

Problem 1.

Consider two macroscopic systems “A” and “B” having the same specific heat c . The systems start with initial temperatures T_A and T_B , respectively. Suppose that the two systems are placed in contact and thermally isolated from the outside world and that heat is allowed to slowly pass between them until they reach a common final temperature, T_f . The volumes and particle numbers of each system remain fixed throughout this process and the specific heat c does not depend on temperature.

- Find the final temperature T_f .
- What is the change of the entropy of each system?
- What is the change of the entropy of the universe? Is it positive or negative?

Solution

Let $T_B > T_A$. First, $T_f = \frac{n_A T_A + n_B T_B}{n_A + n_B}$ where n_A and n_B are masses of systems “A” and “B”. Second,

$$dS_A = \frac{dQ}{T_1} = cn_A \frac{dT_1}{T_1} \Rightarrow \Delta S = cn_A \int_{T_A}^{T_f} \frac{dT_1}{T_1} = cn_A \ln \frac{T_f}{T_A}$$

Similarly,

$$dS_B = -\frac{dQ}{T_2} = cn_B \frac{dT_2}{T_2} \Rightarrow \Delta S = cn_B \int_{T_B}^{T_f} \frac{dT_2}{T_2} = -cn_B \ln \frac{T_B}{T_f}$$

Change of the entropy of the universe

$$\Delta S = cn_A \ln \frac{T_f}{T_A} - cn_B \ln \frac{T_B}{T_f} > 0$$

If $n_A = n_B$ it is obvious: $\Delta S = cn_A \ln \frac{(T_A + T_B)^2}{4T_A T_B} > 0$

Problem 2.

Liquid helium-4 has a normal boiling point of 4.2 K at 1 atm (= 760 mm of mercury). However, at a pressure of 1 mm of mercury, it boils at 1.2 K. Estimate the average latent heat of vaporization of helium in this temperature range. Assume that helium gas is an ideal gas and that the latent heat does not depend on temperature.

Hint: use Clausius-Clapeyron equation

Solution

$$\frac{dP(T)}{dT} = \frac{L}{T(v''' - v'')} \simeq \frac{L}{Tv''}$$

Since $Pv''' = RT$

$$\frac{dP(T)}{dT} = \frac{L}{T(v''' - v'')} \simeq \frac{L}{RT^2}P(T) \Leftrightarrow \frac{dP}{P} = \frac{L}{R} \frac{dT}{T^2}$$

Assuming $L = \text{const}$, we get

$$\ln \frac{P}{P_0} = \frac{L}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \Rightarrow L = R \frac{\ln P/P_0}{\frac{1}{T_0} - \frac{1}{T}} \simeq 93 \frac{\text{kJ}}{\text{kmol}}$$

Problem 3.

An entropy of a substance of n moles at a volume V and temperature T with total internal energy U has the form

$$S = \frac{3}{2}nR \ln \left(\frac{U}{nu_0} + \lambda \right) + nR \left(\ln \frac{V}{V_0} + \frac{3}{2} \right)$$

where U_0, V_0 , and λ are positive constants.

Find:

- Temperature as a function of U, V , and n .
- Equation of state (P as a function of n, V , and T).
- Chemical potential as a function of T, P , and V .

Solution

$$dS = \frac{3}{2} \frac{nR}{U + \lambda nu_0} dU + \frac{nR}{V} dV + \frac{3}{2} R \left[\ln \left(\frac{U}{nu_0} + \lambda \right) + \frac{\lambda nu_0}{U + \lambda nu_0} + \frac{2}{3} \ln \frac{v}{v_0} \right] = \frac{dU}{T} + \frac{PdV}{T} - \frac{\mu dn}{T}$$

$$\Rightarrow T = \frac{2U + \lambda nu_0}{3nR}, \quad P = \frac{nRT}{V}, \quad \mu = -R \left[\frac{3}{2} \ln \frac{3RT}{2u_0} + \frac{\lambda u_0}{RT} + \ln \frac{V}{V_0} \right]$$

Problem 4.

The flux s given by Eq. (9.11) $\Phi = \bar{v} \frac{n(t)}{4} = \bar{v} \frac{N(t)}{4V}$ so we get the differential equation

$$\frac{dN(t)}{dt} = A\Phi = \frac{A\bar{v}}{4V} N(t)$$

with initial condition $N(t)|_{t=0} = N$.

Solution:

$$N = N_0 \times e^{-\frac{A\bar{v}}{4V}t}$$

The number of particles will be $\frac{N}{2}$ when $e^{-\frac{A\bar{v}}{4V}t} = \frac{1}{2}$ which gives

$$t = \frac{4V \ln 2}{A\bar{v}}$$