

FÍSICA ESTADÍSTICA I-PCF

TAREA 3

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■ Problemas

1. Cuando una máquina de Carnot opera cuasi-estáticamente la potencia de la máquina se anula debido al tiempo infinito que requiere para realizar un ciclo. Demuestre que la eficiencia η a potencia máxima está dada por

$$\eta = 1 - \left(\frac{T_2}{T_1} \right)^{1/2},$$

donde $T_1 > T_2$ son las temperaturas de los reservorios en los que opera la máquina (ver Curzon, Am. J. Phys. 43, 22 1975, adjunto a este documento).

2. Demuestre que:
 - a) En una transformación termodinámica de un sistema aislado mecánicamente y mantenido a temperatura constante, la energía libre de Helmholtz no aumenta y que el estado de equilibrio termodinámico corresponde al estado que la minimiza.
 - b) En una transformación termodinámica de un sistema mantenido a temperatura y presión constantes, el potencial de Gibbs nunca aumenta y que el estado de equilibrio termodinámico corresponde al estado que lo minimiza.
3. Construya el potencial termodinámico correspondiente a la situación física en la que temperatura T , volumen V y potencial químico μ corresponden a las variables termodinámicas del sistema (variables que se pueden controlar en el laboratorio). Dicho potencial es llamado **gran potencial**. Discuta sobre la concavidad de este potencial respecto a cada variable así como las condiciones de estabilidad.
4. Pruebe que

$$\left(\frac{\partial P}{\partial T} \right)_V \xrightarrow{T \rightarrow 0} 0$$

es consecuencia de la tercera ley de la termodinámica.

5. Experimentalmente se encuentra que la capacidad calorífica a presión constante C_P puede escribirse a bajas temperaturas como

$$C_P = T^\sigma [A_0(P) + A_1(P)T + A_2(P)T^2 + \dots]$$

con $\sigma > 0$, V el volumen y α el coeficiente de expansión térmica. $A_i(P)$, $i = 0, 1, 2, \dots$ son funciones sólo de P . Muestre que

$$\frac{V\alpha}{C_P} \xrightarrow{T \rightarrow 0} \frac{d}{dP} \ln[A_0(P)]^{-1/\sigma}$$

y discuta, como consecuencia de este resultado, que no es posible enfriar un sistema hasta cero Kelvin realizando un cambio finito de sus parámetros termodinámicos.

Efficiency of a Carnot Engine at Maximum Power Output

F. L. CURZON

B. AHLBORN

*Department of Physics**University of British Columbia**Vancouver, B.C., Canada*

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The efficiency of a Carnot engine is treated for the case where the power output is limited by the rates of heat transfer to and from the working substance. It is shown that the efficiency, η , at maximum power output is given by the expression $\eta = 1 - (T_2/T_1)^{1/2}$ where T_1 and T_2 are the respective temperatures of the heat source and heat sink. It is also shown that the efficiency of existing engines is well described by the above result.

INTRODUCTION

It is well known that practical heat engines are not as efficient as the classical Carnot cycle. Standard texts point out that inefficiencies occur because of heat leaks, or degradation of kinetic energy into heat by means of friction, etc.¹⁻³

We have found it instructive in our classes on thermodynamics to consider another fundamental limitation on efficiency which is caused by the rate at which heat can be exchanged between the working material and the heat reservoirs.

To achieve the theoretical efficiency, the isothermal parts of the cycle have to be carried out infinitely slowly so that the working substance can come into thermal equilibrium with the heat reservoirs (i.e., no temperature gradients occur across the walls of the container which encloses the working material). Under these conditions the power output is clearly zero since it takes an infinite time to do a finite amount of work.

To obtain a finite power output the cycle is speeded up. However, to drive the heat flux during the isothermal expansion of the working substance, the substance must be colder than the heat source. Conversely, during the isothermal compression the working substance cannot reject heat to the sink unless it is hotter than the sink. Ultimately, the two isothermal stages take place with no change in temperature of the working substance, so that heat flows straight from the source to the sink, and no mechanical work is performed by the engine. Hence the power output is zero and the engine has zero efficiency. Somewhere between these two extremes of zero power (i.e., optimum or zero efficiency) the engine clearly has a maximum power output. The efficiency under conditions of maximum power output is evaluated below.

THEORETICAL MODEL

We assume that heat fluxes through the vessel containing the working substance are proportional to the temperature difference across the walls of the vessel. In the isothermal expansion stage we therefore have

$$F_1 = \alpha(T_1 - T_{1w}) \quad (1)$$

where F_1 is the heat flux, α is a constant depending on the thickness and thermal conductivity of the wall; T_1 is the temperature of the heat source and T_{1w} , the temperature of the working substance. If the isothermal expansion lasts t_1 seconds, the input energy W_1 is

$$W_1 = F_1 t_1 = \alpha t_1 (T_1 - T_{1w}). \quad (2)$$

We assume the adiabatic expansion is completely reversible (no heat exchanges with the surroundings). On the isothermal compression, heat W_2 is rejected to the heat sink where

$$W_2 = \beta t_2 (T_{2w} - T_2). \quad (3)$$

In the above equation t_2 is the duration of the compression, T_2 is the temperature of the heat sink, β , its heat transfer coefficient, and T_{2w} the temperature of working material. The final adiabatic compression brings the working substance back to its original volume and temperature.

Since the adiabatic stages are reversible, we must have that

$$(W_1/T_{1w}) = (W_2/T_{2w})$$

i.e.,

$$(t_1/t_2) = \beta T_{1w}(T_{2w} - T_2)/T_{2w}\alpha(T_1 - T_{1w}) \quad (4)$$

(see Eqs. 2 and 3 above).

The power (P) of the engine is then given by the expression

$$P = (W_1 - W_2)/(t_1 + t_2)\gamma, \quad (5)$$

where $(\gamma - 1)(t_1 + t_2)$ is the time taken to complete the adiabatic cycles. Hence we assume that as the heat engine is speeded up, the time to complete the adiabatic processes remains proportional to the time required for the isothermal processes.

Using Eq. (4) to eliminate t_1/t_2 leads to the results

$$P = \frac{\alpha\beta xy(T_1 - T_2 - x - y)}{\gamma[\beta T_1 y + \alpha T_2 x + xy(\alpha - \beta)]}, \quad (6)$$

$$x = T_1 - T_{1w}, \quad y = T_{2w} - T_2. \quad (7)$$

P is maximized by values of x and y satisfying the following equations:

$$(\partial P/\partial x) = 0,$$

i.e.,

$$\beta T_1 y(T_1 - T_2 - x - y) = x[\beta T_1 y + \alpha T_2 x + xy(\alpha - \beta)] \quad (8a)$$

$$(\partial P/\partial y) = 0,$$

i.e.,

$$\alpha T_2 x(T_1 - T_2 - x - y) = y[\beta T_1 y + \alpha T_2 x + xy(\alpha - \beta)]. \quad (8b)$$

From this it follows that

$$y = (\alpha T_2/\beta T_1)^{1/2} x \quad (9)$$

which is then used to eliminate y from Eq. (8a) to give the following quadratic equation for $x/T_1 = \mu$:

$$[1 - (\alpha/\beta)]\mu^2 - 2[(\alpha T_2/\beta T_1)^{1/2} + 1]\mu + [1 - (T_2/T_1)] = 0. \quad (10)$$

Since $\mu < 1$, the physically relevant solution of this equation is readily shown to be:

$$\mu = \frac{x}{T_1} = \frac{1 - (T_2/T_1)^{1/2}}{1 + (\alpha/\beta)^{1/2}}. \quad (11)$$

From Eq. (9) it follows that

$$\frac{y}{T_2} = \frac{(T_1/T_2)^{1/2} - 1}{1 + (\beta/\alpha)^{1/2}}. \quad (12)$$

The efficiency of the engine (η') at maximum power is given by

$$\begin{aligned} \eta' &= (W_1 - W_2)/W_1 \\ &= 1 - (T_{2w}/T_{1w}) \\ &= 1 - [(T_2 + y)/(T_1 - x)]. \end{aligned} \quad (13)$$

Using Eqs. (11) and (12) to eliminate x and y from the expressions for η' leads to the result

$$\eta' = 1 - (T_2/T_1)^{1/2}. \quad (14)$$

At maximum power, it follows from Eqs. (4) and (7) that

$$(t_1/t_2) = \beta T_{1w} y / \alpha T_{2w} x. \quad (15)$$

Eliminating (y/x) by using Eq. (9) and noting that $T_{2w}/T_{1w} = (T_2/T_1)^{1/2}$ [see Eq. (14)] leads to the conclusion that

$$t_1/t_2 = (\beta/\alpha)^{1/2}. \quad (16)$$

From Eqs. (11) and (12), the working temperatures in the isothermal parts of the Carnot cycle

TABLE I. Observed performance of real heat engines.

Power source	T_2 (°C)	T_1 (°C)	η (Carnot)	η' (Eq. 14)	η (observed)
West Thurrock (U.K.) ² Coal Fired Steam Plant	~25	565	64.1%	40%	36%
CANDU (Canada) ⁴ PHW Nuclear Reactor	~25	300	48.0	28%	30%
Larderello (Italy) ⁵ Geothermal Steam Plant	80	250	32.3%	17.5%	16%

are:

$$T_{1w} = CT_1^{1/2}, \quad T_{2w} = CT_2^{1/2}, \quad (17)$$

where

$$C = [(\alpha T_1)^{1/2} + (\beta T_2)^{1/2}] / [(\alpha)^{1/2} + (\beta)^{1/2}]. \quad (18)$$

Finally, using the above equations, it is readily shown that the maximum power (P_{\max}) is

$$P_{\max} = (\alpha\beta/\gamma) [(T_1^{1/2} - T_2^{1/2}) / (\alpha^{1/2} + \beta^{1/2})]^2. \quad (19)$$

The most interesting feature of the above results is Eq. (14) which shows that the efficiency does not depend on the heat transfer coefficients (α and β), and has the attractive feature, that, as with the efficiency for an ideal Carnot engine [$\eta = 1 - (T_2/T_1)$] it depends only on the temper-

ature of the heat reservoirs. However the result also has the interesting property that it serves as quite an accurate guide to the best observed performance of real heat engines, as is shown by Table I.

¹ G. J. Van Wylen and R. E. Sonntag, *Fundamentals of Classical Thermodynamics* (Wiley, New York, 1973), 2nd ed., pp. 170-195.

² D. B. Spalding and E. H. Cole, *Engineering Thermodynamics* (Edward Arnold, London, 1966), 2nd ed., pp. 200-286, table on p. 209.

³ B. D. Wood, *Applications of Thermodynamics* (Addison Wesley, London, Ontario, 1969), pp. 1-86. See also the list of standard texts given on p. xv of this book.

⁴ G. M. Griffiths, *Phys. Can.* **30**, 2 (1974); reference to efficiency is on p. 5.

⁵ A. Chierici, *Planning of a Geothermal Power Plant: Technical and Economic Principles* (U. N. Conference on New Sources of Energy, New York, 1964), Vol. 3, pp. 299-311.