

6.11

The mean separation,  $\bar{x}$ , is found from the probability that the separation is between  $x$  and  $x+dx$ .

$$P(x)dx \propto e^{-\frac{U(x)}{kT}} dx \quad \text{where } U(x) = U_0 \left[ \left(\frac{a}{x}\right)^2 - 2\left(\frac{a}{x}\right)^6 \right]$$

It's easily verified that the minimum of the potential is at  $x=a$ . Since departures from this position are small, we may expand  $U(x)$  about  $a$  to obtain

$$U(x) \approx -U_0 + \frac{36U_0}{a^2}(x-a)^2 - \frac{252U_0}{a^3}(x-a)^3$$

where we have kept only the first three terms. It follows that

$$P(x)dx = C \exp \left[ -\frac{36U_0(x-a)^2}{a^2 kT} + \frac{252U_0(x-a)^3}{a^3 kT} \right] dx$$

We have absorbed the irrelevant constant term,  $e^{-\frac{U_0}{kT}}$ , into the normalization constant  $C$ . This constant is evaluated from the usual requirement

$$\int_{-\infty}^{\infty} P(x)dx = C \int_{-\infty}^{\infty} \exp \left[ -\frac{36U_0(x-a)^2}{a^2 kT} \right] \exp \left[ \frac{252U_0(x-a)^3}{a^3 kT} \right] dx = 1$$

The predominant factor in the integrand is  $\exp \left[ -\frac{36U_0(x-a)^2}{a^2 kT} \right]$  so the second factor may be expanded in a Taylor's series as in Appendix A.6. Furthermore, the region of integration can be extended to  $-\infty$  since the exponential is negligibly small except near  $a$ .

$$\text{Thus } I = C \int_{-\infty}^{\infty} \exp \left[ -\frac{36U_0(x-a)^2}{a^2 kT} \right] \left( 1 + \frac{252U_0(x-a)^3}{a^3 kT} \right) dx \quad (1)$$

where we neglect all but the first two terms. The first integral is evaluated in Appendix A.4 while the second is 0 since the integrand is an odd function.

$$\text{Then } C = \frac{6}{a} \left( \frac{U_0}{\pi kT} \right)^{\frac{1}{2}}$$

By definition,  $\bar{x} = \int_{-\infty}^{\infty} x P(x)dx$ , and to the same approximation as in (1) we have

$$\bar{x} = \int_{-\infty}^{\infty} x \left( \frac{6}{a} \left( \frac{U_0}{\pi kT} \right)^{\frac{1}{2}} \exp \left[ -\frac{36U_0(x-a)^2}{a^2 kT} \right] \left( 1 + \frac{252U_0(x-a)^3}{a^3 kT} \right) dx \right)$$

The first term in the integrand is a Gaussian times  $x$  and the integral is just  $a$ . The second may be evaluated by making the substitution  $\xi = x-a$

$$\bar{x} = a + \frac{6}{a} \left( \frac{U_0}{\pi kT} \right)^{\frac{1}{2}} \frac{252U_0}{a^3 kT} \left[ \int_{-\infty}^{\infty} \xi^4 \exp \left[ -\left( \frac{36U_0}{a^2 kT} \right) \xi^2 \right] d\xi + \int_{-\infty}^{\infty} a \xi^3 \exp \left[ -\left( \frac{36U_0}{a^2 kT} \right) \xi^2 \right] d\xi \right]$$

Noting that the second integral is 0 since the integrand is an odd function, and evaluating the first by Appendix A.4, we find  $\bar{x} = a \left( 1 + \frac{0.15 kT}{U_0} \right)$

$$\text{Thus } \alpha = \frac{1}{\bar{x}} \frac{d\bar{x}}{dT} = \frac{0.15 k}{a U_0 + (0.15) a k T} \approx \frac{0.15 k}{U_0} \quad \text{since } U_0 \gg kT$$

7.1

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

$$Z' = \int \exp \left[ -\frac{\beta}{2m_1} (\underline{p}_{11}^2 + \dots + \underline{p}_{1N_1}^2) - \dots - \frac{\beta}{2m_K} (\underline{p}_{K1}^2 + \dots + \underline{p}_{KN_K}^2) \right] \frac{d^3r_{11} \dots d^3r_{KN_K} d^3p_{11} \dots d^3p_{KN_K}}{h_0^{3N_1} \dots h_0^{3N_K}}$$

The integrations over  $r$  yield the volume,  $V$ , while the  $p$  integrals are identical. Since there are  $N_1 + N_2 + \dots + N_K$  integrations, we have

$$Z' = V^{(N_1 + \dots + N_K)} \left[ \int e^{-\frac{\beta p^2}{2m}} \frac{d^3p}{h_0^3} \right]^{(N_1 + \dots + N_K)}$$

The term in brackets is independent of volume, consequently

$$\ln Z' = (N_1 + \dots + N_K) \ln V + \ln(\text{constant})$$

$$\text{and } \bar{p} = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Z' = (N_1 + \dots + N_K) \frac{1}{\beta V}$$

$$\bar{p}V = (N_1 + \dots + N_K) kT = (v_1 + \dots + v_K) RT \quad (1)$$

(b) For the  $i^{\text{th}}$  gas,  $p_i V = v_i RT$ , hence by (1)  $\bar{p} = \sum_i \bar{p}_i$

7.2

(a) By the equipartition theorem the average value of the kinetic energy of a particle is  $\bar{E} = \frac{3}{2} kT$ .

(b) The average potential energy is  $\bar{U} = \frac{\int_0^L mgz e^{-\beta mgz} dz}{\int_0^L e^{-\beta mgz} dz}$

$$\text{Then } \bar{U} = -\frac{\partial}{\partial \beta} \ln \int_0^L e^{-\beta mgz} dz = -\frac{\partial}{\partial \beta} \ln \frac{e^{-\beta mgL} - 1}{-\beta mg}$$

$$\text{On carrying out the differentiation, we find } \bar{U} = kT + \frac{mgL}{1 - e^{mgL/kT}}$$

7.3

(a) Before the partition is removed, we have on the left,  $\rho V = vRT$ . After removal the pressure is

$$P_f = \frac{2vRT}{(1+b)V} = \frac{2P}{1+b}$$

(b) The initial and final entropies of the system for different gases are

$$S_i = \nu R \left[ \ln \frac{V}{N_A \nu} + \frac{3}{2} \ln T + \bar{\sigma}_i \right] + \nu R \left[ \ln \frac{bV}{N_A \nu} + \frac{3}{2} \ln T + \bar{\sigma}_2 \right]$$

$$S_f = \nu R \left[ \ln \frac{(1+b)V}{N_A \nu} + \frac{3}{2} \ln T + \bar{\sigma}_i \right] + \nu R \left[ \ln \frac{(1+b)V}{N_A \nu} + \frac{3}{2} \ln T + \bar{\sigma}_2 \right]$$

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

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

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

$$S_i = \nu R \left[ \ln \frac{V}{N_A \nu} + \frac{3}{2} \ln T + \bar{\sigma}_o \right] + \nu R \left[ \ln \frac{bV}{N_A \nu} + \frac{3}{2} \ln T + \bar{\sigma}_o \right]$$

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

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

#### Q.4

(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

$$\Delta E_1 + \Delta E_2 = C_V \nu_1 (T_f - T_i) + C_V \nu_2 (T_f - T_2) = 0$$

$$\text{or } T_f = \frac{\nu_1 T_i + \nu_2 T_2}{\nu_1 + \nu_2}$$

The total volume is found from the equation of state

$$V = \frac{\nu_1 R T_i}{P_1} + \frac{\nu_2 R T_2}{P_2}$$

$$\text{Thus the final pressure is } P_f = \frac{(\nu_1 + \nu_2) R T_f}{V} = \frac{\nu_1 T_i + \nu_2 T_2}{(\nu_1 T_i / P_1) + (\nu_2 T_2 / P_2)}$$

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

$$S_i = \nu_1 R \left[ \ln \frac{k T_i}{P_1} + \frac{3}{2} \ln T_i + \bar{\sigma}_i \right] + \nu_2 R \left[ \ln \frac{k T_2}{P_2} + \ln T_2 + \bar{\sigma}_2 \right]$$

$$S_f = \nu R \left[ \ln \frac{k}{\nu_1} \left( \frac{\nu_1 T_i + \nu_2 T_2}{P_1} \right) + \frac{3}{2} \ln \frac{\nu_1 T_i + \nu_2 T_2}{\nu_1 + \nu_2} + \bar{\sigma}_i \right] + \nu_2 R \left[ \ln \frac{k}{\nu_2} \left( \frac{\nu_1 T_i + \nu_2 T_2}{P_2} \right) + \frac{3}{2} \ln \frac{\nu_1 T_i + \nu_2 T_2}{\nu_1 + \nu_2} + \bar{\sigma}_2 \right]$$

$$\text{Thus } \Delta S = S_f - S_i = \nu R \left[ \ln \left( 1 + \frac{\nu_2 T_2 P_1}{\nu_1 T_1 P_2} \right) + \frac{3}{2} \ln \frac{\nu_1 T_1 + \nu_2 T_2}{(\nu_1 + \nu_2) T_1} \right] + \nu_2 R \left[ \ln \left( 1 + \frac{\nu_1 T_1 P_2}{\nu_2 T_2 P_1} \right) + \frac{3}{2} \ln \frac{\nu_1 T_1 + \nu_2 T_2}{(\nu_1 + \nu_2) T_2} \right]$$

(C) For identical gases

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

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

$$\Delta S = \nu_1 R \left[ \ln \frac{1}{\nu_1 + \nu_2} \left( \nu_1 + \frac{\nu_2 T_2 P_1}{T_1 P_2} \right) + \frac{3}{2} \ln \frac{\nu_1 T_1 + \nu_2 T_2}{(\nu_1 + \nu_2) T_1} \right] + \nu_2 R \left[ \ln \frac{1}{\nu_1 + \nu_2} \left( \nu_2 + \frac{\nu_1 T_1 P_2}{T_2 P_1} \right) + \frac{3}{2} \ln \frac{\nu_1 T_1 + \nu_2 T_2}{(\nu_1 + \nu_2) T_2} \right]$$