AXIOMATIC FORMULATION
OF THERMODYNAMICS IDEAL GAS LAWS

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Abstract

The relationships between physical quantities determining thermodynamic state of an ideal gas are analysed in the paper. It will be proved that such relationships can be obtained based on convex analysis of the formula describing specific energy of the gas. This formula is expressed as a functional with specific volume and specific entropy being its constrains. The resulting constitutive equations of ideal gas, determining pressure and temperature as a function of entropy and specific volume, are given. It will be proved that the equation of the ideal gas formulated by Clapeyron, can be easy obtain from the constitutive equations, eliminating the variable describing entropy. Moreover, it will be shown that the functional of specific energy of ideal gas is convex. Because of this mathematical property of the functional, Legendre transform is used in order to determine three conjugated functionals, i.e. enthalpy, free enthalpy and free energy. The method of description of thermodynamic relationships to be introduced herein, differs from well-known classic handbook's presentations. Moreover, it permits a better understanding of the structure of thermodynamics equations.

Keywords: thermodynamics, ideal gas laws, convex analysis

1. Introduction

We analyse the relationships between physical quantities determining thermodynamic state of an ideal gas. The primary quantity describing the state of the gas, is the mass energy density to be accumulated in. It is called the specific energy and is defined as an amount of energy per unit mass. We take into account energetic transformation of a one-kilogram gas sample, filling a container with changing volume. We assume that the state of the gas is homogeneous in every point inside the container.

Thermodynamic state of the gas is described using four physical quantities given below:

v – specific volume $\left[\dfrac{m^3}{kg} \right]$, p – pressure $\left[Pa \right]$, s – specific entropy $\left[\dfrac{J}{kg\ K} \right]$, T – temperature $\left[K \right]$.

The equation of an ideal gas, formulated by Clapeyron in 1834, determines a relationship between the three above introduced quantities and is as follows

$$p\,v = R\,T \ ,$$

where $R \left[\dfrac{J}{kg \; K} \right]$ denotes the universal gas constant.

The gas constant R is related to another parameters, characterizing the properties of ideal gas [5], [6]

c_v – specific heat under constant volume conditions,

c_p – specific heat under constant pressure conditions,

$\kappa = \dfrac{c_p}{c_v}$ – adiabatic fraction , $\kappa > 1$,
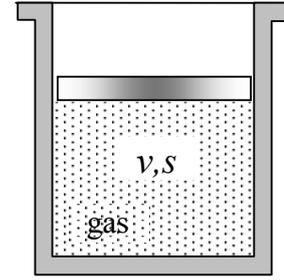
Fig. 1. Ideal gas container

$$R = c_p - c_v = c_v (\kappa - 1).$$

In the paper we will demonstrate that the relationships between the quantities determining thermodynamic state of ideal gas, can be obtained based on the convex analysis of formula describing specific energy of the gas.

Such a presentation of laws of thermodynamics, differs from well-known classic formulations we can find in handbooks. In our opinion, the method to be proposed herein, serves for better understanding of the structure of thermodynamics relations. In many cases it also facilitates the process of formulation of thermodynamics problems. Moreover, the method we propose, is an example of application of the universal physical system laws to the analysis of thermodynamics system.

2. Specific Energy of Ideal Gas

We treat the energy as a physical quantity, which can be perceived, based on experiments, in various forms, via various related physical quantities. Le we assume that in the set of quantities, related to certain form of energy, we can separate a primary quantity from which any quantity can be derived. The results of well-known experiments as well as observations of physical systems, prove this assumption and indicate that the amount of energy accumulated in a separate physical system can be evaluated based on the measurement of the primary physical quantity.

In the case of the ideal gas we analyse the two forms of energy. It is mechanical potential (strain) energy and heat energy. The primary quantities related to these forms of energy are specific volume (v) and specific entropy (s).

Within the classical thermodynamics, the problems to be analysed concern the processes with relatively small velocities of gas particles. In [5], this velocity range was given of 40 m/s. For this reason, the model of an ideal gas can be suited because there is no need, the kinetic energy to be taken into account .

The phenomenon of energy accumulation is described using a function determining an amount of energy with respect to the primary physical quantities. This function, called the energy functional, determines changes in amount of energy to be accumulated in the system with respect to reference state.

The specific energy accumulated in ideal gas is described by the functional $E(v,s)$, which has the following form

$$E(v,s) = E_o \left[\left(\frac{v_o}{v} \right)^{\kappa-1} e^{\frac{s-s_o}{c_v}} - 1 \right],$$

(1)

where:

E_o — gas energy in reference state,

(v_o, s_o) — specific volume and specific entropy in reference state,

κ, c_v — parameters of ideal gas.

The above presented expression, introduced in a similar form in [7], constitutes a synthesis of description of thermodynamics relationships, i.e. the relationships between physical quantities determining the ideal gas state. It means that after mathematical manipulation of this formula, we can obtain the constitutive relations.

The derivative of the energy functional, determines a physical quantity called reciprocal quantity or energetic conjugated quantity with respect to the primary quantity. In the case of energy functional of ideal gas, reciprocal quantities are as follows:

σ_I — one-dimensional stress determining volumetric (isotropic) stress state in the gas,

T — temperature.

The relationships between reciprocal quantities (σ_I, T) and primary quantities (v,s) result from the following equations

$$\sigma_I = \frac{\partial}{\partial v} E(v,s), \qquad T = \frac{\partial}{\partial s} E(v,s).$$

(2)

The values of σ_I obtained from the above expression are negative. Because of this we will use an opposite-sign quantity called pressure

$$p := -\sigma_I, \qquad p = -\frac{\partial}{\partial v} E(v,s).$$

(3)

Differentiating the energy functional we obtain the following constitutive relations of the ideal gas

$$p = \frac{(\kappa-1)E_o}{v_o} \left(\frac{v_o}{v} \right)^{\kappa} e^{\frac{s-s_o}{c_v}}, \qquad T = \frac{E_o}{c_v} \left(\frac{v_o}{v} \right)^{\kappa-1} e^{\frac{s-s_o}{c_v}}.$$

(4)

Let we note, that eliminating the quantity describing entropy *s,* gives the equation of state of the ideal gas formulated by Clapeyron

$$pv = RT.$$

(5)

Based on (4) we can also obtain relationships between p_o, T_o, E_o, occurring in reference state. Substituting $v = v_o$ and $s = s_o$ into (4), gives

$$p_o = \frac{(\kappa-1)E_o}{v_o}, \qquad T_o = \frac{E_o}{c_v}.$$

(6)

Taking into account equations (6), we can obtain new form of relations (4), to be as follows

$$p = p_o \left(\frac{v_o}{v} \right)^\kappa e^{\frac{s-s_o}{c_v}}, \qquad T = T_o \left(\frac{v_o}{v} \right)^{\kappa-1} e^{\frac{s-s_o}{c_v}}. \tag{7}$$

Using (4_2) and (6_2) we may obtain, from equation (1), the following well-known formula for evaluation of gas energy based on temperature value

$$\boldsymbol{E}(v,s) = c_v (T - T_o) \quad \text{if} \quad T = \frac{\partial}{\partial s} \boldsymbol{E}(v,s). \tag{8}$$

The important mathematical property of a functional is convexity, resulting that the matrix of its second derivative is positive definite. In the case of the energy functional, given by equation (1), this matrix has a form

$$\left[\frac{\partial^2 \boldsymbol{E}}{\partial v \partial s} \right] = \alpha(v,s) \begin{bmatrix} \dfrac{\kappa c_v}{v} & , & -1 \\ -1 & , & \dfrac{v}{R} \end{bmatrix}, \quad \alpha(v,s) := (\kappa-1) \frac{T_o}{v_o} \left(\frac{v_o}{v} \right)^\kappa e^{\frac{s-s_o}{c_v}}. \tag{9}$$

It can be proved that the above matrix is positive definite for every $s > 0$ and $v > 0$. Thus, the energy functional of ideal gas is convex with respect to both variables.

3. Conjugated Functionals

In the case of convex functional, it is possible to assign a conjugated functional using Legendre transform, given by

$$F^*\left(x^* \right) := \sup_x \left\{ x^* x - F(x) \right\}, \tag{10}$$

where:

x, x^* – primary and conjugated variables,

F, F^* – primary and conjugated functionals.

We assign to the energy functional of the ideal gas $\boldsymbol{E}$, three conjugated functionals

$$\boldsymbol{E}^*(p,T) := \sup_{v,s} \left\{ -pv + Ts - \boldsymbol{E}(v,s) \right\}, \tag{11}$$

$$\boldsymbol{E}_1^*(p,s) := \sup_v \left\{ -pv - \boldsymbol{E}(v,s) \right\}, \tag{12}$$

$$\boldsymbol{E}_2^*(v,T) := \sup_s \left\{ Ts - \boldsymbol{E}(v,s) \right\}. \tag{13}$$

The above presented funtionals are used in thermodynamics but with an opposite-sign-form (see [1], [3]), to be as follows

– the functional G called free entalpy or Gibs function

$$G(p,T) = -\boldsymbol{E}^*(p,T), \tag{14}$$

– the functional H called entalpy

$$H(p,s) = -E_1^*(p,s), \tag{15}$$

– the functional F called free energy or Helmholtz function

$$F(v,T) = -E_2^*(v,T). \tag{16}$$

Let we use in expressions (11), (12) and (13), the formula describing the gas energy $E(v,s)$ from (1). Thus, we obtain

$$E^*(p,T) = E_o + (s_o - c_p)\,T + c_p T \ln\frac{T}{T_o} + RT \ln\frac{p_o}{p}, \tag{17}$$

$$E_1^*(p,s) = E_o - \frac{\kappa}{\kappa-1}\,pv_o\left[\frac{p_o}{p}\,e^{\frac{s-s_o}{c_v}}\right]^{\frac{1}{\kappa}}, \tag{18}$$

$$E_2^*(v,T) = E_o + (s_o - c_v)\,T + c_v T \ln\frac{T}{T_o} + RT \ln\frac{v}{v_o}. \tag{19}$$

The functional E^* is convex with respect to both variables while E_1^* and E_2^* are convex with respect to conjugated variables (p,T) and non-convex with respect to primary variables (v,s).

Using these functionals it is possible to formulate the following relationships between thermodynamic quantities

$$v = -\frac{\partial E^*(p,T)}{\partial p}, \qquad s = \frac{\partial E^*(p,T)}{\partial T}, \tag{20a}$$

$$v = -\frac{\partial E_1^*(p,s)}{\partial p}, \qquad T = -\frac{\partial E_1^*(p,s)}{\partial s}, \tag{20b}$$

$$p = \frac{\partial E_2^*(v,T)}{\partial v}, \qquad s = \frac{\partial E_2^*(v,T)}{\partial T}. \tag{20c}$$

Let we note that the equations (20a) describe an inverse form of relations given by (2). Differentiating (20a) we obtain

$$v = \frac{RT}{p}, \qquad s = s_o + c_p \ln\frac{T}{T_o} + R\ln\frac{p_o}{p}, \tag{21}$$

while using (20b) gives

$$v = v_o\left(\frac{p_o}{p}\,e^{\frac{s-s_o}{c_v}}\right)^{\frac{1}{\kappa}}, \qquad T = T_o\left[\left(\frac{p_o}{p}\right)^{\kappa-1}e^{\frac{s-s_o}{c_v}}\right]^{\frac{1}{\kappa}}. \tag{22}$$

4. Thermodynamic Equilibrium

Thermodynamic system and its surroundings are considered to be in a state of equilibrium when pressure and temperature of both are the same.

In Fig. 2, we've shown a container with an ideal gas put within a surroundings having the pressure p_z and the temperature T_z to be constant. The static problem of the system, consists in evaluation of specific volume v_z and entropy s_z of the gas, when its pressure and temperature within container are of the same value as in surroundings p_z, T_z.

This problem could be solved using various methods, for example we can use equations (21). The same result will be obtained if we formulate the static problem in an optimization form. In such a case we sould determine the pair (v_z, s_z) minimizing the fonctional

Fig. 2. Gas container and its surroundings

$$\mathbf{E}_c(v, s) := \mathbf{E}(v, s) + p_z v - T_z s . \tag{23a}$$

Thus, we can write

$$(v_z, s_z) = \arg \min_{v,s} \mathbf{E}_c(v, s), \tag{23b}$$

where the functional $\mathbf{E}$ is given by (1).

The solution of the problem (23) determines the relationships between (v_z, s_z) and (p_z, T_z) to be given by (2) and (3). The explicit form of these relations was expressed by (4) or (7). Thus, we can evaluate the pair (v_z, s_z). Having evaluated specific volume and specific entropy (v_z, s_z), determining the state of thermodynamic equilibrium, we can determine an amount of energy to be taken by gas from surroundings, using equation (1). It should be emphasized that the static problem does not describe the process of gas transformation from initial state (v_o, s_o) to the state of equilibrium (v_z, s_z).

5. Thermodynamic Transformations

Thermodynamic transformation is a process consisting in gas state change from initial sate (v_1, s_1), (p_1, T_1) to fianal state (v_2, s_2), (p_2, T_2). Usually, so called quasistatic problems are considered (see [1], [2]). We assume that for quasistatic problem, the state of the gas changes slowly. Thus, the state of the gas can be even out within the container in such a way, the thermodynamic equilibrium to be satisfied in every moment. This assumption makes possible to use the ideal gas model in analysis of the above described processes called reversible processes.

Let we analyse a reversible thermodynamic transformation from the state (v_1, s_1), (p_1, T_1) to the (v_2, s_2), (p_2, T_2). The type of transformation depends on the path, the system follows from the initial state to the final one. This path is determined by the curve ℓ corresponding to arcs ℓ_{vp} and ℓ_{sT}, in coordinate systems to be shown in Fig. 3.

Fig. 3. Termodynamic process chart

During the transformation process, the energy moves from surroundings to the system. The energy increase is determined by a differential, calculated using equations (1), (2) and (3)

$$dE = -p\,dv + T\,ds\,, \qquad p = -\frac{\partial E}{\partial v}\,, \qquad T = \frac{\partial E}{\partial s}\,, \tag{24}$$

Thus, we obtain the description of the transformation via the following contour integral

$$E(v_2, s_2) - E(v_1, s_1) = \int_{\bar{\ell}} \frac{\partial E}{\partial v}\,dv + \int_{\bar{\ell}} \frac{\partial E}{\partial s}\,ds\,. \tag{25}$$

The above equation can be expressed as an energy balance

$$\Delta E_{12}(v_1, s_1; v_2, s_2) = \Delta L_{12}(\ell) + \Delta Q_{12}(\ell), \tag{26a}$$

where the component

$$\Delta E_{12}(v_1, s_1; v_2, s_2) = E(v_2, s_2) - E(v_1, s_1), \tag{26b}$$

determines energy increase in the system. Moreover, the elements depending on the path ℓ

$$\Delta L_{12}(\ell) := \int_{\bar{\ell}} \frac{\partial E}{\partial v}\,dv\,, \qquad \Delta Q_{12}(\ell) := \int_{\bar{\ell}} \frac{\partial E}{\partial s}\,ds$$

determine an amount of energy in mechanical form ΔL_{12} and in heat form ΔQ_{12} to be transferred to the system during transformation. The ΔL_{12} is usually called the work and the ΔQ_{12} - the heat delivered to the system [4].

The above presented equations show that the increase of energy ΔE_{12} is determined only by limit states of the system while the work ΔL_{12} and the heat ΔQ_{12} transferred to the system during transformation, depend on the curve describing the path joining these limit states.

6. Conclusions

It was demonstrated in the paper, how to formulate well-known thermodynamic relations using the energetic description of physical systems. In comparison with classical methods, the procedure to be proposed herein is distinct by the fact of its compact mathematical description. We were analysing only quasistatic processes. Taking into account additional variables describing kinetic energy of the gas, we can obtain functionals suited for dynamic processes analysis.

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