

Finite-time exergy with a finite heat reservoir and generalized radiative heat transfer law

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The problem of the maximum work that can be extracted from a system consisting of one finite heat reservoir and one subsystem with the generalized radiative heat transfer law [$q \propto \Delta(T^n)$] is investigated in this paper. Finite-time exergy is derived for a fixed duration and a given initial state of the subsystem by applying optimal control theory. The optimal subsystem temperature configuration for the finite-time exergy consists of three segments, including the initial and final instantaneous adiabatic branches and the intermediate heat transfer branch. Analyses for special examples show that the optimal configuration of the heat transfer branch with Newton's heat transfer law [$q \propto \Delta(T)$] is that the temperatures of the reservoir and the subsystem change exponentially with time and the temperature ratio between them is a constant; The optimal configuration of the heat transfer branch with the linear phenomenological heat transfer law [$q \propto \Delta(T^{-1})$] is such that the temperatures of the reservoir and the subsystem change linearly and non-linearly with time, respectively, and the difference in reciprocal temperature between them is a constant. The optimal configuration of the heat transfer branch with the radiative heat transfer law [$q \propto \Delta(T^4)$] is significantly different from those with the former two different heat transfer laws. Numerical examples are given, effects of changes in the reservoir's heat capacity on the optimized results are analyzed, and the results for the cases with some special heat transfer laws are also compared with each other. The results show that heat transfer laws have significant effects on the finite-time exergy and the corresponding optimal thermodynamic process. The finite-time exergy tends to the classical thermodynamic exergy and the average power tends to zero when the process duration tends to infinitely large. Some modifications are also made to the results from recent literatures.

Keywords: Finite time thermodynamics; finite-time exergy; finite heat reservoir; generalized radiative heat transfer law; optimal control.

En este trabajo se investiga el problema del máximo trabajo que es posible extraer del sistema consistente en un recipiente térmico finito y un subsistema con la ley generalizada de transferencia de calor por radiación [$q \propto \Delta(T^n)$]. Se obtiene la exergía de tiempo finito para una duración fija y un estado inicial del subsistema dado aplicando la teoría de control óptimo. La configuración óptima de temperatura del subsistema para la exergía de tiempo finito consiste en tres segmentos: la rama instantánea adiabática inicial y final, y la rama de transferencia de calor intermedia. El análisis de ejemplos especiales muestra que la configuración óptima de la rama de transferencia de calor con la ley de Newton de transferencia térmica [$q \propto \Delta(T)$] es aquella en la que la temperatura del recipiente y del subsistema cambian exponencialmente con el tiempo y la razón de temperaturas es constante. La configuración óptima de la rama de transferencia térmica con la ley lineal fenomenológica [$q \propto \Delta(T^{-1})$] es aquella en la que las temperaturas del recipiente y del subsistema cambian lineal y no linealmente con el tiempo respectivamente y la diferencia en la temperatura recíproca entre ellos es constante. La configuración óptima para la rama de transferencia térmica con la ley radiativa de transferencia de calor [$q \propto \Delta(T^4)$] es significativamente diferente de las que emplean las dos leyes anteriores. Se dan ejemplos numéricos, se analizan los efectos de los cambios en la capacidad calorífica del recipiente en los resultados optimizados, y los resultados para los casos con alguna ley especial de transferencia térmica se comparan unos con otros. Los resultados muestran que las leyes de transferencia térmica tienen efectos significativos en la exergía de tiempos finitos y en el proceso termodinámico óptimo correspondiente. La exergía de tiempos finitos tiende a la de la termodinámica clásica y la potencia promedio tiende a cero cuando la duración del proceso tiende a ser infinitamente largo. También se hacen algunas modificaciones a resultados recientemente publicados.

Descriptores: Termodinámica a tiempos finitos; exergía a tiempos finitos; recipiente térmico finito; ley generalizada de transferencia de calor por radiación; control óptimo.

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1. Introduction

One of the classical problems of thermodynamics has been the determination of the maximum work that might be extracted when a prepared system is allowed to undergo a transformation from its initial state to a designated final state. When that final state is defined by the condition of equilibrium between the system and some environment, the maximum extractable work is generally known as the exergy. Exergy concept and exergy analysis have been applied to perfor-

mance analysis and optimization for various thermodynamic processes, cycles and devices [1-10]. The conventional exergy is the classical thermodynamic exergy and the solution methodology of classical thermodynamics problems assumes reversible thermodynamic processes, *i.e.*, processes in which the system preserves internal equilibrium, the total entropy of the system and the environment does not increase; the differences between the values of intensive variables (temperatures, pressures, chemical potentials *et al.*) of the system and those of the environment are infinitely small, and the

process duration is infinitely large. Performance limits obtained with the aid of reversible processes are independent of the equation of state of the system and are limiting in the sense that they remain unattainable in all real processes. All real thermodynamic processes are irreversible since the rate of exchange between the system and the environment is not infinitesimally small, the system does not maintain internal equilibrium, and the process duration is finite.

In 1975, Curzon and Ahlborn [11] postulated a real Carnot engine, with power output limited by the rates of heat transfer to and from the working substance, and showed that the hot- and cold-end temperatures of a power plant can be optimized such that the power output is maximal. The efficiency at maximum power point is $\eta_{CA} = 1 - \sqrt{T_L/T_H}$. This provided a new performance limit, which is different from Carnot efficiency, for the heat engine characterized by finite rate, finite duration, and finite-size. Since the mid 1970s, finite time thermodynamics, *i.e.* the research into identifying the performance limits of thermodynamic processes and optimizing thermodynamic processes has made great progress in the fields of physics and engineering [12-21]. Ondrechen *et al.*, [22] investigated the problem of maximizing work output from a finite heat reservoir by infinite sequential Carnot cycles. Yan [23] derived the efficiency of a sequence of Carnot cycles operating between a finite source and an infinite sink at maximum power output. Andresen *et al.*, [24] first put forward the concept of finite-time exergy. With the help of a conventional exergy analysis approach, Mironova *et al.*, [25] introduced the criterion of thermodynamic ideality, which is defined as the ratio of actual rate of entropy production to the minimum rate of entropy production, and applied it to the evaluation of performances of thermodynamic systems. Sieniutycz and von Sparkovsky [26] obtained the optimal reservoir temperature profiles of multistage endoreversible continuous CA heat engine [11] systems operating between a finite source and an infinite sink for maximum work output (also called finite time exergy in Ref. 25), in which the heat transfer between the working fluid and the reservoirs obeys Newton's heat transfer law [$q \propto \Delta(T)$]. Sieniutycz [27] further obtained those of multistage endoreversible discrete heat engine systems for maximum work output. Tsirlin [15,18], Berry *et al.*, [16] and Mironova *et al.*, [17] investigated the problem of the maximal work that can be extracted from a system consisting of one infinite heat reservoir and one subsystem with the generalized radiative heat transfer law [$q \propto \Delta(T^n)$], and further investigated the problem of the maximal work that can be extracted from a system consisting of one finite heat reservoir and one subsystem with Newton's heat transfer law. Tsirlin and Kazakov [28] investigated the maximum work problems of several subsystems with an infinite heat reservoir and one subsystem with an infinite mass reservoir. Sieniutycz [29,30] obtained a finite-rate generalization of the maximum-work potential called generalized (rate-dependent) exergy with the method of variational calculus [29], and further investigated the effects of heat transfer laws on the rate-dependent exergy [30].

Based on Refs. 15 to 18, this paper will further investigate the problem of the maximum work that can be extracted from a system consisting of one finite heat reservoir and one subsystem, in which heat transfer obeys the generalized radiative heat transfer law [$q \propto (\Delta T^n)$] [31-39], and drive the finite-time exergy for a fixed duration and a given initial state of the subsystem by using optimal control theory.

2. System model

The model to be considered in this paper is illustrated in Fig. 1, which consists of one finite heat reservoir and one subsystem. There is no mechanical interaction or mass transfer between the subsystem and the reservoir and only heat transfer between them. The heat reservoir has a finite thermal capacity, and its thermal capacity, temperature, entropy, pressure, volume, and internal energy are denoted as C_1 , T_1 , S_1 , p_1 , V_1 , and E_1 , respectively, while the corresponding parameters of the subsystem are denoted as T_2 , S_2 , p_2 , V_2 , and E_2 , respectively. The heat transfer between the reservoir and the subsystem obeys the generalized radiative heat transfer law $q(T_1, T_2) = k(T_1^n - T_2^n)$, where k is the heat conductance, and different values of power exponent n denote different heat transfer laws. Both the reservoir and the subsystem have fixed composition and are assumed to be in internal equilibrium, so their states could be described by two independent thermodynamic variables. Once these two independent variables are chosen, the other variables are determined by the independent variables via the equation of state. For example, when the independent variables of internal energy E and volume V are chosen to describe the state of the system, one has the following relationships:

$$S = S(E, V), \quad 1/T = \partial S/\partial E, \quad p/T = \partial S/\partial V \quad (1)$$

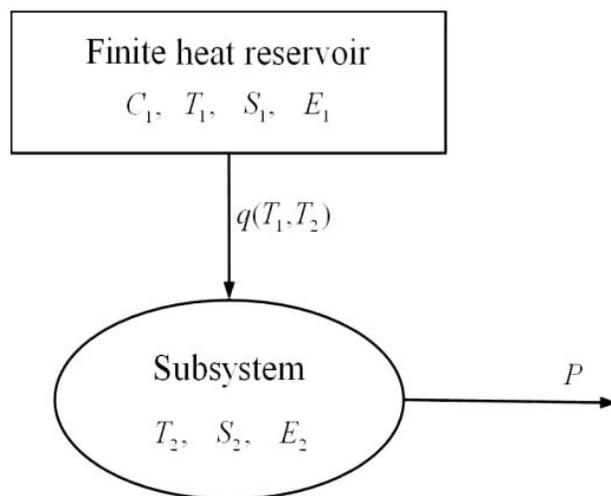


FIGURE 1. Model of one finite heat reservoir and one subsystem.

The independent variables of entropy S and volume V are chosen, and so

$$E = E(S, V), \quad T = \partial E / \partial S, \quad p = -\partial E / \partial V \quad (2)$$

If the reservoir has an infinite heat capacity, its temperature T_1 and pressure p_1 are constants. From Eq. (1), one obtains

$$1/T_1 = \partial S_1 / \partial E_1, \quad p_1/T_1 = \partial S_1 / \partial V_1 \quad (3)$$

The right hand sides of Eq. (3) are constants; then combining Eqs. (1) and (3) yields

$$S_1 = E_1/T_1 + p_1 V_1/T_1, \quad (4)$$

If the working fluid of the subsystem is an ideal gas, its constant volume heat capacity C_{V2} and mole number N_2 are constants. From Eq. (1), one can obtain

$$S_2 = C_{V2} \ln E_2 + N_2 R \ln V_2, \\ T = E_2/C_{V2}, \quad p_2 = N_2 R T_2/V_2 \quad (5)$$

where R is the universal gas constant. The reservoir's heat capacity and its initial temperature are given by C_1 and $T_1(0) = T_{10}$, respectively. The initial internal energy and temperature of the subsystem are given by $E_2(0)$ and $T_2(0)$, respectively. The amount of the heat transfer and the process duration are given by Q and τ , respectively. Exergy is a relative concept, which depends on the choosing of the referee environment. If the referee environment is considered to be a finite heat reservoir, when the capacity of the reservoir tends to infinity ($C_1 \rightarrow \infty$), the obtained results would reduce to those obtained with an infinite heat reservoir (*i.e.* the universal environment) [15-18]. Now suppose that the duration of the process τ is a finite value. Then the maximal work output A^* of the system is smaller than the classical exergy A_{rev} that is achieved in a reversible process, *i.e.* a process in which the parameters of the system are infinitesimally separated from those of the environment and the process duration is effectively infinitely large. It is natural to call $A^*(\tau)$ the finite-time exergy or finite-time availability [24].

In terms of the first law of thermodynamics, for the reservoir and the subsystem, one has

$$\dot{E}_1 = -q(T_1, T_2), \quad \dot{S}_1 = \sigma_1 = -q(T_1, T_2)/T_1, \\ \dot{E}_2 = q(T_1, T_2) - P, \quad \dot{S}_2 = \sigma_2 = q(T_1, T_2)/T_2 \quad (6)$$

where σ_1 and σ_2 are the entropy change rates of the reservoir and the subsystem, respectively, and $\dot{E}_1 = dE_1/dt$, the dot notation signifies the time derivative. From the second law of thermodynamics, the total entropy generation in the heat transfer process ΔS is given by

$$\Delta S = \int_0^\tau q(T_1, T_2)(1/T_2 - 1/T_1)dt = \Delta S_1 + \Delta S_2 \quad (7)$$

where

$$\Delta S_1 = \int_0^\tau [-q(T_1, T_2)/T_1]dt$$

and

$$\Delta S_2 = \int_0^\tau [q(T_1, T_2)/T_2]dt$$

are the entropy changes of the reservoir and the subsystem, respectively. The work done by the subsystem is

$$A = \int_0^\tau P(t)dt$$

and its absorbed heat is

$$Q = \int_0^\tau q dt.$$

From Eq. (6), one obtains

$$A = Q - \Delta E_2 = Q + E_2(0) - E_2(\tau) \quad (8)$$

Determining the finite-time exergy A^* is equivalent to minimizing the internal energy change of the subsystem ΔE_2 due to the fact that the amount of heat transfer is known. One can see that $\partial E_2 / \partial S_2 = T_2 > 0$ holds from Eq. (2). Then minimizing ΔE_2 could be further equivalent to minimizing the entropy change of the subsystem ΔS_2 . The reservoir's heat capacity C_1 is a finite value; then

$$C_1 \dot{T}_1 = -q(T_1, T_2), \quad T_1(0) = T_{10} \quad (9)$$

3. Finite-time exergy

From the above analysis, for the given amount of heat Q , determining the finite-time exergy A^* with a finite heat reservoir is equivalent to minimizing the entropy change of the subsystem ΔS_2 . Let ΔS_2 be the objective function; one has

$$\min \Delta S_2 = \int_0^\tau [q(T_1, T_2)/T_2]dt \quad (10)$$

The corresponding constraints are given by

$$\int_0^\tau q(T_1, T_2)dt = Q \quad (11)$$

$$\dot{T}_1 = \frac{-q(T_1, T_2)}{C_1}, \quad T_1(0) = T_{10} \quad (12)$$

Equation (11) shows that the amount of heat transfer is fixed, and Eq. (12) shows that the thermal capacity of the

heat reservoir is a finite value. This is a typical average optimal control problem in optimal control theory. The problem could be simplified if one replaces the variable of time t by the control variable of temperature T_1 . From Eqs. (11) and (12), for the given Q and T_{10} , the final temperature of the reservoir is given by $T_1(\tau) = T_{10} - Q/C$. Substituting Eq. (12) into Eq. (10) yields

$$\min \Delta S_2 = \int_{T_1(\tau)}^{T_{10}} (C_1/T_2)dT_1 \quad (13)$$

Combining Eq. (11) with Eq. (12) yields

$$\int_0^\tau dt = \int_{T_1(\tau)}^{T_{10}} [C_1/q(T_1, T_2)]dT_1 = \tau \quad (14)$$

Our problem now is to find the minimal value of ΔS_2 in Eq. (13) and the corresponding optimal temperature configuration of the subsystem subject to the finite time constraint of Eq. (14). The problem is similar to that of determining the optimal configurations of heat engines operating between a finite source and an infinite sink for maximum power output [40-48]. The modified Lagrange function is given by

$$L(T_2, \lambda) = C_1[1/T_2 + \lambda/q(T_1, T_2)] \quad (15)$$

where λ is a Lagrange constant. From the extreme condition $\partial L/\partial T_2 = 0$, one has

$$\lambda \partial q/\partial T_2 = -[q(T_1, T_2)/T_2]^2 \quad (16)$$

Assume that the reservoir's heat capacity C_1 does not depend on its temperature T_1 ; then substituting $q = k(T_1^n - T_2^n)$ into Eqs. (12) and (14), respectively, yields

$$T_2^{n+1} = \frac{k(T_1^n - T_2^n)^2}{(\lambda n)} \quad (17)$$

$$\int_{T_{10}-Q/C_1}^{T_{10}} [1/(T_1^n - T_2^n)]dT_1 = k\tau/C_1 \quad (18)$$

Equations (17) and (18) determine the optimal temperature profiles of the reservoir and the subsystem, and they can be solved analytically for only some special heat transfer laws, for instance, Newton's heat transfer law ($n = 1$) and the linear phenomenological heat transfer law ($n = -1$). For other heat transfer laws, they need to be solved numerically. Equation (17) has the same expression as that of the optimal temperature profiles of the finite high-temperature source and the hot-side working fluid of the heat engine operating between a finite source and an infinite sink for maximum power output with the generalized radiative heat transfer law [43, 48]. One could obtain the optimal temperature profiles of the reservoir $T_1^*(t)$ and the subsystem $T_2^*(t)$ from Eqs. (17) and (18). Substituting $T_1^*(t)$ and $T_2^*(t)$ into Eq. (10) yields the minimum

entropy change $\Delta S_2^*(\tau)$. From Eq. (8), the finite-time exergy A^* is given by

$$A^* = Q - \Delta E_2(\Delta S_2^*(\tau), V_2^*(\tau)) \quad (19)$$

Assume that the working fluid in the subsystem is an ideal gas; from Eq. (5), one has

$$\Delta S_2(\tau) = C_{V2} \ln \left[\frac{T_2(\tau)}{T_2(0)} \right] + R \ln \left[\frac{V_2(\tau)}{V_2(0)} \right] \quad (20)$$

$$\Delta E_2 = C_{V2}[T_2(\tau) - T_2(0)] = E_2(0) \left[\frac{T_2(\tau)}{T_2(0)} - 1 \right] \quad (21)$$

Combining Eq. (20) with Eq. (21) yields

$$\Delta E_2 = E_2(0) \left[\left(\frac{V_2(\tau)}{V_2(0)} \right)^{-R/C_{V2}} \exp \left(\frac{\Delta S_2(\tau)}{C_{V2}} \right) - 1 \right] \quad (22)$$

Substituting Eq. (22) into Eq. (19) yields the finite-time exergy A^*

$$A^* = Q - E_2(0) \left[\left(\frac{V^*(\tau)}{V(0)} \right)^{-R/C_{V2}} \times \exp \left(\frac{\Delta S_2^*(\tau)}{C_{V2}} \right) - 1 \right] \quad (23)$$

4. Analyses for special examples

4.1. The results for the case with Newton's heat transfer law

In this case, $n = 1$. Since $T_1 > T_2$, from Eq. (17), one obtains

$$T_2 = \frac{T_1 \sqrt{k/\lambda}}{(1 + \sqrt{k/\lambda})} \quad (24)$$

Substituting Eq. (24) into Eq. (18) yields

$$\frac{\ln[T_{10}/(T_{10} - Q/C_1)]}{[1 - \sqrt{k/\lambda}/(1 + \sqrt{k/\lambda})]} = k\tau/C_1 \quad (25)$$

Combining Eq. (24) with Eq. (25) yields the optimal relation between the reservoir temperature and the subsystem temperature:

$$T_2^*(T_1) = T_1 \{1 - C_1 \ln[T_{10}/(T_{10} - Q/C_1)]/k\tau\} \quad (26)$$

Substituting Eq. (26) into Eq. (9) yields the optimal temperature of the reservoir versus time:

$$T_1^*(t) = T_{10} [(T_{10} - Q/C_1)/T_{10}]^{(t/\tau)} \quad (27)$$

Substituting Eq. (27) into Eq. (26) yields the optimal temperature of the subsystem versus time:

$$T_2^*(t) = T_{10} \{1 - C_1 \ln[T_{10}/(T_{10} - Q/C_1)]/k\tau\} \times [(T_{10} - Q/C_1)/T_{10}]^{(t/\tau)} \quad (28)$$

The optimal temperature configuration of the subsystem for the finite-time exergy consists of three segments, including the initial and final instantaneous adiabatic branches and the intermediate heat transfer branch, as follows: at $t = 0$, the subsystem jumps instantly from the given initial $T_2(0)$ to the $T_2^*(0)$; then $T_2^*(t)$ changes according to Eq. (28) during the time interval $(0, \tau)$; finally, at $t = \tau$, the temperature of the subsystem jumps again, and its final state is defined by the equation of state and the optimal volume $V^*(\tau)$, which is to be found from the condition $V^*(\tau) = \arg \min_{V_2} E_2(S_2^*(\tau), V_2(\tau))$, *i.e.* the volume of the working fluid corresponding to the minimum $E_2^*(\tau)$ among the admissible set of volume $V_2(\tau)$. From Eq. (27)

and Eq. (28), one can see that the optimal configuration of the heat transfer process for the finite-time exergy with Newton's heat transfer law such is that the temperatures of the reservoir and the subsystem change exponentially with time and the temperature ratio between the reservoir and the subsystem is a constant. They are the same as those obtained in Refs. 41 to 44 and 48. Substituting Eq. (26) into Eq. (13) yields the minimal entropy change $\Delta S_2^*(\tau)$:

$$\Delta S_2^*(\tau) = \frac{k\tau C_1 \ln[T_{10}/(T_{10} - Q/C_1)]}{\{k\tau - C_1 \ln[T_{10}/(T_{10} - Q/C_1)]\}} \quad (29)$$

Substituting Eq. (29) into Eq. (23) yields

$$A^* = Q - E_2(0) \left\{ \left(\frac{V_2^*(\tau)}{V_2(0)} \right)^{-(R/C_{V2})} \exp \left\{ \frac{k\tau C_1 \ln[T_{10}/(T_{10} - Q/C_1)]}{C_{V2} \{k\tau - C_1 \ln[T_{10}/(T_{10} - Q/C_1)]\}} \right\} - 1 \right\} \quad (30)$$

Equations (29) and (30) are the same as those obtained in Refs. 15 to 18. It is noted that the optimal relation between the reservoir temperature and the subsystem temperature and the optimal temperature of the subsystem versus time obtained in Refs. 15 to 18 are as follows:

$$T_2^*(T_1) = T_1 \frac{k\tau - C_1 \ln[T_{10}/(T_{10} - Q/C_1)]}{k\tau} \quad (31)$$

$$T_2^*(t) = (T_{10} - Q/C_1) \times \frac{k\tau - C_1 \ln[T_{10}/(T_{10} - Q/C_1)]}{k\tau} \exp\left(\frac{t}{\tau}\right) \quad (32)$$

Equation (31) is correct, which is the same as Eq. (26) in this paper, while Eq. (32) is wrong. This could be proved easily. Assume Eq. (32) is correct; then from Eqs. (31) and (32), one obtains the optimal temperature of the reservoir versus time, as follows:

$$T_1^*(t) = (T_{10} - Q/C_1) \exp\left(\frac{t}{\tau}\right) \quad (33)$$

From Eq. (33), $T_1^*(0) = T_{10} - Q/C_1$ when $t = 0$, and $T_1^*(\tau) = (T_{10} - Q/C_1)e$ when $t = \tau$. It does not coincide with the given boundary conditions of the reservoir temperature, *i.e.* $T_1^*(0) = T_{10}$ and $T_1^*(\tau) = T_{10} - Q/C_1$.

Therefore, Eq. (5.45) on page 209 in Ref. 16 and the same equation on page 215 in Ref. 15, page 209 in Ref. 17, and page 78 in Ref. 18 (Eq. (32) in this paper) should be replaced by Eq. (28) in this paper. Because the minimal entropy change $[\Delta S_2^*(\tau)]$ of the system in Refs. 15 to 18 was obtained based on Eq. (31) rather than Eq. (32) in this paper, it is correct.

4.2. The results for the case with the linear phenomenological heat transfer law

In this case, $n = -1$, and the heat conductance k is negative. Since $T_1 > T_2$, from Eq. (17), one obtains

$$T_2^{-1} - T_1^{-1} = \sqrt{-\lambda/k} \quad (34)$$

Substituting Eq. (34) into Eq. (18) yields

$$\sqrt{-k/\lambda} = -k\tau/Q \quad (35)$$

Combining Eq. (34) with Eq. (35) yields the optimal relation between the reservoir temperature and the subsystem temperature,

$$T_1^*(t) = T_{10} [(T_{10} - Q/C_1)/T_{10}]^{(t/\tau)} \quad (36)$$

Substituting Eq. (36) into Eq. (9) yields the optimal temperature of the reservoir versus time:

$$T_1^*(t) = T_{10} - Qt/(C_1\tau) \quad (37)$$

Substituting Eq. (37) into Eq. (36) yields the optimal temperature of the subsystem versus time:

$$T_2^*(t) = \frac{k\tau(C_1 T_{10} \tau - Qt)}{[C_1 k \tau^2 - Q(C_1 T_{10} \tau - Qt)]} \quad (38)$$

The optimal temperature configuration of the subsystem for the finite-time exergy consists of three segments, including the initial and final instantaneous adiabatic branches and the intermediate heat transfer branch, as follows: at $t = 0$, the subsystem jumps instantly from the given initial $T_2(0)$ to the $T_2^*(0)$; then $T_2^*(t)$ changes according to Eq. (38) during the time interval $(0, \tau)$; finally, at $t = \tau$,

the temperature of the subsystem jumps again, and its final state is defined by the equation of state and the optimal volume $V^*(\tau)$, which can be found from the condition $V^*(\tau) = \arg \min_{V_2} E_2[S_2^*(\tau), V_2(\tau)]$. From Eq. (37) and Eq. (38), the optimal configuration of the heat transfer process for the finite-time exergy with the linear phenomenological heat transfer law is such that the temperatures of the reservoir and the subsystem change linearly and non-linearly with time, respectively, and the difference in reciprocal temperature between the reservoir and the subsystem is a constant. They are the same as those obtained in Refs. 42, 43, and 48. Substituting Eq. (36) into Eq. (13) yields the minimal entropy change $\Delta S_2^*(\tau)$, as follows:

$$\Delta S_2^*(\tau) = C_1 \ln[T_{10}/(T_{10} - Q/C_1)] - Q^2/(k\tau) \quad (39)$$

Assume that the working fluid in the subsystem is an ideal gas; substituting Eq. (39) into Eq. (23) yields

$$A^* = Q - E_2(0) \left[\left(\frac{V^*(\tau)}{V(0)} \right)^{-(R/C_{V2})} \times \exp \left(\frac{k\tau C_1 \ln[T_{10}/(T_{10} - Q/C_1)] - Q^2}{k\tau C_{V2}} \right) - 1 \right] \quad (40)$$

4.3. The results for the case with the radiative heat transfer law

In this case, $n = 4$. Eqs. (9) and (17) further give

$$C_1 \dot{T}_1 = -k(T_1^4 - T_2^4), \quad T_1(0) = T_{10} \quad (41)$$

$$T_2^5 = k(T_1^4 - T_2^4)^2/(4\lambda) \quad (42)$$

respectively. There are no analytical solutions for $T_1^*(t)$ and $T_2^*(t)$, which should be solved numerically. It is shown that the optimal temperature configuration of the subsystem for the finite-time exergy consists of three segments, including the initial and final instantaneous adiabatic branches and the intermediate heat transfer branch, as follows: at $t = 0$, the subsystem jumps instantly from the given initial $T_2(0)$ to the $T_2^*(0)$; then $T_2^*(t)$ changes according to Eq. (42) during the time interval $(0, \tau)$; finally, at $t = \tau$, the temperature of the subsystem jumps again, and its final state is defined by the equation of state and the optimal volume $V^*(\tau)$, which can be found from the condition

$$V^*(\tau) = \arg \min_{V_2} E_2(S_2^*(\tau), V_2(\tau)).$$

The minimal entropy change $\Delta S_2^*(\tau)$ is also obtained numerically. Assume that the working fluid in the subsystem is an ideal gas, substituting $\Delta S_2^*(\tau)$ into Eq. (23) yields

$$A^* = Q - E_2(0) \times \left[\left(\frac{V^*(\tau)}{V(0)} \right)^{-(R/C_{V2})} \exp \left(\frac{\Delta S_2^*(\tau)}{C_{V2}} \right) - 1 \right] \quad (43)$$

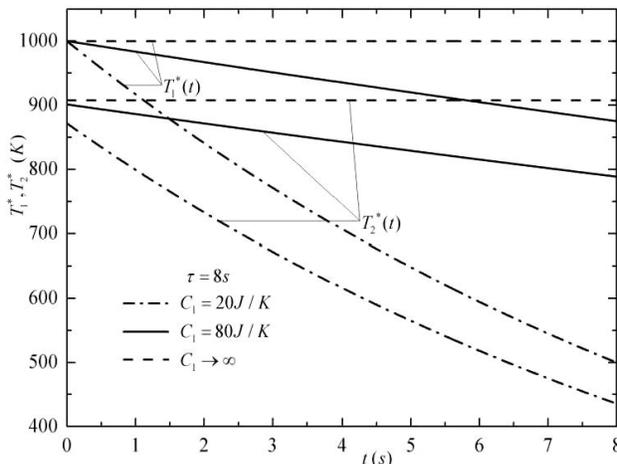


FIGURE 2. Optimal temperature configurations for the finite-time exergy during the heat transfer processes with Newton's heat transfer law.

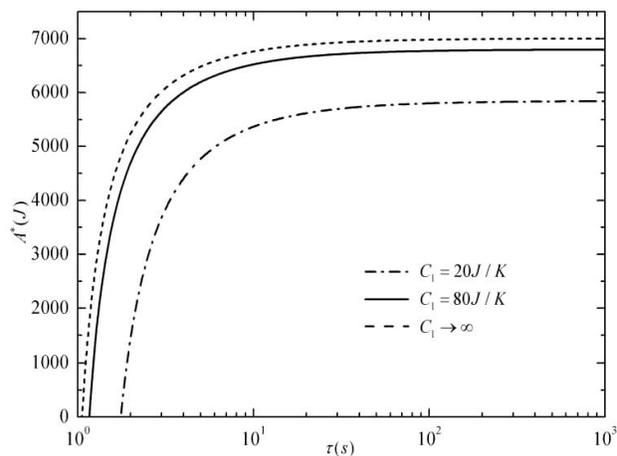


FIGURE 3. Finite-time exergy versus process duration for the case with Newton's heat transfer law.

4.4. The results for the case with infinite thermal capacity reservoir

In this case, $C_1 \rightarrow \infty$. Now the finite-time exergy with a finite reservoir reduces to that with an infinite reservoir. According to Refs. 15 to 18, the optimal thermodynamic processes for the finite-time exergy with Newton's, linear phenomenological, and radiative heat transfer law are those for which the temperature of the subsystem is a constant and the temperature difference between the reservoir and the subsystem is also a constant during the heat transfer process without exception. Then the temperature of the working fluid is a constant and equal to T_2^* ; from Eq. (13) one obtains

$$\Delta S_2^*(\tau) = Q/T_2^* \quad (44)$$

Substituting Eq. (44) into Eq. (23) yields

$$A^* = Q - E_2(0) \times \left[\left(\frac{V^*(\tau)}{V(0)} \right)^{-(R/C_{V2})} \exp \left(\frac{Q}{C_{V2}T_2^*} \right) - 1 \right] \quad (45)$$

Since T_2^* is non-negative, $A^*(\tau)$ is defined for

$$\tau > \tau_{\min} = Q / (kT_1^n).$$

5. Numerical examples and discussions

In the calculations, the initial temperature of the heat reservoir is $T_{10} = 1000$ K, the subsystem is 1 mol ideal gas, the universal gas constant is $R = 8.314$ J/(mol · K), the mole constant volume heat capacity is $C_{V2} = 3R/2$, the initial volume is $V_2(0) = 22.4$ liter, the initial temperature is $T_2(0) = 300$ K, the amount of heat transfer is $Q = 1 \times 10^4$ J, and the initial internal energy is $E_2(0) = 3741.5$ J. In order to analyze effects of changes of the heat capacity on the optimized results, the heat capacity of the reservoir is set to be $C_1 = 20$ J/K, $C_1 = 80$ J/K, and $C_1 \rightarrow \infty$, respectively.

5.1. Numerical example for the case with Newton's heat transfer law

In this case, the heat conductance is set as $k = 13.5$ W/K. Figure 2 shows the optimal temperature configurations for the finite-time exergy during the heat transfer processes with $\tau = 8$ s. Figure 3 shows the finite-time exergy versus process duration. From Fig. 2, one can see that the optimal temperature configuration during the heat transfer process is such that the temperatures of the reservoir and the subsystem change exponentially with time, and the temperature ratio between the reservoir and the subsystem is a constant. The amounts of temperature changes of the reservoir and the subsystem decrease with the increase in the heat capacity of the reservoir. When the heat capacity of the reservoir tends to infinitely large, the optimal configuration of the heat transfer branch is such that the subsystem temperature is a constant, and the temperature difference between the reservoir and the subsystem is also a constant during the heat transfer process. From Fig. 3, one can see that with the increase of the process duration, the finite time exergy tends to a constant, *i.e.* the classical thermodynamic exergy. For the same process duration, the finite-time exergy is an increasing function of the heat capacity of the reservoir, *i.e.* the finite-time exergy with a finite thermal capacity heat reservoir is less than that with an infinite thermal capacity heat reservoir under the same condition. For a fixed process duration τ , the maximum average power is $P(\tau) = A^*(\tau)/\tau$, which is equal to the tangent of the slope of the line segment connecting the origin with the point $A^*(\tau)$ in Fig. 3. Figure 4 shows the maximum average power P versus process duration τ . From Fig. 4, one can see that the maximum average power attains its maximum value at one point along the axis of process duration, and the average power tends to zero when the process time tends to infinitely large, *i.e.* the power for the reversible process is zero. It is evident that the finite-time exergy is a more realistic, stronger limit compared to the classical thermodynamic exergy.

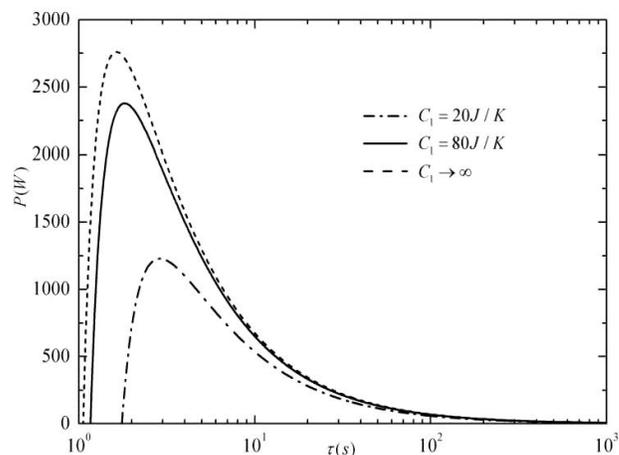


FIGURE 4. Maximum average power versus process duration for the case with Newton's heat transfer law.

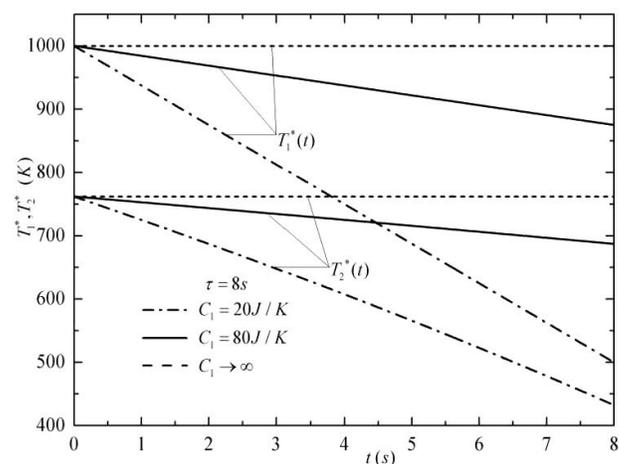


FIGURE 5. Optimal temperature configurations for the finite-time exergy during the heat transfer processes with the linear phenomenological heat transfer law.

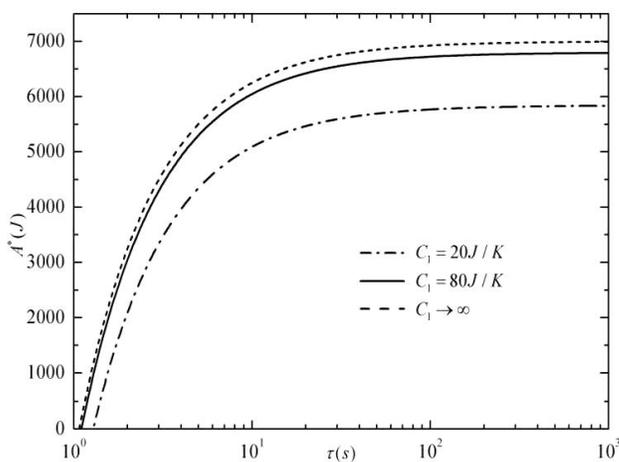


FIGURE 6. Finite-time exergy versus process duration for the case with the linear phenomenological heat transfer law.

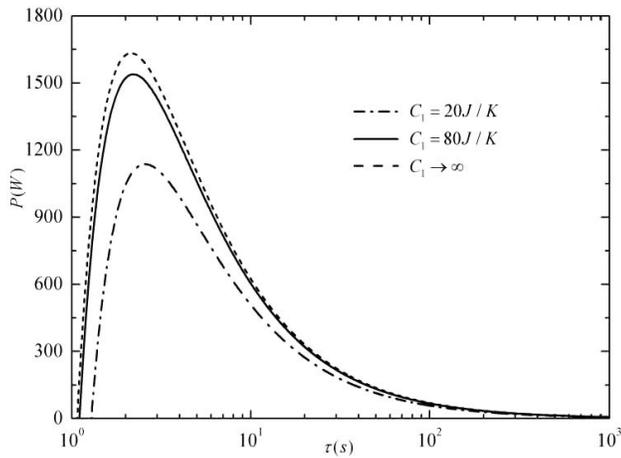


FIGURE 7. Maximum average power versus process duration for the case with the linear phenomenological heat transfer law.

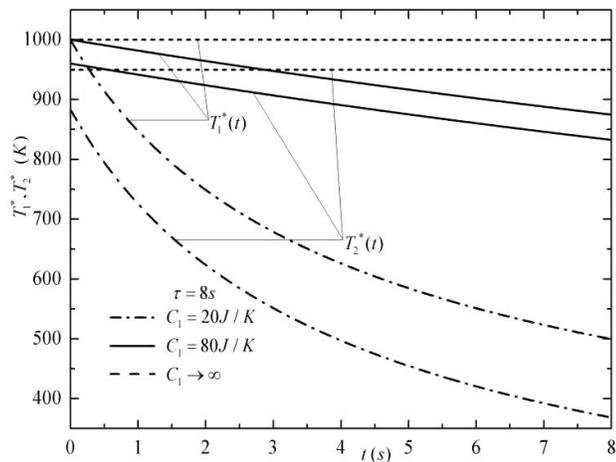


FIGURE 8. Optimal temperature configurations for the finite-time exergy during the heat transfer processes with the radiative heat transfer law.

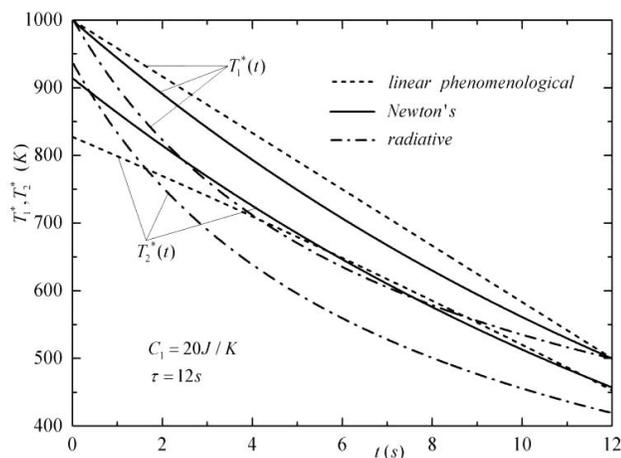


FIGURE 9. Optimal temperature configurations for the finite-time exergy during the heat transfer processes with different heat transfer laws.

5.2. Numerical example for the case with the linear phenomenological heat transfer law

In this case, the heat conductance is set as $k = -4.0 \times 10^6 \text{ W} \cdot \text{K}$. Figure 5 shows the optimal temperature configurations for the finite-time exergy during the heat transfer processes with $\tau = 8 \text{ s}$. Figure 6 shows the finite-time exergy versus process duration. From Fig. 5, one can see that the optimal temperature configuration during the heat transfer process is such that the temperatures of the reservoir and the subsystem change linearly and non-linearly with time, respectively, and the difference in reciprocal temperature between them is a constant. The amounts of temperature changes in the reservoir and the subsystem decrease with the increase in the heat capacity of the reservoir. When the heat capacity of the reservoir tends to infinitely large, the optimal configuration of the heat transfer branch is such that the subsystem temperature is a constant, and the temperature difference between the reservoir and the subsystem is also a constant during the heat transfer process. From Fig. 6, one can see that with the increase in process duration, the finite time exergy tends to a constant, *i.e.* the classical thermodynamic exergy. For the same process duration, the finite-time exergy is an increasing function of the heat capacity of the reservoir, *i.e.* the finite-time exergy with a finite thermal capacity heat reservoir is less than that with an infinite thermal capacity heat reservoir under the same condition. Figure 7 shows the maximum average power P versus process duration τ for the case. From Fig. 7, one can see that the maximum average power also attains its maximum value at one point along the axis of process duration, and the average power tends to zero when the process time tends to infinitely large, *i.e.* the power for the reversible process is zero. It is evident that the finite-time exergy is a more realistic, stronger limit compared to the classical thermodynamic exergy.

5.3. Numerical example for the case with the radiative heat transfer law

In this case, the heat conductance is set as $k = 1.0 \times 10^{-8} \text{ W/K}^4$. Figure 8 shows the optimal temperature configurations for the finite-time exergy during the heat transfer processes $\tau = 8 \text{ s}$. From Fig. 8, one can see that the optimal temperature configuration during the heat transfer process is such that the temperatures of the reservoir and the subsystem change linearly with time. The amounts of temperature changes in the reservoir and the subsystem decrease with the increase in the heat capacity of the reservoir. When the heat capacity of the reservoir tends to infinitely large, the optimal configuration of the heat transfer branch is also such that the subsystem temperature is a constant, and the temperature difference between the reservoir and the subsystem is also a constant during the heat transfer process. According to the calculation results, the same conclusions as those obtained for the cases with Newton's and linear phenomenological heat transfer law are obtained.

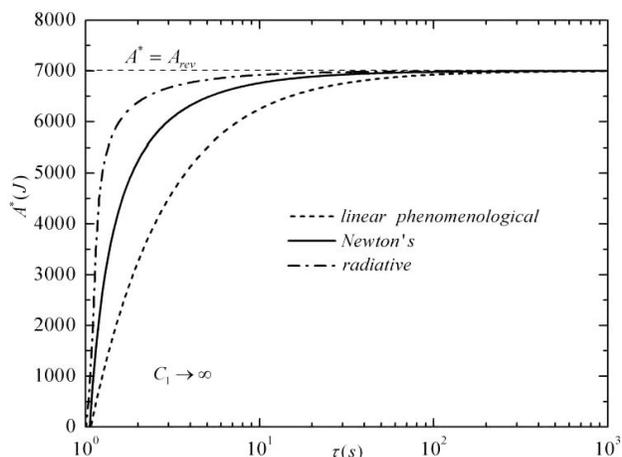


FIGURE 10. Finite-time exergy versus process duration for the cases with different heat transfer laws.

6. Performance comparison for different heat transfer laws

Figure 9 shows the optimal temperature configurations for the finite-time exergy during the heat transfer processes with different heat transfer laws ($C_1 = 20 \text{ J/K}$ and $\tau = 12 \text{ s}$). From Fig. 9, one can see that the optimal temperature configurations of the reservoir and the subsystem for the finite-time exergy with different heat transfer laws are different from each other significantly, see detail mentioned above. Figure 10 shows the finite-time exergy versus process duration with different heat transfer laws and $C_1 \rightarrow \infty$. For the same process duration, the finite-time exergy for the case with the radiative heat transfer law is the largest, the finite-time exergy for the case with the linear phenomenological heat transfer law is the smallest, and the finite-time exergy for the case with the Newton's heat transfer law lies between them. Heat transfer laws have significant effects on the finite-time exergy and the corresponding optimal thermodynamic process, so it is necessary to investigate the results with different heat transfer laws.

7. Conclusion

On the basis of Refs. 15 to 18, the problem of the maximal work that can be extracted from a system consisting of one

finite heat reservoir and one subsystem with generalized radiative heat transfer law [$q \propto \Delta(T^n)$] is investigated in this paper. Finite time exergy is derived for the fixed duration of the process and the given initial state of the subsystem by applying optimal control theory. The optimal temperature configuration of the subsystem for the finite-time exergy consists of three segments, including the initial and final instantaneous adiabatic branches and the intermediate heat transfer branch. The optimal configuration of the heat transfer branch with Newton's heat transfer law [$q \propto \Delta(T)$] is such that the temperatures of the reservoir and the subsystem change exponentially with time and the temperature ratio between the reservoir and the subsystem is a constant. The optimal configuration of the heat transfer branch with the linear phenomenological heat transfer law [$q \propto \Delta(T^{-1})$] is such that the temperatures of the reservoir and the subsystem change linearly and non-linearly with time, respectively, and the difference in the reciprocal temperature between the reservoir and the subsystem is a constant. The optimal configuration of the heat transfer branch with the radiative heat transfer law [$q \propto \Delta(T^4)$] is significantly different from those with the former two different heat transfer laws. Some modifications are made to the results in Refs. 15 to 18, and the obtained results in this paper become those with an infinite heat reservoir [15-18] when the capacity of the reservoir tends to infinity. The finite-time exergy in this paper is derived under the constraint that the process duration is finite and the assumption that both the reservoir and the subsystem are in internal equilibrium. If the internal irreversibility of the subsystem is further considered, the corresponding maximum work output is lower than the finite-time exergy obtained in this paper. The finite-time exergy tends to the classical thermodynamic exergy and the average power tends to zero when the process duration tends to infinitely large.

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