Study on the Circulation Efficiency of Different Nonideal Gases

Yuwei Yin*

School of Science, Tianjin University, Tianjin, 300000, China

*Corresponding Author: yinyuwei0912_@tju.edu.cn

Abstract. The thermodynamic properties of two kinds of representative non-ideal real gases van der Waals gas and Onnes gas are expounded and discussed by common thermodynamic methods, and the specific expressions of heat engine efficiency based on Carnot cycle, Stirling cycle and Otto cycle with these two real gases as working fluids are derived through theoretical derivation and calculation. On this basis, the variation rules of various thermal efficiency corresponding to heat engine with cycle parameters (such as high-temperature heat source temperature T1, low-temperature heat source temperature T2, the isovolumetric molar heat capacity of gas, initial volume V in the cycle process, gas volume expansion ratio r) are analyzed, and the general rules which are helpful to improve the efficiency of heat engine are found. This work will provide some theoretical reference for the optimal design of the actual operating conditions of the heat engine.

Keywords: Van Der Waals Gas; Onnes Gas; Carnot Cycle; Stirling Cycle; Otto Cycle.

1. Introduction

Heat engine, a kind of machine that converts heat energy into mechanical energy, is widely used in industrial production. Heat engine cycle has always been an important part of heat engine research [1]. The heat engine cycle has various advantages, but its energy conversion efficiency has been at a low level [2]. Too low heat conversion efficiency will cause a lot of energy loss, which is not in line with the current trend of green development. In recent years, the topic of how to improve the thermal efficiency of heat engine has attracted wide attention [3]. Recently, the topic of how to improve the thermal efficiency of heat engine has attracted extensive attention [4]. Existing studies have confirmed that the maximum thermal efficiency of traditional cylinder-piston steam engines is about 20%, the efficiency of improved steam engines is about 40% [5], the efficiency of mass-produced gasoline engines is about 40% [6], and the thermal efficiency of diesel engines is about 45%~50% [7-8]. The thermal efficiency of single-engine gas turbine is generally 32%~45%, while the efficiency of dual-engine combined cycle heat units is about 52%~66% [9-10]. Obviously, the energy utilization efficiency of heat engine needs to be further improved, so it is of great significance to analyze and study the efficiency of heat engine.

In the theoretical analysis, the ideal gas is conventionally used as the analysis object, but its equation of state deviates obviously under the actual conditions of high pressure and low temperature. In addition, in industrial production, the actual gas as a working medium is a non-ideal real gas. It is known that van der Waals gas and Onnes gas are two representative non-ideal gas models [11], so this paper studies these two gases. In the aspect of heat engine thermal cycle efficiency, a large number of scholars have carried out a great deal of related work in recent years. Ye Xingmei et al analyzed the heat loss process of van der Waals gas using Otto cycle as working fluid. Jiang Guisheng et al. provided the efficiency expression of the Diesel cycle with an ideal gas as the working substance, obtained the efficiency expression of the Diesel cycle with an ideal quantum gas as the working substance according to its equation of state and its thermodynamic properties by taking an ideal Fermi gas as an example, and summarized the main ways to improve the efficiency of the actual heat engine by comparison. However, the research on the specific expression of heat engine efficiency needs to be further improved.

Accordingly, van der Waals gas and Onnes gas, two non-ideal gas models, are applied as simulation objects to analyze and study the thermal efficiency of Carnot cycle, Stirling cycle and Otto cycle, the expression of cycle efficiency is derived by thermodynamic method, the variation law of

thermal efficiency with cycle parameters(high-temperature heat source temperature T1, low-temperature heat source temperature T2, isovolumetric molar heat capacity of gas, initial volume V of the cycle process and gas volume expansion ratio r) is analyzed, and the general law which is beneficial to the improvement of heat engine efficiency is obtained.

2. Thermodynamic Processes of Two Nonideal Gases

2.1 Basic Thermodynamic Relationships

For infinitesimal thermodynamic processes, it can be known from the first law of thermodynamics that [12,13]:

$$dQ = dU + PdV \tag{1}$$

Wherein, Q represents the heat exchanged between the gas and the outside world, U represents the internal energy of the gas, P represents the pressure of the gas, and V represents the volume of the gas.

Taking temperature and volume as independent variables, then the internal energy U [5] is $U(T,V)$, and its total differential is

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{2}$$

According to thermodynamic theory, it can be proved by applying Carnot's theorem [7,9]:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{3}$$

The above Eqs. (1) to (3) are the most basic thermodynamic formulas, and are applicable to any gas model, both for van der Waals and Onnes gas.

2.2. Thermodynamic process of van der Waals gas

Considering that gas molecules attract and repel each other, Dutch physicists van der Waals and Clausius modified the ideal gas equation of state to obtain the van der Waals equation [14]. The equation of state for 1molvan der Waals gas is:

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \tag{4}$$

Wherein, R represents a universal gas constant, V represents the molar volume of a gas, and a and b are constants for a certain gas [7,11]. According to the experimental results, the correction of gas pressure by attraction and repulsion between actual gases is described respectively. The equation (1) is substituted for the thermodynamic relationship [12]:

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0$$

This means that the isovolumetric molar heat capacity C_V of van der Waals gas is only a function of temperature and has nothing to do with volume [9,11]. The characteristic temperature of the internal thermal motion of the gas molecule is relatively high. at the usual temperature, the contribution of the internal thermal motion to the heat capacity can not be considered, but only the heat capacity caused by the translation and rotation of the molecule can be considered. In this case, the isovolumetric molar heat capacity CV can be regarded as a constant independent of temperature, which can be recorded as:

$$C_V = C_V^0$$

From the definition of equal volume molar heat capacity [5], it is expressed as:

$$C_V = C_V^0 = \left(\frac{\partial U}{\partial T}\right)_V$$

And the Eqs. (3) and (4) are combined to:

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$$

Substitute into Eq. (2) to get:

$$dU = C_V^0 dT + \frac{a}{V^2} dV \tag{5}$$

Substitute Eq. (5) into Eq. (1):

$$dQ = C_V^0 dT + \frac{RT}{V-b} dV \tag{6}$$

The following discusses the related formulas of several typical processes: (let the subscript of the initial state be 1 and the subscript of the final state be 2).

In the adiabatic process, the system has no energy exchange with the outside world, so $dQ = 0$, therefore:

$$T(V-b)^{\frac{R}{C_V^0}} = const \tag{7}$$

Combining Eq. (1), since $dQ = 0$:

$$W = -\Delta U = -\int_1^2 dU = C_V^0 (T_1 - T_2) + \frac{a}{V_2} - \frac{a}{V_1} \tag{8}$$

Isothermal process:

In this process $dT = 0$, substitute into Eq. (5),

$$\Delta U = \int_1^2 dU = \frac{a}{V_1} - \frac{a}{V_2} \tag{9}$$

Combined with Eq. (6),

$$Q = \int_1^2 dQ = RT \ln\left(\frac{V_2 - b}{V_1 - b}\right) \tag{10}$$

Combined with Eq. (1),

$$W = Q - \Delta U = RT \ln\left(\frac{V_2 - b}{V_1 - b}\right) + \frac{a}{V_2} - \frac{a}{V_1} \tag{11}$$

Isometric process:

Taking the volume V as an invariant, so

$$W = \int_1^2 PdV = 0 \tag{12}$$

$$Q = \int_1^2 dQ = C_V^0 (T_2 - T_1) \tag{13}$$

2.2 Thermodynamic process of Onnes gas

Onnes gas's equation of state is the equation of state of gas expressed by series expansion according to the property that the real gas tends to be an ideal gas when the pressure tends to zero [7,12]. The equation of state of 1molOnnes gas is [5]:

$$PV = A + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \cdots$$

Wherein, A, B, C, D, … represent the first [3], second, third, fourth, ... virial coefficients, which are functions of temperature, and since $A = RT$, so:

$$PV = RT + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \cdots \tag{14}$$

From Eq. (3), it is,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{R}{V}+\frac{\partial B}{\partial T}\frac{1}{V^2}+\frac{\partial C}{\partial T}\frac{1}{V^3}+\frac{\partial D}{\partial T}\frac{1}{V^4}+\cdots\right)-\left(\frac{RT}{V}+\frac{B}{V^2}+\frac{C}{V^3}+\frac{D}{V^4}+\cdots\right)$$

So,

$$dU = C_V^1 dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{15}$$

Wherein, C_V^1 represents the isovolumetric molar heat capacity of Onnes gas. The magnitude of B, C, D, ... decreases rapidly and the value is small, so when the temperature T does not change much, $\frac{\partial B}{\partial T}$, $\frac{\partial C}{\partial T}$ and $\frac{\partial D}{\partial T}$ can be used as invariants [3]. Because of this, the following infinite virial coefficients can be ignored in practical applications [5]. The first four virial coefficients are considered when calculating efficiency.

Substitute Eq. (16) for the thermodynamic relationship [12]:

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0$$

This shows that the isovolumetric molar heat capacity C_V^1 of Onnes gas is only a function of temperature and has nothing to do with volume [9,11].

In addition, when the range of temperature variation in the problem under discussion is not large, the isovolumetric molar heat capacity C_V^1 can be regarded as a constant [3].

Substitute Eq. (7) into Eq. (1), it is obtained:

$$dQ = C_V^1 dT + T\left(\frac{R}{V}+\frac{\partial B}{\partial T}\frac{1}{V^2}+\frac{\partial C}{\partial T}\frac{1}{V^3}+\frac{\partial D}{\partial T}\frac{1}{V^4}+\cdots\right)dV \tag{16}$$

When in an adiabatic process, $dQ = 0$, so $\frac{dQ}{T} = 0$, the integral is:

$$C_V^1 \ln T + R\ln V + \frac{\partial B}{\partial T}\left(\frac{-1}{V}\right)+\frac{\partial C}{\partial T}\left(\frac{-1}{2V^2}\right)+\frac{\partial D}{\partial T}\left(\frac{-1}{3V^3}\right)+\cdots = const \tag{17}$$

3. Ideal Carnot Cycle

Carnot cycle is an ideal cycle that does not exist in the actual heat engine. Carnot theorem shows that the efficiency of any actual heat engine can not exceed that of Carnot cycle, because the efficiency of Carnot cycle is the theoretical extreme value of the efficiency of actual heat engine. As shown in Fig. 1, the Carnot cycle includes isothermal expansion from state 1->state 2, adiabatic expansion from state 2->state 3, isothermal compression from state 3->state 4, and adiabatic compression from state 4->state 1. The following will analyze the efficiency of Carnot cycle when van der Waals gas and Onnes gas are used as real gas models, respectively.

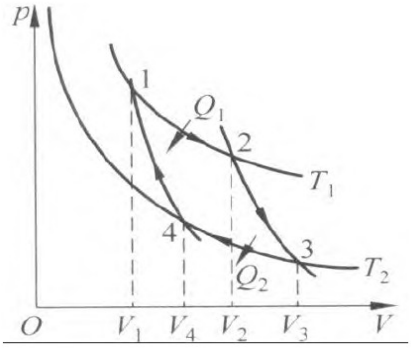


Fig. 1 P-V diagram of the Carnot cycle [14]

3.1 Van Der Waals Gas

State 1—>State 2:

$$W_{12} = RT_1 \ln\left(\frac{V_2 - b}{V_1 - b}\right) + \frac{a}{V_2} - \frac{a}{V_1} > 0$$

$$Q_1 = RT_1 \ln\left(\frac{V_2 - b}{V_1 - b}\right) > 0$$

State 2—>State 3: $Q = 0$

$$W_{23} = C_V^0 \left(T_1 - T_2\right) + \frac{a}{V_3} - \frac{a}{V_2} > 0$$

State 3—>State 4:

$$W_{34} = RT_2 \ln\left(\frac{V_4 - b}{V_3 - b}\right) + \frac{a}{V_4} - \frac{a}{V_3} < 0$$

State 4—>State 1: $Q = 0$

$$W_{41} = C_V^0 \left(T_2 - T_1\right) + \frac{a}{V_1} - \frac{a}{V_4} < 0$$

So, the efficiency is:

$$\eta_1 = \frac{W_{12} + W_{23} + W_{34} + W_{41}}{Q_1} = \frac{RT_1 \ln\left(\frac{V_2 - b}{V_1 - b}\right) + RT_2 \ln\left(\frac{V_4 - b}{V_3 - b}\right)}{RT_1 \ln\left(\frac{V_2 - b}{V_1 - b}\right)}$$

Then, in combination with Eq. (7),

$$T_1 \left(V_2 - b\right)^{\frac{R}{C_V^0}} = T_2 \left(V_3 - b\right)^{\frac{R}{C_V^0}}$$

$$T_1 \left(V_1 - b\right)^{\frac{R}{C_V^0}} = T_2 \left(V_4 - b\right)^{\frac{R}{C_V^0}}$$

Substitute these two expressions into the efficiency expression:

$$\eta_1 = 1 - \frac{T_2}{T_1} \tag{18}$$

3.2 Onnes gas

State 1—>State 2:

$$Q_1 = \int_1^2 dQ = RT_1 \ln\frac{V_2}{V_1} + T_1 \frac{\partial B}{\partial T}\left(\frac{1}{V_1} - \frac{1}{V_2}\right) + T_1 \frac{\partial C}{\partial T}\left(\frac{1}{2V_1^2} - \frac{1}{2V_2^2}\right) + T_1 \frac{\partial D}{\partial T}\left(\frac{1}{3V_1^3} - \frac{1}{3V_2^3}\right) + \cdots > 0$$

State 2—>State 3: $Q = 0$

State 3—>State 4:

$$Q_2 = \int_3^4 dQ = RT_2 \ln\frac{V_4}{V_3} + T_2 \frac{\partial B}{\partial T}\left(\frac{1}{V_3} - \frac{1}{V_4}\right) + T_2 \frac{\partial C}{\partial T}\left(\frac{1}{2V_3^2} - \frac{1}{2V_4^2}\right) + T_2 \frac{\partial D}{\partial T}\left(\frac{1}{3V_3^3} - \frac{1}{3V_4^3}\right) + \cdots < 0$$

State 4—>State 1: $Q = 0$

So, the efficiency is:

$$\eta_2 = \frac{Q_1 + Q_2}{Q_1} = 1 + \frac{Q_2}{Q_1}$$

Apply Eq. (19) to State 2—> State 3 and State 4—> State 1,

$$C_V^1 \ln T_1 + R\ln V_2 + \frac{\partial B}{\partial T}\left(\frac{-1}{V_2}\right) + \frac{\partial C}{\partial T}\left(\frac{-1}{2V_2^2}\right) + \frac{\partial D}{\partial T}\left(\frac{-1}{3V_2^3}\right) + \cdots = C_V^1 \ln T_2 + R\ln V_3 + \frac{\partial B}{\partial T}\left(\frac{-1}{V_3}\right) + \frac{\partial C}{\partial T}\left(\frac{-1}{2V_3^2}\right) + \frac{\partial D}{\partial T}\left(\frac{-1}{3V_3^3}\right) + \cdots$$

$$C_V^1 \ln T_1 + R\ln V_1 + \frac{\partial B}{\partial T}\left(\frac{-1}{V_1}\right) + \frac{\partial C}{\partial T}\left(\frac{-1}{2V_1^2}\right) + \frac{\partial D}{\partial T}\left(\frac{-1}{3V_1^3}\right) + \cdots = C_V^1 \ln T_2 + R\ln V_4 + \frac{\partial B}{\partial T}\left(\frac{-1}{V_4}\right) + \frac{\partial C}{\partial T}\left(\frac{-1}{2V_4^2}\right) + \frac{\partial D}{\partial T}\left(\frac{-1}{3V_4^3}\right) + \cdots$$

Substitute these two expressions into the efficiency expression:

$$\eta_2 = 1 - \frac{T_2}{T_1} \tag{19}$$

In the above discussion, the actual gas model applied is different, but the efficiency of Carnot cycle is the same, and the expression (18) (19) reflects that the Carnot efficiency is only related to the temperature of the heat source and has nothing to do with other factors. Obviously, improving high-temperature heat source temperature and reducing low-temperature heat source temperature will contribute to improving Carnot cycle efficiency. According to the relevant contents of Carnot theorem, it is also helpful to improve the theoretical limit of actual heat engine efficiency under the same high temperature heat source and low temperature heat source.

4. Non-Ideal Cycle

4.1 Stirling Cycle

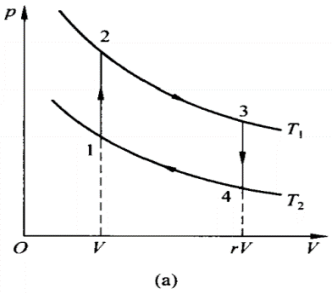


Fig. 2 P-V diagram of Stirling cycle [11]

Stirling cycle is a cycle that can be applied to an actual heat engine. As shown in Fig. 2, the stirring cycle includes the isovolumetric endotherm of state 1->state 2, the isothermal expansion of state 2->state 3, the isothermal heat release of state 3->state 4, and the isothermal compression of state 4->state 1. In the following, the van der Waals gas model and the Onnes gas model will be used to analyze and calculate the efficiency of the stirring cycle.

4.1.1. Van Der Waals Gas

State 1—>State 2: The volume is constant

$$Q_1 = \int_1^2 dQ = C_V^0 \left(T_1 - T_2\right) > 0$$

State 2—>State 3:

$$Q_2 = \int_2^3 dQ = RT_1 \ln\left(\frac{rV - b}{V - b}\right) > 0$$

State 3—>State 4: The volume is constant

$$Q_3 = \int_3^4 dQ = C_V^0 \left(T_2 - T_1\right) < 0$$

State 4—>State 1:

$$Q_4 = \int_4^1 dQ = RT_2 \ln\left(\frac{V - b}{rV - b}\right) < 0$$

So,

$$\eta_3 = \frac{Q_1 + Q_2 + Q_3 + Q_4}{Q_1 + Q_2} = \frac{1 - \frac{T_2}{T_1}}{1 + \frac{C_V^0}{R}\left(1 - \frac{T_2}{T_1}\right)\left[\ln\left(\frac{rV - b}{V - b}\right)\right]^{-1}} \tag{20}$$

Wherein, r represents the volume expansion ratio, V represents the initial volume during the cycle, and T_2 represents low-temperature heat source temperature, T_1 represents high-temperature heat source temperature, C_V^0 represents the isovolumetric molar heat capacity of van der Waals gas.

So,

$$\eta_3 < \frac{1-\frac{T_2}{T_1}}{1} = 1-\frac{T_2}{T_1}$$

This verifies the correctness of Carnot theorem to a certain extent, and the theoretical extreme value of Stirling cycle with van der Waals gas as working medium is the Carnot cycle efficiency under the same working conditions (high temperature heat source and low temperature heat source are the same).

When analyzing the variation of efficiency with parameters, let:

$$x = \ln\left(\frac{rV-b}{V-b}\right) > 0$$

So,

$$\eta_3 = \frac{1-\frac{T_2}{T_1}}{1+\frac{C_V^0}{R}\left(1-\frac{T_2}{T_1}\right)x^{-1}} \tag{21}$$

Taking the partial derivatives for each parameter, we get:

$$\frac{\partial \eta_3}{\partial x} > 0 \tag{22}$$

$$\frac{\partial \eta_3}{\partial\left(1-\frac{T_2}{T_1}\right)} > 0 \tag{23}$$

$$\frac{\partial \eta_3}{\partial C_V^0} < 0 \tag{24}$$

Then take the partial derivative of x with respect to r and V, since (b>0 [7,12]), we can get:

$$\frac{\partial x}{\partial V} < 0 \tag{25}$$

$$\frac{\partial x}{\partial r} > 0 \tag{26}$$

4.1.2. Onnes gas

State 1—>State 2: The volume is constant, $dV = 0$

$$Q_1 = \int_1^2 dQ = C_V^1\left(T_1 - T_2\right) > 0$$

State 2—>State 3: The temperature is constant

$$Q_2 = \int_2^3 dQ = RT_1 \ln r + T_1\frac{\partial B}{\partial T}\left(\frac{1}{V}-\frac{1}{rV}\right) + T_1\frac{\partial C}{\partial T}\left(\frac{1}{2V^2}-\frac{1}{2r^2V^2}\right) + T_1\frac{\partial D}{\partial T}\left(\frac{1}{3V^3}-\frac{1}{3r^3V^3}\right) + \cdots > 0$$

State 3—>State 4: The volume is constant

$$Q_3 = \int_3^4 dQ = C_V^1\left(T_2 - T_1\right) < 0$$

State 4—>State 1: The temperature has always been T_2

$$Q_4 = \int_4^1 dQ = -RT_2 \ln r - T_2\frac{\partial B}{\partial T}\left(\frac{1}{V}-\frac{1}{rV}\right) - T_2\frac{\partial C}{\partial T}\left(\frac{1}{2V^2}-\frac{1}{2r^2V^2}\right) - T_2\frac{\partial D}{\partial T}\left(\frac{1}{3V^3}-\frac{1}{3r^3V^3}\right) + \cdots < 0$$

So, the efficiency is:

$$\eta_4 = \frac{Q_1 + Q_2 + Q_3 + Q_4}{Q_1 + Q_2} = \frac{\left(1 - \frac{T_2}{T_1}\right) y}{y + C_V^1 \left(1 - \frac{T_2}{T_1}\right)} \tag{27}$$

Wherein:

$$y = R \ln r + \frac{\partial B}{\partial T}\left(\frac{1}{V} - \frac{1}{rV}\right) + \frac{\partial C}{\partial T}\left(\frac{1}{2V^2} - \frac{1}{2r^2V^2}\right) + \frac{\partial D}{\partial T}\left(\frac{1}{3V^3} - \frac{1}{3r^3V^3}\right)$$

So,

$$\eta_4 < \frac{\left(1 - \frac{T_2}{T_1}\right) y}{y} = 1 - \frac{T_2}{T_1}$$

This verifies the correctness of Carnot's theorem to a certain extent, and the efficiency of Carnot cycle is indeed the theoretical limit that can not be achieved when Onnes gas is used as the working medium of Stirling cycle.

By calculating the partial derivative, the following can be obtained:

$$\frac{\partial \eta_4}{\partial y} > 0 \tag{28}$$

$$\frac{\partial \eta_4}{\partial \left(1 - \frac{T_2}{T_1}\right)} > 0 \tag{29}$$

$$\frac{\partial \eta_4}{\partial C_V^1} < 0 \tag{30}$$

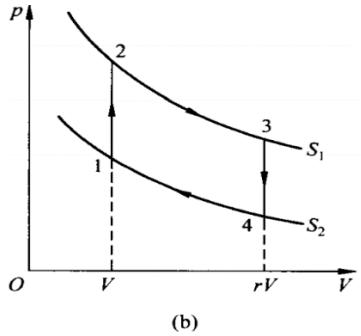
Considering that the order of magnitude of the virial coefficients B, C, D, ... decreases rapidly and their values are small [3]. By referring to figure 26.8 of reference [14], it is found that the virial coefficient B increases monotonously with the increase of temperature, so $\frac{\partial B}{\partial T}$, $\frac{\partial C}{\partial T}$ and $\frac{\partial D}{\partial T}$ can be approximately treated as positive constants. Therefore, taking the partial derivatives of y with respect to r and V, respectively, we get:

$$\frac{\partial y}{\partial r} > 0 \tag{31}$$

$$\frac{\partial y}{\partial V} < 0 \tag{32}$$

According to the above analysis, the Stirling cycle efficiency of the two real gas models is related to the parameters such as high-temperature heat source temperature T_1, low-temperature heat source temperature T_2, the isovolumetric molar heat capacity of gas, initial volume V in the cycle process and gas volume expansion ratio r. With the combination of Eqs. (22)-(26) and (28)-(32), the effects of various parameters on the Stirling cycle efficiency using two different real gas models as working fluids have something in common: the higher the high-temperature heat source temperature T_1, the lower the low-temperature heat source temperature T_2, the smaller the isovolumetric molar heat capacity of gas, the smaller the initial volume V in the cycle process, and the larger the gas volume expansion ratio r, the more beneficial to the improvement of Stirling cycle efficiency.

4.2 Otto cycle



(b)

Fig. 3 P-V diagram of the Otto cycle [11]

Otto cycle can be used for actual heat engine. As shown in Figure 3, the Otto cycle includes the isovolumic endotherm of state 1->state 2, the adiabatic expansion of state 2->state 3, the isovolumic heat release of state 3->state 4, and the adiabatic compression of state 4->state 1 . In the following, the van der Waals gas model and the Onnes gas model will be used to analyze and calculate the efficiency of the Otto cycle.

4.2.1. Van Der Waals Gas

State 1—>State 2: The volume is constant

$$Q_1 = \int_1^2 dQ = C_V^0 \left(T_2 - T_1\right) > 0$$

State 2—>State 3: Adiabatic process,

$$dQ = 0$$

$$T_3 \left(rV - b\right)^{\frac{R}{C_V^0}} = T_2 \left(V - b\right)^{\frac{R}{C_V^0}}$$

State 3—>State 4: The volume is constant

$$Q_2 = \int_3^4 dQ = C_V^0 \left(T_4 - T_3\right) < 0$$

State 4—>State 1: Adiabatic process,

$$dQ = 0$$

$$T_1 \left(V - b\right)^{\frac{R}{C_V^0}} = T_4 \left(rV - b\right)^{\frac{R}{C_V^0}}$$

So the efficiency is:

$$\eta_5 = \frac{Q_1 + Q_2}{Q_1} = 1 + \frac{Q_2}{Q_1} = 1 + \frac{T_4 - T_3}{T_2 - T_1}$$

In view of the inconvenience of discussing the four temperatures, we can combine the conservation formula of the adiabatic process and get:

$$\eta_5 = 1 - \left(\frac{V - b}{rV - b}\right)^{\frac{R}{C_V^0}} = 1 - \frac{T_3}{T_2} = 1 - \frac{T_4}{T_1} \tag{33}$$

Let η_5 take the partial derivatives with respect to *r*, *V* and C_V^0, respectively, we can get:

$$\frac{\partial \eta_5}{\partial r} > 0 \tag{34}$$

$$\frac{\partial \eta_5}{\partial C_V^0} < 0 \tag{35}$$

$$\frac{\partial \eta_5}{\partial V} < 0 \tag{36}$$

4.2.2. Onnes Gas

State 1—>State 2: The volume is constant

$$Q_1 = \int_1^2 dQ = C_V^1 \left(T_2 - T_1\right) > 0$$

State 2—>State 3: Adiabatic process, $dQ=0$

$$C_V^1\ln T_2+R\ln V+\frac{\partial B}{\partial T}\left(\frac{-1}{V}\right)+\frac{\partial C}{\partial T}\left(\frac{-1}{2V^2}\right)+\frac{\partial D}{\partial T}\left(\frac{-1}{3V^3}\right)+\cdots=C_V^1\ln T_3+R\ln(rV)+\frac{\partial B}{\partial T}\left(\frac{-1}{rV}\right)+\frac{\partial C}{\partial T}\left(\frac{-1}{2r^2V^2}\right)+\frac{\partial D}{\partial T}\left(\frac{-1}{3r^3V^3}\right)+\cdots$$

State 3—>State 4: The volume is constant

$$Q_2=\int_3^4 dQ=C_V^1\left(T_4-T_3\right)<0$$

State 4—>State 1: Adiabatic process, $dQ=0$

$$C_V^1\ln T_1+R\ln V+\frac{\partial B}{\partial T}\left(\frac{-1}{V}\right)+\frac{\partial C}{\partial T}\left(\frac{-1}{2V^2}\right)+\frac{\partial D}{\partial T}\left(\frac{-1}{3V^3}\right)+\cdots=C_V^1\ln T_4+R\ln(rV)+\frac{\partial B}{\partial T}\left(\frac{-1}{rV}\right)+\frac{\partial C}{\partial T}\left(\frac{-1}{2r^2V^2}\right)+\frac{\partial D}{\partial T}\left(\frac{-1}{3r^3V^3}\right)+\cdots$$

So, the efficiency is:

$$\eta_6=\frac{Q_1+Q_2}{Q_1}=1+\frac{Q_2}{Q_1}=1+\frac{T_4-T_3}{T_2-T_1}$$

Simultaneously with the conservation of adiabatic process, we can get:

$$\eta_6=1-e^{\frac{f(V)-f(rV)}{C_V^1}}=1-\frac{T_3}{T_2}=1-\frac{T_4}{T_1} \tag{37}$$

Wherein, the function f is the constructor:

$$f(x)=R\ln x+\frac{\partial B}{\partial T}\left(\frac{-1}{x}\right)+\frac{\partial C}{\partial T}\left(\frac{-1}{2x^2}\right)+\frac{\partial D}{\partial T}\left(\frac{-1}{3x^3}\right)+\cdots$$

It is known that $\frac{\partial B}{\partial T}$, $\frac{\partial C}{\partial T}$ and $\frac{\partial D}{\partial T}$ can be treated as positive constants approximately, so we can obtain:

$$\frac{df}{dx}>0$$

Let the partial derivative of the efficiency with respect to *r*, *V* and C_V^1, respectively, and obtain:

$$\frac{\partial\eta_6}{\partial V}<0 \tag{38}$$

$$\frac{\partial\eta_6}{\partial C_V^1}<0 \tag{39}$$

$$\frac{\partial\eta_6}{\partial r}>0 \tag{40}$$

In the above analysis and calculation, as shown in Eqs. (33) and (37). For the expression of efficiency, the temperature parameter can be replaced by the volume expansion ratio *r*, the initial volume *V*, and the isovolumetric molar heat capacity for the sake of brevity of discussion. After analyzing these three parameters, Eqs. (34)-(36) and (38)-(40) suggest that the efficiency of Otto cycle can be improved by reducing the initial volume *V*, selecting an actual gas with a small equimolar heat capacity as the working fluid, or increasing the volume expansion ratio during the cycle.

For the temperature parameters, equation (33) (37) suggests that if the temperature difference before and after the adiabatic process in the Otto cycle process can be increased, that is, the specific high-temperature heat source temperature before and after the adiabatic process is increased and the relative low-temperature heat source temperature is reduced, it is also beneficial to the improvement of Otto cycle efficiency.

5. Conclusion

Carnot cycle efficiency is the theoretical limit of the actual heat engine efficiency under the same heat source, so the Carnot cycle efficiency can be improved by increasing high-temperature heat source temperature and reducing low-temperature heat source temperature, thus improving the actual heat engine efficiency.

Considering the effect of the volume compression ratio on the efficiency of the cycle process, generally speaking, for the cycle process involving volume change, the larger the volume expansion

ratio, the more beneficial to improve the efficiency. Combined with the formula 4.1 and 4.2, the increase of initial volume will reduce the heat engine efficiency in Otto cycle and Stirling. Therefore, in the actual manufacturing, the initial volume should be reduced as much as possible, while the volume expansion ratio should be increased.

In general, the greater the isovolumetric molar heat capacity of the working fluid gas, the lower the efficiency of the heat engine. Therefore, when selecting working fluid gas, we can give priority to low heat capacity gas on the basis of meeting the cost requirements.

The thermal efficiency of three kinds of heat engine cycles is analyzed by using van der Waals gas and Onnes gas non-ideal gas models as working fluids, and the heat engine efficiency expressions based on Carnot cycle, Stirling cycle and Otto cycle are derived. On this basis, the law of the cycle efficiency of each heat engine changing with various parameters is clarified, and the common law which is helpful to improve the heat engine efficiency is obtained, which provides an important theoretical basis for the optimization design of the actual operation conditions of the heat engine.

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