

Problem 7-29 solution

Q: Is $C = AT^{1/2} + BT^3$ OK?

A: Yes, since $C \rightarrow 0$ as $T \rightarrow 0$ and

$$S(V, T) = \int_0^T \frac{C}{T} dT = \int_0^T dT (AT^{-1/2} + BT^2) \xrightarrow{T \rightarrow 0} 0$$

Problem 8-1 solution

(a):

From Eq. (6.45)

$$\left. \begin{aligned} S_A &= n_A \left(c_v \ln \frac{T}{T_0} + R \ln \frac{V_1}{V_0} \right) + S_{0A} \\ S_B &= n_B \left(c_v \ln \frac{T}{T_0} + R \ln \frac{V_2}{V_0} \right) + S_{0B} \end{aligned} \right\} \xrightarrow{\text{partition removed}} \left\{ \begin{aligned} S'_A &= n_A \left(c_v \ln \frac{T}{T_0} + R \ln \frac{V_1+V_2}{V_0} \right) + S_{0A} \\ S'_B &= n_B \left(c_v \ln \frac{T}{T_0} + R \ln \frac{V_1+V_2}{V_0} \right) + S_{0B} \end{aligned} \right.$$

$$\Rightarrow \Delta S = S'_A + S'_B - S_A - S_B = Rn_A \ln \frac{V_1+V_2}{V_1} + Rn_B \ln \frac{V_1+V_2}{V_2} = Rn_A \ln \frac{n_A+n_B}{n_A} + Rn_B \ln \frac{n_A+n_B}{n_B}$$

(b)

If gas is the same, partition is irrelevant \Rightarrow should be $\Delta S = 0$ rather than : Gibbs' paradox.

Resolution: in quantum mechanics (suppose the gas is monoatomic so $c_v = \frac{3}{2}R$)

$$S = Nk_B \left[\ln \frac{V}{N} + \frac{3}{2} \ln k_B T \right] + Nk_B \left[\frac{5}{2} + \frac{3}{2} \ln \left(\frac{m}{2\pi\hbar^2} \right) \right] \quad (1)$$

where N is a number of molecules (number of moles is $n = \frac{N}{N_A}$ where N_A is the Avogadro number).

Now for different gases

$$\left. \begin{aligned} S_A &= N_A k_B \left[\ln \frac{V_1}{N_A} + \frac{3}{2} \ln k_B T \right] + N_A k_B \left[\frac{5}{2} + \frac{3}{2} \ln \left(\frac{m}{2\pi\hbar^2} \right) \right] \\ S_B &= N_B k_B \left[\ln \frac{V_2}{N_B} + \frac{3}{2} \ln k_B T \right] + N_B k_B \left[\frac{5}{2} + \frac{3}{2} \ln \left(\frac{m}{2\pi\hbar^2} \right) \right] \end{aligned} \right\} \xrightarrow{\text{partition removed}}$$

$$\rightarrow \left\{ \begin{aligned} S'_A &= N_A k_B \left[\ln \frac{V_1+V_2}{N_A} + \frac{3}{2} \ln k_B T \right] + N_A k_B \left[\frac{5}{2} + \frac{3}{2} \ln \left(\frac{m}{2\pi\hbar^2} \right) \right] \\ S'_B &= N_B k_B \left[\ln \frac{V_1+V_2}{N_B} + \frac{3}{2} \ln k_B T \right] + N_B k_B \left[\frac{5}{2} + \frac{3}{2} \ln \left(\frac{m}{2\pi\hbar^2} \right) \right] \end{aligned} \right.$$

$$\Rightarrow \Delta S = S'_A + S'_B - S_A - S_B = k_B N_A \ln \frac{V_1+V_2}{V_1} + k_B N_B \ln \frac{V_1+V_2}{V_2}$$

same as before, while for identical gases

$$\left. \begin{aligned} S_A &= N_A k_B \left[\ln \frac{V}{N_A} + \frac{3}{2} \ln k_B T \right] + N_A k_B \left[\frac{5}{2} + \frac{3}{2} \ln \left(\frac{m}{2\pi\hbar^2} \right) \right] \\ S_B &= N_B k_B \left[\ln \frac{V}{N_B} + \frac{3}{2} \ln k_B T \right] + N_B k_B \left[\frac{5}{2} + \frac{3}{2} \ln \left(\frac{m}{2\pi\hbar^2} \right) \right] \end{aligned} \right\} \xrightarrow{\text{partition removed}}$$

$$\rightarrow S'_{A+B} = (N_A + N_B) k_B \left[\ln \frac{V_1+V_2}{N_A+N_B} + \frac{3}{2} \ln k_B T \right] + (N_A + N_B) k_B \left[\frac{5}{2} + \frac{3}{2} \ln \left(\frac{m}{2\pi\hbar^2} \right) \right]$$

$$\Rightarrow \Delta S = S'_A + S'_B - S_A - S_B = k_B (N_A + N_B) \ln \frac{V_1+V_2}{N_A+N_B} - k_B N_A \ln \frac{V_1}{N_A} - k_B N_B \ln \frac{V_2}{N_B} = 0$$

since $\frac{V_1}{N_A} = \frac{V_2}{N_B} = \frac{V_1+V_2}{N_A+N_B} = v$

Problem 8-3 solution

(a)

Analog of Eq. (8-15) $dG = -SdT + VdP + \mu dn$:

$$dG = -SdT + VdP + \mu_1 dn_1 + \mu_2 dn_2$$

(b)

dG is exact \Rightarrow Maxwell's equations:

$$\begin{aligned} \left(\frac{\partial V}{\partial T} \right)_{P, n_1, n_2} &= - \left(\frac{\partial S}{\partial P} \right)_{T, n_1, n_2} &= \frac{\partial^2 G(P, T, n_1, n_2)}{\partial P \partial T}, & \left(\frac{\partial \mu_1}{\partial n_2} \right)_{P, T, n_1} &= \left(\frac{\partial \mu_2}{\partial n_1} \right)_{T, P, n_2} &= \frac{\partial^2 G(P, T, n_1, n_2)}{\partial n_1 \partial n_2} \\ \left(\frac{\partial V}{\partial n_1} \right)_{P, T, n_2} &= \left(\frac{\partial \mu_1}{\partial P} \right)_{T, n_1, n_2} &= \frac{\partial^2 G(P, T, n_1, n_2)}{\partial P \partial n_1}, & \left(\frac{\partial V}{\partial P} \right)_{P, T, n_1} &= \left(\frac{\partial \mu_2}{\partial P} \right)_{T, n_1, n_2} &= \frac{\partial^2 G(P, T, n_1, n_2)}{\partial P \partial n_2} \\ - \left(\frac{\partial S}{\partial n_1} \right)_{P, T, n_2} &= \left(\frac{\partial \mu_1}{\partial T} \right)_{P, n_1, n_2} &= \frac{\partial^2 G(P, T, n_1, n_2)}{\partial T \partial n_1}, & - \left(\frac{\partial S}{\partial n_2} \right)_{P, T, n_1} &= \left(\frac{\partial \mu_1}{\partial T} \right)_{P, n_1, n_2} &= \frac{\partial^2 G(P, T, n_1, n_2)}{\partial T \partial n_2}, \\ - \left(\frac{\partial S}{\partial n_1} \right)_{P, T, n_2} &= \left(\frac{\partial \mu_1}{\partial T} \right)_{P, n_1, n_2} &= \frac{\partial^2 G(P, T, n_1, n_2)}{\partial T \partial n_1}, & - \left(\frac{\partial S}{\partial n_2} \right)_{P, T, n_1} &= \left(\frac{\partial \mu_1}{\partial T} \right)_{P, n_1, n_2} &= \frac{\partial^2 G(P, T, n_1, n_2)}{\partial T \partial n_2}, \end{aligned}$$