热力学与统计物理-第八次作业

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Problem 7.1

Answer:

(a)

We label the positions and momenta such that r_{ij} and p_{ij} refer to the $\mathbf{j}th$ molecule of type i. There are N_i molecules of species i. Then the classical partition function for the mixture of ideal gas is:

$$z' = \int \exp\left[-\frac{\beta}{2m_1}\left(p_{11}^2+\ldots+p_{1N_1}^2\right)\ldots-\frac{\beta}{2m_k}\left(p_{k1}^2+\ldots+p_{kN_k}^2\right)\right]\frac{d^3r_{11}\ldots d^3r_{kN_k}d^3p_{11}\ldots d^3p_{kN_k}}{h_0^{3N_1}\ldots h_0^{3N_k}} \tag{1.1}$$

This integration over r yield the volume, V, while the p integrals are identical. Since there are $N_1+N_2+\ldots+N_k$ integration, we have:

$$z' = V^{(N_1+\ldots+N_k)}\left[\int e^{-\frac{\beta p^2}{2m}}\frac{d^3p}{h_0^3}\right]^{(N_1+\ldots+N_k)} \tag{1.2}$$

The term in brackets is independent of volume, consequently:

$$\ln z' = (N_1+\ldots+N_{\mathrm{K}})\ln V + \ln(\text{ constant }) \tag{1.3}$$

And:

$$\bar{p} = \frac{1}{\beta}\frac{\partial}{\partial V}\ln z' = (N_1+\ldots+N_k)\frac{1}{\beta V} \tag{1.4}$$

$$\overline{\mathrm{p}}V = (\mathrm{N}_1+\ldots+\mathrm{N}_{\mathrm{k}})\,\mathrm{kT} = (\nu_1+\ldots+\nu_{\mathrm{k}})\,\mathrm{RT} \tag{1.5}$$

(b)

For the i^{th} gas, $\mathrm{p}_i\mathrm{V} = \nu_i\mathrm{RT}$, from (1.5):

$$\bar{p} = \sum_i \bar{p}_i \tag{1.6}$$

Problem 7.3

Answer:

Before the partition is removed, we have on the left, pV = νRT. After removal the pressure is:

$$p_f = \frac{2\nu}{(1+b)V} = \frac{2p}{1+b} \tag{2.1}$$

(b)

The initial and final entropies of the system for different gases are:

$$\mathrm{S_i} = \nu\mathrm{R}\left[\ln\frac{\mathrm{V}}{\mathrm{N_A}\nu} + \frac{3}{2}\ln\mathrm{T} + \sigma_1\right] + \nu\mathrm{R}\left[\ln\frac{\mathrm{bV}}{\mathrm{N_A}\nu} + \frac{3}{2}\ln\mathrm{T} + \sigma_2\right] \tag{2.2}$$

$$S_f = \nu R\left[\ln\frac{(1+b)V}{N_A\nu} + \frac{3}{2}\ln T + \sigma_1\right] + \nu R\left[\ln\frac{(1+b)V}{N_A\nu} + \frac{3}{2}\ln T + \sigma_2\right] \tag{2.3}$$

Here one adds the entropies of the gases in the left and right compartments for $\mathrm{S_i}$ while $\mathrm{S_f}$ is the entropy of two different gases in volume $(1+b)V$. Then:

$$\Delta S = S_f - S_i = \nu R\left[2\ln\frac{V(1+b)}{N_A\nu} - \ln\frac{V}{N_A\nu} - \ln\frac{bV}{N_A\nu}\right] = \nu R\ln\frac{(1+b)^2}{b} \tag{2.4}$$

(c)

In the case of identical gases, $\mathrm{S_i}$ is again the sum of the entropies of the left and right compartments. $\mathrm{S_f}$ is the entropy of 2ν moles in a volume $(1+\mathrm{b})\mathrm{V}$

$$S_i = \nu R\left[\ln\frac{V}{N_A\nu} + \frac{3}{2}\ln T + \sigma_0\right] + \nu R\left[\ln\frac{bV}{N_A\nu} + \frac{3}{2}\ln T + \sigma_0\right] \tag{2.5}$$

$$S_f = 2\nu R\left[\ln\frac{(1+b)V}{2N_A\nu} + \frac{3}{2}\ln T + \sigma_0\right] \tag{2.6}$$

Thus:

$$\Delta S = \nu R\left[\ln\frac{(1+b)V}{2N_A\nu} - \ln\frac{V}{N_A\nu} - \ln\frac{bV}{N_A\nu}\right] = \nu R\ln\frac{(1+b)^2}{4b} \tag{2.7}$$

Problem 7.4

Answer:

(a)

The system is isolated so its total energy is constant, and since the energy of an ideal gas depends only on temperature, we have

$$\Delta E_1 + \Delta E_2 = C_V\left(T_f - I_1\right) + C_V\left(T_f - T_2\right) = 0 \tag{3.1}$$

Or

$$T_f = \frac{T_1 + T_2}{2} \tag{3.2}$$

The total volume is found fram the equation of state

$$V = \frac{\nu_1 R T_1}{p_1} + \frac{\nu_2 R T_2}{p_2} \tag{3.3}$$

Thus the final pressure is

$$p_f = \frac{(\nu_1 + \nu_2)\,\mathrm{R}T_\mathrm{f}}{\mathrm{V}} = \frac{(\nu_1 + \nu_2)}{2}\left(\frac{\mathrm{T_1 + T_2}}{(\nu_1 \mathrm{T_1/p_1}) + (\nu_2 \mathrm{T_2/p_2})}\right) \tag{3.4}$$

(b)

Using $\frac{V}{N} = \frac{kT}{p}$, we have for the initial and final entropies of different gases

$$S_i = \nu_1 R\left[\ln\frac{kT_1}{p_1} + \frac{3}{2}\ln T_1 + \sigma_1\right] + \nu_2 R\left[\ln\frac{kT_2}{p_2} + \ln T_2 + \sigma_2\right] \tag{3.5}$$

$$\begin{aligned}\mathrm{S_f} = \nu_1 \mathrm{R}\left[\ln\frac{\mathrm{k}}{\nu_1}\left(\frac{\nu_1\mathrm{T_1}}{\mathrm{p_1}} + \frac{\nu_2\mathrm{T_2}}{\mathrm{p_2}}\right) + \frac{3}{2}\ln\frac{\mathrm{T_1 + T_2}}{2} + \sigma_1\right]\\ + \nu_2\mathrm{R}\left[\ln\frac{\mathrm{k}}{\nu_2}\left(\frac{\nu_1\mathrm{T_1}}{\mathrm{p_1}} + \frac{\nu_2\mathrm{T_2}}{\mathrm{z_2}}\right) + \frac{3}{2}\ln\frac{\mathrm{T_1 + T_2}}{2} + \sigma_2\right]\end{aligned} \tag{3.6}$$

So:

$$\begin{aligned}\Delta S = S_f - S_i = \nu_1 R\left[\ln\left(1 + \frac{\nu_2 T_2 p_1}{\nu_1 T_1 p_2}\right) + \frac{3}{2}\ln\frac{T_1 + T_2}{2T_1}\right]\\ + \nu_2 R\left[\ln\left(1 + \frac{v_1 T_1 p_2}{v_2 T_2 p_1}\right) + \frac{3}{2}\ln\frac{T_1 + T_2}{2T_2}\right]\end{aligned} \tag{3.7}$$

(c)

For identical gases:

$$S_i = \nu_1 R\left[\ln\frac{kT_1}{p_1} + \frac{3}{2}\ln T_1 + \sigma_0\right] + \nu_2 R\left[\ln\frac{kT_2}{p_2} + \frac{3}{2}\ln T_2 + \sigma_0\right] \tag{3.8}$$

$$S_f = (\nu_1 + \nu_2)\,R\left[\ln\frac{k}{(\nu_1 + \nu_2)}\left(\frac{\nu_1 T_1}{p_1} + \frac{\nu_2 T_2}{p_2}\right) + \frac{3}{2}\ln\frac{T_1 + T_2}{2} + \sigma_0\right] \tag{3.9}$$

So:

$$\begin{aligned}\Delta S = v_1 R\left[\ln\frac{1}{(v_1 + v_2)}\left(v_1 + \frac{v_2 T_2 p_1}{T_1 p_2}\right) + \frac{3}{2}\ln\frac{T_1 + T_2}{2T_1}\right]\\ + v_2 R\left[\ln\frac{1}{(v_1 + v_2)}\left(v_2 + \frac{v_1 \mathrm{T_1 p_2}}{\mathrm{T_2 p_1}}\right) + \frac{3}{2}\ln\frac{\mathrm{T_1 + T_2}}{\mathrm{2T_2}}\right]\end{aligned} \tag{3.9}$$

Problem 7.5

Answer:

We take the zero of potential energy so that if a segment is oriented parallel to the vertical it contributes energy Wa and if antiparallel it contributes $-Wa$ to the total energy of the rubber band (Thus if the rubber band were fully extended, the total energy would be $-NWa$). Since the segments are non-interacting,

$$\bar{l} = N\frac{\mathrm{ae}^{-\mathrm{Wa}\beta} - \mathrm{ae}^{\mathrm{Wa}\beta}}{\mathrm{e}^{-\mathrm{Wa}\beta} + \mathrm{e}^{\mathrm{Wa}\beta}} = \mathrm{Na}\tanh\frac{\mathrm{Wa}}{\mathrm{kT}} \tag{4.1}$$

Problem 7.6

Answer:

Since the total energy is additive:

$$E_i = \epsilon_i\left(p_i\right) + U\left(q_1 \cdots q_n\right) = \frac{p^2}{2m} + U\left(q_1 \cdots q_n\right) \tag{5.1}$$

where U is the energy of interaction, the equipartition theorem still applies and

$$\bar{\epsilon} = \frac{3}{2}\mathrm{kT} \tag{5.2}$$

Problem 7.7

Answer:

If the gas is ideal, its mean energy per particle is

$$\bar{\epsilon} = \frac{\overline{p_x^2}}{2m} + \frac{\overline{p_y^2}}{2m} = kT \tag{6.1}$$

and the mean energy per mole becomes $\bar{E} = N_A kT$:

$$C = \frac{\partial\bar{E}}{\partial T} = N_A k = R \tag{6.2}$$

Problem 7.10

Answer:

(a)

Let the restoring force be - αx. Then the mean energy of N particles is

$$\overline{\mathrm{E}} = \mathrm{N}\left(\frac{1}{2}\mathrm{m}\overline{\mathrm{x}^2} + \frac{1}{2}\alpha\overline{\mathrm{x}^2}\right) \tag{7.1}$$

Then:

$$\overline{\mathrm{E}} = \mathrm{N}\left(\frac{1}{2}\mathrm{kT} + \frac{1}{2}\mathrm{kT}\right) = \mathrm{NkT} \tag{7.2}$$

So:

$$c = \frac{\partial \bar{E}}{\partial T} = Nk \tag{7.3}$$

(b)

If the restoring force is $-\alpha x^3$, the mean energy per particle is

$$\bar{\epsilon} = \frac{1}{2}m\bar{\dot{x}^2} + \frac{1}{4}\alpha\bar{x} \tag{7.4}$$

So, similarly with (a), we can get:

$$C = \frac{\partial \bar{E}}{\partial T} = \frac{3}{4}Nk \tag{7.5}$$

Problem 7.12

Answer:

(a)

Consider a cube of side a. The force necessary to decrease the length of a side by Δ a is κ_0Ae and therefore the pressure is $\Delta \mathrm{p} = \kappa_0 \Delta \mathrm{a}/\mathrm{a}^2$. The change in volume is $\Delta \mathrm{V} = -\mathrm{a}^2 \Delta \mathrm{a}$

$$\kappa = -\frac{1}{V}\left(\frac{\Delta V}{\Delta p}\right) = -\frac{1}{a^3}\left(-\frac{a^2\Delta a}{\kappa_0 \Delta a/a^2}\right) = \frac{a}{\kappa_0} \tag{8.1}$$

(b)

The Einstein temperature is $\theta_{\mathrm{E}} = \hbar\omega/\mathrm{k}$. Since $\omega = \sqrt{\kappa_{\mathrm{O}}/\mathrm{m}}$ where m is mass, we have from (8.1)

$$\theta_E = \frac{\hbar}{\mathrm{k}}\sqrt{\frac{\kappa}{\mathrm{m}}} = \frac{\hbar}{\mathrm{k}}\sqrt{\frac{\mathrm{a}}{\mathrm{m}_\kappa}} \tag{8.2}$$

So:

$$a = \left(\frac{\mu}{\rho N_A}\right)^{1/3} = \left(\frac{63 \cdot 5}{(8.9)\,(6 \times 10^{23})}\right)^{1/3} = 2.3 \times 10^{-8}\mathrm{cm} \tag{8.3}$$

So:

$$\theta_E \approx 150^{\circ}\mathrm{K} \tag{8.4}$$