Problem 7-10 solution

$$\Phi \equiv S - \frac{U+PV}{T} \quad \Rightarrow \quad d\Phi = dS - \frac{1}{T}(dU + PdV + VdP) + \frac{dT}{T^2}(U+PV)$$

$$TdS = dU + PdV \quad \Rightarrow \quad d\Phi = -\frac{V}{T}dP + \frac{dT}{T^2}(U+PV) \quad \Rightarrow \quad \Big(\frac{\partial \Phi}{\partial P}\Big)_T = -\frac{V}{T}$$

$$\Big(\frac{\partial \Phi}{\partial P}\Big)_T = -V, \quad \Big(\frac{\partial \Phi}{\partial T}\Big)_P = \frac{U+PV}{T^2} \quad \Rightarrow \quad T\Big(\frac{\partial \Phi}{\partial T}\Big)_P + P\Big(\frac{\partial \Phi}{\partial P}\Big)_T = \frac{U}{T}$$

$$T\Big(\frac{\partial \Phi}{\partial T}\Big)_P + \Phi = \frac{U+PV}{T^2} + S - \frac{U+PV}{T} = S$$

Problem 7-29 solution

Q: Is $C = AT^{1/2} + BT^3$ OK?
A: Yes, since $C \to 0$ as $T \to 0$ and

$$S(V,T) = \int_0^T \frac{C}{T}dT = \int_0^T d\mathcal{T}\,\left(A\mathcal{T}^{-1/2} + B\mathcal{T}^2\right) \stackrel{T\to 0}{\to} 0$$

Problem 8-1 solution

(a):
From Eq. (6.45)

$$\left.\begin{array}{l} S_A = n_A\big(c_v \ln\frac{T}{T_0} + R\ln\frac{V_1}{V_0}\big) + S_{0A} \\ S_B = n_B\big(c_v \ln\frac{T}{T_0} + R\ln\frac{V_2}{V_0}\big) + S_{0B} \end{array}\right\} \xrightarrow{\text{partition removed}} \left\{\begin{array}{l} S'_A = n_A\big(c_v \ln\frac{T}{T_0} + R\ln\frac{V_1+V_2}{V_0}\big) + S_{0A} \\ S'_B = n_B\big(c_v \ln\frac{T}{T_0} + R\ln\frac{V_1+V_2}{V_0}\big) + S_{0B} \end{array}\right.$$
$$\Rightarrow \quad \Delta S = S'_A + S'_B - S_A - S_B = Rn_A \ln\frac{V_1+V_2}{V_1} + Rn_B \ln\frac{V_1+V_2}{V_2} = Rn_A \ln\frac{n_A+n_B}{n_A} + Rn_B\ln\frac{n_A+n_B}{n_B}$$

(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 $c_v = \frac{3}{2}R$)

$$S = Nk_B\Big[\ln\frac{V}{N} + \frac{3}{2}\ln k_BT\Big] + Nk_B\Big[\frac{5}{2} + \frac{3}{2}\ln\big(\frac{m}{2\pi\hbar^2}\big)\Big] \tag{1}$$

where N is a number of molecules (number of moles is $n = \frac{N}{\mathcal{N}_A}$ where $\mathcal{N}_A$ is the Avogadro number).
Now for different gases

$$\left.\begin{array}{l} S_A = N_Ak_B\Big[\ln\frac{V_1}{N_A} + \frac{3}{2}\ln k_BT\Big] + N_Ak_B\Big[\frac{5}{2} + \frac{3}{2}\ln\big(\frac{m}{2\pi\hbar^2}\big)\Big] \\ S_B = N_Bk_B\Big[\ln\frac{V_2}{N_B} + \frac{3}{2}\ln k_BT\Big] + N_Bk_B\Big[\frac{5}{2} + \frac{3}{2}\ln\big(\frac{m}{2\pi\hbar^2}\big)\Big] \end{array}\right\} \xrightarrow{\text{partition removed}}$$
$$\to \left\{\begin{array}{l} S'_A = N_Ak_B\Big[\ln\frac{V_1+V_2}{N_A} + \frac{3}{2}\ln k_BT\Big] + N_Ak_B\Big[\frac{5}{2} + \frac{3}{2}\ln\big(\frac{m}{2\pi\hbar^2}\big)\Big] \\ S'_B = N_Bk_B\Big[\ln\frac{V_1+V_2}{N_B} + \frac{3}{2}\ln k_BT\Big] + N_Bk_B\Big[\frac{5}{2} + \frac{3}{2}\ln\big(\frac{m}{2\pi\hbar^2}\big)\Big] \end{array}\right.$$
$$\Rightarrow \quad \Delta S = S'_A + S'_B - S_A - S_B = \;= k_BN_A\ln\frac{V_1+V_2}{V_1} + k_BN_B\ln\frac{V_1+V_2}{V_2}$$

same as before, while for identical gases

$$\left.\begin{array}{l} S_A = N_Ak_B\Big[\ln\frac{V}{N_A} + \frac{3}{2}\ln k_BT\Big] + N_Ak_B\Big[\frac{5}{2} + \frac{3}{2}\ln\big(\frac{m}{2\pi\hbar^2}\big)\Big] \\ S_B = N_Bk_B\Big[\ln\frac{V}{N_B} + \frac{3}{2}\ln k_BT\Big] + N_Bk_B\Big[\frac{5}{2} + \frac{3}{2}\ln\big(\frac{m}{2\pi\hbar^2}\big)\Big] \end{array}\right\} \xrightarrow{\text{partition removed}}$$
$$\to \quad S'_{A+B} = (N_A+N_B)k_B\Big[\ln\frac{V_1+V_2}{N_A+N_B} + \frac{3}{2}\ln k_BT\Big] + (N_A+N_B)k_B\Big[\frac{5}{2} + \frac{3}{2}\ln\big(\frac{m}{2\pi\hbar^2}\big)\Big]$$
$$\Rightarrow \quad \Delta S = S'_A + S'_B - S_A - S_B = k_B(N_A+N_B)\ln\frac{V_1+V_2}{N_A+N_B} - k_BN_A\ln\frac{V_1}{N_A} - -k_BN_B\ln\frac{V_2}{N_B} = 0$$

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:

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