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REGARDING THE APPLICATION LIMITATIONS OF THE CARNOT'S THEOREM

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***Abstract**: The purpose of this article is to perform a comparative study of a reversible heat engine with an ideal or real gas as a working fluid and to determine the change in its efficiency depending on the thermodynamic characteristics of the working fluid. The main research method is the method of thermodynamic potentials, based primarily on the analysis of changes in the free and internal energy of an ideal and real gas in a cyclic process. The theory of thermodynamic potentials is used to consider the Carnot quasistatic heat engine. A comparative analysis of its operation is carried out, for a cycle with both an ideal and a real gas as a working fluid. The possibility of analyzing cyclic processes occurring in heat engines using the method of thermodynamic potentials has been identified and substantiated. The study has shown that the existing formulation of the Carnot's theorem is valid only for ideal gas as a working fluid. Based on the work carried out, the Carnot's theorem in the general case can be formulated, for example, as follows: the efficiency of the heat engine ηr, when it operates at the reversible Carnot cycle with real gas as a working fluid, is determined by the following expression:*

$$\eta_r = 1 - \frac{T_B}{T_A} + \varepsilon,$$

where T_A and T_B are the temperatures of the upper and lower isotherms of the Carnot cycle, respectively; ε is the correction term (positive or negative), depending on the thermodynamic properties of a real gas, which tends to zero as the properties of a real gas approach the properties of an ideal gas.

***Key words**: heat engine; thermodynamic potentials; characteristic functions; Gibbs energy; Helmholtz energy; Carnot's theorem; Carnot cycle; quasistatic process; reversible cyclic process; efficiency of the Carnot cycle; efficiency of heat engines; efficiency.*

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ОБ ОГРАНИЧЕННОСТИ ОБЛАСТИ ПРИМЕНЕНИЯ ТЕОРЕМЫ КАРНО

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***Резюме:** Целью написания данной статьи является сравнительное исследование обратимого теплового двигателя с идеальным или реальным газом в качестве рабочего тела и определение изменения его коэффициента полезного действия в зависимости от* *термодинамических характеристик рабочего тела. Основным методом исследования является метод термодинамических потенциалов, базирующийся, прежде всего на анализе изменения свободной и внутренней энергии идеального и реального газа в циклическом процессе. В статье на основе теории термодинамических потенциалов произведено рассмотрение квазистатического теплового двигателя Карно, в рамках которого осуществлен сравнительный анализ его работы, как для цикла с рабочим телом идеальный газ, так и для цикла с рабочим телом реальный газ. В работе выявлена и обоснована возможность анализа циклических процессов, протекающих в тепловых двигателях с использованием метода термодинамических потенциалов. На основе проведённого исследования установлено, что существующая формулировка теоремы Карно справедлива только для рабочего тела «идеальный газ». В общем случае, на основании проведённой работы, теорема Карно может быть сформулирована, например, следующим образом: коэффициент полезного действия тепловой машины* η_r*, при её функционировании по обратимому циклу Карно с рабочим телом реальный газ, определяется следующей формулой:*

$$\eta_r = 1 - \frac{T_B}{T_A} + \varepsilon,$$

где T_A *и* T_B *— температура, соответственно, верхней и нижней изотерм цикла Карно;* ε *– поправка (положительная или отрицательная), зависящая от термодинамических свойств реального газа, которая стремится к нулю при приближении свойств реального газа к свойствам газа идеального.*

Ключевые слова: *тепловой двигатель; термодинамические потенциалы; характеристические функции; энергия Гиббса; энергия Гельмгольца; теорема Карно; цикл Карно; квазистатический процесс; обратимый циклический процесс; КПД цикла Карно; КПД тепловых двигателей; коэффициент полезного действия.*

Introduction

In a number of previous publications [1, 2, 3], the author used the method of thermodynamic potentials [4, 5] to analyze the simplest thermodynamic processes (mixing of ideal gases and isothermic equilibrium and non-equilibrium expansion of an ideal gas). This work explores the behavior of real gas in thermodynamic cycles and the influence of its properties on the efficiency of heat engines basing on the basic principles underlying the earlier publications. It should be noted that application of the theory of thermodynamic potentials to the “ideal gas mixture” system was a key factor in the appearance of an article entitled “The Gibbs Paradox and its Solution” [1]. So, the author poses the second task of the present work: to indirectly confirm the basic principles underlying this earlier publication. It should be noted that this problem is very actively discussed as a matter of modern thermodynamics, as evidenced, in particular, by the following works [6-10].

In accordance with I. Prigogin [11, p. 81], “Carnot showed that a reversible cyclic heat engine must perform the maximum work (driving force) ...”. Later he [11, p. 81] reports: “If any heat engine could perform more work than a reversible cyclic engine, then an infinite amount of work could be done. First, using a more efficient engine, it was necessary to transfer heat from the hot tank to the cold, then, using a reversible heat engine, return the same amount of heat to the hot tank. Since the direct process gives more work than it is required to complete the reverse process, the result is a gain in work. ... Carnot argued that this was impossible." Note that in this discussion there is a substitution of concepts. In fact, Carnot actually speaks only of volumetric-mechanical work (and only about it), into which the heat supplied to the system is converted (or vice versa, the work is converted to heat), and this phenomenon is observed only when a heat engine with an ideal gas as working fluid is used. At the same time, “Joule and Thomson showed that the vast majority of gases studied by them are cooled during free expansion, since such expansion is associated with work against the internal forces of interaction between gas particles" [12, p. 35]. There is the possibility of heating real gases during expansion [p[1] . 249], however, an increase in gas temperature is a rather rare phenomenon, therefore, in the framework of this work we mainly restrict ourselves to considering the first case. Thus, when using non-ideal gas as a working fluid in the upper Carnot isotherm, the heat supplied to the system is spent both on the performance of volumetric-mechanical work and on maintaining a constant temperature of the "self-cooling" gas. As a result, the isotherm of the real gas will be below the isotherm of the ideal gas [13, p. 22], which should be interpreted as the presence of some internal compressive pressure of real gas. This thesis is illustrated by Fig. 1 "Isotherms for ideal (1) and real (2) gases."

Thus, it can be stated that under isothermal expansion of one mole of a real gas at relatively low pressures (when its volatility coefficient is less than one), the work performed by it will be less than that performed by one mole of an ideal gas at the same pressure change. This is driven by the fact that part of heat received by the non-ideal gas from the hot tank will be spent on maintaining its temperature, which is necessary for an isothermal process due to the presence of its "self-cooling" effect, that is, it is spent on chemical work against the Van der Waals forces. A similar situation, except for the sign, is also observed for the lower isotherm of the Carnot cycle. In this case, attraction of real gas molecules to each other takes place, so when it is compressed by external forces, in addition to heat generated due to mechanical work (as it is observed, for example, for an ideal gas) its self-heating occurs due to strengthening of Van der Waals bonds. So, in this case the chemical work will be performed by the substance itself. This leads to increased, in comparison with the amount of volumetric-mechanical work performed, heat transfer to the refrigerator of the system in question. In addition, we note that it is necessary to take into account the internal energy of a real gas, the change of which actually determines the volumetric-mechanical work of adiabats of the Carnot cycle. It is known that in the general case it depends on the volume of real gas [11, p. 163] and, therefore, the volumetric-mechanical work performed in adiabats (by the system and being done on the system) in this case is not subject to reduction. So it can be argued that when carrying out the Carnot cycle with the participation of real gas, along with the use of heat for performing volumetric-mechanical work, it is also used for performing chemical work, which has an influence on the system efficiency. This phenomenon will be considered in more detail in subsequent sections of this work. In addition, it should be noted that there are no doubts that the considered effects and their values depend on the type of reversible heat engine (thermodynamic cycle), which requires analysis of this factor, but is clearly beyond the scope of this work.

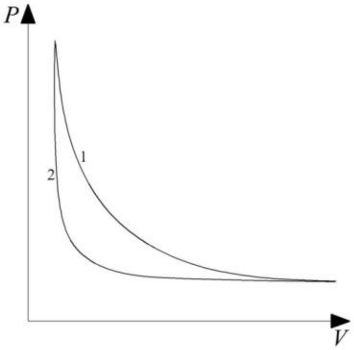

Fig. 1. Isotherms for ideal (1) and real (2) gases

We now return to the Carnot's theorem itself. Its traditional formulation, given, for example, in the monograph by I. Prigogin [11, p. 83], states that the discovery of Carnot "... comes

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[1] Yavorsky B.M. Справочник по физике: справочник / B.M. Yavorsky, A.A. Detlaf. Moscow: Nauka, 1974. (In Russ).

down to the statement that the efficiency of a reversible heat engine is maximum, does not depend on the properties of the heat engine and is a function of only the temperatures of the hot and cold tanks:

$$\eta = 1 - \frac{Q_1}{Q_2} = 1 - f(t_1, t_2) \qquad (1)$$

where $f(t_1, t_2)$ are the function of only temperatures t_1 and t_2 of hot and cold tanks."

Earlier we showed that in the case of real gas this statement is not true. Therefore, the aforecited conclusion of the Carnot's theorem should be attributed exclusively to the working fluid "ideal gas". In case of a real gas, expression (1) becomes simply incorrect, since there appears relationship between η and the gas properties. In the following sections of this article, we show the validity of the stated thesis using specific examples.

Materials and methods

Analysis of the work of the Carnot thermodynamic cycle with the "ideal gas" working fluid can be found in almost any course of thermodynamics. Therefore, we will use one of the variants for studying this issue, basing, for example, on the monograph of I. Prigogin [11, pp. 83–86]. Together with it, we will use the method proposed by the author and presented, in particular, in his work, "Philips and Carnot Heat Engines from the Point of View of the Theory of Thermodynamic Potentials" [3].

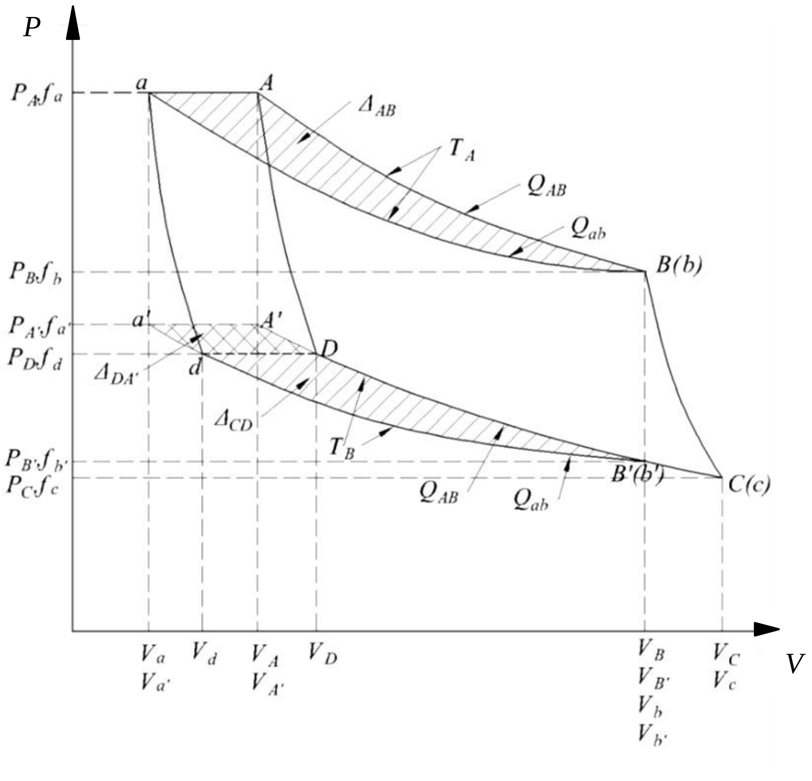

Fig. 2. Carnot cycle in P-V coordinates for ideal and real gas

Fig. 2 shows a graph of the cyclic operation of the Carnot machine in pressure-volume coordinates for one mole of ideal gas and one mole of real gas. Moreover, without loss of generality, it is accepted that the right adiabats and the right parts of isotherms of thermodynamic cycles of real and ideal gases coincide. In other words, the real gas in this case becomes ideal. Using this technique allows us to consider any Carnot cycle with the participation of the real gas

$a - ab - dc - d$ as the difference of two Carnot cycles ("large" $a - b - c - d$ and "small" $ab - b - c - dc$), in which, in their right part, the expansion of real gas is so significant that it becomes an ideal gas. An explanation of this thesis is presented in Fig. 3. In addition, in order to simplify further calculations, we assume that the device under consideration, operating with either ideal or real gas, is in vacuum, and to analyze its operation we use the theory of thermodynamic potentials, assuming that only one mole of gas is always used in the system.

Stage 1. Isothermal transitions at temperature T_A.

Ideal gas. Transition A - B.

In this case, in accordance with I. Prigogin [11, p. 84], external work performed by one mole of ideal gas A_{AB} is determined by the expression

$$A_{AB} = \int_A^B PdV = RT_A \ln \frac{V_B}{V_A}, \tag{2}$$

where P is the gas pressure; V is the current gas volume; V_A and V_B are the ideal gas volumes at the beginning and at the end of the upper isotherm of the Carnot cycle, respectively; T_A is the gas temperature of the upper isotherm of the Carnot cycle, R is the universal gas constant.

When using pressure as an independent variable, the last expression can be rewritten [14, p. 22] in the following form:

$$A_{AB} = \int_A^B VdP = -RT_A \ln \frac{P_B}{P_A}, \tag{3}$$

where P_A and P_B are the ideal gas pressures at the beginning and at the end of the upper isotherm of the Carnot cycle, respectively.

In such an isothermal process involving an ideal gas, heat Q_{AB} is absorbed from the reservoir, and the following equality is fulfilled:

$$A_{AB} = Q_{AB}. \tag{4}$$

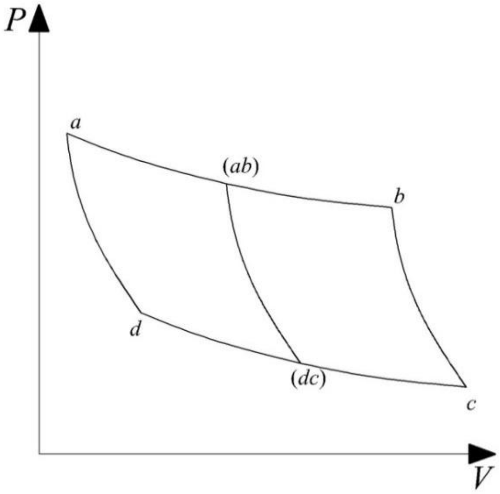

Fig. 3. The scheme of transformation of Carnot cycles with real gas as a working fluid

Real gas. Transition a - b.

In this case, external work performed by real gas A_{ab} is determined by the ratio [14, p. 22]

$$A_{ab} = \int_a^b VdP = -RT_A \ln \frac{f_b}{f_a} \tag{5}$$

where f_a and f_b are the volatilities of real gas at the beginning and end of the upper isotherm of the Carnot cycle, respectively.

Further, the difference between the volumetric-mechanical work of a real gas A_{real} and the volumetric-mechanical work of an ideal gas A_{ideal} will be a certain amount Δ_{AB}, which N. Izmailov calls the excessive work of expansion and is determined [13, p. 22], with the system of signs adopted by us, as follows :

$$\Delta_{AB} = RT_A \ln \frac{P_A}{f_A} = A_{\text{ideal}} - A_{\text{real}}, \tag{6}$$

where A_{ideal} is the isothermal work performed by ideal gas when expanding from pressure P_A to pressure P_B; A_{real} is the isothermal work performed by real gas when expanding from pressure P_A, corresponding to volatility f_a to pressure P_B, at which the real gas becomes an ideal one.

In this case, it can be stated (see Fig. 2) that heat received by the system with real gas (when volatility coefficient is less than one) is consumed both for performing external work A_{ab} and for working against internal pressure forces Δ_{AB}, i.e., the mutual attraction of gas particles. It should be noted that in the *a* - *b* isotherm the amount of heat absorbed by the real gas Q_{ab} remains unchanged, that is, it is equal to the heat absorbed by the ideal gas Q_{AB} in the isotherm *A* - *B*. Thus, for the upper isotherm of the Carnot cycle with alternating participation of the real and ideal gas it can be written:

$$Q_{AB} = Q_{ab}, \tag{7}$$

$$A_{AB} - A_{ab} = \Delta_{AB} > 0\,. \tag{8}$$

Stage 2. Adiabatic transition.

Ideal gas. Transition B - C.

It is known that the only source of energy for performing external work A_{BC}, under adiabatic expansion of an ideal gas, is a change in its internal energy ΔU [14, p. 42]. Therefore, in this case, we can write

$$-\Delta U = C_v(T_A - T_B) = A_{BC}, \tag{9}$$

where C_v is the heat capacity of an ideal gas at a constant pressure, and T_B is the gas temperature in the lower isotherm of the Carnot cycle.

Due to the preconditions imposed on the considered Carnot cycles, an analysis of the adiabatic transition *b* - *c* for a real gas is not required (all its parameters coincide with the parameters of an ideal gas), i.e. in particular $A_{BC} = A_{bc}$.

At the same time, for further research, we need to know the characteristics of an ideal gas at the moment of the end of the right adiabat at a temperature T_B (the beginning of the “lower” isotherm of ideal and real gas). For this purpose, the transition from point B to point C is carried out in two stages. In the first case, we move at a constant volume of ideal gas from point *B* to point *B′* located on the lower isotherm of the Carnot cycle, which will lead to a corresponding change in its internal energy [3]:

$$-\Delta U_{BB'} = C_v(T_A - T_B)\,. \tag{10}$$

The heat released as a result of this process we will direct to a battery, which has a temperature T_B. It should be noted that the volumetric-mechanical work in this case, due to the constancy of the volume of gas, is zero. The further transition of one mole of ideal gas is carried out along the isotherm from point *B′* to point *C*. In this case, as we found out earlier, the external work performed is limited by the amount of heat supplied to the system and going to actually carry out this work (in our case, the amount of heat released as a result of a decrease in internal energy).

Thus, we can write [13, p. 22], taking into account the isothermal equivalence of the Helmholtz and Gibbs energy changes, the following expression:

$$A_{BC} = A_{B'C} = \int_{B'}^{C} PdV = RT_B \ln \frac{V_C}{V_{B'}} = -RT_B \ln \frac{P_C}{P_{B'}}\,. \tag{11}$$

In this case, a combination of equations (10) and (11) allows one to determine the values V_C and P_C corresponding to the volume and pressure of an ideal gas at point *C* of the lower isotherm. Indeed, from these expressions it follows that

$$C_v(T_A - T_B) = RT_B \ln \frac{V_C}{V_{B'}} = -RT_B \ln \frac{P_C}{P_{B'}}\,. \tag{12}$$

In these two equations, only V_C and P_C are unknown. In turn, the external work A_{BC} or A_{bc} of the considered system during its adiabatic transition from point *B* to point *C* will be equal to:

$$A_{BC} = A_{bc} = C_v(T_A - T_B)\,. \tag{13}$$

Stage 3. Isothermal transitions at temperature T_B *.*

Ideal gas. Transition C - D.

We will consider this process by analogy with stage 1.

In this case, in accordance with I. Prigogin [11, p. 85], external work (negative) performed on an ideal gas is determined by the expression

$$A_{CD} = \int_{C}^{D} PdV = RT_B \ln \frac{V_D}{V_C}\,. \tag{14}$$

When using pressure as an independent variable, the last relation can be rewritten [13, p. 22] in the following form:

$$A_{CD} = \int_{C}^{D} VdP = -RT_B \ln \frac{P_D}{P_C}\,. \tag{15}$$

In such an isothermal process involving an ideal gas, heat Q_{CD} is transferred to the refrigerator, and the following equality is fulfilled:

$$A_{CD} = Q_{CD}\,. \tag{16}$$

Real gas. Transition c - d.

In this case, external work (negative) A_{cd} performed on real gas is determined by the equation

$$A_{cd} = \int_{c}^{d} PdV = RT_B \ln \frac{V_d}{V_c}\,. \tag{17}$$

When using pressure as an independent variable and volatility f, the last relation can be rewritten [13, p. 22]:

$$A_{cd} = \int_{c}^{d} VdP = -RT_B \ln \frac{f_d}{f_c} = -RT_B \ln \frac{f_d}{P_c}\,. \tag{18}$$

In turn, the difference between the values of the work of the real and ideal gases will be a certain amount Δ_{CD} (negative), which N. Izmailov calls the excess work of expansion and is determined in this case [13, p. 22] as follows:

$$\Delta_{CD} = -RT_B \ln \frac{P_D}{f_d} = A_{CD} - A_{cd}\,. \tag{19}$$

Therefore, the heat Q_{CD} generated by the system with real gas in the isothermal process *c* – *d* and transferred to the refrigerator can be decomposed into two components:

– Heat received as a result of the actual transformation of mechanical work with the participation of external forces acting on the system, and quantitatively equal to this work: $-RT_B \ln \frac{f_d}{P_c}$;

– Heat received as a result of work performed due to the attraction of molecules (Van der Waals forces), which is equal to Δ_{CD}.

Thus, it can be stated that in this case, external work is completely converted into heat; moreover, heat is also generated due to the work caused by the forces of Van der Waals.

Stage 4. Adiabatic transitions.

Perfect gas. Transition D - A.

In this subsection, we will use the results obtained by us when analyzing stage 2, which will have opposite signs due to the fact that the process under consideration proceeds in the opposite direction. All necessary explanations can be obtained from the analysis of Fig. 2: it can be seen that the considered transition is divided into two parts: isothermal *D* - *A′* and isochoric *A′* - *A*. It is known that under adiabatic compression of an ideal gas, a change in its internal energy is numerically equal to the volumetric-mechanical work performed on it [14, p. 42]. Therefore, in this case, an increase in internal energy is observed, and the following relation can be written:

$$\Delta U_{DA} = C_v (T_A - T_B) = -A_{DA}. \tag{20}$$

Thus, for transition *D* - *A*, given the the Helmholtz and Gibbs energies change equivalence in this case, we can write [15, p. 42]:

$$A_{DA} = A_{DA'} = \int_D^{A'} PdV = RT_B \ln \frac{V_{A'}}{V_D} = -RT_B \ln \frac{P_{A'}}{P_D}. \tag{21}$$

The combination of the last two equations allows one to determine V_D and P_D, corresponding to the volume and pressure of an ideal gas at point *D* of the lower isotherm. Indeed, from these equalities it follows that

$$-C_v (T_A - T_B) = RT_B \ln \frac{V_{A'}}{V_D} = -RT_B \ln \frac{P_{A'}}{P_D}. \tag{22}$$

In turn, from the latter expressions one can easily calculate the considered values V_D and P_D by means of simple algebraic transformations.

Real gas. Transition d - a

We will analyze this process by analogy with the *D* - *A* transition, replacing the corresponding pressures by volatilities, and the molar volumes of an ideal gas by molar volumes of real gas. All necessary explanations can be obtained by analyzing Fig. 2, from which it can be seen that the transition under consideration is divided into two parts: the isothermal *d* - *a′* and the isochoric *a′* - *a*.

It is known that during adiabatic compression of gas, a change in its internal energy is numerically equal to the volumetric-mechanical work performed on it [14, p. 42]. Therefore, in this case, an increase in internal energy is observed, and the following relation can be written:

$$\Delta U_{da} = C_r (T_A - T_B) = -A_{da} \tag{23}$$

where C_r is the heat capacity of real gas at a constant volume V_a, which in general case can be a function of both temperature and volume. In our discussions, without loss of generality, in order to simplify the analysis, we accept it depending only on the real gas volume. As for the previous discussions, the volumetric-mechanical work is concentrated in the section *d* - *a′*, and accordingly it is equal to zero in the section *a′* - *a*. Then, taking into account the comments made, we get:

$$A_{da} = A_{da'} = \int_d^{a'} PdV = RT_A \ln \frac{V_{a'}}{V_d} = -RT_A \ln \frac{f_{a'}}{f_d}. \tag{24}$$

The last two equations allow, using simple algebraic transformations, to calculate the parameters of the real gas V_d and f_d at the point *d*.

3. Results and discussion

3.1 Efficiency of the Carnot cycle with ideal gas

In accordance with I. Prigogin [11, p. 86], the efficiency of the Carnot cycle with an ideal gas η_i is determined by the formula

$$\eta_i = \frac{A_i}{Q_{AB}} = 1 - \frac{T_B}{T_A}, \tag{25}$$

where A_i is the total amount of work produced by the considered system.

We show that the results we obtained in the previous paragraph using the method of thermodynamic potentials coincide with the latter formula. To do this, we use fig. 2. The amount of heat entering the system in our case, as well as in the usual version of analysis of this process, is equal to Q_{AB} and equals to work performed at this stage A_{AB}.

To determine the work on the adiabat *B* - *C*, one can use the results of the previous paragraph (stage 2). In this case, the third-external work performed by the system is “concentrated” on the isotherm with temperature T_B and is determined by the following expression:

$$A_{BC} = C_v(T_A - T_B). \tag{26}$$

A similar situation, except for the sign, is observed when considering the transition along the adiabat *D* - *A*. External work performed on the system is concentrated on the isotherm with temperature T_B and is determined in this case by the formula

$$A_{DA} = -C_v(T_A - T_B) = -A_{BC}. \tag{27}$$

Thus, the total work performed on the upper isotherm and two adiabats, i.e., on the section D - A - B - C, will be equal to

$$A_{DABC} = A_{AB} + A_{BC} + A_{DA}. \tag{28}$$

However, knowing that

$$A_{DA} = -A_{BC}, \tag{29}$$

we obtain

$$A_{DABC} = A_{AB} = RT_A \ln\frac{V_B}{V_A}. \tag{30}$$

It is known that for negative external work performed on the lower isotherm of the Carnot cycle, we can write:

$$A_{CD} = RT_B \ln\frac{V_D}{V_C}. \tag{31}$$

In addition, consideration of the geometry of Fig. 2 allows us to state that the following equality is true

$$\ln\frac{V_B}{V_A} = \ln\frac{V_{B'}}{V_{A'}}. \tag{32}$$

At the same time, taking into account the fact that on the lower isotherm the same amount of work, determined by expression $A_{BC} = -A_{DA} = C_v(T_A - T_B)$ is added and subtracted to the work $A_{A'B'} = RT_B \ln\frac{V_{B'}}{V_{A'}}$, it becomes possible to assert that its value remains unchanged and, therefore, the following relation is true:

$$RT_B \ln\frac{V_B{}'}{V_A{}'} = RT_B \ln\frac{V_C}{V_D}. \tag{33}$$

And finally, compiling the last equation with the previous one, we get

$$\ln\frac{V_B}{V_A}=\ln\frac{V_C}{V_D}\,. \tag{34}$$

Taking into account the last three expressions and substituting the expressions for work A_{CD} and A_{DABC} into the expression that determines the efficiency of an ideal gas allows us to obtain the following formula:

$$\eta_i=\frac{RT_A\ln\frac{V_B}{V_A}+RT_B\ln\frac{V_D}{V_C}}{RT_A\ln\frac{V_B}{V_A}}=1-\frac{T_B}{T_A}\,. \tag{35}$$

This expression for the Carnot cycle efficiency completely coincides with a similar relation obtained in traditional way [1, p. 86], which confirms the correctness of the method of thermodynamic potentials for solving the problems under consideration. In the next subsection of this publication, we complicate the task somewhat by applying the method of thermodynamic potentials to analyze the efficiency of the Carnot cycle with the “real gas” working fluid.

3.2. Efficiency of the Carnot cycle with real gas

In case of Carnot cycle with a “real gas” working fluid, its efficiency η_r can be calculated using a formula similar to the corresponding formula for an ideal gas:

$$\eta_r=\frac{A_r}{Q_{ab}}\,. \tag{36}$$

However, the expression for the work, we denote it here A_r, will look somewhat different, since we have to use the concept of volatility instead of pressure in these calculation, and instead of the ideal gas volume, we use the real gas volume. In this case (see Fig. 2), the determination of the cycle efficiency can be carried out using the technique used in the previous paragraph of this paper. As before, we assume that the amount of heat Q_{ab} is equal to heat entering the system. And, in turn, the work performed by the system in the section *a* - *b* will be determined by the formula

$$A_{ab}=RT_A\ln\frac{V_b}{V_a}=-RT_A\ln\frac{f_b}{f_a}\,. \tag{37}$$

Note that in this case, in accordance with the analysis carried out in Paragraph 4, A_{ab} and Q_{ab} and are not equal to each other. To determine the work A_{bc} in section b - c from point b of the upper isotherm along the isochore, we descend to the intersection with the lower isotherm at point b′, and then we move along the lower isotherm to point *c*. Then the total work on the section *b* - *b′* - *c*, due to the constancy of the volume, on the isochore will be concentrated on the segment b′ - c and is equal to the following value:

$$A_{bb'c}=A_{b'c}=RT_B\ln\frac{V_c}{V_{b'}}=-RT_B\ln\frac{f_c}{f_{b'}}=-RT_B\ln\frac{P_c}{P_{b'}}=C_v(T_A-T_B)\ . \tag{38}$$

Note that according to the terms of the problem, the properties of ideal and real gases coincide in this area, and the corresponding heat capacities are equal to each other. At the same time, the solution of the latter relation relative to f_c, P_c and V_c allows one to determine the properties of the considered gas at point *c*.

To determine the point *d* - the end of the lower isotherm of the Carnot cycle - we use the following technique. From point *a* of the upper isotherm *a* - *b*, along the isochor *a* - *a′* we descend to the point *a′* located on the continuation of the lower isotherm *c* - *d*, and then move along the isotherm *a′* - *c* to point *d*.

In fact, in the Carnot cycle, the movement along the adiabat under consideration proceeds in the opposite direction, which requires appropriate consideration by setting the signs in the following formula:

$$A_{da'a} = A_{da'} = -A_{a'd} = RT_B \ln \frac{V_{a'}}{V_d} = -RT_B \ln \frac{f_{a'}}{f_d} = -C_r(T_A - T_B)\,. \tag{39}$$

where C_r is the heat capacity of real gas, at a constant volume V_a .

We note that the solution of the last expression in relation to f_d and V_d allows one to determine the properties of a real gas at point *c*.

Thus, the total work performed on the upper isotherm and two adiabats, i.e., on the section *d* - *a* - *b* - *c*, will be equal to:

$$A_{dabc} = A_{ab} + A_{b'c} + A_{da'}\,. \tag{40}$$

However, due to the fact that in this case, for the adiabats *b* - *c* and *d* - *a*, the heat capacities are not equal to each other, i.e. $C_r \neq C_v$, so

$$A_{b'c} \neq -A_{da'}\,. \tag{41}$$

Thus, based on the last two formulas, we obtain the expression:

$$\begin{aligned} A_{dabc} &= RT_A \ln \frac{V_b}{V_a} + RT_B \ln \frac{V_c}{V_{b'}} + RT_B \ln \frac{V_{a'}}{V_d} = \\ &= -RT_A \ln \frac{f_b}{f_a} - RT_B \ln \frac{f_c}{f_{b'}} - RT_B \ln \frac{f_{a'}}{f_d}. \end{aligned} \tag{42}$$

At the same time, taking into account the data from the previous paragraph, for work (negative), which was performed on the system on the isotherm c - d, we obtain the following expression:

$$A_{cd} = RT_B \ln \frac{V_d}{V_c} = -RT_B \ln \frac{f_d}{f_c}\,. \tag{43}$$

It is more convenient to present the last two ratios in the form

$$A_{dabc} = RT_A \ln \frac{V_B}{V_A} - \Delta_{AB} + RT_B \ln \frac{V_C}{V_{B'}} - \Delta_{B'C} + RT_B \ln \frac{V_{A'}}{V_D} - \Delta_{DA'}\,, \tag{44}$$

$$A_{cd} = RT_B \ln \frac{V_D}{V_C} - \Delta_{CD}\,, \tag{45}$$

where Δ_{AB}, $\Delta_{B'C}$, $\Delta_{DA'}$ and Δ_{CD} is the corresponding redundant expansion work, and according to the conditions of the problem $\Delta_{B'C} = 0$.

Substitution of expressions for work A_{cd} and A_{dabc} in expression that determines the efficiency allows us to obtain the formula

$$\begin{aligned} \eta_r &= \frac{RT_A \ln \frac{V_B}{V_A} - \Delta_{AB} + RT_B \ln \frac{V_C}{V_{B'}} - \Delta_{B'C} + RT_B \ln \frac{V_{A'}}{V_D} - \Delta_{DA'}}{RT_A \ln \frac{V_B}{V_A}} + \\ &+ \frac{RT_B \ln \frac{V_D}{V_C} - \Delta_{CD}}{RT_A \ln \frac{V_B}{V_A}} = 1 - \frac{T_B}{T_A} + \varepsilon \end{aligned}\,. \tag{46}$$

It is more convenient to present the obtained equation in the form:

$$\eta_r = \eta_i + \varepsilon\,, \tag{47}$$

where

$$\varepsilon = \frac{-\Delta_{AB} + RT_B \ln \dfrac{V_C}{V_{B'}} - \Delta_{B'C} + RT_B \ln \dfrac{V_{A'}}{V_D} - \Delta_{DA'} - \Delta_{CD}}{RT_A \ln \dfrac{V_B}{V_A}}. \tag{48}$$

Analysis of the last formula allows us to state that the value ε that distinguishes the efficiency of the Carnot cycle with a working fluid “real gas” from the efficiency of the Carnot cycle with a working fluid “ideal gas” is a complex function of temperature of the cycle isotherms and the thermodynamic properties of the real gas that distinguish it from the ideal gas. In addition, it can be concluded that the efficiency of a real gas can, depending on the value of the volatility coefficient of a real gas, exceed or be less than the efficiency of an ideal gas. A more detailed analysis of the issue can be performed only taking into account the specific properties of the working fluid, that is, including the analysis of the contribution of various quantities Δ to the correction term ε.

An indirect confirmation of the validity of the obtained formula is the fact that when the equality $\Delta_{AB} = \Delta_{B'C} = \Delta_{DA'} = \Delta_{CD} = 0$ is true, that is, during the transformation of real gas into ideal gas, the following quantities are simultaneously reduced in the last formula: $RT_B \ln \dfrac{V_C}{V_{B'}}$ and $RT_B \ln \dfrac{V_{A'}}{V_D}$. Thus, in this case, the correction term ε becomes equal to zero, and the real gas is transformed into ideal gas.

Consequently, it can be stated that the efficiency of the quasistatic Carnot cycle is determined, in particular by the properties of a real gas. From the point of view of electrochemistry [15, p. 18], this result is quite expected, since it is known that with the equilibrium course of electrochemical reactions, the external work carried out by means of chemical energy can occur both with absorption and with the release of heat. In other words, a quasistatic system can perform additional, for example, volumetric-mechanical, work due to a chemical process that takes place with the absorption of heat from the environment or vice versa, with the release of heat into the environment. In this article this well-known principle is applied to a new object - the Carnot thermodynamic cycle.

4. Conclusions

Thus, based on the performed work, the following conclusions can be drawn:

1. The existing formulation of the Carnot – Clausius theorem is valid only for the “ideal gas” working fluid.

2. In general case, based on the presented calculations, the Carnot – Clausius theorem can be formulated, for example, as follows: the efficiency of a heat engine η_r when it is operated on a reversible Carnot cycle with a “real gas” working fluid is determined by the following formula:

$$\eta_r = 1 - \frac{T_B}{T_A} + \varepsilon \tag{49}$$

where T_A and T_B are the temperatures of the upper and lower isotherms of the Carnot cycle, respectively; ε is the correction term (positive or negative), depending on the thermodynamic properties of a real gas, which tends to zero as the properties of a real gas approach the properties of an ideal gas.

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