

## TP – A SOLUTION

For an ideal monatomic gas  $U=3/2nRT$ ,  $C_v = 3/2R$  and  $C_p = 3/2R + R = 5/2R$ .

Since the process is at constant pressure  $\Delta Q = C_p n \Delta T$  giving

a:  $n = \Delta Q / (5/2R\Delta T) = 1000 / (5/2 * 8.31 * 10)$

$$\Delta U = 3/2nR\Delta T = (3/2)R\Delta T(\Delta Q / 5/2R\Delta T) = 3\Delta Q / 5$$

$$\Delta U = \Delta Q - P\Delta V$$

b:  $P\Delta V = \Delta Q - \Delta U = 2/5 \Delta Q$

$$\Delta V = 2/5\Delta Q / P = (2/5)1000/10^5 \text{ m}^3$$

c:  $T(dS) = dQ = C_p n(dT)$

$$\Delta S = \frac{5}{2}nR \int \frac{dT}{T} = \frac{5}{2}nR \ln\left(\frac{T_0 + 10}{T_0}\right)$$

## TP - B SOLUTION

(a) If the ground level energy is defined as zero and  $E$  is the energy of excited level:

$$Z = \sum_i d_i \exp(-\beta \varepsilon_i) = 2 + 6 \exp(-\beta E)$$

The probability that the atom is in its excited level:

$$P(E) = \frac{6 \exp(-\beta E)}{Z} = \frac{3 \exp(-\beta E)}{1 + 3 \exp(-\beta E)} = \frac{3}{3 + \exp(\beta E)}$$

Since  $E = 1.2$  eV,  $T = 6000$ K ( $\sim 0.5$  eV),  $\beta E = 2.32$ ,  $\exp(\beta E) \approx 10$  we get:  $P(E) = \frac{3}{3+10} = 0.23$

(b) The average energy per atom is:

$$\langle \varepsilon \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{\varepsilon \times 6 \exp(-\beta \varepsilon)}{2 + 6 \exp(-\beta \varepsilon)} = \frac{3\varepsilon}{\exp(\beta \varepsilon) + 3}$$

(c) The specific heat is:

$$C_V = \left( \frac{\partial \langle \varepsilon \rangle}{\partial T} \right)_V = \frac{-3\varepsilon \times \varepsilon \exp(\beta \varepsilon) \frac{\partial \beta}{\partial T}}{[\exp(\beta \varepsilon) + 3]^2} = k_B \frac{3(\beta \varepsilon)^2 \exp(\beta \varepsilon)}{[\exp(\beta \varepsilon) + 3]^2}$$

## TP — C1 SOLUTION

In equilibrium the chemical potential of the molecules on the surface sites must equal to the chemical potential  $\mu$  of the gas outside the surface. Thus the required expression is given by substitution of the latter chemical potential into the Fermi distribution of the adsorbed molecules  $[e^{(E-\mu)/kT} + 1]^{-1}$ . The chemical potential for the gas molecules ( $\mu$ ) can be related to the number of gas molecules per unit volume ( $n$ ) by integrating the Maxwell-Boltzmann distribution over momentum:

$$n = \int \frac{d^3p}{(2\pi\hbar)^3} \exp\left(-\frac{\frac{p^2}{2M} - \mu}{kT}\right).$$

Then, if  $n$  is eliminated using the ideal gas law ( $P = nkT$ ), one can solve for the chemical potential  $\mu$ , and put it back into the Fermi distribution for the adsorbed molecules. The resulting expression for the adsorbed fraction is

$$\frac{CP}{1 + CP},$$

where

$$C = \frac{\Lambda^3}{kT} \exp\left(-\frac{E}{kT}\right),$$

and

$$\Lambda = \sqrt{\frac{2\pi\hbar^2}{MkT}}.$$

$\Lambda$  is proportional to the thermal de Broglie wavelength, so that the combination  $CP$  is dimensionless by analogy with the ideal gas law.

## TP – C2 SOLUTION

$$(a) \quad J = \frac{P_{Sun}}{4\pi R_{orbit}^2} = \frac{4 \cdot 10^{26} W}{4\pi (5.8 \cdot 10^{10} m)^2} = 9.46 \cdot 10^3 W / m^2$$

$$(b) \quad P_{Mercury} = J \cdot \pi R_{Mercury}^2 = 9.46 \cdot 10^3 W / m^2 \cdot \pi (2.44 \cdot 10^6 m)^2 = 1.77 \cdot 10^{17} W$$

$$(c) \quad \text{Consider Mercury as a hemisphere, then: } P_{Mercury} = 2\pi R_{Mercury}^2 \sigma T_{Mercury}^4$$

Solving for the temperature we have:

$$T_{Mercury} = \left( \frac{P_{Mercury}}{2\pi R_{Mercury}^2 \sigma} \right)^{1/4} = \left[ \frac{1.77 \cdot 10^{17} W}{2\pi (2.44 \cdot 10^6 m)^2 5.76 \cdot 10^{-8} W / K^4 m^2} \right]^{1/4} = 535 K$$

$$(d) \quad T_{Sun} = \left( \frac{P_{Sun}}{4\pi R_{Sun}^2 \sigma} \right)^{1/4} = \left( \frac{4 \cdot 10^{26} W}{4\pi (7 \cdot 10^8 m)^2 5.76 \cdot 10^{-8} W / K^4 m^2} \right)^{1/4} = 5,795 K$$

$$v_{max}^{received} = 2.8 \frac{k_B T_{Sun}}{h} = 2.8 \frac{1.38 \cdot 10^{-23} J / K \times 5,795 K}{6.62 \cdot 10^{-34} Js} = 3.4 \cdot 10^{14} Hz$$

$$(e) \quad v_{max}^{emitted} = 2.8 \frac{k_B T_{Mercury}}{h} = 2.8 \frac{1.38 \cdot 10^{-23} J / K \times 535 K}{6.62 \cdot 10^{-34} Js} = 3.1 \cdot 10^{13} Hz$$

## TP – D1 SOLUTION

a) Final temperature stays the same at 300K.

Total pressure stays the same. Individual pressures are given by the law of partial pressures with helium pressure at  $1/6 \cdot 2 = 1/3$  atm, neon pressure at  $2/6 \cdot 2 = 2/3$  atm and argon pressure at  $3/6 \cdot 2 = 1$  atm.

Note the volume is not initially divided equally but is in proportion to mole fractions using  $PV = nRT$  or  $V/n = RT/P$  which is a constant.

Helium volume =  $1/6V$ , neon volume =  $1/3V$ , argon volume =  $1/2V$ .

b)  $U$  only depends on  $T$  and not  $V$  for an ideal gas  $\Delta U = 0$

c)  $dG = -SdT + VdP + udn$ .  $dG = V(dP)$  at constant  $T$ .  $dG = (nRT/P)(dP)$

$$\Delta G = nRT \ln \frac{P_f}{P_i} \text{ for each component}$$

$$\Delta G = RT (n_{He} \ln(1/6) + n_{Ne} \ln(1/3) + n_{Ar} \ln(1/2)) =$$

$$8.31 \cdot 300 \cdot 10^3 (1 \ln(1/6) + 2 \ln(1/3) + 3 \ln(1/2)) = -1.5 \cdot 10^7 \text{ J}$$

c) For an ideal gas  $U = 3/2 nRT$  and  $dU = 3/2 nR(dT)$

$$dU = T(dS) - P(dV) + u(dN)$$

$$dS = 3/2 nR dT/T + nR dV/V \text{ with } dN = 0$$

$$\text{Thus } S = 3/2 nR \ln T + nR \ln V + \text{constant or } S = nR \ln T^{3/2} V / C_0 = k_B N \ln T^{3/2} V / NC_1.$$

The constant  $C_0 = NC_1$  to keep the entropy extensive.

Use  $V = Nk_B T / P$  to get

$$S = nR \ln T^{5/2} / PC_1$$

Thus

$$\Delta S = -\Delta G / T = 1.5 \cdot 10^7 / 300 = 5 \cdot 10^4 \text{ J/K}$$

## TP — D2 SOLUTION

For the density, we have

$$n \propto \int d^d p f(\epsilon_p) \propto \int_0^\infty dp p^{d-1} f(\epsilon_p), \quad (1)$$

where  $f$  is the Fermi function

$$f(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)} + 1}, \quad (2)$$

with  $\beta = (kT)^{-1}$ . Using the fact that  $\epsilon_p \propto p^2$ , it is convenient to change dummy integration variables, writing

$$n \propto \int_{-\infty}^{\infty} d\epsilon g(\epsilon) f(\epsilon), \quad (3)$$

where

$$g(\epsilon) \propto \epsilon^{(d-2)/2} \theta(\epsilon), \quad (4)$$

where  $\theta$  is the unit step function that vanishes for negative arguments. Noting that the zero temperature Fermi function is a unit step function, we now may write

$$0 = n(T) - n(T=0) = \int_{-\infty}^{\infty} d\epsilon g(\epsilon) \left[ \frac{1}{e^{\beta(\epsilon-\mu)} + 1} - \theta(\mu_0 - \epsilon) \right]. \quad (5)$$

Using the fact that we are looking only for a small change, we may write this as

$$\begin{aligned} (\mu - \mu_0)g(\mu_0) &\approx \int_{-\infty}^{\infty} d\epsilon g(\epsilon) [\theta(\mu - \epsilon) - \theta(\mu_0 - \epsilon)] \\ &= - \int_{-\infty}^{\infty} d\epsilon g(\epsilon) \left[ \frac{1}{e^{\beta(\epsilon-\mu)} + 1} - \theta(\mu - \epsilon) \right]. \end{aligned} \quad (6)$$

The integrand in the final integral has contributions that go to zero exponentially when  $|\epsilon - \mu| > kT$ , so we can expand in  $T$  by expanding  $g(\epsilon)$  around  $\mu$  letting

$$g(\epsilon) \approx g(\mu) + (\epsilon - \mu)g'(\mu) + \dots \quad (7)$$

Substituting above, we note that the integral over the first term in the series vanishes. In the integral resulting from the second term, we integrate by parts, and noting that the integrated part vanishes exponentially at  $\pm\infty$ , we find

$$(\mu - \mu_0)g(\mu_0) \approx g'(\mu) \frac{1}{2} \int_{-\infty}^{\infty} d\epsilon (\epsilon - \mu)^2 \frac{d}{d\epsilon} \left[ \frac{1}{e^{\beta(\epsilon - \mu)} + 1} - \theta(\mu - \epsilon) \right] \quad (8)$$

Carrying out the differentiation, and changing the dummy integration variable to  $x = \beta(\epsilon - \mu)$  gives

$$\mu - \mu_0 \approx -\alpha \frac{g'(\mu)}{g(\mu_0)} (kT)^2 \approx -\alpha \frac{g'(\mu_0)}{g(\mu_0)} (kT)^2, \quad (9)$$

where

$$\alpha = \int_0^{\infty} dx \frac{x^2 e^x}{(e^x + 1)^2} = \frac{\pi^2}{6}. \quad (10)$$

Substituting  $g$  from Eq. (4) gives

$$\mu - \mu_0 \approx -\alpha \left( \frac{d-2}{2} \right) \frac{(kT)^2}{\mu_0}. \quad (11)$$

We see that for  $d > 2$ ,  $\mu$  decreases as we increase the temperature. For  $d = 1$  it increases with temperature, while the crossover where it doesn't vary is at  $d = 2$ .