Pathria + Beale, Chapter 1

Problem 1.4

We consider a gas of N hard spheres, each with radius r_0 and volume $v_0 = \frac{4}{3}\pi r_0^3$, confined to a region of volume V.

The factor in $\Omega = e^S$ that depends on V is the product of N factors, one for each of the successive particles inserted into the volume.

The center-of-mass of a hard sphere must be a distance r_0 away from the boundary of the container. The volume for the first particle is therefore $V - Ar_0$, where A is the area of the container.

The center-of mass of the second hard sphere must be a distance r_0 away from the boundary and also a distance $2r_0$ away from the center-of-mass of the first hard sphere. The volume factor for the second particle is therefore $V - Ar_0 - \frac{4}{3}\pi(2r_0)^3$.

The volume factor for each successive hard sphere is smaller by the same term. The complete volume factor in $\Omega = e^S$ is therefore

$$\prod_{n=1}^{N}\left(V - Ar_0 - (n-1)\,8v_0\right)$$

$$= \left(V-Ar_0\right)^N \prod_{n=1}^{N}\left(1 - (n-1)\frac{8v_0}{V-Ar_0}\right)$$

$$= \left(V-Ar_0\right)^N \exp\left(\sum_{n=1}^{N} \log\left(1-(n-1)\frac{8v_0}{V-Ar_0}\right)\right)$$

If $Nv_0 \ll V$, the logarithm can be approximated by the first term in its expansion in powers of $v_0/V-Ar_0$.

$$\log\left(1-(n-1)\frac{8v_0}{V-Ar_0}\right) \simeq -(n-1)\frac{8v_0}{V-Ar_0}$$

The sum then reduces to

$$\sum_{n=1}^{N}\left(-(n-1)\frac{8v_0}{V-Ar_0}\right)$$

$$= -\frac{8v_0}{V-Ar_0}\sum_{n=1}^{N}(n-1)$$

$$= -\frac{8v_0}{V-Ar_0}\,\frac{(N-1)N}{2}$$

$$\simeq -\frac{4v_0N^2}{V-Ar_0}$$

The volume factor in $\Omega = e^S$ reduces to

$$\left(V-Ar_0\right)^N \exp\left(-\frac{4v_0N^2}{V-Ar_0}\right)$$

$$= \left[\left(V-Ar_0\right)\exp\left(-\frac{4v_0N}{V-Ar_0}\right)\right]^N$$

If $N v_0 << V$, the exponential can be expanded to first order in $N v_0 / V - A r_0$. The volume factor reduces to

$$\left[(V - A r_0) \left(1 - \frac{4 v_0 N}{V - A r_0}\right) \right]^N$$

$$= \left(V - A r_0 - 4 N v_0 \right)^N$$

If the length scale for the container is L, the volume scales as L^3 and the area scales as L^2. In the thermodynamic limit, the term $A r_0$ is negligible compared to V. The volume factor therefore reduces to

$$\left(V - 4 N v_0 \right)^N$$

The volume V is decreased by 4 times the total volume of the N hard spheres.

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Problem 1.6

The thermodynamic variables of a monatomic gas satisfy

$$PV = NkT \qquad E = \tfrac{3}{2}NkT$$

The initial temperature, pressure, and volume are

$$kT = \left(1.38\times10^{-23}\,\tfrac{J}{K}\right)(300K) = 4.14\times10^{-21}\,J$$

$$P = 1\,atm = 1.01\times10^{5}\,\tfrac{J}{m^3}$$

$$V = (1\,m)\,\pi\,(0.1\,m/2)^2 = 7.85\times10^{-3}\,m^3$$

The number of atoms is

$$N = \frac{PV}{kT}$$

$$= \frac{(1.01\times10^{5}\,J/m^3)(7.85\times10^{-3}\,m^3)}{4.14\times10^{-21}\,J}$$

$$= 1.92\times10^{23}$$

The initial energy is

$$E = \tfrac{3}{2}NkT$$

$$= \frac{3}{2}(1.92 \times 10^{23})(4.14 \times 10^{-21}\ J)$$

$$= 1190\ J$$

The electrical discharge adds an energy of 10^4 J. The resulting energy is $E_1 = 11{,}190$ J. The final temperature is

$$T = \frac{E_1}{\frac{3}{2} N k}$$

$$= \frac{11{,}190\ J}{\frac{3}{2}(1.92 \times 10^{23})(1.38 \times 10^{-23}\ J/K)}$$

$$= 2820\ K$$

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Problem 1.9

Since N, V, E and the entropy S are all extensive quantities, the entropy satisfies

$$S(\lambda N, \lambda V, \lambda E) = \lambda S(N, V, E)$$

Differentiating with respect λ and then setting $\lambda = 1$, we obtain

$$\left(\frac{\partial S}{\partial N}\right)_{V,E} N + \left(\frac{\partial S}{\partial V}\right)_{N,E} V + \left(\frac{\partial S}{\partial E}\right)_{N,V} E = S$$

The fundamental thermodynamic relation is

$$dE = T dS - P dV + \mu dN$$

The differential of S can be expressed as

$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$$

We can now identify the partial derivativese of S:

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T} \quad \left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{P}{T} \quad \left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{\mu}{T}$$

Inserting these into the extensivity relation, we get

$$-\frac{\mu}{T}N + \frac{P}{T}V + \frac{1}{T}E = S$$

This can be rewritten

$$N\mu = E + PV - TS$$

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Problem 1.11

At room temperature and pressure, nitrogen and oxygen are both diatomic gases. For separated gases consisting of ν_i moles of diatomic molecules with mass m_i, the ideal gas law is

$$PV = \nu_i N_A kT$$

The entropy is

$$S = \nu_i N_A k \left[\log \frac{V}{\nu_i N_A} + \frac{3}{2} \log \frac{m_i kT}{2\pi\hbar^2} + f_i(T) \right]$$

where $f_i(T)$ takes into account vibrations and rotations.

Separate gases of 1 mole of O_2 and 4 moles of N_2 at temperature T and pressure P will have volumes $V_{O_2} = N_A kT/P$ and $4V_{O_2}$ respectively. Their entropies are

$$S_{O_2} = N_A k \left[\log \frac{V_{O_2}}{N_A} + \frac{3}{2} \log \frac{m_{O_2} kT}{2\pi\hbar^2} + f_{O_2}(T) \right]$$

$$S_{N_2} = 4N_A k \left[\log \frac{4V_{O_2}}{4N_A} + \frac{3}{2} \log \frac{m_{N_2} kT}{2\pi\hbar^2} + f_{N_2}(T) \right]$$

If the two gases are allowed to mix, the resulting air will have volume $5V_{O_2}$. Its entropy will be

$$S_{air} = N_A k\left[\log \frac{5V_{O_2}}{N_A} + \frac{3}{2}\log \frac{m_{O_2}kT}{2\pi\hbar^2} + f_{O_2}(T)\right]$$

$$+ 4N_A k\left[\log \frac{5V_{O_2}}{4N_A} + \frac{3}{2}\log \frac{m_{N_2}kT}{2\pi\hbar^2} + f_{N_2}(T)\right]$$

The entropy of mixing is

$$S_{mixing} = S_{air} - (S_{O_2} + S_{N_2})$$

$$= N_A k \log 5 + 4N_A k \log \frac{5}{4}$$

$$= 2(\log 5 - \log 2) N_A k$$

The entropy of mixing per mole of the air is

$$\frac{S_{mixing}}{5} = \frac{2}{5}(\log 5 - \log 2) R$$

where $R = N_A k$ is the gas constant.