

You are graded on your work (with partial credit where it is deserved) so please do not just write down answers with no explanation (or skip important steps)!

Please give clear, well-organized, understandable solutions.

$h = 6.63 \times 10^{-34} \text{ J s}$	[Planck's constant]	$k = 1.38 \times 10^{-23} \text{ J/K}$	[Boltzmann constant]
$c = 3.00 \times 10^8 \text{ m/s}$	[speed of light]	$m_e = 9.11 \times 10^{-31} \text{ kg}$	[mass of electron]
$\sigma_B = 5.67 \times 10^{-8} \frac{\text{W}}{\text{m}^2 \cdot \text{K}^4}$	[Stefan-Boltzmann constant]	$G = 6.67 \times 10^{-11} \frac{\text{N m}^2}{\text{kg}^2}$	[gravitational constant]
$1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$	and $\frac{1 \text{ eV}}{k} = 11,600 \text{ K}$	$R_\odot = 6.96 \times 10^8 \text{ m}$	[radius of Sun]
average distance of Earth from Sun = $1.50 \times 10^{11} \text{ m}$		$R_\oplus = 6.38 \times 10^6 \text{ m}$	[radius of Earth]

See back page for small integral table.

The variables have their usual meanings:  $E$  = energy,  $S$  = entropy,  $V$  = volume,  $N$  = number of particles,  $T$  = temperature,  $P$  = pressure,  $\mu$  = chemical potential,  $B$  = applied magnetic field,  $C_V$  = heat capacity at constant volume,  $k$  = Boltzmann constant. Also,  $\langle \dots \rangle$  represents an average.

You should know this, but:

$$\langle n(\epsilon_i) \rangle = \frac{1}{e^{(\epsilon_i - \mu)/kT} \pm 1} ; \quad dE = TdS - PdV + \mu dN ; \quad E = TS - PV + \mu N$$

1. Let us calculate the isothermal compressibility  $\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$  for the free electron model

(an ideal gas of electrons), which gives reasonably good estimates for some metals. We will consider nonrelativistic electrons at  $T = 0$ .

(a) (5) We found that  $E = \frac{3}{5} N \epsilon_F$  with  $\epsilon_F = \left( \frac{3}{8\pi} \right)^{2/3} \frac{h^2}{2m} \left( \frac{N}{V} \right)^{2/3}$ .

(Here  $E = \langle E \rangle$  is the thermodynamic or average energy of the system.)

Use these relations to show that  $P = a \frac{E}{V}$  while at the same time obtaining the constant  $a$ .

$$E = A V^{-2/3} \Rightarrow \boxed{P = -\frac{\partial E}{\partial V}} = + A \cdot \frac{2}{3} V^{-5/3} = \frac{2}{3} \frac{1}{V} A V^{-2/3} = \boxed{\frac{2}{3} \frac{E}{V}}$$

(b) (5) Using the result of part (a), show that

$$\left( \frac{\partial P}{\partial V} \right)_T = b \frac{P}{V}$$

while at the same time obtaining the constant  $b$ .

$$\boxed{\frac{\partial P}{\partial V}} = \frac{\partial}{\partial V} \left( A \cdot \frac{2}{3} V^{-5/3} \right) = \frac{2}{3} A \left( -\frac{5}{3} V^{-8/3} \right) = -\frac{5}{3} \cdot \frac{1}{V} \cdot \frac{2}{3} A V^{-5/3} = \boxed{-\frac{5}{3} \frac{P}{V}}$$

(c) (5) Using the relations given and obtained in part (a), show that

$$P = c n \mathcal{E}_F \quad \text{where} \quad n = \frac{N}{V}$$

while at the same time obtaining the constant  $c$ .

$$\boxed{P =} \frac{2}{3} \frac{1}{V} \cdot \frac{3}{5} N \mathcal{E}_F = \boxed{\frac{2}{5} n \mathcal{E}_F}$$

(d) (5) Obtain  $\kappa_T$  in terms of  $\mathcal{E}_F$  and  $n$ .

$$\begin{aligned} \boxed{\kappa_T} &= -\frac{1}{V} \left( -\frac{3}{5} \frac{V}{P} \right) \quad \text{since} \quad \left( \frac{\partial V}{\partial P} \right)_T = \frac{1}{(\partial P / \partial V)_T} \\ &= \frac{3}{5} \cdot \frac{5}{2} \frac{1}{n \mathcal{E}_F} \\ &= \boxed{\frac{3}{2 n \mathcal{E}_F}} \end{aligned}$$

(e) (5) The number density of electrons in aluminum is  $1.8 \times 10^{29} \text{ m}^{-3}$  and the Fermi energy is 11.6 eV, where  $1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$ . Calculate the electronic pressure  $P$  and the compressibility  $\kappa_T$  for aluminum. Give both answers in GPa or  $\text{GPa}^{-1}$ , where  $1 \text{ GPa} = 10^9 \text{ Pa} = 10^9 \text{ N/m}^2$ . Why does this enormous pressure not blast the material apart?

$$\begin{aligned} \boxed{P} &= \frac{2}{5} n \mathcal{E}_F = \frac{2}{5} (1.8 \times 10^{29} \text{ m}^{-3}) (11.6 \text{ eV}) (1.60 \times 10^{-19} \frac{\text{J}}{\text{eV}}) \\ &= 0.13 \times 10^{12} \text{ Pa} \\ &= \boxed{130 \text{ GPa}} \end{aligned}$$

$$\begin{aligned} \boxed{\kappa_T} &= \frac{3}{2 n \mathcal{E}_F} = 4.5 \times 10^{-12} \text{ Pa}^{-1} = 4.5 \times 10^{-3} \text{ GPa}^{-1} \\ &= \boxed{0.0045 \text{ GPa}^{-1}} \end{aligned}$$

[This is about  $\frac{1}{3}$  the measured value.]

Positive ions exert the opposite attractive force.

2. A system has the Gibbs free energy

$$G = -NkT \ln \left( \frac{aT^{7/2}}{P} \right)$$

where  $a$  is a constant. Recall that  $dG = -SdT + VdP + \mu dN$ . Calculate the following quantities as functions of the natural variables of  $G(T, P, N)$ .

(a) (4) The entropy  $S$

$$\boxed{S =} - \frac{\partial G}{\partial T} = +Nk \frac{\partial}{\partial T} \left( T \ln \left( \frac{aT^{7/2}}{P} \right) \right) = Nk \left[ \ln \left( \frac{aT^{7/2}}{P} \right) + T \frac{\partial}{\partial T} \frac{7}{2} \ln T \right]$$

$$= \boxed{Nk \ln \left( \frac{aT^{7/2}}{P} \right) + \frac{7}{2} Nk}$$

(b) (4) The heat capacity at constant pressure,  $C_p$

$$\boxed{C_p =} T \left( \frac{\partial S}{\partial T} \right)_P = T \frac{\partial}{\partial T} \left( \frac{7}{2} \ln T + \ln a + \ln P \right) \cdot Nk$$

$$= T \frac{7}{2} \frac{1}{T} \cdot Nk = \boxed{\frac{7}{2} Nk}$$

(c) (4) The volume  $V$  -- and then write the equation of state for the system

$$\boxed{V =} \frac{\partial G}{\partial P} = -NkT \frac{\partial}{\partial P} \left( \ln a + \ln T^{7/2} - \ln P \right)$$

$$= \boxed{+NkT \frac{1}{P}} \quad \text{so} \quad \boxed{PV = NkT}$$

(d) (4) The chemical potential  $\mu$

$$\boxed{\mu =} \frac{\partial G}{\partial N} = \boxed{-kT \ln \left( \frac{aT^{7/2}}{P} \right)}$$

(e) (4) The energy  $E$ , which you can obtain from Euler's theorem. (If you have forgotten Euler's theorem, look at the front page of this exam.)

$$\boxed{E =} TS - PV + \mu N$$

$$= \left( T Nk \ln \left( \frac{aT^{7/2}}{P} \right) + \frac{7}{2} NkT \right) - NkT - NkT \ln \left( \frac{aT^{7/2}}{P} \right)$$

$$= \boxed{\frac{5}{2} NkT}$$

(f) (4) The heat capacity at constant volume,  $C_v$

$$\boxed{C_v =} \frac{\partial E}{\partial T} = \boxed{\frac{5}{2} Nk}$$

(g) (1) What system has this equation of state?

: diatomic ideal gas

3. The classical Maxwell-Boltzmann distribution of velocities is given by the function

$$\tilde{f}(v)dv = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT} \cdot 4\pi v^2 dv$$

(a) (8) By using the definition of the average of  $v^2$ , and evaluating this integral (see last page of this exam for an integral table), obtain the root-mean-square velocity  $v_{rms}$  at a temperature  $T$ .

$$\begin{aligned} \langle v^2 \rangle &= \left(\frac{m}{2\pi kT}\right)^{3/2} \cdot 4\pi \int_0^\infty v^2 e^{-mv^2/2kT} v^2 dv \\ &= \left(\frac{m}{2\pi kT}\right)^{3/2} \cdot 4\pi \cdot \left(\frac{2kT}{m}\right)^{5/2} \int_0^\infty dx \cdot x^4 e^{-x^2} \quad x \equiv \left(\frac{m}{2kT}\right)^{1/2} v \\ &= \frac{4}{\pi^{1/2}} \left(\frac{2kT}{m}\right) \cdot \frac{3}{2} \cdot \frac{1}{4} \pi^{1/2} \quad [n=2 \text{ in integral table, } a=1] \\ &= 3 \frac{kT}{m} \\ \Rightarrow \boxed{v_{rms}} &\equiv \langle v^2 \rangle^{1/2} = \boxed{\sqrt{\frac{3kT}{m}}} \quad \left[ \text{and } \frac{1}{2} m v_{rms}^2 = \frac{3}{2} kT \right. \\ &\quad \left. \text{or } E_{trans} = \frac{3}{2} NkT \right] \end{aligned}$$

(b) (9) Calculate  $v_{rms}$  at  $T = 300$  K for a nitrogen molecule, with a mass of 28.0 u, and a hydrogen molecule, with a mass of 2.02 u, where  $1 \text{ u} = 1.66 \times 10^{-27} \text{ kg}$ . Hydrogen is by far the most common element in the universe, so why is there so little in the Earth's atmosphere?

$$\begin{aligned} \boxed{v_{rms}^{N_2}} &= \sqrt{\frac{(3)(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}{(28.0 \text{ u})(1.66 \times 10^{-27} \text{ kg/u})}} \\ &= \boxed{517 \frac{\text{m}}{\text{s}}} \\ \boxed{v_{rms}^{H_2}} &= \sqrt{\frac{m_{N_2}}{m_{H_2}}} = \sqrt{\frac{28.0 \text{ u}}{2.02 \text{ u}}} \left(517 \frac{\text{m}}{\text{s}}\right) = \boxed{1925 \frac{\text{m}}{\text{s}}} \end{aligned}$$

$H_2$  molecules reach escape velocity more easily.

(c) (8) In this part we are still considering a classical system in equilibrium, but extending the treatment to any classical variable  $x$  which occurs quadratically in the energy  $\epsilon$  of a single particle:

$$\epsilon = bx^2 + \text{other terms}$$

where  $b$  is a constant and the other terms do not depend on  $x$ . Given the fact that the classical probability is proportional to  $e^{-\epsilon/kT}$ , show that the variable  $x$  makes a contribution to the total energy which is proportional to  $kT$ ,

$$\langle bx^2 \rangle = c kT,$$

while at the same time obtaining the constant  $c$ .

$$\langle bx^2 \rangle = \frac{\int_0^{\infty} dx \cdot bx^2 e^{-bx^2/kT} \int d(\text{other variables}) e^{-E_{\text{other}}/kT}}{\int_0^{\infty} dx e^{-bx^2/kT} \int d(\text{other variables}) e^{-E_{\text{other}}/kT}}$$

$$= \frac{b \cdot \frac{1}{4} \sqrt{\frac{\pi}{(b/kT)^3}}}{\frac{1}{2} \sqrt{\frac{\pi}{b/kT}}}$$

$$= \frac{1}{2} b \frac{kT}{b}$$

$$\boxed{= \frac{1}{2} kT}$$

4. For the ionization reaction  $H \rightleftharpoons H^+ + e^-$ , the law of mass action gives

$$\frac{[H^+][e^-]}{[H]} = K(T), \quad K(T) = \frac{\lambda_{H^+}^{-3} \lambda_{e^-}^{-3} Z_{H^+}(\text{int}) Z_{e^-}(\text{int})}{\lambda_H^{-3} Z_H(\text{int})}, \quad \lambda = \frac{h}{(2\pi m k T)^{1/2}}$$

The masses of  $H$  and  $H^+$  can be taken to be the same in the present context (to a good approximation). Also,  $Z(\text{int}) = 2$  for  $H^+$  and  $e^-$  (spin up or down with zero energy), and  $Z_H(\text{int}) = 2 \times 2 e^{-\epsilon_{gs}/kT}$  (spin up or down for both electron and proton) with ground state energy  $\epsilon_{gs} = -13.6$  eV.

(a) (20) Taking  $[H] \approx 10^{19} \text{ m}^{-3}$  and  $T = 6000$  K (temperature at surface of Sun), with  $[e^-] = [H^+]$

(for charge neutrality), so that  $\frac{[H^+]^2}{[H]^2} = \frac{K(T)}{[H]}$ , estimate  $\frac{[H^+]}{[H]}$ .

$$K(T) \approx \lambda_{e^-}^{-3} \frac{2 \times 2}{2 \times 2 \times e^{-\epsilon_{gs}/kT}} \quad \text{since } \lambda_{H^+} \approx \lambda_H$$

$$\lambda_{e^-} = \frac{h}{(2\pi m_e k T)^{1/2}} = \frac{6.63 \times 10^{-34} \text{ J}\cdot\text{s}}{(2\pi)(9.11 \times 10^{-31} \text{ kg})(1.38 \times 10^{-23} \text{ J/K})(6000 \text{ K})^{1/2}}$$

$$= 9.6 \times 10^{-10} \text{ m} \quad [\text{or } 9.6 \text{ \AA}; (\text{kg}\cdot\text{J})^{1/2} = \text{kg m/s} \text{ and } \text{J}\cdot\text{s} = \text{kg m}^2/\text{s}]$$

$$\frac{\epsilon_{gs}}{kT} = -\frac{(13.6 \text{ eV})(1.60 \times 10^{-19} \text{ J/eV})}{(1.38 \times 10^{-23} \text{ J/K})(6000 \text{ K})} = -26.3$$

$$\therefore K(T) = (9.6 \times 10^{-10} \text{ m})^{-3} \frac{2 \times 2}{2 \times 2 \times e^{+26.3}} = 4.3 \times 10^{15} \text{ m}^{-3}$$

$$\boxed{\frac{[H^+]}{[H]} = \left( \frac{K(T)}{[H]} \right)^{1/2} = \left( \frac{4.3 \times 10^{15} \text{ m}^{-3}}{10^{19} \text{ m}^{-3}} \right)^{1/2} = \boxed{0.021 \text{ or } 2.1\%}}$$

(b) (5) Calculate  $e^{+\epsilon_{gs}/kT} = e^{-13.6 \text{ eV}/kT}$ , the Boltzmann factor for  $H^+$  and  $e^-$  (with energy 0) relative to  $H$  (with energy -13.6 eV). Why is  $\frac{[H^+]}{[H]}$  so much bigger than this factor, which we would naively expect if only energy were involved?

$$\text{From above, } e^{+\epsilon_{gs}/kT} = e^{-26.3} = \boxed{3.8 \times 10^{-12}}$$

Entropy is also important.

$$\int_0^{\infty} e^{-ax^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{a}} \text{ for } a > 0 \text{ (the Gaussian integral)}$$

$$\int_0^{\infty} x^2 e^{-ax^2} dx = \frac{1}{4} \sqrt{\frac{\pi}{a^3}} \text{ for } a > 0$$

$$\int_0^{\infty} x^{2n} e^{-ax^2} dx = \frac{2n-1}{2a} \int_0^{\infty} x^{2(n-1)} e^{-ax^2} dx$$

$$\int_0^{\infty} x^3 e^{-ax^2} dx = \frac{1}{2a^2} \text{ when } a > 0$$

$$\int_{-\infty}^{\infty} dx x^2 \frac{e^x}{(e^x+1)^2} = \frac{1}{3} \pi^2$$