

Physics 3410 Homework #6

5 problems

Solutions

▷ 1.

Calculate the chemical potential of an ideal gas, given the Sackur-Tetrode equation.

Answer:_____

The Sackur-Tetrode equation says that

$$S = kN \left[\ln \frac{V}{N} + \frac{3}{2} \ln \frac{U}{N} + C \right]$$

where $C = \frac{5}{2} + \frac{3}{2} \ln \frac{4\pi m}{3h^2}$ is a constant. From the thermodynamic potential

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

we can get the relationship

$$\mu = -T \left(\frac{\partial S}{\partial N} \right)_{U,V}$$

so we need to take the N derivative of the Sackur-Tetrode equation. It's easier if we expand it out a little bit. Assuming U and V are constant in what follows:

$$\begin{aligned} \frac{dS}{dN} &= \frac{d}{dN} \left[kN \left(\ln V - \ln N + \frac{3}{2} \ln U - \frac{3}{2} \ln N + C \right) \right] \\ &= k \left(\ln V - \ln N + \frac{3}{2} \ln U - \frac{3}{2} \ln N + C \right) + kN \left(-\frac{1}{N} - \frac{3}{2N} \right) \\ &= k \left(\ln V - \ln N + \frac{3}{2} \ln U - \frac{3}{2} \ln N + \frac{5}{2} + \frac{3}{2} \ln \frac{4\pi m}{3h^2} \right) - \frac{5}{2}k \\ &= k \left(\ln V - \ln N + \frac{3}{2} \ln U - \frac{3}{2} \ln N + \frac{3}{2} \ln \frac{4\pi m}{3h^2} \right) \\ &= k \left(\ln \frac{V}{N} + \frac{3}{2} \ln \frac{U}{N} + \frac{3}{2} \ln \frac{4\pi m}{3h^2} \right) \\ \implies \mu &= -kT \left(\ln \frac{V}{N} + \frac{3}{2} \ln \frac{U}{N} + \frac{3}{2} \ln \frac{4\pi m}{3h^2} \right) \\ &= kT \left(\ln \frac{N}{V} - \frac{3}{2} \ln \frac{U}{N} - \frac{3}{2} \ln \frac{4\pi m}{3h^2} \right) \end{aligned}$$

Notice that the chemical potential is related to the number density $\frac{N}{V}$: the more particles a system has, the higher its chemical potential, and the more likely it is to give particles to other systems.

That's fine for an answer, but we can also use the fact that an ideal gas obeys the equipartition theorem: $\frac{U}{N} = \frac{f}{2}kT$ and so

$$\begin{aligned}\mu &= kT \left(\ln \frac{N}{V} - \frac{3}{2} \ln \left(\frac{f}{2} kT \right) - \frac{3}{2} \ln \frac{4\pi m}{3h^2} \right) \\ &= \boxed{kT \left(\ln \frac{N}{V} - \frac{3}{2} \ln \frac{2\pi f m kT}{3h^2} \right)}\end{aligned}$$

▷ **2.**

Consider an Einstein solid in the low-temperature limit $N \gg q \gg 1$, which as you'll recall has the multiplicity

$$\Omega = \left(\frac{eN}{q} \right)^q$$

(a) Find a formula for the temperature of an Einstein solid in the limit $q \ll N$. Let $U = q\varepsilon$ where ε is the energy per quantum.

(b) Solve for the energy as a function of temperature to obtain $U = N\varepsilon e^{-\varepsilon/kT}$.

Answer:_____

(a) The number of microstates of an Einstein solid in the “low-temperature” limit $q \ll N$ is

$$\Omega = \left(\frac{eN}{q} \right)^q$$

where $q = \frac{U}{\varepsilon}$, ε being the size of each energy unit. Thus the entropy is

$$\begin{aligned}S &= k \ln \Omega = k \ln \left(\frac{eN}{q} \right)^q \\ &= kq [\ln e + \ln N - \ln q] \\ &= k \frac{U}{\varepsilon} [\ln N - \ln U + \ln \varepsilon + 1]\end{aligned}$$

The temperature is given by

$$\begin{aligned}\frac{1}{T} &= \frac{\partial S}{\partial U} \\ &= \frac{k}{\varepsilon} [\ln N - \ln U + \ln \varepsilon + 1] - k \frac{U}{\varepsilon} \frac{1}{U} \\ &= \frac{k}{\varepsilon} \ln \left(\frac{N\varepsilon}{U} \right)\end{aligned}$$

or

$$T = \frac{\varepsilon}{k \ln(N\varepsilon/U)}$$

(b)

$$\begin{aligned}\frac{1}{T} &= \frac{k}{\varepsilon} \ln \left(\frac{N\varepsilon}{U} \right) \\ \implies \frac{\varepsilon}{kT} &= \ln \left(\frac{N\varepsilon}{U} \right) \\ \implies e^{\varepsilon/kT} &= \frac{N\varepsilon}{U} \\ \implies U &= N\varepsilon e^{-\varepsilon/kT}\end{aligned}$$

which is what we wanted to show. Note that as $T \rightarrow 0$, the exponent goes to $-\infty$, and so the energy goes to zero as one would expect.

▷ **3.**

Consider a $V = 1 \text{ m}^3$ solid block of lead at standard temperature and pressure. The coefficient of volume expansion for lead is $\beta = 70 \times 10^{-6} / \text{K}$, where

$$\beta V = \left(\frac{\partial V}{\partial T} \right)_{P,N}$$

Assume that the metal has $f = 6$ degrees of freedom per atom, and it obeys the equipartition theorem.

(a) If the block's temperature increases by 2 K at constant pressure, what is its increase in enthalpy? (*Hint: use β to find the change in volume.*)

(b) What is the block's heat capacity C_P at constant pressure, given this data?

Answer: _____

(a) If the pressure is constant, then $dH = P dV$ and the enthalpy's change is proportional to the change in volume. We know that the block's volume will increase as its temperature rises, according to

$$\beta V = \frac{dV}{dT} \implies dV = \beta V dT$$

and so

$$dH = dU + P dV$$

$$dH = N \frac{f}{2} k dT + P(\beta V dT)$$

We can get the number of atoms N using the density and atomic weight of lead. First we get its mass using the mass density $\rho = 11.34 \text{ g/cm}^3$.

$$m = 11.34 \frac{\text{g}}{\text{cm}^3} \times 1 \text{ m}^3 = 11.34 \text{ g} \left(\frac{\text{m}}{\text{cm}} \right)^3 = 11.34 \times 10^6 \text{ g}$$

(A meter divided by a centimeter is 100.) Using the atomic weight of lead, 207.2, we find the number of moles:

$$n = \frac{11.34 \times 10^6 \text{ g}}{207.2 \text{ g/mol}} = 5.47 \times 10^4 \text{ mol}$$

and finally, Avogadro's number gives us

$$N = nN_A = (5.47 \times 10^4 \text{ mol})(6.02 \times 10^{23} / \text{mol}) = 3.29 \times 10^{28}$$

Therefore,

$$\begin{aligned} dH &= N \frac{f}{2} k dT + P(\beta V dT) \\ &= (3.29 \times 10^{28})(3)(1.38 \times 10^{-23} \text{ J/K})(2 \text{ K}) + (10^5 \text{ Pa})(70 \times 10^{-6} / \text{K})(1 \text{ m}^3)(2 \text{ K}) \\ &= \boxed{2.7 \text{ MJ}} = 2.7 \times 10^6 \text{ J} \end{aligned}$$

(b) The heat capacity at constant pressure is

$$C_P = \frac{dH}{dT} = \frac{2.7 \text{ MJ}}{2 \text{ K}} = \boxed{1.4 \text{ MJ/K}} = 1.4 \times 10^6 \text{ J/K}$$

▷ 4.

During a particular quasistatic chemical reaction at constant temperature and pressure, the thermal potentials undergo the following changes:

$$\Delta U = +40 \text{ kJ} \quad \Delta H = +10 \text{ kJ} \quad \Delta F = +50 \text{ kJ} \quad \Delta G = +20 \text{ kJ}$$

Answer the following questions:

- (a) How much heat flows into or out of the system?
- (b) What is the total work done on the system by the environment (or vice versa)?
- (c) How much of that work is not due to the compression or expansion of the system?
- (d) Does the system expand or contract?

Answer:_____

(a) At constant pressure, $\Delta H = Q + W_{nc}$, and at constant pressure and temperature $\Delta G = W_{nc}$. Thus the total amount of heat flow is

$$Q = \Delta H - \Delta G = 10 \text{ kJ} - 20 \text{ kJ} = \boxed{-10 \text{ kJ}}$$

This is negative so there is a net flow of heat *out* of the system.

(b) At constant temperature, $\Delta F = \boxed{50 \text{ kJ}}$ is the total work done on the system; it's positive so the total work is *into* the system.

(c) At constant temperature and pressure, $\Delta G = \boxed{20 \text{ kJ}}$ is the total noncompression work at constant temperature and pressure; it's positive so the total noncompression work is *into* the system.

(d) The total compression work is

$$W_c = W_{total} - W_{nc} = \Delta F - \Delta G = 50 \text{ kJ} - 20 \text{ kJ} = 30 \text{ kJ}$$

This is positive so compression work is flowing into the system; thus the system must be *contracting*.

▷ 5.

At constant temperature and pressure, explain why

$$\Delta H + \Delta F = \Delta U + \Delta G$$

Answer:_____

At constant temperature and pressure (and assuming a process is quasistatic), we have

$$\Delta H = Q + W_{nc} \quad \Delta F = W_c + W_{nc} \quad \Delta G = W_{nc}$$

where Q is the heat into the system, W_c is the compression work done on the system, and ΔG is the noncompression work. Also the 1st law of thermodynamic says that

$$\Delta U = Q + W_c + W_{nc}$$

and so

$$\begin{aligned}\Delta H + \Delta F &= (Q + W_{nc}) + (W_c + W_{nc}) \\ &= (Q + W_c + W_{nc}) + W_{nc} \\ &= \Delta U + \Delta G\end{aligned}$$

Q.E.D.