is not thermodynamic. Specific information about the properties of a substance are introduced into thermodynamics from outside. It turns out to be possible to set up certain substantial demands with respect to the structure of the equation of state within the framework of thermodynamics but not to determine the form of the function at all.

The problem of the equation of state, and in a more general formulation of the methods of predicting and calculating the thermodynamic and transfer properties of substances, is with its bibliography (see [1]) an independent scientific direction substantially. It is understood that thermodynamic investigation facilities are utilized quite extensively here, that permit not only any relationships characterizing the substance properties to be obtained, but also the setting up of a connection between the most diverse quantitative data obtained experimentally or borrowed from other divisions of physics.

Investigation of the problem under consideration is separated into two main directions. Extensive utilization of an electron computer is characteristic for the first of them, whereupon selection of the mode of representing the experimental data is subjected primarily to requirements of convenience of machine processing. This would result in the appearance of approximations in the form of polynomials with a large number of individual coefficients (for instance, the equation of state of water contains 167 coefficients [1]). It is understood that it is not even possible to speak about the generalization of relationships so difficult to review.

Dependences obtained on the basis of the conception of the thermodynamic similarity of substances are more promising in this sense. The main statement in this method was formulated by van der Waals in the form of the celebrated law of corresponding states. As is known [1, 2], this law can be extended to any other, non-van der Waals substance if only their equation of state contains two individual parameters (constants) in addition to the specific gas constant.

Multiparametric equations of state must be used in investigations encompassing a broad range of variation of physical conditions for real substances. However, if the investigation is limited to a narrower range of state parameter variation (the limits of one phase, say), then in many cases it turns out to be possible to be satisfied by three constants. Therefore, in principle the possibility is created for separating groups of similar substances according to a criterion on identity of the values of an appropriate similarity criterion. The critical coefficient of compressibility is taken most often as such a criterion. Other generalized parameters [1] are also utilized recently for this purpose.

Any macroscopic properties for thermodynamically similar substances can be represented in dimensionless form as universal functions of reduced parameters. This permits not only the computation of properties of some substances according to the same properties of others, but also the modeling of sufficiently complex processes (the transfer process [2]). The main difficulty that occurs here is in the separation of the groups of thermodynamically similar substances. It should be acknowledged that no sufficiently reliable method of solv-

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ing this problem exists at this time. All this obliges examination of the practical realization of the thermodynamic similarity method as a very approximate approximation.

The theory of thermodynamic similarity is a particular case of applying generalized analysis. Values of the thermodynamic parameters at the critical point are used here most often as the reference scales of variables, which corresponds to the method of characteristic scales [3]. Selection of these scales is dictated substantially by considerations of convenience, since the critical parameters for many substances are determined with a sufficiently high degree of accuracy (with the exception, perhaps, of the specific volume). To represent the appropriate equations of state in dimensionless form in courses on thermodynamics, a connection is ordinarily set up between the critical parameters and the individual constants of the equation under consideration by using conditions at the critical point

$$\left(\frac{\partial p}{\partial v}\right)_T^{cr} = 0; \quad \left(\frac{\partial^2 p}{\partial v^2}\right)_T^{cr} = 0. \quad (1)$$

A simpler and more natural means from the viewpoint of generalized analysis can be proposed here that is not associated with going over to conditions of the type (1). For instance, for the van der Waals equation of state

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \quad (2)$$

the corresponding independent equations of scale relations [3, 4] can be written in the form

$$p_* v_* = p_* b = \frac{a}{v_*} = RT_*, \quad (3)$$

from which there follows directly

$$(p_+ + v_+^{-2})(v_+ - 1) = T_+, \quad (4)$$

where the quantities

$$p_* = a/b^2; \quad v_* = b; \quad T_* = a/(bR). \quad (5)$$

are utilized as characteristic pressure, specific volume, and temperature scales.

It is clear at once that quantities of the type (5) or critical parameter values related to them cannot be chosen as reference scales for the state domain of the substance that is close to an ideal gas in its properties. The substance properties are quite specific here because certain physical effects degenerate completely. Among them are the internal (cohesive) pressure and the finiteness of the molecule sizes whose influence is taken into account in the equations of state of real substances by appropriate individual parameters (the constants a and b in the van der Waals equation, say).

At the same time, despite the simplicity of the thermodynamic relationships for an ideal gas, their examination on the basis of applying generalized analysis methods can turn out to be quite useful. This is explained first by the circumstance that many fundamental statements of thermodynamics, the foundation for the selection of the properties of a thermometric body, the construction of an absolute temperature scale, the properties of entropy, etc., are related closely to precisely the problem of the existence and the study of the properties of an ideal gas.

Before proceeding to the solution of these problems, we briefly examine the apparatus of generalized analysis that will henceforth be utilized. We speak about the scale relations equations, i.e., about the relationships that connect the reference scales of the variables and parameters of the problem. The system (3) is an example of such relationships obtained from the equations of the problem by using proportional transformations of variables [3, 4]. If the equations of the problem are not known, then the defining equations of dimensional analysis can be utilized for this purpose with the subsequent elimination of reference scales of those primary quantities that do not enter directly into the list of essentials, from them [5]. All the reference scales are initially assumed not defined, which produces additional possibilities for making the solution universal and makes the method more flexible.

Two modes of ultimately making the solution universal exist [3, 4]: self-similarity and a self-similar (similar) solution. Self-similarity is understood to be the limit case

of degeneration of all the criteria of the problem. There follows directly from the condition of incontrovertibility of the system of equations of scale relations that the number of equations of the scale relations should not exceed the number of variables being transformed in this case. If the form of the desired function can be determined or the transformation of variables for which the "dimensionality" of the problem is diminished can be realized (i.e., the degeneracy of the independent variable is clarified) on the basis of generalized analysis, then this problem has a self-similar (similar) solution. It is most often necessary to deal with the passage from a two- to a one-dimensional problem. The partial differential equations are here transformed into ordinary differential equations. However, this circumstance, that is of primary value in many areas of physics and engineering, is again not very essential for the application of generalized analysis to thermodynamics. For the problem to have a self-similar solution it is sufficient that the number of scale relations equations be less than the number of variables being transformed. Those equations should here be eliminated from the number of scale relations equations that result in the appearance of criteria containing only physical parameters (see [3] for more details). It must be noted that a self-similar (similar) solution can be obtained in the case of the one-dimensional problem only in the form of a power-law or logarithmic function [3, 4].

Thus, returning to the main topic of the paper, we proceed to a discussion of one of the key thermodynamic problems that is formed, as follows in conformity with the structurally logical system of constructing thermodynamics [6] that we assumed (a system based on the hypothesis of the existence of thermal coordinates of state and, therefore, a thermal interaction potential). To set up requirements whose satisfaction assures realization of the necessary and sufficient conditions for temperature identification is empirical, determined directly in terms of measurement of certain other quantities (the thermometric properties), and absolute (thermal potential), independent of the individual characteristics of the thermometric substance.

Later, just a thermally deformed system will be examined. It is consequently natural to try to choose a deformation parameter (pressure, volume, or some function of these quantities) as the thermometric property.

The state of a thermally deformed system is determined by giving two coordinates, the volume v and entropy s . Each of the potentials is here a single-valued function of them:

$$p = p(v, s); T = T(v, s). \quad (6)$$

Taking into account that the absolute temperature T should be associated uniquely with the empiric θ and eliminating the entropy, we obtain from (6)

$$f(p, v, \theta) = 0. \quad (7)$$

The thermometric substance will be the closer to the absolute, the less the individual characteristics enter into its definition. Therefore, from the viewpoint of generalized analysis the selection of an optimal thermometric substances reduces to seeking that of its states for which the problem of determining the specific mode of the equation of state allows of ultimate universalization, i.e., has a self-similar solution. Test shows that in the simplest case an equation of state of the type (7) contains just one dimensional constant. Most often used as this is the specific gas constant R . From dimensionality formulas of the quantities essential for the problem under consideration the following system of scale relations equations can be obtained (the reference scales of the appropriate variables are denoted with an asterisk):

$$p_* = \frac{m_*}{\tau_*^2 l_*}; v_* = \frac{l_*^3}{m_*}; R = \frac{l_*^2}{\tau_*^2 \theta_*}. \quad (8)$$

Eliminating the primary quantities not entering in the list of essentials (mass m_* , time τ_* , extension l_*) from this system of scales, we obtain just one scale relations equation in the form

$$R = \frac{p_* v_*}{\theta_*}. \quad (9)$$

We have three transformable variables connected by a single equation; consequently, the desired function is either a power-law or logarithmic function exactly as for the one-dimensional problem. Indeed, this case can be considered as the successive passage first

from a two- to a one-dimensional problem of general form, and then to a degenerate problem for which the specific form of the desired function can be determined on the basis of generalized analysis. In other words, this solution can be represented in the form

$$\frac{pv}{R\theta} = A_1 = \text{const.} \quad (10)$$

Analogously (on the basis of dimensionality formulas for the internal energy considered as a function of v and θ), we have from the equations of scale relations

$$u_* = \frac{l_*^2}{\tau_*^2}; \quad v_* = \frac{l_*^3}{m_*}; \quad R = \frac{l_*^2}{\tau_*^2 \theta_*} \quad (11)$$

the equation

$$\frac{u}{R\theta} = A_2 = \text{const.} \quad (12)$$

For $A_1 = 1$, Eq. (10) agrees with the Clapeyron equation. However, it must be emphasized that (10) is related continuously to the relationship (12) that sets up a linear dependence between the internal energy and the empirical temperature. Therefore, the equation of state of a substance containing just one dimensional constant does not correspond to an ideal gas but is its particular case, a perfect gas (an ideal gas with constant specific heat). The Clapeyron equation for the general case of an ideal gas should apparently be considered approximate even in the case when the internal energy of the substance depends only on the temperature (but this dependence is not linear). This is confirmed sufficiently well by comparing experimental data for monatomic (with almost constant specific heat) and those gases (di- and multiatomic) whose specific heat varies noticeably with temperature.

Although the specific gas constant has different values for each gas, it is not fully an individual constant of any substance. Its appearance among the parameters of the problem is explained primarily by the fact that the specific and not the molar values of the additive quantities are considered here. However, this constant can generally be eliminated from the conditions of the problem by using a known recipe, by translating one of the primary quantities (the temperature in this case) into a category of secondary quantities [5]. If an energetic temperature unit is introduced following Bridgman [7], then (by using specific quantities as before) we rewrite the system of scale relations equations (8) as follows:

$$p_* = \frac{m_*}{\tau_*^2 l_*}; \quad v_* = \frac{l_*^3}{m_*}; \quad \theta_* = \frac{l_*^2}{\tau_*^2}, \quad (13)$$

from which, by the usual procedure, we obtain

$$pv = A_1 \theta, \quad (14)$$

and from system (11), respectively,

$$u/\theta = A_2. \quad (15)$$

Expressions (14) and (15) are interesting in the respect that they do not generally contain any individual characteristics of the substance.

The conditions to obtain relationships containing the entropy on the basis of a generalized analysis are rather more complex. The elementary quantity of heat is determined by the expression

$$dq = Tds, \quad (16)$$

from which there follows directly

$$q_* = T_* s_*. \quad (17)$$

If it is taken into account that from the equation for the first principle of thermodynamics

$$dq = du + pdv \quad (18)$$

we obtain

$$q_* = u_* = p_* v_*, \quad (19)$$

then we rewrite the relationship (17) to identify the reference scales of the temperature θ_* and T_* in the form

$$u_* = \theta_* s_* \quad (17')$$

As is easy to see, when using the energetic temperature unit, (17) means that the entropy is a dimensionless quantity. This circumstance indicates that relationships containing the entropy cannot be obtained directly by using generalized analysis. In this connection, it is interesting to note that application of the apparatus of generalized analysis to relationships containing the entropy results in an internal contradictory system of scale relations equations. This is characteristic also for equations of the type (6) and for their analogs represented in the more customary form

$$s = s(v, \theta), \quad (20)$$

i.e., expressions in which the entropy is formally a dimensional quantity. It must be said that such a situation must also be encountered in other cases of the application of generalized analysis to solve physical problems. The best-known example is the problem of the logarithmic profile of the average velocity in a near-wall turbulent stream. A method is known which can sometimes be used to bypass the difficulties arising successfully. To do this, one should go from consideration of the function itself over to examination of the derivative (derivatives). Such derivatives for the relationship (20) are

$$\left(\frac{\partial s}{\partial v}\right)_\theta = f_1(v, \theta), \quad (21)$$

$$\left(\frac{\partial s}{\partial \theta}\right)_v = f_2(v, \theta). \quad (22)$$

Ordinarily it is possible to obtain

$$\left(\frac{\partial s}{\partial v}\right)_\theta = \frac{A_3'}{v}; \quad \left(\frac{\partial s}{\partial \theta}\right)_v = \frac{A_4'}{\theta}; \quad (23)$$

$$ds = \left(\frac{\partial s}{\partial v}\right)_\theta dv + \left(\frac{\partial s}{\partial \theta}\right)_v d\theta$$

by using generalized analysis and after integration

$$\Delta s = A_3 (\ln v + A_4 \ln \theta). \quad (24)$$

If we start from the scale relations equations containing the specific gas constant, then in this case (24) can be represented in the form

$$\Delta s = A_3 R (\ln v + A_4 \ln \theta). \quad (24')$$

Here the entropy has the same dimensionality as the quantity R . If we set $A_3 = 1$ and $A_4 = c_v/R$, then (24) acquires its usual form:

$$\Delta s = R \ln v + c_v \ln \theta. \quad (24'')$$

Briefly, the absolute temperature can be defined as the integrating divisor for the elementary quantity of heat that does not contain any individual characteristics of the thermometric substance and is a thermal interaction potential. It is easy to see that a perfect gas satisfies all these requirements as a thermometric substance; consequently, the temperature of such a gas can be identified with the absolute temperature. A special proof is not required here that this temperature is an integrating divisor for the elementary quantity of heat since any of the relationships of the type (24) determines the entropy of a perfect gas as a function of the state. It is understood that this proof can be realized, if desired, by the usual manner.

It should again be emphasized that we speak of precisely the perfect gas temperature and not of the ideal gas temperature. As already noted, the Clapeyron equation in the more

general case of an ideal gas with variable specific heat should be considered as approximate since more than one constant will be contained here in the conditions of the problem.

The natural question occurs of whether utilization of the gas constant as the fundamental constant of the problem is the uniquely possible solution and whether there are generally other variants in the selection of the thermometric body. This question can be answered affirmatively at once, since one such variant is known in physics, where the thermodynamics of equilibrium radiation comes to mind.

In examining this problem we start from the hypotheses ordinarily accepted [8]. We will consider radiation filling a certain cavity to be a photon gas in a state of thermal equilibrium with the surrounding bodies. Since a photon has no rest mass, the specific (referred to unit mass) values of the quantities cannot possibly be used here. The total values of the energy, entropy, and volume will be used to determine the properties of the appropriate thermodynamic system together with the equilibrium radiation temperature and light pressure. Just one dimensional constant, the Stefan-Boltzmann constant σ , will be among the arguments of the problem in addition to the variables. By using generalized analysis we set up the equation of state of the system under consideration as well as certain other relationships.

First, we compile the system of scale relations equations on the basis of the defining equation. None of the defined quantities corresponding to the International System of Units (SI) will certainly be selected at all as primary. By conserving their number, those may be examined that will be most convenient for this specific problem. The system of scale relations equations for the pressure as a function of the volume and entropy has the following form:

$$p_* = \frac{U_*}{V_*}; \quad \sigma = \frac{U_*}{V_* T_*^4}; \quad S_* = \frac{U_*}{T_*}. \quad (25)$$

Eliminating the reference scales of quantities not entering directly into the desired dependence (U_* and T_*) from system (25), which is equivalent to eliminating the dimensionalities of the corresponding primary quantities, we obtain

$$p_* = \sqrt[3]{\frac{S_*^4}{\sigma V_*^4}} \quad (26)$$

and

$$\frac{p}{p_*} = f\left(\frac{V}{V_*}; \frac{S}{S_*}\right). \quad (27)$$

The three variables turn out to be related only by the one equation (26); consequently, even here the passage from the two-dimensional problem (27) is first possible to a one-dimensional problem of general form

$$\frac{p}{p_*} = f_1\left(\frac{V \sqrt[3]{\sigma^3 p_*^3}}{S}\right), \quad (28)$$

and then to a degenerate one-dimensional problem whose solution can be represented in the form of the power-law function

$$\frac{p V^{4/3} \sigma^{1/3}}{S^{4/3}} = B_1. \quad (29)$$

Expressions for the temperature and internal energy are obtained in an analogous manner:

$$\frac{T V^{1/3} \sigma^{1/3}}{S^{1/3}} = B_2, \quad (30)$$

$$\frac{U V^{1/3} \sigma^{1/3}}{S^{4/3}} = B_3, \quad (31)$$

and as a consequence of comparing relationships (29)-(31)

$$\frac{U}{V} = \sigma T^4, \quad (32)$$

$$p = \frac{B_1}{B_3} \frac{U}{V}. \quad (33)$$

Expression (32) contains no dimensionless constants since (without limiting the generality of the problem formulation) it is included in the constant σ . Specific properties of the temperature as an integrating divisor for the elementary quantity of heat can be used to determine the numerical value of the quantity B_1/B_3 . Consequently, we have

$$dS = \frac{dQ}{T} = \frac{1}{T} dU + \frac{p}{T} dV \quad (34)$$

and, therefore, the condition

$$\left\{ \frac{\partial}{\partial V} \left(\frac{1}{T} \right) \right\}_U = \left\{ \frac{\partial}{\partial U} \left(\frac{p}{T} \right) \right\}_V \quad (35)$$

should be satisfied. It is easy to see that

$$B_1/B_3 = 1/3 \quad (36)$$

and, correspondingly,

$$p = \frac{1}{3} \frac{U}{V} \quad (33')$$

are obtained from a comparison of (35) with (32) and (33). This last equation is the relationship between the light pressure and the volume energy density known from electrodynamics.

In certain cases the power-law dependences analogous to relationships (29)-(33) for the photon gas can be obtained even for an ordinary perfect gas. However, discussion of the questions associated with this is beyond the scope of this paper.

NOTATION

a , b are constants in the van der Waals equation of state; c_V , the isochoric specific heat; l , the extension; m , the mass; p , the pressure; q , the specific heat; R , the specific gas constant; S , the entropy, s , the specific entropy; Δs , the increment in the specific entropy; T , the absolute temperature; U , the internal energy; u , the specific internal energy; V , the volume; v , the specific volume; σ , the Stefan-Boltzmann constant; θ , the empirical temperature; τ , the time. Subscripts: cr , critical parameters; $*$, reference scales of appropriate quantities; $+$, dimensionless quantities.

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