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Abstract. We derive an expression for the efficiency of a Carnot engine using a van der Waals gas as the working substance.

Zusammenfassung. Wir geben eine Herleitung für die Leistungsfahigkeit einer Carnot Engine unter Verwendung von van der Waal Gas als Wirkungssubstanz.

1. Introduction

The discussion of the Carnot cycle and its efficiency is an integral part of any course in undergraduate thermodynamics (Feynman *et al* 1963, Abbott and Van Ness 1972a, b, c, Warren 1979, Halliday and Resnick 1988). The customary treatment (Abbott and Van Ness 1972a, Halliday and Resnick 1988) of this topic is based on the use of the equation of state $PV = RT$ for a perfect gas as the working substance which, in turn, leads to the expression for the efficiency:

$$\eta = 1 - T_C/T_H \tag{1}$$

where T_C and T_H refer to the absolute temperatures of the cold sink and hot source, respectively. Furthermore, invoking the second law of thermodynamics it is shown in the textbooks that η of a reversible engine is independent of the nature of the working substance.

While teaching this course in undergraduate classes it occurred to us whether the above mentioned statements about the Carnot engine can be verified for other equations of state (Abbott and Van Ness 1972b) such as e.g. the well known van der Waals equation. We tackle this question in section 2 by recapitulating the expressions of pressure and internal energy of a van der Waals gas, calculating the heats taken in or given out along the Carnot cycle, and finally deducing the desired formula for the efficiency. In section 3 we point out the difficulties which might be encountered if the same procedure is carried out for more complicated equations of state and suggest a possible method to overcome these difficulties.

2. Thermodynamics of an imperfect gas

2.1. Equation of state

The van der Waals equation (Abbott and Van Ness 1972b) for a mole of an imperfect gas reads

$$P = RT/(V - b) - a/V^2 \tag{2}$$

where P, V, T and R have the usual meanings and the parameters a and b are assumed to be constants which can be related to the critical values (designated by the subscript c) as $a = 9RT_c V_c/8$ and $b = V_c/3$. In order to be able to discuss the Carnot cycle it is essential to supplement equation (2) by a formula for the internal energy U as well. To do this, we start from the standard thermodynamic relation (Abbott and Van Ness 1972c):

$$dU = C_V dT + [T(\partial P/\partial T)_V - P]dV \tag{3}$$

where C_V is the specific heat capacity at constant volume. Since dU is a perfect differential hence the constraint

$$\partial C_V/\partial V = (\partial/\partial T)[T(\partial P/\partial T)_V - P] = T(\partial^2 P/\partial T^2)_V \tag{4}$$

has to be fulfilled. Now for P given by equation (2) $T(\partial^2 P/\partial T^2)_V = 0$ implying that $\partial C_V/\partial V = 0$, i.e. the value of C_V for a van der Waals gas is a function of the temperature only. Using equation (2) and (3) we get the expression for the infinitesimal heat dQ as

$$dQ = dU + PdV$$
$$= C_V dT + RT dV/(V - b). \tag{5}$$
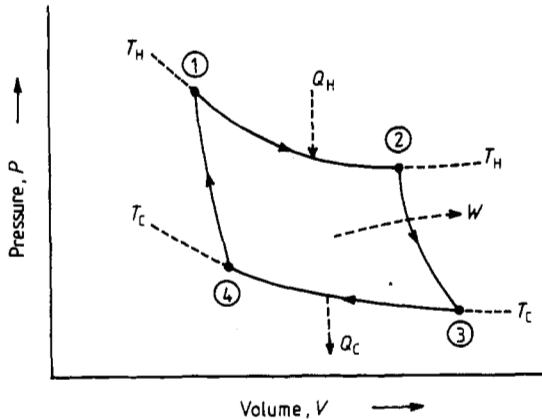
Figure 1. Indicator diagram showing the Carnot cycle 1–2–3–4. The initial state of the working substance is represented by the point 1. The enclosed area stands for the work W done during the process.

2.2. Carnot cycle

Referring to figure 1 and employing equation (5) the heat absorbed along the isothermal expansion arm 1–2 at temperature T_H becomes

$$Q_H = \int_1^2 dQ = RT_H \ln[(V_2 - b)/(V_1 - b)]. \quad (6)$$

Next, the heat change along the adiabatic expansion arm 2–3 is zero, implying

$$\int_2^3 C_V \, dT/T + R \ln[(V_3 - b)/(V_2 - b)] = 0. \quad (7)$$

In analogy with equation (6) the heat absorbed along the isotherm 3–4 at temperature T_C reads

$$Q_C = \int_3^4 dQ = RT_C \ln[(V_4 - b)/(V_3 - b)]. \quad (8)$$

Finally, along the adiabat 4–1 analogy with equation (7) yields

$$\int_4^1 C_V \, dT/T + R \ln[(V_1 - b)/(V_4 - b)] = 0. \quad (9)$$

Now we recall that C_V/T is a function of T only and $T_1 = T_2 = T_H$ and $T_3 = T_4 = T_C$. Therefore, addition of equations (7) and (9) gives a useful condition

$$\ln[(V_3 - b)/(V_2 - b)] = -\ln[(V_1 - b)/(V_4 - b)]. \quad (10)$$

2.3. Efficiency

By definition the efficiency of the engine is given by

$$\eta \equiv (Q_H + Q_C)/Q_H$$
$$= 1 + (T_C/T_H) \ln[(V_4 - b)/(V_3 - b)]/$$
$$\ln[(V_2 - b)/(V_1 - b)]$$
$$= 1 - T_C/T_H \quad (11)$$

where use has been made of equations (6) and (8) along with the condition equation (10). This is our desired result which agrees with equation (1) deduced originally for an ideal gas as the working substance. For the sake of ready reference we give in table 1 a comparison of the relevant thermodynamic properties of a Carnot cycle having perfect or van der Waals gases as the working substances.

3. Discussion

The question of checking the validity of equation (1) for substances not obeying the perfect gas law is non-trivial. Our derivation presented in section 2 has accomplished this explicitly for a van der Waals gas —the reason why the procedure succeeds is that the specific heat transpires to be a function of the temperature only. However, the same procedure applied to other known equations of state may not be so successful. For example, consider the Redlich–Kwong (Abbott and Van Ness 1972b) equation

$$. P = RT/(V - b) - a/[T^{1/2} V(V + b)] \quad (12)$$

for which $[\partial^2 P/\partial T^2]_V \neq 0$, i.e. C_V generally depends on the volume also; therefore the $\int C_V \, dT/T$ terms encountered in equations (7) and (9) may not cancel mutually.

Obviously if the working substance in the Carnot cycle is arbitrary, i.e. the functional dependence among P, V, T is arbitrary, it is difficult to apply the above philosophy for a *finite* cycle. However, we have been able to rederive equation (1) even in these cases for an *infinitesimal* cycle by a suitable Taylor expansion of thermodynamic variables carried out about the point 1 in figure 1 and the details of our calculations will be communicated in a future paper.

Table 1. Comparison of relevant thermodynamic properties used in a Carnot cycle for ideal and van der Waals gases.

S No	Property	Ideal gas	van der Waals gas
1	C_V	Constant	Function of temperature
2	dU	$C_V dT$	$C_V dT + (a/V^2) dV$
3	Equation of adiabat	$(C_V/T)(dT/dV) = -R/V$	$(C_V/T)(dT/dV) = -R/(V - b)$
4	Efficiency of Carnot engine, η	$1 - T_C/T_H$	$1 - T_C/T_H$

Acknowledgments

References

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