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1 Garrod #6.2: Equilibrium Constant Conversion.

Suppose the equilibrium constant for the reaction $A \leftrightarrow 2B$ is $2e-4m^{-3}$ and that for the reaction $B \leftrightarrow C$ is 0.3. What is the equilibrium constant for the reaction $A \leftrightarrow 2C$?

The equilibrium constant K for a general reaction can be written¹ in terms of the chemical concentrations, as

$$K = \frac{n_R^r n_S^s \dots}{n_A^a n_B^b \dots}, \quad (1)$$

where A, B, \dots are the reactants with stoichiometric coefficients a, b, \dots and R, S, \dots are the products with coefficients r, s, \dots . Therefore the equilibrium constant for $A \leftrightarrow 2B$ is

$$K_{AB} = \frac{n_B^2}{n_A} \Rightarrow \frac{1}{n_A} = \frac{K_{AB}}{n_B^2}, \quad (2)$$

for $B \leftrightarrow C$ the constant is

$$K_{BC} = \frac{n_C}{n_B} \Rightarrow n_C = n_B K_{BC}. \quad (3)$$

We are interested in the equilibrium constant for $A \leftrightarrow 2C$, which is given by

$$K_{AC} = \frac{n_C^2}{n_A} = n_B^2 K_{BC}^2 \left(\frac{K_{AB}}{n_B^2} \right) = K_{AB} K_{BC}^2 = (2e-4m^{-3})(0.3)^2 = 1.8e-5m^{-3} = K_{AC}. \quad (4)$$

¹Garrod, equation 6.9.

2 Garrod #7.4: Two-Dimensional Adsorption Model.

If the adsorbed particles on a surface are free to move across the surface, then they may sometimes be approximated as a two-dimensional ideal gas in which the energy of a particle of momentum (p_x, p_y) is $\epsilon(\mathbf{p}) = (p_x^2 + p_y^2)/2m - \epsilon_0$, where ϵ_0 is the binding energy of the particle to the surface. Using this approximation, calculate the surface density of adsorbed particles if the pressure in the three-dimensional gas, in equilibrium with the adsorbed particles on its surface, is p .

The Boltzmann factor for an adsorbed particle is

$$e^{-\beta\epsilon(\mathbf{p})} = e^{\beta\epsilon_0} e^{-(p_x^2 + p_y^2) \frac{\beta}{2m}}, \quad (5)$$

so the canonical partition function for a single adsorbed particle is

$$z_a = e^{\beta\epsilon_0} \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y e^{-(p_x^2 + p_y^2) \frac{\beta}{2m}} \iint dz dy, \quad (6)$$

which if we restrict the adsorption surface to have an area A , we see the partition function is

$$z_a = A e^{\beta\epsilon_0} \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y e^{-(p_x^2 + p_y^2) \frac{\beta}{2m}} = A \frac{2\pi m}{\beta} e^{\beta\epsilon_0}, \quad (7)$$

using the well known formula for Gaussian integrals². Since the gas in question can be treated as an ideal gas, Garrod equation 7.28 holds for the affinity of the gas yet to be adsorbed. If we equate this with the affinity for the adsorbed particles, Garrod equation 7.22, we see

$$g(T) = \beta^{-5/2} \frac{(2\pi m)^{3/2}}{h^3}, \quad (8)$$

because the pressure p of the gas particles and adsorbed particles in equilibrium. The occupation fraction of the adsorption sites at pressure p is

$$f_a = \frac{p}{p + \beta^{-5/2} \frac{(2\pi m)^{3/2}}{h^3} \left(\frac{\beta}{2\pi m A} e^{-\beta\epsilon_0} \right)} = \frac{p}{p + \frac{1}{Ah^3} \left(\frac{2\pi m}{\beta^3} \right)^{1/2} e^{-\beta\epsilon_0}}, \quad (9)$$

so the surface density ρ (occupation fraction per unit area) is

$$\rho = \frac{N}{A} \frac{f_a K}{A} = \frac{pK}{pA + \frac{1}{h^3} \left(\frac{2\pi m}{\beta^3} \right)^{1/2} e^{-\beta\epsilon_0}}. \quad (10)$$

²Gaussian integral: $\int_{-\infty}^{\infty} e^{-ax^2} = \sqrt{\pi/a}$.

3 Garrod #7.5: Occupation Fraction of Diatomic Molecule.

Diatomic molecules are sometimes decomposed, upon adsorption, into their constituent atoms, attached to the surface. Consider a gas of diatomic nitrogen (N_2), and assume that the vibrational excitations can be ignored, so that Garrod equation 4.65 is applicable. Assuming that the gas is in equilibrium with K atomic adsorption sites, derive the equivalent of Garrod equation 7.24 for the fraction of occupied sites.

Since the gas decomposes to its constituent atoms when it is adsorbed, the affinity of the adsorbed gas is twice that of the molecular gas. Therefore, when we equate the affinity of the molecular gas to the adsorbed atomic gas, we must have

$$2 \left[\log \left(\frac{1 - f_a}{f_a} \right) + \log z_a \right] = -\log p + \log g, \quad (11)$$

where z_a is the partition function for a single occupied adsorption site. If we solve the above equation to get the equivalent of Garrod equations 7.23 and 7.24, we get

$$\log \sqrt{\frac{g}{p}} = \log \left(\frac{1 - f_a}{f_a} \right) + \log z_a \Rightarrow f_a = \frac{\sqrt{p}}{\sqrt{p} + \sqrt{g(T)/z_a}}, \quad (12)$$

where $g(T)$ can be determined from form of the affinity for the diatomic molecules with no vibrational excitations. We can find the affinity from the canonical potential of a diatomic gas (Garrod equation 4.65) and the definition of the affinity:

$$\alpha = \frac{\partial \phi(N, \beta, V)}{\partial N} = \left[\log \left(\frac{V}{N} \right) - \frac{5}{2} \log(\beta) + \log \left(2I \left[\frac{m}{2\pi} \right]^{3/2} \hbar^{-5} \right) + 1 \right] + N \left(-\frac{1}{N} \right) \quad (13)$$

$$= \log \left(\frac{1}{\beta p} \right) - \frac{5}{2} \log(\beta) + \log \left(2I \left[\frac{m}{2\pi} \right]^{3/2} \hbar^{-5} \right), \quad (14)$$

using the ideal gas law so that $V/N = 1/\beta p$. It should be noted that Garrod introduced an extra factor of $\log k^{5/2}$ when he collected terms of β between both lines of Garrod equation 4.65. If we separate the first log, we see

$$\alpha = -\log(p) - \frac{7}{2} \log(\beta) + \log \left(2I \left[\frac{m}{2\pi} \right]^{3/2} \hbar^{-5} \right) = -\log(p) + \log \left(2I \beta^{-7/2} \left[\frac{m}{2\pi} \right]^{3/2} \hbar^{-5} \right), \quad (15)$$

which by comparison with Garrod equation 7.22, we find

$$g(T) = \frac{2I}{\hbar^5} \sqrt{\frac{m^3}{8\pi^3 \beta^7}}, \quad (16)$$

so from Equation 12, the occupation fraction of adsorption sites (analog to Garrod equation 7.24) is

$$f_a = \frac{\sqrt{p}}{\sqrt{p} + \frac{1}{z_a} \sqrt{\frac{2I}{\hbar^5} \left(\frac{m}{2\pi} \right)^{3/4} (kT)^{7/4}}}, \quad (17)$$

where z_a is given above. If we assume each atomic adsorption site has binding energy $-\epsilon_0$ (with $\epsilon_0 > 0$) then this partition function is

$$z_a = e^{\beta \epsilon_0}, \quad (18)$$

for a single atomic adsorption site.

4 Garrod #7.9: Hydrogen in Magnetic Field.

If a hydrogen atom is placed in a magnetic field, its nucleus (a proton) can have its spin, and therefore its magnetic moment, oriented either parallel or antiparallel to the field. The energy levels of the two orientations are $\pm\mu B$, where $\mu = 2.79255\mu_N$. ($\mu_N = e\hbar/2M_p = 5.05e27$ J/T is the Bohr nuclear magneton.)

4.1 Ratio of Spin Orientations.

In a field of 2 Tesla, at a temperature of 300 K, what is the ratio $R(T) = (N_- - N_+)/ (N_- + N_+)$. (N_- and N_+ are the numbers of parallel and antiparallel spins, respectively.)

If there are N total hydrogen atoms, then we clearly have $N_- + N_+ = N$, which is a fixed number of particles, so we may ignore the affinity α of the hydrogen atom. The energy of a hydrogen atom's interaction with the magnetic field is $E = -\boldsymbol{\mu} \cdot \mathbf{B}$, so the energies are negative for the aligned states and positive for the anti-aligned states. If this is the case, we get the number of particles for each spin alignment from the Fermi-Dirac distribution

$$N_- = \frac{N}{e^{(-\mu B)\beta} + 1} \quad N_+ = \frac{N}{e^{(\mu B)\beta} + 1} . \quad (19)$$

Consider the difference:

$$N_- - N_+ = \frac{N}{e^{-\beta\mu B} + 1} - \frac{N}{e^{\beta\mu B} + 1} = N \frac{(e^{\beta\mu B} + 1) - (e^{-\beta\mu B} + 1)}{(e^{\beta\mu B} + 1)(e^{-\beta\mu B} + 1)} \quad (20)$$

$$= N \frac{2 \sinh(\beta\mu B)}{2 \cosh(\beta\mu B) + 2} . \quad (21)$$

If we use the double angle formulae³ for hyperbolic sine and cosine, we see the difference can be written

$$N_- - N_+ = N \frac{\sinh(\beta\mu B)}{\cosh(\beta\mu B) + 1} = N \frac{2 \sinh(\frac{1}{2}\beta\mu B) \cosh(\frac{1}{2}\beta\mu B)}{(2 \cosh^2(\frac{1}{2}\beta\mu B) - 1) + 1} = N \frac{\sinh(\frac{1}{2}\beta\mu B)}{\cosh(\frac{1}{2}\beta\mu B)} \quad (22)$$

$$= N \tanh(\frac{1}{2}\beta\mu B) . \quad (23)$$

Armed with this knowledge, the ratio of interest is trivial to compute (using $N_- + N_+ = N$):

$$R(T) = \frac{N_- - N_+}{N_- + N_+} = \tanh(\frac{1}{2}\beta\mu B) = \tanh\left(\frac{\mu B}{2k_B T}\right) , \quad (24)$$

where k_B is the Boltzmann constant. For the parameters given, this ratio is

$$R(300\text{K}) = 3.4e-6 , \quad (25)$$

so the number of atoms with their spins aligned is comparable to the number of atoms with their spins anti-aligned with the magnetic field, at room temperature.

³ $\sinh(2z) = 2 \sinh(z) \cosh(z)$ and $\cosh(2z) = 2 \cosh^2(z) - 1$

4.2 Nuclear Magnetic Resonance Frequency.

If a substance containing hydrogen is placed in a magnetic field and subjected to electromagnetic radiation at a frequency $\nu = 2\mu B/h$, energy will be absorbed from the radiation field, causing transitions between the two nuclear magnetic energy states. The absorption rate is proportional to $R(T)$. This is the phenomenon of nuclear magnetic resonance. For a field of 2 T, in what range is the nuclear magnetic resonance frequency (infrared, microwave, etc.)?

The energy difference between the aligned and anti aligned states is $\Delta E = 2\mu B$. Therefore the frequency of EM radiation required for NMR is simply

$$\nu = \frac{\Delta E}{h} = \frac{2\mu B}{h} = 8.5e7 \text{ Hz} = 85 \text{ MHz} , \quad (26)$$

which is in the micro- and radio- wave regime of the EM spectrum. More specifically, this is between the high-frequency (HF) to very high-frequency (VHF) regimes.

5 Garrod #7.15: Neutrino Gas.

Neutrinos are zero-mass spin- $\frac{1}{2}$ Fermi-Dirac particles. Although neutrinos have spin- $\frac{1}{2}$, there is only one neutrino state for each momentum, because of the fact that the spin angular momentum of a neutrino is always antiparallel to its momentum vector. Treating the neutrino number as a strictly conserved quantity, obtain expansions for p and E/N , up to order τ^2 , for a neutrino gas.

If we assume the neutrinos have no mass, they have an energy-momentum relationship given by $\epsilon = |\mathbf{p}|c$, where c is the speed of light. Additionally, these particles obey Fermi-Dirac statistics, so we may use the integral form of the grand potential given by Garrod equation 7.46. In this integral form the factor of two is due to the two-spin states per momentum eigenstate, in our case there is only one state per momentum eigenstate. Using this information, the grand potential of a neutrino gas confined to a volume V is given by the integral

$$\psi = \frac{V}{h^3} \int \log[1 + e^{-(\alpha + \beta\epsilon(\mathbf{p}))}] d^3\mathbf{p}, \quad (27)$$

where $\epsilon(\mathbf{p})$ is the energy-momentum relationship for neutrinos. We can reduce the momentum vector to its magnitude and its polar and azimuthal angles, and write the volume element as $d^3\mathbf{p} = p^2 \sin\theta dp d\theta d\phi$. Since the energy only depends on the magnitude, we can immediately integrate the solid angle to acquire a factor of 4π . Using the energy-momentum relationship, we see $d\epsilon = cd p$, so we can write the integral in terms of the energy instead of the momentum:

$$\psi = \frac{4\pi}{c^3 h^3} V \int_0^\infty \log[1 + e^{-(\alpha + \beta\epsilon)}] \epsilon^2 d\epsilon, \quad (28)$$

and we define $\gamma_\nu = 4\pi/c^3 h^3$. Quickly let us note the derivatives of the logarithm:

$$-\frac{\partial}{\partial\alpha} \log[1 + e^{-(\alpha + \beta\epsilon)}] = \frac{1}{1 + e^{-(\alpha + \beta\epsilon)}} \quad (29)$$

$$-\frac{\partial}{\partial\beta} \log[1 + e^{-(\alpha + \beta\epsilon)}] = \frac{\epsilon}{1 + e^{-(\alpha + \beta\epsilon)}}. \quad (30)$$

Using these derivatives, the definitions in Garrod equations 7.42 and 7.43, and introducing the chemical potential $\mu = -\alpha/\beta$, and the temperature $\tau = \beta^{-1} = kT$, we can write the total energy and total number of neutrinos as

$$\frac{N}{V} = \gamma_\nu \int_0^\infty \frac{\epsilon^2 d\epsilon}{e^{(\epsilon - \mu)/\tau} + 1} \quad (31)$$

$$\frac{E}{V} = \gamma_\nu \int_0^\infty \frac{\epsilon^3 d\epsilon}{e^{(\epsilon - \mu)/\tau} + 1}. \quad (32)$$

In the low temperature limit, we see the denominator of the integrands is 1 for $\epsilon < \mu$ and 0 for $\epsilon > \mu$, so we can evaluate this integral at low temperatures:

$$\frac{N}{\gamma_\nu V} = \int_0^{\epsilon_F} \epsilon^2 d\epsilon = \frac{1}{3} \epsilon_F^3, \quad (33)$$

note the upper limit of integration is the Fermi energy (equal to the chemical potential at zero temperature), because past this the integrand is zero. We will now define the average particle density $\bar{n} = N/V$ and the energy density $\bar{\epsilon} = E/V$. The integrals can be evaluated for finite

temperature using the expansion for low temperature given by Garrod equation 7.55. For the N/V integral $g(\epsilon) = \epsilon^2$, and for the E/V integral, $g(\epsilon) = \epsilon^3$, so we see, to second order in τ ,

$$\frac{\bar{n}}{\gamma_\nu} = \frac{N}{\gamma_\nu V} = \int_0^\mu \epsilon^2 d\epsilon + \frac{\pi^2 \tau^2}{6} (2\mu) = \frac{1}{3} \mu (\mu^2 + \pi^2 \tau^2) \quad (34)$$

$$\frac{\bar{\epsilon}}{\gamma_\nu} = \frac{E}{\gamma_\nu V} = \int_0^\mu \epsilon^3 d\epsilon + \frac{\pi^2 \tau^2}{6} (3\mu^2) = \frac{1}{4} \mu^2 (\mu^2 + 2\pi^2 \tau^2) , \quad (35)$$

so the average energy per particle is

$$\frac{E}{N} = \frac{\bar{\epsilon}}{\bar{n}} = \frac{3}{4} \mu \frac{\mu^2 + 2\pi^2 \tau^2}{\mu^2 + \pi^2 \tau^2} , \quad (36)$$

but we must find an expression for the chemical potential at finite temperature in terms of the Fermi energy. To do this we can equate Equations 33 and 34 to see

$$\frac{1}{3} \epsilon_F^3 = \frac{1}{3} \mu (\mu^2 + \pi^2 \tau^2) \quad \Rightarrow \quad \mu^3 = \epsilon_F^3 - \pi^2 \tau^2 \mu \quad (37)$$

$$\frac{\mu}{\epsilon_F} = \left(1 - \frac{\pi^2 \tau^2}{\epsilon_F^2} \right)^{1/3} . \quad (38)$$

Since the term is of order τ^2 , we can replace μ by ϵ_F on the right-hand side of Equation 37, with negligible errors (as in Garrod, page 174). If the temperature is small, as in the derivation of Equation 33, we can Taylor expand the exponential to see

$$\frac{\mu}{\epsilon_F} = 1 - \frac{\pi^2 \tau^2}{3\epsilon_F^2} \quad \Rightarrow \quad \mu = \epsilon_F - \frac{\pi^2 \tau^2}{3\epsilon_F} . \quad (39)$$

For a relativistic gas, the pressure is given by $p = \frac{1}{3}(E/V)$, so inserting μ into the expression for E/V and dividing by three yields

$$p = \frac{1}{3} \frac{E}{V} = \frac{1}{3} \frac{\gamma_\nu}{4} \mu^2 (\mu^2 + 2\pi^2 \tau^2) = \frac{1}{3} \frac{\gamma_\nu}{4} \left[\epsilon_F - \frac{\pi^2 \tau^2}{3\epsilon_F} \right]^2 \left[\left(\epsilon_F - \frac{\pi^2 \tau^2}{3\epsilon_F} \right)^2 + 2\pi^2 \tau^2 \right] \quad (40)$$

which is the pressure of a neutrino gas, recall that $\gamma_\nu = 4\pi/c^3 h^3$. If we expand this expression and keep terms up to order τ^2 , we get the result

$$p \simeq \frac{1}{4} \frac{\gamma_\nu}{3} \left[\epsilon_F^2 - \frac{2}{3} \pi^2 \tau^2 \right] \left[\epsilon_F^2 + \frac{4}{3} \pi^2 \tau^2 \right] \simeq \frac{1}{4} \frac{\gamma_\nu}{3} \left[\epsilon_F^4 + \frac{2}{3} \pi^2 \tau^2 \epsilon_F^2 \right] = \frac{1}{4} \frac{1}{3} \gamma_\nu \epsilon_F^3 \left[\epsilon_F + \frac{2}{3} \frac{\pi^2 \tau^2}{\epsilon_F} \right] , \quad (41)$$

using the definition of the neutrino density (Equation 33), we see

$$p = \frac{\bar{n}}{4} \left[\epsilon_F + \frac{2}{3} \frac{\pi^2}{\beta^2 \epsilon_F} \right] \equiv n_\nu f(\beta) . \quad (42)$$

6 Garrod #7.16: Neutrino and Antineutrino Gas.

The antiparticle to the neutrino is the antineutrino, a particle with the same properties as the neutrino, but with its spin angular momentum always parallel to its linear momentum. In fact, the neutrino number N_ν and the antineutrino number $N_{\bar{\nu}}$ are not separately conserved, but only the lepton number, $L = N_\nu - N_{\bar{\nu}}$, is conserved. Due to creation of neutrino-antineutrino pairs, the total number of particles, $N = N_\nu + N_{\bar{\nu}}$, can change spontaneously. A neutrino-antineutrino gas may be treated as two interpenetrating Fermi-Dirac ideal gases with a chemical reaction, $N_\nu + N_{\bar{\nu}} \leftrightarrow 0$. Using the chemical equilibrium equation, calculate the pressure of such a system as an expansion in τ , separately, for the two cases $L = 0$ and $L > 0$. (Note: This problem requires the solution of Problem 7.15.)

Let us define the lepton number density $\ell = L/V = n_\nu - n_{\bar{\nu}}$, using the result from Garrod 7.15, we see

$$f(\beta)\ell = p_\nu - p_{\bar{\nu}} , \quad (43)$$

where $f(\beta)$ is the expansion to order τ^2 found in the previous problem, and the individual pressures are $p_{\nu/\bar{\nu}} = f(\beta)n_{\nu/\bar{\nu}}$. Using the given reaction equation, we can write the equilibrium constant as

$$K_{\text{eq}} = \frac{(\tilde{n})^0}{(n_\nu)^1(n_{\bar{\nu}})^1} , \quad (44)$$

using Garrod equation 6.9, where \tilde{n} is the density of the products (there are none, hence the zero power). Therefore $n_{\bar{\nu}} = 1/K_{\text{eq}}n_\nu$. If we add twice the pressure of antineutrinos to both sides of Equation 43, we see

$$p_\nu + p_{\bar{\nu}} = 2p_{\bar{\nu}} + f(\beta)\ell = 2f(\beta)n_{\bar{\nu}} + f(\beta)\ell , \quad (45)$$

and if we assume Dalton's law of partial pressures holds true for a quantum ideal gas, we see the left-hand side is just the total pressure. This makes sense because the neutrino-antineutrino gas is in equilibrium so the annihilation rate is equal to the creation rate, and so instantaneously the sum of their pressures is constant for given particle densities at a specific temperature. Substituting the expression for $n_{\bar{\nu}}$ into this result, we get

$$p = f(\beta) \left(\ell + \frac{2}{K_{\text{eq}}n_\nu} \right) = f(\beta)(n_\nu + n_{\bar{\nu}}) , \quad (46)$$

which is true up to order τ^2 . We see the pressure is proportional to the sum of the neutrino and antineutrino densities. In the case $L = 0$, the pressure is proportional to twice the inverse density of the neutrino density (which is equal to the antineutrino density if $L = 0$). For $L > 0$, the pressure is proportional to the sum of the neutrino density and the inverse of the neutrino density.

7 Garrod #7.18: The Baloneyon.

The baloneyon is an imaginary Fermi-Dirac particle with spin- $\frac{1}{2}$ and the following relationship between energy and momentum:

$$E = B|\mathbf{p}|^4, \quad (47)$$

where B is the baloney constant. What is the Fermi energy of a system of baloneyons as a function of the particle density?

To determine the Fermi energy of a system of these particles, we will follow the derivation in Garrod section 7.5 (because this derivation is valid for spin- $\frac{1}{2}$ particles. We can begin by writing the grand potential:

$$\psi = 2 \frac{V}{h^3} \int \log \left[1 + e^{-(\alpha + \beta \epsilon(\mathbf{p}))} \right] d^3 \mathbf{p}, \quad (48)$$

where $\epsilon(\mathbf{p}) = B|\mathbf{p}|^4$, and the system is confined to a volume V . In spherical momentum space, this integral is

$$\psi = 8\pi \frac{V}{h^3} \int \log \left[1 + e^{-(\alpha + \beta B p^4)} \right] p^2 dp, \quad (49)$$

where the factor of 4π came from evaluating the angular integrals. We can transform this to be over the energy variable ϵ . If we rearrange the energy-momentum relationship, we find

$$p = \left(\frac{\epsilon}{B} \right)^{1/4} \Rightarrow dp = \frac{1}{4B} \left(\frac{\epsilon}{B} \right)^{-3/4} d\epsilon, \quad (50)$$

and as such, the volume element is $p^2 dp = (4B(\epsilon/B)^{1/4})^{-1}$. The grand potential is now given by the integral

$$\psi = 2\pi \frac{VB^{-3/4}}{h^3} \int \log \left[1 + e^{-(\alpha + \beta \epsilon)} \right] \epsilon^{-1/4} d\epsilon. \quad (51)$$

We can find the average number of baloneyons in this system by taking the negative derivative of this with respect to the affinity:

$$N = -\frac{\partial \psi}{\partial \alpha} = -2\pi \frac{VB^{-3/4}}{h^3} \int \epsilon^{-1/4} d\epsilon \frac{\partial}{\partial \alpha} \log \left[1 + e^{-(\alpha + \beta \epsilon)} \right] \quad (52)$$

$$= 2\pi \frac{VB^{-3/4}}{h^3} \int \epsilon^{-1/4} d\epsilon \frac{1}{e^{\alpha + \beta \epsilon} + 1}, \quad (53)$$

after carrying out the derivative⁴. If we divide through by the volume and introduce the chemical potential $\mu = -\alpha/\beta$, the particle density is

$$n = \frac{N}{V} = 2\pi \frac{B^{3/4}}{h^3} \int \frac{\epsilon^{-1/4} d\epsilon}{e^{\beta(\epsilon - \mu)} + 1}. \quad (54)$$

The Fermi energy is equivalent to the chemical potential at zero temperature⁵, so we can take the limit as $\beta \rightarrow \infty$ of this expression, to find

$$n = \frac{2\pi}{(B^{1/4}h)^3} \int \epsilon^{-1/4} \lim_{\beta \rightarrow \infty} \frac{1}{e^{\beta(\epsilon - \mu)} + 1} d\epsilon, \quad (55)$$

⁴ $\frac{\partial}{\partial \alpha} \log \left[1 + e^{-(\alpha + \beta \epsilon)} \right] = \frac{(-1)e^{-(\alpha + \beta \epsilon)}}{1 + e^{-(\alpha + \beta \epsilon)}} = -\frac{1}{e^{\alpha + \beta \epsilon} + 1}$

⁵ Garrod, page 174.

and using Garrod equation 7.53, the limit is unity for $\epsilon < \mu$ (which in our case, is valid for energies below the Fermi energy). We are left with a trivial integral to evaluate to find the particle density:

$$n = \frac{2\pi}{(B^{1/4}\hbar)^3} \int_0^{\epsilon_F} \epsilon^{-1/4} d\epsilon = \frac{2\pi}{(B^{1/4}\hbar)^3} \left(\frac{4}{3} \epsilon_F^{3/4} \right), \quad (56)$$

note we are not integrating to infinite energy, because past $\epsilon = \epsilon_F$, the integrand is zero. If we rearrange this result, we find

$$\epsilon_F = \left(\frac{3(B^{1/4}\hbar)^3}{8\pi} n \right)^{4/3} = \hbar^4 B \left(\frac{3}{8\pi} n \right)^{4/3} \quad (57)$$

which is the Fermi energy, as a function of particle density.

8 Garrod #7.19: Electron and α -Particle Interspersed Gas.

Consider a mixture of N α particles and $2N$ electrons within a volume V . When the average kinetic energy of the electrons, due to the Pauli Exclusion Principle, is much larger than the binding energy of an electron bound to an α particle, then the electrons will be stripped off the α particles and the system can be approximated as an interpenetrating Fermi-Dirac electron gas and a classical gas of α particles, rather than as a gas of helium atoms, which it would become at lower densities. This situation exists in high-density stars.

8.1 Mass Density at 0K.

Determine the mass density of the system when the average kinetic energy of the electrons (at 0 K) is ten times the binding energy of a single electron to an α particle in free space.

The average kinetic energy of the electrons at zero temperature is, for this system

$$\epsilon = 10\epsilon_b, \quad (58)$$

where ϵ_b is the binding energy of an electron to an α particle. This binding energy is $\epsilon_b = Z^2\epsilon_0$, where Z is the atomic number (for an α particle, $Z = 2$), and ϵ_0 is the Rydberg constant for hydrogen ($\epsilon_0 \simeq 13.6$ eV). At absolute zero, using Garrod equation 7.61, we see the Fermi energy is related to the average energy per particle by

$$\epsilon_F = \frac{5}{3}\epsilon = \frac{50}{3}\epsilon_b = \frac{200}{3}\epsilon_0. \quad (59)$$

Using Garrod equation 7.50, we can find the electron density

$$\frac{N_e}{V} = 2\gamma \int \frac{\epsilon^{1/2}}{e^{\beta(\epsilon-\mu)} + 1} d\epsilon, \quad (60)$$

where $\gamma = 2\pi(2m/\hbar^2)^{3/2}$. Using the method in Garrod, this integral can be evaluated by noting that for $\epsilon < \mu$, in the low-temperature limit, the denominator is one. This integral gives the result

$$\frac{N_e}{V} = \frac{4}{3}\gamma\epsilon_F^{3/2} = \frac{4}{3}\gamma \left(\frac{200}{3}\epsilon_0\right)^{3/2} = \frac{2N}{V}, \quad (61)$$

which is the density of electrons. Given that $N_\alpha = 2N_e$ for the same volume, we may write the mass density of the system of both gases as

$$m = \frac{M}{V} = m_e \frac{N_e}{V} + m_\alpha \frac{N_\alpha}{V} = \frac{N}{V}(2m_e + m_\alpha) = \frac{4}{3}\gamma \left(\frac{200}{3}\epsilon_0\right)^{3/2} (2m_e + m_\alpha), \quad (62)$$

where m_e is the mass of the electron and m_α is the mass of the α particle, and N/V is the density of α particles.

8.2 Stellar Mass Densities.

How does it compare with the estimated mass densities at the center of the sun ($1e5$ kg/m³) and in a white dwarf ($2e9$ kg/m³)?

We can evaluate the mass density:

$$m = \frac{M}{V} = \frac{4}{3}\gamma \left(\frac{200}{3}\epsilon_0 \right)^{3/2} (2m_e + m_\alpha) = 8.2e5 \text{ kg m}^{-3} , \quad (63)$$

which is about eight times more dense than the center of the sun, and much less dense than a white dwarf star.

8.3 Fermi Energy in White Dwarf.

The internal temperature of white dwarf stars is about 10^7 K. What is the ratio of τ to ϵ_F in a white dwarf? (This ratio determines whether the zero-temperature approximation is accurate.)

The relationship between the temperature, energy per particle, and Fermi energy is given by Garrod equation 7.61. In the zero-temperature approximation, we can drop the term that is quadratic in temperature, yielding

$$\epsilon_F = \frac{5}{3}\epsilon , \quad (64)$$

and if we assume the energy per particle in a white dwarf is equivalent to the binding energy of an electron to an α particle, we see

$$\epsilon_F = \frac{200}{3}\epsilon_0 \simeq 1.45e-16 \text{ J} = 906.6 \text{ eV} . \quad (65)$$

The temperature of the white dwarf is

$$\tau = k_B T = 1.38e-16 \text{ J} = 861.3 \text{ eV} , \quad (66)$$

so the ratio is

$$\frac{\tau}{\epsilon_F} = 0.95 , \quad (67)$$

which says the Fermi energy is of the same magnitude as the temperature of the star.

Alternatively, we can solve our expression for the mass density of the electron- α particle gas for the Fermi energy, to obtain

$$\left(\frac{3m}{2\gamma} \frac{1}{2m_e + m_\alpha} \right)^{2/3} = \epsilon_F = 4.2e-14 \text{ J} = 262 \text{ keV} , \quad (68)$$

this result does not apply the zero-temperature approximation. In this case the ratio is

$$\frac{\tau}{\epsilon_F} = 0.0033 . \quad (69)$$

9 Garrod #7.26: 2D Bose-Einstein Gas.

9.1 Number of Momentum Eigenstates in Energy Interval.

For a two-dimensional gas of spin-zero particles in a periodic box of area L^2 , calculate the number of momentum eigenstates with energies within the interval ϵ to $\epsilon + d\epsilon$.

The average occupation of one momentum eigenstate is given by Garrod equation 2.69,

$$N = \frac{1}{e^{\alpha + \beta \epsilon(\mathbf{p})} - 1}, \quad (70)$$

if we take a differential of this, we get the number of momentum eigenstates within the interval $\mathbf{p} + d\mathbf{p}$. This differential is

$$dN = d^2\mathbf{p} \frac{1}{e^{\alpha + \beta \epsilon(\mathbf{p})} - 1} \left(\frac{A}{\hbar^2} \right), \quad (71)$$

where the $\frac{A}{\hbar^2}$ term is the momentum density (the quantum of momentum in 2 dimensions). We can reduce this to an integral over only the magnitude of the momentum by inserting $d\mathbf{p} = p dp d\theta$, and immediately integrate the θ dependence out over the region $0 < \theta < 2\pi$, which yields

$$dN = \frac{2\pi A}{\hbar^2} \frac{p dp}{e^{\alpha + \beta \epsilon(\mathbf{p})} - 1}. \quad (72)$$

Using the relationship of energy and momentum, $\epsilon = p^2/2m$, we can write the differential energy as

$$d\epsilon = \frac{p}{m} dp. \quad (73)$$

Inserting this into the previous equation, we see the number of momentum eigenstates in the interval $\epsilon + d\epsilon$ is

$$dN = \frac{Am}{2\pi\hbar^2} \frac{d\epsilon}{e^{\alpha + \beta \epsilon} - 1}, \quad (74)$$

where now ϵ is independent of the momentum.

9.2 Areal Particle Density.

Use the result of 4.1 to obtain an integral formula for N/A as a function of α and τ for a 2D Bose-Einstein gas.

The expression in Equation 74 can be integrated over $d\epsilon$ to find the total number, dividing this by the area yields

$$\frac{\int dN}{A} = \frac{m}{2\pi\hbar^2} \int \frac{d\epsilon}{e^{\alpha + \beta \epsilon} - 1}, \quad (75)$$

noting that $\beta = 1/\tau$. Introducing the chemical potential $\mu = -\frac{\alpha}{\beta}$, we see

$$\frac{N}{A} = \frac{m}{2\pi\hbar^2} \int \frac{d\epsilon}{e^{\tau(\epsilon - \mu)} - 1}, \quad (76)$$

which is an integral formula for the areal density of the particles.

9.3 2D Bose-Einstein Condensate?

Show that the result obtained in 4.2 implies that no Bose-Einstein condensation occurs for the two-dimensional ideal Bose-Einstein gas.

Bose-Einstein condensation occurs at densities greater than some critical density n_c . This critical density occurs at the maximum of the integrand, which is $\alpha = 0 \rightarrow \mu = 0$. The critical density for this system is given by

$$n_c = \frac{m}{2\pi\hbar^2} \int_0^\infty \frac{d\epsilon}{e^{\tau\epsilon} - 1}, \quad (77)$$

which diverges on this interval (as $\epsilon \rightarrow \infty$). Since the critical density is infinite, no density above the critical can exist, and as such no Bose-Einstein condensation may occur.

10 Garrod #7.27: Relativistic Bosons.

10.1 Linear Energy-Momentum Relationship.

Consider a system of conserved bosons for which the relationship between energy and momentum is not $\epsilon = p^2/2m$, but $\epsilon = cp$, where $p = |\mathbf{p}|$. For this system, calculate the Bose-Einstein condensation temperature τ_C as a function of the particle density.

Similar to the derivation of the ideal Fermi gas, we can write the density of bosons in this system as

$$\frac{N}{V} = \frac{1}{h^3} \int \frac{1}{e^{\alpha+\beta\epsilon(\mathbf{p})} - 1} d^3\mathbf{p}, \quad (78)$$

found by differentiating the grand potential given by Garrod equation 7.46 with respect to the negative affinity, first removing the factor of two due to spin degeneracy, and swapping the sign of the one to obey Bose-Einstein statistics. If we write the volume element as $d^3\mathbf{p} = p^2 dp d\Omega$, we see

$$n \equiv \frac{N}{V} = \frac{4\pi}{h^3} \int \frac{p^2 dp}{e^{\alpha+\beta\epsilon(p)} - 1}, \quad (79)$$

after carrying out the integration over solid angle. Using the energy-momentum relationship, we can transform this integral to one over energy as

$$n = \frac{4\pi}{c^3 h^3} \int_0^\infty \frac{\epsilon^2 d\epsilon}{e^{\alpha+\beta\epsilon} - 1} = \frac{4\pi}{c^3 h^3} \tau^3 \int_0^\infty \frac{x^2 dx}{e^{\alpha+x} - 1}, \quad (80)$$

after making another change of variables such that $x = \beta\epsilon$, with the temperature $\tau = 1/\beta$. Rearranging this yields an expression for the inverse temperature in terms of the density:

$$\tau^{-3} = \frac{4\pi}{c^3 h^3} n \int_0^\infty \frac{x^2 dx}{e^{\alpha+x} - 1}. \quad (81)$$

The critical temperature occurs at the maximum value of this integral, which is when the affinity is zero. This is

$$\tau_C^{-3} = \frac{4\pi}{c^3 h^3} n \int_0^\infty \frac{x^2 dx}{e^x - 1} = \frac{4\pi}{c^3 h^3} n (2\zeta(3)), \quad (82)$$

using the identity given by Garrod equation 7.68, where $\zeta(x)$ is the Riemann zeta function (note $\Gamma(3) = 2$). Solving for the critical temperature yields

$$\tau_C = hc \left[\frac{n}{8\pi\zeta(3)} \right]^{1/3}. \quad (83)$$

10.2 Cubic Energy-Momentum Relationship.

For a system of particles in which $\epsilon = cp^3$, show that there is no Bose-Einstein condensation.

Starting from Equation 79, and inserting the energy momentum relation $p = (\epsilon/c)^{1/3}$, we can write the density as

$$n = \frac{4\pi}{h^3} \int_0^\infty \frac{(\epsilon/c)^{2/3} \left[\frac{1}{3} \left(\frac{\epsilon}{c} \right)^{-2/3} \frac{d\epsilon}{c} \right]}{e^{\alpha+\beta\epsilon} - 1} = \frac{4\pi}{3c} \int_0^\infty \frac{d\epsilon}{e^{\alpha+\beta\epsilon} - 1}. \quad (84)$$

The critical density is this expression integrated with $\alpha = 0$. This results in a divergent integral, so the critical density is infinite. Therefore no Bose-Einstein condensation can occur because the density of bosons can never be greater than infinity.

11 Garrod #8.4: Repulsive Potential of Arbitrary Power.

11.1 The Cluster Integral.

Determine the cluster integral, $C_2(T)$, for particles with a repulsive interaction potential, $v(r) = a/r^\lambda$, where $\lambda > 3$. [Hint: $\int_0^\infty \exp(-x)x^s dx = \Gamma(s-1)$.]

Let us begin by noting another of Garrod's errors, the hint should read⁶:

$$\int_0^\infty \exp(-x)x^s dx = \Gamma(s+1) . \quad (85)$$

Using Garrod equation 8.15, the second cluster integral for this potential is given by

$$C_2(T) = 2\pi \int_0^\infty \left(e^{-\beta ar^{-\lambda}} - 1 \right) r^2 dr . \quad (86)$$

We can integrate this by parts using

$$dv = r^2 dr \quad \Rightarrow \quad v = \frac{1}{3} r^3 \quad (87)$$

$$u = e^{-\beta ar^{-\lambda}} - 1 \quad \Rightarrow \quad du = e^{-\beta ar^{-\lambda}} (\lambda \beta ar^{-\lambda-1}) dr \quad (88)$$

so the integral can be expressed

$$C_2(T) = 2\pi \left\{ \left[\frac{1}{3} r^3 (e^{-\beta ar^{-\lambda}} - 1) \right] \Big|_{r=0}^\infty - \int_0^\infty \frac{1}{3} r^3 e^{-\beta ar^{-\lambda}} (\lambda \beta ar^{-\lambda-1}) dr \right\} , \quad (89)$$

and we can note the boundary term vanishes provided $\lambda > 3$, which is the case for this potential. This can be seen by investigating the limiting behavior of

$$r^3 (e^{-1/r^\lambda} - 1) , \quad (90)$$

with $\lambda > 3$. For the $r \rightarrow 0$ limit, the cubic term is zero and the exponential is finite, so this limit is zero. In the large r limit, the r term diverges, while the exponential converges to one, so the two-term factor converges to zero faster than the cubic diverges. The remaining integral can be evaluated using a change of variables such that

$$x = \beta ar^{-\lambda} \quad (91)$$

$$dx = -\lambda \beta ar^{-\lambda-1} dr \quad (92)$$

$$r = \left(\frac{x}{\beta a} \right)^{-1/\lambda} , \quad (93)$$

so

$$C_2(T) = 2\pi \int_0^\infty \frac{1}{3} r^3 e^{-\beta ar^{-\lambda}} (-\lambda \beta ar^{-\lambda-1}) dr = \frac{2}{3} \pi \int_\infty^0 \left(\frac{x}{\beta a} \right)^{-3/\lambda} e^{-x} dx . \quad (94)$$

Using the (corrected) hint from Garrod, we see this integral is

$$C_2(T) = -\frac{2}{3} \pi (\beta a)^{3/\lambda} \Gamma(1 - \frac{3}{\lambda}) . \quad (95)$$

⁶Zwillinger, CRC Standard Mathematical Tables and Formulae, 31 ed. Equation 641.

11.2 Parameters as Expansions in Particle Density.

Write expressions for βp and E/N as expansions in the particle density n up to second order.

Using Garrod equation 8.16, we can write the first expansion to second order in the activity ζ as

$$\beta p = \zeta + C_2(T)\zeta^2 + \mathcal{O}(\zeta^3) , \quad (96)$$

which if we assume the activity is related to the particle density as in an ideal gas⁷, then we see this expansion is also to second order in the particle density n . This is given by

$$\beta p = n - \frac{2}{3}\pi (\beta a)^{3/\lambda} \Gamma(1 - \frac{3}{\lambda})n^2 + \mathcal{O}(n^3) . \quad (97)$$

We can now use Garrod equation 8.21 to write the energy density as

$$\frac{E}{N} = \frac{3}{2} \frac{1}{\beta} - \frac{1}{n} (C'_2(\beta)n^2 + C'_3(\beta)n^3 + \mathcal{O}(n^4)) , \quad (98)$$

where the prime denotes a derivative with respect to β . We can see we must calculate $C_3(T)$ to go to second order in n . Which we could do if we were interested using Garrod equation 8.12. If we did this we would see

$$\frac{E}{N} = \frac{3}{2} \frac{1}{\beta} - \frac{\partial C_2}{\partial \beta} n - \frac{\partial C'_3}{\partial \beta} n^2 + \mathcal{O}(n^3) \quad (99)$$

$$= \frac{3}{2} \frac{1}{\beta} + \frac{2\pi}{\lambda} a^{3/\lambda} \Gamma(1 - \frac{3}{\lambda}) \beta^{\frac{3}{\lambda}-1} n - \frac{\partial C'_3}{\partial \beta} n^2 + \mathcal{O}(n^3) . \quad (100)$$

⁷Not necessarily a great assumption because Garrod equation 8.17 is an expansion for the particle density in term of the activity. The cluster integrals of second or ghighter order are zero for an ideal gas.

12 Garrod #8.5: Virial Coefficients for a Dieterici Gas.

Determine the virial coefficients, $B_2(T)$ and $B_3(T)$, for a gas that satisfies Dieterici's equation of state, $p(v - b) = RT \exp(-a/vT)$, where a and b are constants and v is the molar volume.

We can rearrange Dieterici's equation to write

$$\frac{p}{T} = \frac{1}{v - b} R e^{-a/vT}, \quad (101)$$

and if we divide both sides by the Boltzmann constant k , the left-hand side will be in the correct form to perform a virial expansion, and the right-hand side will have a term R/k . This term is simply Avogadro's constant N_A , or one mole. Since v is the molar volume, we have $N_A/v = n$, where n is the particle density. We will take $N_A = 1$, because v is the volume occupied by one mole of the gas. Our virial expansion is then of the form

$$\frac{1}{v - b} e^{-a/vT} = \frac{1}{v} + B_2 \left(\frac{1}{v}\right)^2 + B_3 \left(\frac{1}{v}\right)^3 + \dots \quad (102)$$

Taylor expanding the exponential yields

$$e^{-a/vT} = 1 - \frac{a}{T} \frac{1}{v} + \frac{a^2}{2T^2} \left(\frac{1}{v}\right)^2 - \frac{a^3}{6T^3} \left(\frac{1}{v}\right)^3 + \mathcal{O}(v^{-4}). \quad (103)$$

When we multiply this by the factor $(v - b)^{-1}$, we get the result

$$\frac{p}{kT} = \frac{1}{v - b} - \frac{a}{T} \frac{1}{v(v - b)} + \frac{a^2}{2T^2} \frac{1}{v^2(v - b)} + \mathcal{O}(v^{-4}). \quad (104)$$

We can note:

$$\frac{1}{v - b} = \frac{1}{v} + b \frac{1}{v(v - b)} \quad (105)$$

$$\frac{1}{v(v - b)} = \frac{1}{v^2} + b \frac{1}{v^2(v - b)} \quad (106)$$

$$\frac{1}{v^2(v - b)} = \frac{1}{v^3} + b \frac{1}{v^3(v - b)}, \quad (107)$$

which we may insert into the virial expansion:

$$\frac{p}{kT} = \left(\frac{1}{v} + b \frac{1}{v(v - b)}\right) - \frac{a}{T} \left(\frac{1}{v^2} + b \frac{1}{v^2(v - b)}\right) + \frac{a^2}{2T^2} \left(\frac{1}{v^3}\right) + \mathcal{O}(v^{-4}) \quad (108)$$

$$= \frac{1}{v} - \frac{a}{T} \left(\frac{1}{v}\right)^2 + \frac{a^2}{2T^2} \left(\frac{1}{v}\right)^3 + \left(b \frac{1}{v(v - b)} - \frac{ab}{T} \frac{1}{v^2(v - b)}\right) + \mathcal{O}(v^{-4}) \quad (109)$$

$$= \frac{1}{v} - \frac{a}{T} \left(\frac{1}{v}\right)^2 + \frac{a^2}{2T^2} \left(\frac{1}{v}\right)^3 + b \left(\frac{1}{v^2} + b \frac{1}{v^2(v - b)} - \frac{a}{T} \frac{1}{v^3}\right) + \mathcal{O}(v^{-4}) \quad (110)$$

$$= \frac{1}{v} + \left(b - \frac{a}{T}\right) \left(\frac{1}{v}\right)^2 + \left(\frac{a^2}{2T^2} - \frac{ab}{T}\right) \left(\frac{1}{v}\right)^3 + b \left(\frac{1}{v^2(v - b)}\right) + \mathcal{O}(v^{-4}) \quad (111)$$

$$= \frac{1}{v} + \left(b - \frac{a}{T}\right) \left(\frac{1}{v}\right)^2 + \left(\frac{a^2}{2T^2} - \frac{ab}{T} + b^2\right) \left(\frac{1}{v}\right)^3 + \mathcal{O}(v^{-4}), \quad (112)$$

so the first two coefficients in the virial expansion are

$$B_2(T) = b - \frac{a}{T} \quad \text{and} \quad B_3(T) = \frac{a^2}{2T^2} - \frac{ab}{T} + b^2. \quad (113)$$