

# The Thermodynamics Cycles with a Reversible Chemical Reaction

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**Abstract:** The relevance: In the modern world, there is an urgent need for the efficient use of all possible heat sources for the subsequent production of mechanical work or electrical energy. The gradual depletion of fossil fuels on the planet is bringing humanity closer to a large-scale energy crisis. Since the conversion of heat into freely convertible work or electrical energy is possible with the help of heat engines, it is necessary to look for new ways to improve them. One of these ways can be the use of thermodynamic cycles with reversible chemical reactions. The main aim of the investigation of thermodynamic cycles with reversible chemical reactions, comparison and analysis of the results obtained and formulation of conclusions. Object: thermodynamic cycles of Carnot, Brighton and Stirling; mixtures of gases capable of changing their composition as a result of a reversible chemical reaction; chemical work. Methods: solving the problem of finding the efficiency coefficient using analytical methods solving the problem of finding the efficiency coefficient using analytical methods. Results: A Brighton, Carnot and Stirling thermodynamic cycles is considered in which the working substance is a chemically reacting gas with molar weight and heat capacity changing as a result of a reversible chemical reaction. By way of example, the reactions  $N_2 + 3H_2 \rightarrow 2NH_3$  and  $CO + 2H_2 \leftrightarrow CH_3OH$  is considered. For a constant heat supply, the cycles is characterized by the lower ( $T_{low}$ ) and upper ( $T_{top}$ ) temperature boundaries of existence; between these boundaries, the efficiency  $\eta$  can change from 0 to 1. Such peculiar properties are manifested because of two factors: reversibility of the chemical reaction and the special role of the chemical work in the conversion of heat into mechanical work, which minimizes the heat loss to the surrounding space in a closed thermodynamic cycles. The possibility of achieving a thermal efficiency in them equal to 1 in a limited temperature range does not depend on the type of cycle. The value of efficiency in Carnot and Stirling machines depends on the method of heat supply and removal at isotherms. Each of the Carnot, Stirling and Brighton cycles is characterized, respectively, by its parameter  $\alpha_C$ ,  $\alpha_{St}$  and  $\alpha_{Br}$ , which determines the condition for achieving efficiency  $\eta = 1$ . Heat engines operating on thermodynamic cycles with reversible chemical reactions are most efficient when using low potential heat sources.

**Keywords:** Thermodynamic Cycle, Reversible Chemical Reaction, Chemical Work, Efficiency

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## 1. Introduction

In modern physics, the second law of thermodynamics is associated with the impossibility of creating heat engines with efficiency equal to or greater than one [1, 2]. At the same time, as a justification for such a statement, in particular, a reversible thermodynamic Carnot cycle is considered, where in order to produce mechanical work from the incoming (specific) heat  $q_{in}$  and close the cycle, it is necessary to dissipate part of the thermal energy entering the machine into the environment.

The environment together with the heat engine forms an

extended adiabatic system, then heat dissipation (specific anergy  $q_{out}$ ) by the machine can be called energy dissipation of the first kind, corresponding to a small change in (specific) entropy [1, 2]<sup>1</sup>

$$d_e s = \frac{\delta q_{out}}{T}, \quad (1)$$

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<sup>1</sup> In [3],  $q_{in}$  is used instead of  $q_{out}$ , but since it refers to the entropy produced by the machine in the environment,  $q_{in}$  is replaced by  $q_{out}$ .

where  $T$  is the temperature. The part of the received heat  $q_{ex}$  exergy that is converted into work does not lead to an increase in entropy, for ideal machines  $q_{ex} = q_{in} - q_{out}$ .

At the same time, in real machines, energy dissipation also occurs due to friction forces of various nature and radiation, the entropy differential for such a dissipation of the second kind is equal to  $d_i s$ . Any energy dissipation leads to an increase in entropy, but its increment in a short time  $dt$  in the second case  $d_i s$  is proportional to the product of thermodynamic forces  $X_k$  and flows  $J_k$ ,  $k = 1, 2, \dots$ :

$$d_i s = dt \sum_k X_k J_k. \quad (2)$$

The total change in entropy  $ds$  is equal to the sum of  $d_e s$  and  $d_i s$ :

$$ds = \frac{\delta q_{out}}{T} + dt \sum_k X_k J_k. \quad (3)$$

The above two types of dissipation do not allow in real machines to achieve the efficiency value = 1 in principle, since  $d_i s > 0$  is always present. Any thermal machine produces entropy along with work. A distinctive feature of the dissipation of the first kind and des is that they can theoretically be reduced to zero (but not equal to zero) by using a refrigerator with a temperature near absolute zero or efficient use of energy inside the machine.

Modern approaches to increasing efficiency are based on the choice of new thermodynamic cycles [3–5], the selection of working substances [6–8], and the reduction of energy losses to the ambient level [9–11]. However, if the working substance can change its properties as a result of a chemical transformation, the process of conversion of specific heat  $q_{in}$  into specific work  $w$  involves chemical work  $w_{ch}$ . If  $I$  components of a mixture of substances with  $n_i$  molecules or atoms ( $i = 1, 2, \dots, I$ ) are transformed into one another, change  $dw_{ch}$  in the chemical work is given by [1].

$$dw_{ch} = \sum_{i=1}^I \frac{\partial u}{\partial n_i} dn_i, \quad (4)$$

where  $u$  is the internal specific energy. Number of particles  $n_i$  of the mixture components with mass  $m$  can be defined in terms of relative mass concentrations  $g_i$ :

$$n_i = \frac{m N_A}{\mu_i} g_i. \quad (5)$$

Here,  $N_A$  is the Avogadro number and  $\mu_i$  is the molar mass of the  $i$ -th substance.

This article will show the possibility of creating new heat engines, in which the working substance can change physical properties as a result of a reversible chemical reaction. Theoretically, such machines (cycles) have a very high thermal efficiency. Therefore, they are of interest for practice, since they can have a serious impact on the energy sector in the near future.

## 2. A Model of Chemical Transformation and the form of Writing the First Law of Thermodynamics

A simple model of chemical transformation is used below [12]: the working substance (ideal gas) takes two extreme states A and C, these states are identified as gases A and C. They are characterized by molar masses  $\mu_A$  and  $\mu_C$ , heat capacities at constant volume  $c_{v,A} = \text{const}$  and  $c_{v,C} = \text{const}$ , and heat capacities at constant pressure  $c_{p,A} = \text{const}$  and  $c_{p,C} = \text{const}$ .

In the initial mixture, gas A at the maximum temperature (heater)  $T_{\max}$  during the chemical reaction turns into product C, at the minimum temperature (cooler)  $T_{\min}$ , the reverse reaction occurs, and C turns into A. This is represented by general chemical equations

$$T = T_{\max}: A \rightarrow C; T = T_{\min}: C \rightarrow A.$$

In the area of the chemical reaction, both substance A and product C are contained. The thermal effect of a chemical reaction is assumed to be zero to simplify calculations. The chemical transformation is tracked by the relative mass concentration of the first substance  $g_A$ , the concentration of the second substance  $g_C = 1 - g_A$ ,

$$g_A = \frac{m_A}{m}, \quad g_C = \frac{m_C}{m},$$

where  $m_A$  and  $m_C$  are the masses of components A and C. The gas mixture is characterized by its heat capacity at constant volume  $c_v$ , constant pressure  $c_p$  and mass  $m = m_A + m_C$ .

In general, the differentials of the specific internal energy  $du$  and the enthalpy  $dh$  are determined by the equalities [12].

$$du = c_v dT + (c_{v,A} - c_{v,C}) T dg_A, \quad (6)$$

$$c_v = (c_{v,A} - c_{v,C}) g_A + c_{v,C};$$

$$dh = c_p dT + (c_{p,A} - c_{p,C}) T dg_A, \quad (7)$$

$$c_p = (c_{p,A} - c_{p,C}) g_A + c_{p,C}.$$

Here, the terms containing the  $dg_A$  differential represent chemical work. Then the first law of thermodynamics can be written in two forms:

$$c_v dT + (c_{v,A} - c_{p,C}) T dg_A = -p dv + \delta q; \quad (8)$$

$$c_p dT + (c_{p,A} - c_{p,C}) T dg_A = v dp + \delta q, \quad (9)$$

where  $q$  and  $v$  are specific heat and volume;  $p$  is pressure.

Since an ideal gas is considered below, there are no additives of heat of mixing and dissolution in (6) and (8).

Equations (6) and (8) are the basic equalities for studying thermodynamic cycles with reversible chemical reactions.

In a conditional initial state, gas A at a high temperature  $T >$

$T_{\text{mid}}$  is converted in the course of a chemical reaction into product C; at a low temperature  $T < T_{\text{mid}}$ , the reverse reaction occurs, and C is converted into A. Here,  $T_{\text{mid}}$  is the middle temperature at which chemical equilibrium sets in, and the rate of direct reaction equals the rate of the reverse reaction. This can be expressed by the general chemical equation.

In the general case, temperature  $T_{\text{mid}}$  depends on pressure  $p$  [13], but, to simplify the analysis, this dependence is assumed to be weak. At an arbitrary instant, the region in which the chemical reaction occurs contains both substance A and product C. Both components of the mixture have heat capacities at constant volume  $c_{v,A} = \text{const}$  and  $c_{v,C} = \text{const}$ , molar masses  $\mu_A$  and  $\mu_C$ , and constant adiabatic exponents  $\gamma_A$  and  $\gamma_C$ , respectively.

### 3. Brighton Cycle

In practice, the Brighton cycle is used in gas turbine units (Figure 1); in the upper heat exchanger at pressure  $p_{\text{max}}$ , specific heat  $q_{2 \rightarrow 3}$ , J/kg, is supplied to the working gas; through the lower heat exchanger, heat per unit mass  $q_{1 \rightarrow 4}$ , J/kg, is removed at pressure  $p_{\text{min}}$ ; the total specific mechanical work is denoted by  $w_{\Sigma}$ , J/kg.

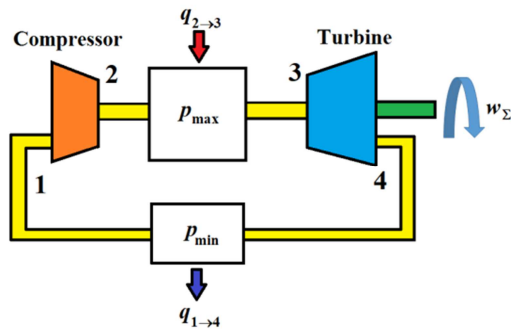


Figure 1. Diagram of a gas-turbine engine with the Brayton cycle; digits indicate nodal points for determining thermodynamic parameters.

The Brighton cycle is shown on pressure  $p$  vs. specific volume  $v$  diagram (Figure 2), where the reaction  $A \rightarrow C$  occurs in the upper isobar segment  $2 \rightarrow 3$  at pressure  $p_{\text{max}} = \text{const}$ , while the reaction  $C \rightarrow A$  occurs on the lower segment  $4 \rightarrow 1$  at pressure  $p_{\text{min}} = \text{const}$ . The change in the gas composition is traced from the value of relative mass concentration  $g_A$  of the first substance. Gas A is compressed on adiabat  $1 \rightarrow 2$ , while gas C expands on adiabat  $3 \rightarrow 4$ .

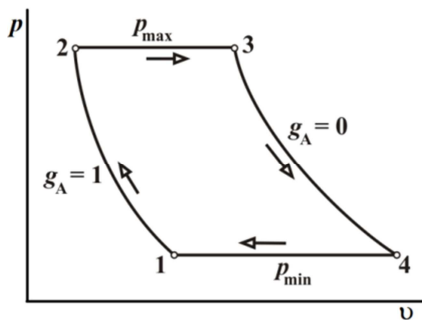


Figure 2. Thermodynamic Brighton cycle with a reversible chemical reaction and concentrations  $g_A$  on adiabatic segments.

For the thermal efficiency, the formula is found [14].

$$\eta_{\text{Br}} = 1 - \frac{q_{1 \rightarrow 4}}{q_{2 \rightarrow 3}}, \quad (10)$$

$$q_{1 \rightarrow 4} = c_{p,C} T_3 \left( \frac{T_1}{T_2} \right)^\alpha - c_{p,A} T_1,$$

$$q_{2 \rightarrow 3} = c_{p,C} T_3 - c_{p,A} T_2.$$

Temperatures  $T_1$ ,  $T_2$  and  $T_3$  are determined at points 1, 2 and 3.

Here, reversible chemical reactions are assumed to occur in hypothetical machines, as an example, the calculation of heat, work and efficiency was carried out for the reaction of synthesis and decomposition of ammonia  $\text{N}_2 + 3\text{H}_2 \leftrightarrow 2\text{NH}_3$  at a temperature  $T_{\text{min}} = 400$  K and a pressure of 30 MPa [15]. Substance A corresponds to  $\text{NH}_3$ , substance C is a mixture of  $3\text{H}_2/\text{N}_2$ . Molar mass  $\mu_A = 17$  and  $\mu_C = 8.5$  g/mol; heat capacity  $c_{p,A} = 2287$  and  $c_{p,C} = 3430$  J·kg<sup>-1</sup>·K<sup>-1</sup>. The heat capacities and molar masses correspond to the adiabatic values  $\gamma_A = 1.272$  and  $\gamma_C = 1.399$ , they are calculated by the equations [2].

$$\gamma_A = \left( 1 - \frac{R}{c_{p,A} \mu_A} \right)^{-1}, \quad \gamma_C = \left( 1 - \frac{R}{c_{p,C} \mu_C} \right)^{-1}. \quad (11)$$

Figure 3 shows the results of calculation of  $\eta_{\text{Br}}$  (10) and Carnot efficiency  $\eta_0$  [14]:

$$\eta_0 = 1 - \frac{T_{\text{min}}}{T_{\text{max}}}. \quad (12)$$

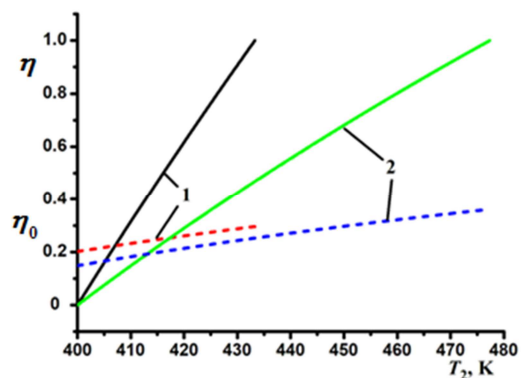


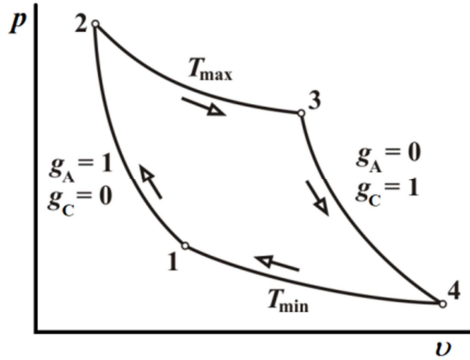
Figure 3. Dependences of efficiencies  $\eta$  (solid curves) and  $\eta_0$  (dashed curves) on compression temperature  $T_2 > T_1$  for the following values of  $q_{2 \rightarrow 3}$ : (curve 1) 0.1 MJ/kg; (curve 2) 0.25 MJ/kg.

This figure shows the possibility of achieving the highest value  $\eta_{\text{Br}} = 1$  in limited temperature ranges.

### 4. Carnot Cycle with a Reversible Chemical Reaction

In practice, the Carnot cycle is difficult to implement, but

the results obtained on the basis of its analysis serve as a good guideline in the development of heat engines with other thermodynamic cycles [1, 2]. Therefore, consideration in the first place of the Carnot cycle with chemical transformations can give practical results. The Carnot cycle in  $p$ - $v$  coordinates is shown in figure 4, where gas A with adiabatic exponent  $\gamma_A$  rises from initial state 1 with temperature  $T_{\min}$  to  $T_{\max}$  by adiabatic compression, point 2 corresponds to this.



**Figure 4.** Constant values of temperature  $T_{\min}$  and  $T_{\max}$  and mass concentration  $g_A$  in different parts of the Carnot cycle.

For the Carnot cycle (and further, for the Stirling cycle), it is necessary to use the dependence  $g_A(\rho)$ ,  $\rho = 1/v$ . Это необходимо для вычисления удельной работы

$$w = \int p dv = RT \int \frac{dv}{\mu v}. \quad (13)$$

The molar mass of the mixture

$$\frac{1}{\mu} = \left( \frac{1}{\mu_A} - \frac{1}{\mu_C} \right) g_A + \frac{1}{\mu_C} \quad (14)$$

contained here depends on the mass fraction  $g_A(\rho) = g_A(v)$ . Therefore, the function  $g_A(\rho)$  is taken as an approximation

$$g_A = \frac{\rho_A}{\rho} \frac{\rho - \rho_C}{\rho_A - \rho_C}, \quad (15)$$

where  $\rho_A$ ,  $\rho_C$  are the densities of the components A and C. This dependence is considered as one of the possible, in fact, there can be infinitely many different forms of  $g_A(\rho)$ .

The equation for the efficiency factor  $\eta_C$  can be written as

$$\eta_C = 1 - \frac{T_{\min}}{T_{\max}} F(\omega_1, \omega_2), \quad (16)$$

$$F(\omega_1, \omega_2) = \frac{F_0 + \ln \omega_1 + \frac{\mu_C - \mu_A}{\mu_A} \frac{\omega_1 \ln \omega_1}{\omega_1 - 1}}{F_0 + \ln \omega_2 + \frac{\mu_C - \mu_A}{\mu_A} \frac{\omega_2 \ln \omega_2}{\omega_2 - 1}},$$

$$F_0 = \frac{\gamma_C}{\gamma_C - 1} - \frac{\mu_C}{\mu_A} \frac{\gamma_A}{\gamma_A - 1},$$

$$\omega_1 = \omega_2 \left( \frac{T_{\max}}{T_{\min}} \right)^{\alpha_C}, \quad \alpha_C = \frac{\gamma_A - \gamma_C}{(\gamma_C - 1)(\gamma_A - 1)}.$$

If  $\mu_A = \mu_C$  and  $\gamma_A = \gamma_C$ , then  $F(\omega_1, \omega_2) = 1$ , and equation (16) yields the Carnot efficiency for a chemically inert working gas  $\eta_0$  (12).

In the theory of the Carnot cycle with a chemically inert working gas ( $\mu_C = \mu_A$ ), the equation [1, 2] holds for the (in points 1...4) pressure ratio

$$\frac{p_2}{p_1} = \frac{p_3}{p_4}. \quad (17)$$

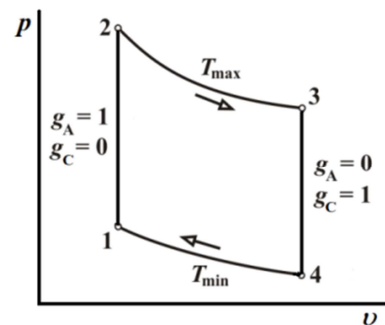
Then and  $\omega_1 = \omega_2$ . But in the presence of a reversible chemical reaction, such a ratio for pressure is not fulfilled,  $\omega_1 \neq \omega_2$ , so Figure 4 should be taken as an approximate image of the Carnot cycle.

When performing the calculation efficiency  $w_{1 \rightarrow 4}$  and  $w_{2 \rightarrow 3}$  should have a positive sign, so not any combination of numeric parameters  $\omega_2$ ,  $\mu_C$ ,  $\mu_A$ ,  $\gamma_C$  and  $\gamma_A$  relationship temperatures  $T_{\max}$  and  $T_{\min}$  have a physical meaning. Thermodynamics considers processes from the most general positions, therefore it is possible to obtain results devoid of physical content.

If the substances A and C are different, then the numerical value of  $F(\omega_1, \omega_2)$  can be either greater or less than one. To fulfill  $\eta_C > \eta_0$  must be  $F(\omega_1, \omega_2) < 1$ . From the last inequality we find the condition  $\alpha_C < 0$ , or,  $\gamma_C > \gamma_A$ . As a rule, the smaller the molar weight of a gas and the number of atoms in its molecule, the greater the adiabatic exponent. But the adiabatic index characterizes the ability of gases to compress (and expand) under external influence. Therefore, we can say that the possibility  $\eta_C > \eta_0$  is determined by the scheme of transformation of substances, and gas A on the left adiabat of Figure 4 must contract/expand weaker than the gas C on the right adiabat.

## 5. Effectiveness of a Stirling Machine With a Reversible Chemical Reaction

The Stirling machine in modern engineering is considered as one of the most promising devices for converting heat into mechanical work and its numerous improved versions are known [9, 16]. The Stirling cycle consists of two isotherms and isochores (Figure 5).



**Figure 5.** Stirling cycle with a reversible chemical reaction in  $p$ - $v$  coordinates.

As in the Carnot cycle (Figure 4), the chemical transformation occurs on isotherms  $2 \rightarrow 3$  and  $4 \rightarrow 1$ , in the isochoric sections  $1 \rightarrow 2$  and  $3 \rightarrow 4$  the composition of the working gas remains constant, work is not performed in them. In section  $1 \rightarrow 2$ , gas A receives heat  $q_{1 \rightarrow 2} = c_{v,A}(T_{\max} - T_{\min})$ , in section  $3 \rightarrow 4$  heat is removed from gas C:  $q_{3 \rightarrow 4} = -c_{v,C}(T_{\max} - T_{\min})$ .

The efficiency of Stirling machine  $\eta_{St}$  is given by the equation

$$\eta_{St} = 1 - \frac{T_{\min}}{T_{\max}} G(\omega), \quad (18)$$

$$G(\omega) = \frac{G_{0,1} + G_1}{G_{0,2} + G_1}, \quad G_1 = \left( 1 + \frac{\mu_C - \mu_A}{\mu_A} \frac{\omega}{\omega - 1} \right) \ln \omega,$$

$$G_{0,1} = \frac{1}{\gamma_C - 1} \frac{T_{\max}}{T_{\min}} - \frac{\mu_C}{\mu_A (\gamma_A - 1)},$$

$$G_{0,2} = \frac{1}{\gamma_C - 1} - \frac{\mu_C}{\mu_A (\gamma_A - 1)} \frac{T_{\min}}{T_{\max}},$$

$$\omega = \omega_1 = \frac{v_4}{v_1} = \frac{v_3}{v_2} = \omega_2.$$

If the chemical composition of the working gas does not change, then  $c_{v,C} = c_{v,A} = c_v$ ,  $\mu_A = \mu_C = \mu$  and  $\gamma_A = \gamma_C = \gamma$ , then the well-known expression [16] is obtained from (18)

$$\eta_{St} = 1 - \frac{T_{\min} + T_*}{T_{\max} + T_*}, \quad T_* = \frac{c_v \mu}{R \ln \omega} (T_{\max} - T_{\min}), \quad (19)$$

where  $R$  is the universal gas constant. The condition  $\eta_{St} > \eta_0$  is satisfied if  $G(\omega) < 1$ . A simple analysis leads to the requirement

$$\alpha_{St} > \frac{T_{\max}}{T_{\min}}, \quad \alpha_{St} = \frac{\mu_C (\gamma_C - 1)}{\mu_A (\gamma_A - 1)}. \quad (20)$$

The parameter  $\alpha_{St}$  defines the property of the working gas, the ratio  $T_{\max}/T_{\min}$  defines the operating condition of the machine. Depending on whether  $\alpha_{St} > 1$  or  $\alpha_{St} < 1$ , you can choose the operating condition of the Stirling machine with the maximum production of mechanical work.

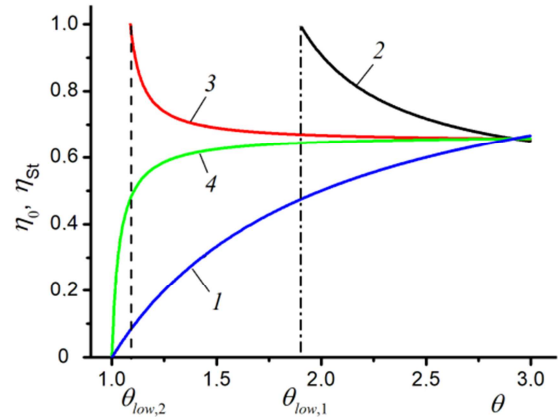
Consider the reaction of the formation of methanol  $\text{CO} + 2\text{H}_2 \leftrightarrow \text{CH}_3\text{OH}$ , at a pressure of 20 MPa and a high temperature (about 400°C), a heavy gas  $\text{CH}_3\text{OH}$  is formed, which at a low temperature (about 20°C) decomposes into a light mixture of hydrogen  $\text{H}_2$  and carbon monoxide  $\text{CO}$ .

Here, substance A is a mixture of  $\text{CO}/\text{H}_2$ , substance C is methanol  $\text{CH}_3\text{OH}$ . There is the following set of parameters: molar masses  $\mu_A = 10.67$  and  $\mu_C = 32$  g/mol; the average values of the heat capacity of hydrogen  $c_{p,\text{H}_2}$  and carbon monoxide  $c_{p,\text{CO}}$  at a pressure of 20 MPa and a temperature range of 20...400°C are  $c_{p,\text{H}_2} = 14.8$ ,  $c_{p,\text{CO}} = 1.16$  kJ·kg<sup>-1</sup>·K<sup>-1</sup> [15].

These data correspond to the adiabatic index of the mixture  $\gamma_A = 1.37$ . The physical properties of methanol vary in a

complex and ambiguous way depending on pressure and temperature, since it is near the critical point, but the reference data [15] approximately indicate  $\gamma_C = 1.36$ . Then the parameter  $\alpha_{St} = 2.92 > 1$ . Temperature  $T_{\min} = 300$  K.

Below are the results obtained on the basis of equations (16) and (18). Here, too, high efficiency values are possible, and the Stirling machine can surpass the Carnot machine in this indicator (Figure 6). The dimensionless temperature  $\theta = T_{\max}/T_{\min}$  is used here.



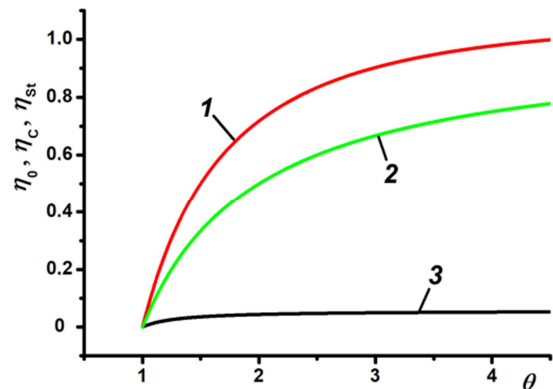
**Figure 6.** Reaction  $\text{CO} + 2\text{H}_2 \leftrightarrow \text{CH}_3\text{OH}$ . Dependences of  $\eta_0$  (line 1) and  $\eta_{St}$  (lines 2–4) and on dimensionless temperature  $\theta$  at various  $\omega = 1.5$  (line 2),  $\omega = 4$  (line 3) and  $\omega = 5$  (line 4). The dashed-dotted and dashed lines indicate the points of the lower temperature limits  $\theta_{low,1}$  and  $\theta_{low,2}$ .

Figure 7 shows the efficiencies  $\eta_C$ ,  $\eta_0$  and  $\eta_{St}$  as functions of the dimensionless temperature  $\theta$  in the case of the reaction  $\text{N}_2 + 3\text{H}_2 \leftrightarrow 2\text{NH}_3$ .

The Carnot cycle considered here has two features:

- 1) the efficiency coefficient  $\eta_C > \eta_0$ , since  $\alpha_C < 0$ ;
- 2) solutions that have physical meaning are not possible at all temperatures  $T_{\max}$ .

The area of existence of the cycle (machine) in Figure 7 is located between the lower  $T_{low} = T_{\min}$  ( $\theta = 1$ ) and the upper  $T_{top} = 1800$  K ( $\theta = 4.5$ ) boundaries of the possible temperature change  $T_{\max}$ . At the lower and upper temperature boundaries, respectively,  $\eta_C = 0$  and  $\eta_C = 1$  (Figure 7), but at the upper boundary  $\eta_0 = 0.57$ .



**Figure 7.** Carnot and Stirling cycle and reaction  $\text{N}_2 + 3\text{H}_2 \leftrightarrow 2\text{NH}_3$ . Dependences of the efficiency  $\eta_C$  (line 1),  $\eta_0$  (line 2) and  $\eta_{St}$  (line 3) on the dimensionless temperature  $\theta$ .

With increasing  $\theta$  (or  $T_{\max}$ ), the heat dissipation  $q_{1 \rightarrow 4} = w_{1 \rightarrow 4} + u_{1 \rightarrow 4}$  decreases and at the upper bound  $q_{1 \rightarrow 4} = 0$  and the entropy differential  $d_e s = 0$ .

At  $T > T_{\text{top}}$ , the heat is  $q_{1 \rightarrow 4} < 0$  ( $q_{4 \rightarrow 1} > 0$ ), but this means heat supply and has no physical meaning.

## 6. Conclusions

In the modern theory of thermal machines [1, 2], the Carnot cycle occupies a special position as having the highest efficiency among all possible, all other cycles are compared with it when evaluating their efficiency. The analysis carried out above shows that in the case of reversible chemical reactions in the working gas, there is no special cycle among the three considered. Each thermodynamic cycle is characterized by its own parameter  $\alpha_C$ ,  $\alpha_{St}$  and  $\alpha_{Br}$ , the value of which determines its greatest efficiency. The expediency of using a particular cycle in practice is determined by the conditions of its operation and the properties of the working gas.

The resulting values of efficiency  $\eta = 1$  in the Brighton cycle [14] and in the Carnot and Stirling cycles with a reversible chemical reaction correspond to an increase in entropy  $d_e s = 0$ , which does not contradict the fundamentals of thermodynamics. This is realized due to the conversion of the energy  $q_{4 \rightarrow 1}$  to zero, since the heat necessary for discharge into the environment is converted into the internal energy of the working gas. At the same time, it becomes possible to close the cyclic process.

Previously, reversible chemical reactions were considered [17-20] as a way of accumulating the internal energy of the working substance from various sources and, if necessary, releasing it for the production of mechanical work or electrical energy. But in [14] and above, reversible reactions are considered as direct participants in the conversion of incoming heat into mechanical work in thermal machines.

Analysis of the Brighton, Carnot and Stirling cycles has revealed a strong effect of the chemical work on the efficiency. Three main physical parameters (the ratio of the maximal and minimal temperatures, the molar mass, and the adiabatic exponent) affecting the reaction have also been established. To obtain high efficiencies of heat engines with the Brayton, Carnot and Stirling cycles, the following conditions must be satisfied:

- (i) the working substance must be chemically reactive reversibly in certain temperature intervals;
- (ii) the physical properties of the working substance must change, and adiabatic exponent  $\gamma_A$  of the gas in the compressor (in Brighton cycle) must be smaller than adiabatic exponent  $\gamma_C$  in the turbine; the same should be the case on the expansion section in the Carnot and Stirling cycles;
- (iii) the chemical work must be comparable in magnitude with the supplied heat and be negative on segment  $4 \rightarrow 1$  for the cycle to become closed due to the chemical work.

Machines with reversible chemical reactions are like biological objects: they can operate in a limited temperature range from  $T_{\text{low}}$  to  $T_{\text{top}}$ , but have a high efficiency [14].

Therefore, it is possible that in the future heat engines will look like living organisms.

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