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GENERALIZED DEFINITION OF THE ADIABATIC EXPONENT

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A generalized definition of the adiabatic exponent, which holds for ideal and real gases, is investigated. The generalized definition makes it possible to apply a number of formulas of engineering thermodynamics and gas dynamics to a real gas, using a parameter called the "ideal" temperature.

The well-known definition of the adiabatic (isentropic) exponent by means of the relation

$$k = c_p/c_v \tag{1}$$

is appropriate only for an ideal gas. For a real gas in a state far removed from the ideal state, this definition leads to completely wrong results. For simplicity, it is often convenient to assume k = const for an ideal gas. But, as can be easily shown, the formulas for the speed of sound $a = \sqrt{kpv}$ and for the critical speed in a nozzle $c_{cr} = \sqrt{k_{cr}p_{cr}v_{cr}} = a_{cr}$ are valid for an ideal gas with k defined by (1) but not constant. Other formulas which include k are also valid if an appropriate average value of k is used, but, in formulas in which k appears both as an exponent and as a multiplying factor, the averaging for the two cases is different.

It is to be expected that an appropriate definition of k for a real gas would lead to analogous formulas, in particular, to an exact formula for the speed of sound, similar to that for the ideal gas. The averaging of k for a real gas, when necessary, may be more complicated than for an ideal gas, for which k depends only on T, since in the case of a real gas k may depend on two parameters.

From the definition (1), using simple differential relations characteristic of the adiabatic process, the equation of the adiabatic of an ideal gas, which is exact for k = const, can be derived. For variable k this equation is exact either when the appropriate average k is used, or for an elementary adiabatic process. The generalized definition of the adiabatic exponent should have the same properties, i.e., it should yield, on the basis of the same relations, an analogous equation for the adiabatic of a real gas, while, in the special case of an ideal gas, this definition should reduce to definition (1) directly, i.e., independently of the differential relations mentioned above.

Since the specific heats c_p and c_v are the temperature derivatives of the enthalpy i and the internal energy u, and in an adiabatic process the entropy s is constant, the definition of k should be connected with these three most important thermodynamic functions of state i, u, s.

Therefore, the adiabatic exponent should be defined as the partial derivative of enthalpy with respect to internal energy at constant entropy, i.e., by the formula [1]

$$k = (\partial i/\partial u)_s. \tag{2}$$

In the case of an ideal gas i and u depend only on T, and therefore the partial derivative in (2) should be replaced by the total derivative di/du, which can be represented as the ratio of the two derivatives di/dT and du/dT, equal to c_p and c_v, respectively. Thus, the generalized definition reduces directly to the special definition (1) in the case of an ideal gas.

Definition (2) can also be represented as the ratio of the two partial derivatives $(\partial i/\partial T)_s$ and $(\partial u/\partial T)_s$, but these are not equal to the specific heats, since $c_p = (\partial i/\partial T)_p$ and $c_v = (\partial u/\partial T)_v$. Definition (1) can be obtained only in the case when these derivatives are identical, and thus it does not hold for a real gas.

However, since i = u + pv, it is possible to replace the partial derivatives of i and u with respect to T by derivatives with respect to pv or, even better, with respect to the parameter

$$\vartheta = pv/R, \tag{3}$$

which may be called the "ideal" temperature of the real gas, since ϑ has the dimensions of temperature and for an ideal gas $\vartheta = T$. This leads to the relations

$$\xi_p = \frac{k}{k-1} = \frac{1}{R}\left(\frac{\partial i}{\partial \vartheta}\right)_s; \quad \xi_v = \frac{1}{k-1} = \frac{1}{R}\left(\frac{\partial u}{\partial \vartheta}\right)_s; \tag{4}$$

$$\xi_p - \xi_v = 1; \tag{5}$$

$$k = \xi_p/\xi_v. \tag{6}$$

For an ideal gas formula (4) becomes

$$\zeta_p = \frac{k}{k-1} = \frac{c_p}{R}; \quad \zeta_v = \frac{1}{k-1} = \frac{c_v}{R}, \tag{4a}$$

and formulas (5) and (6) correspond to Meyer's equation and to definition (1), respectively. The quantities ζ_p and ζ_v are convenient for practical calculations.

From definition (2) and the fundamental differential equation of thermodynamics Tds = du + pdv = di − vdp it follows, assuming ds = 0, that

$$k = -\frac{v}{p}\left(\frac{\partial p}{\partial v}\right)_s = -\left[\frac{\partial(\ln p)}{\partial(\ln v)}\right]_s. \tag{7}$$

Starting from formula (7), we can easily derive the formulas for the speed of sound and for the critical speed mentioned above, taking into account the well-known formula $a = \sqrt{(\partial p/\partial \rho)_s}$ and the fact that c_{cr} is determined by the minimum of the quantity v/c, where $d(c^2/2) = -vdp$.

If we assume that k, as defined by (2), is constant (first approximation), then, starting from (7), we can easily derive the equation of the adiabatic in the form

$$pv^k = \text{const}; \quad p\vartheta^{-\zeta_p} = \text{const}; \quad v\vartheta^{\zeta_v} = \text{const}. \tag{8}$$

Substituting ϑ = T for an ideal gas, and taking account of (4a), we obtain the well-known equations of the adiabatic of an ideal gas with k = const.

If k, as defined by (2), is variable, then, starting from (7), we obtain equations analogous to (8), but the values of k, ζ_p, ζ_v should then be averaged over ϑ at s = const in an appropriate manner, similar to the averaging over T for an ideal gas. Note, that the assumption that k, as defined by (2), is constant holds for superheated steam with approximately the same accuracy as the assumption that k, as defined by (1), is constant for ideal water vapor. With the same accuracy one may take k = k*, where k refers to superheated steam and k* to ideal water vapor.

This property is not accidental, as it might seem from the fact that the adiabatic exponent of superheated steam is an empirical quantity, but is rather a result of the considerations given below and is, apparently, common to the vapors of other liquids.

All ideal gas formulas which contain k, or which are based on the equation of state (for example, formulas for work or for processes at T = const), remain valid for a real gas if the parameter ϑ is substituted for the temperature T. This is also the case when k is variable; if k is averaged in the appropriate way, the role of the derivative dk/dT, which governs the averaging process for an ideal gas, will be played by the derivative $(\partial k/\partial\vartheta)_s$ in the case of a real gas.

Thus, the use of the parameter ϑ instead of T in the generalized definition of the adiabatic exponent is quite effective for the generalization of several engineering formulas; in particular, formulas which describe the flow processes of a gas or a vapor. Therefore, it is convenient to add the parameter ϑ to steam tables, and to introduce the lines ϑ = = const in Mollier charts. Clearly, the substitution of ϑ for T is inadmissible in other cases (in the formulas for entropy, for the efficiency of a Carnot cycle, etc.). The condition k = const is inapplicable in more exact calculations and the variation of k must be taken into account. In the case of an ideal gas k depends only on T, and the total derivative dk/dT exists. This follows from the condition i = i(T), a result of the equation of state of an ideal gas, which can be written in the form ϑ = T. Accordingly, for an ideal gas i = i(ϑ).

In the case of a real gas $\vartheta \neq$ T and, therefore, when i = const T varies (quite considerably) even for quite moderate changes in p or v. This manifests itself in the Joule-Thomson throttling effect, which is positive for $T < T_i$, i.e., in all ordinary steam installations. But the necessary and sufficient condition for the exponent k of a real gas being a function of one variable only is not i = i(T), as in the case of an ideal gas, but i = i(ϑ). Then also u = u(ϑ) and the exponent k, as defined by (2), is a function of ϑ only. From the condition i = i(ϑ) it also follows that for an ideal gas (ϑ = T) i = i(T). The converse is not necessarily true, but there are some indications that i ≈ i(ϑ) may be true for superheated vapors in a wide range of temperature, as is the case for superheated steam.

Let us denote by ϑ^* and T^* the limits of ϑ and T when v → ∞ at i = const. Since as v → ∞ all real gases become ideal, we have $\vartheta^* = T^*$.

Consider the quantities

$$\delta_\vartheta = \vartheta - \vartheta^*; \quad \delta_T = T - T^*; \quad \delta = T - \vartheta = \delta_T - \delta_\vartheta. \tag{9}$$

Clearly, δ = 0 for an ideal gas and increases in absolute value with decreasing v for a real gas. From steam tables we find that δ > 0, but the sign of δ may depend on temperature.

Starting from Van der Waal's equation, it can be shown that

$$\delta = \frac{a}{Rv} - \frac{bT}{v-b}. \tag{10}$$

If the pressure is not very high, then $v \gg b$ and

$$\delta \approx \frac{a}{Rv}\left(1 - \frac{RbT}{a}\right) = \frac{a}{Rv}\left(1 - \frac{8}{27}\frac{T}{T_{cr}}\right). \tag{10a}$$

Consequently, when $T < (27/8)\, T_{cr} = T_i/2$, i.e., in ordinary steam installations, both δ and δ_T are positive and increase with decreasing v at constant i. The quantity δ_ϑ, being the difference of two positive quantities, cannot exceed in absolute value the greater of the two and, since δ and δ_T increase simultaneously, one may expect δ_ϑ to be small. Obviously, this assumption has no rigorous justification, but it is justified empirically.

Thus, in the case of superheated steam [2] at $i \approx 3455 \times 10^3$ J/kg, an increase in pressure from 0.01×10^5 N/m^2 to 98.1×10^5 N/m^2 results in an increase in T in the amount of 47.3 K, whereas ϑ increases by only 6.1 K, i.e., by only 0.8% of ϑ^*. When p increases from 0.01×10^5 N/m^2 to 294.3×10^5 N/m^2, $\delta_T = 116.3$ K and $\delta_\vartheta = -16.8$ K (2.2% of ϑ^*). Even more striking is the example $i \approx 2930 \times 10^3$ J/kg, when the same pressure changes give the following values for δ_T and δ_ϑ, respectively: 124.7 and -7.1 K (1.4% of ϑ^*) in the first case, and 239.8 and -11.1 (2.2% of ϑ^*) in the second. Analogous results are obtained for other (intermediate) values of i for superheated steam in the above pressure range.

Thus, there are indications that, although the temperature T of a real gas changes quite considerably in an isenthalpic process of a real gas, the "ideal" temperature ϑ changes very little. Then in approximate calculations (second approximation), one could assume $i = i(\vartheta)$, replace the partial derivatives in (2) and (4) by the total derivatives di/du, $di/d\vartheta$, and $du/d\vartheta$, and, in averaging k, replace the derivative $(\partial k/\partial\vartheta)_s$ by the derivative $dk/d\vartheta$. This would justify even more strongly the choice of ϑ as one of the parameters of state governing the variation of k – in approximate calculations as the only parameter, in exact calculations as one of two, the second being the entropy s.

Assuming that $i \approx i(\vartheta)$, we obtain $\vartheta \approx \vartheta^* = T^*$ and $k = k^*$. Starting from formula (6), we obtain

$$k \approx c_p^*/c_v^*. \tag{11}$$

Formula (11) is very similar to formula (1), but it is approximate and, what is very important, c_p^* and c_v^* are not the true specific heats of the real gas, but the specific heats of an ideal gas at the same i or at the same ϑ, or (approximately) at the same temperature. By analogy with ϑ we may call these the "ideal" specific heats of a real gas. Now it is clear why in the example of steam the adiabatic exponent was nearly equal to k, the exponent of ideal water vapor at the same temperature. It is also clear why the approximate value k = 1.3, long ago proposed for superheated steam, is still used in approximate calculations. The accuracy of the calculations based on this value is almost the same as the accuracy of calculations for ideal water vapor based on k = const.

Engineering formulas containing the adiabatic exponent of superheated steam and, apparently, other superheated vapors, can be made more exact in the same way as the equations for an ideal gas.

The use of the parameter ϑ is also convenient in the case of saturated steam, where

$$\vartheta = \vartheta' + x(\vartheta'' - \vartheta'). \tag{12}$$

Admittedly, in the case of saturated steam the variation of ϑ at i = const even in approximate calculations cannot be neglected, but δ_ϑ is considerably smaller than δ_T. Starting from (2), and taking into account that i, u, and s are linear functions of the vapor fraction x, we can derive an exact formula for the adiabatic exponent of saturated steam as a function of its parameters p and x, which could replace the usual empirical formulas.

In conclusion, it should be noted again that the arguments for the approximate relation $i \approx i(\vartheta)$, which then leads to $u \approx u(\vartheta)$ and $k \approx k(\vartheta)$, are not rigorous and should be regarded as indications. Despite the fact that this assumption is justified in the case of superheated steam over a wide range of temperature and pressure, the generalization of this assumption and the estimation of its accuracy would require further study.

NOTATION

a – speed of sound; a, b – Van der Waals parameters; c – flow velocity; c_p, c_v – specific heats per unit mass at constant pressure and volume, respectively; i – enthalpy per unit mass; k – adiabatic (isentropic) exponent; p – pressure; R – gas constant; s – entropy per unit mass; T – absolute temperature; T_i – inversion temperature, absolute; T_{cr} – critical temperature, absolute; u – internal energy per unit mass; v – specific volume; x – vapor fraction of saturated steam; δ, δ_{ϑ}, and δ_T — defined by (9); ζ_p, ζ_v — adiabatic exponents in the coordinate systems ζ, p and ζ, v, respectively; ρ — density; ϑ — "ideal" temperature, defined by (3). Subscript cr — values of the parameters a, c, k, p, and v corresponding to the critical pressure ratio in nozzle flow; superscript * — values of c_p, c_v, k, T, and ϑ of an ideal gas at the same value of i as that of a real gas; superscript ' and " — values of the parameter ϑ of liquid and vapor at saturation.

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