

**University of Illinois at Chicago
Department of Physics**

***Thermodynamics & Statistical Mechanics
Qualifying Examination***

***January 9, 2009
9.00 am – 12:00 pm***

Full credit can be achieved from completely correct answers to 4 questions. If the student attempts all 5 questions, all of the answers will be graded, and the top 4 scores will be counted toward the exam's total score.

Problem 1

A vertical cylinder contains n moles of an ideal gas, and is closed off by a piston of mass M and area A . The acceleration due to gravity is g . The molar specific heat C_v (at constant volume) of the gas is a constant independent of temperature. The heat capacities of the piston and the cylinder are negligibly small, and any frictional forces between the piston and the cylinder walls can be neglected. The whole system is thermally isolated. Initially the piston is clamped in position so that the gas has a volume V_o and a temperature T_o . The piston is now released and, after some oscillations, comes to rest in a final equilibrium state corresponding to a larger volume of the gas. Assume that the external air pressure is negligible.

(a) Does the temperature of the gas increase, decrease, or stay the same. Explain your answer.

First law: $\Delta U = Q + W$

System is thermally isolated $\Rightarrow Q = 0$

The expanding gas does work on the surroundings $\Rightarrow W < 0$

Therefore, from first law $\Delta U < 0$

For an ideal gas, U is a function of T only, and hence the gas cools.

(b) Does the entropy of the gas increase, decrease, or remain the same? Explain your answer.

This process is an irreversible expansion of the gas. For a thermally isolated system undergoing an irreversible process, the entropy of the system must increase.

(c) Express the ratio T_f/V_f in terms of M , g , A , n and the gas constant R , where T_f and V_f are the final temperature and volume, respectively, of the gas.

The final pressure, at equilibrium, is given by $P_f = \frac{Mg}{A}$

$$\Rightarrow \frac{Mg}{A} = \frac{nRT_f}{V_f} \Rightarrow \frac{T_f}{V_f} = \frac{Mg}{AnR} .$$

(d) What is the net work done by the gas in this process? Express your answer in terms of V_o , V_f , M , g , and A .

The net work done by the gas in pushing the piston up by a height h is

$$Mgh = \frac{Mg}{A}(Ah) = \frac{Mg}{A}(V_f - V_o)$$

(e) What is the final temperature T_f ? Express your answer in terms of T_o , V_o , M , g , A , C_v , n and R .

The change in the internal energy of the gas can be expressed as

$$\Delta U = nC_v(T_f - T_o)$$

From first law $\Delta U = W$ where W is the work done on the gas.

$$nC_v(T_f - T_o) = -\frac{Mg}{A}(V_f - V_o) = \frac{Mg}{A}V_o - \frac{Mg}{A}V_f$$

Use the result from part(c) to eliminate V_f :

$$nC_v(T_f - T_o) = \frac{Mg}{A}V_o - \frac{Mg}{A}\left(\frac{nRT_f A}{Mg}\right) = \frac{Mg}{A}V_o - nRT_f$$

Rearrange and solve for T_f

$$(nC_v + nR)T_f - nC_vT_o = \frac{Mg}{A}V_o \Rightarrow T_f = \left(C_vT_o + \frac{MgV_o}{nA}\right)\left(\frac{1}{C_v + R}\right)$$

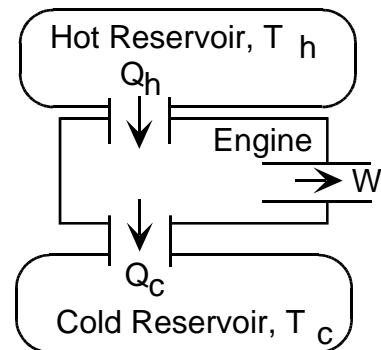
Problem 2

The diagram shows the energy flow in a heat engine.

(a) State the definition of the efficiency of this heat engine in terms of the heat Q_h absorbed from the hot reservoir, and the heat Q_c rejected to the cold reservoir. Do not assume that the engine is reversible.

The efficiency of the engine is given by

$$\eta = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}$$



(b) Based upon entropy considerations, derive an inequality between the efficiency of the engine, and the temperatures of the reservoirs.

The combined entropy of the two reservoirs and the engine cannot decrease in this process, i.e. $\Delta S_h + \Delta S_c + \Delta S_{engine} \geq 0$

where $\Delta S_h = -\frac{Q_h}{T_h}$; $\Delta S_c = -\frac{Q_c}{T_c}$; and $\Delta S_{engine} = 0$

which gives $-\frac{Q_h}{T_h} + \frac{Q_c}{T_c} \geq 0 \Rightarrow \frac{Q_c}{T_c} \geq \frac{Q_h}{T_h} \Rightarrow \frac{Q_c}{Q_h} \geq \frac{T_c}{T_h}$.

Therefore, $\eta = 1 - \frac{Q_c}{Q_h} \leq 1 - \frac{T_c}{T_h}$, where the equality holds for a reversible engine.

For parts (c)-(e), replace the reservoirs by two identical but finite bodies, each characterized by a heat capacity at constant pressure C , which is independent of temperature. The bodies remain at constant pressure and undergo no change of phase. Initially, their temperatures are T_1 and T_2 , respectively; finally, as a result of the operation of the heat engine, the bodies will attain a common final temperature T_f .

(c) What is the total amount of work W done by the engine? Do not assume that the engine is operated reversibly. Express your answer in terms of C , T_1 , T_2 , and T_f .

Apply first law to the combined system consisting of the two bodies and the engine $\Delta U = Q + W \Rightarrow \Delta U = W$, since no heat is absorbed from the surroundings (all heat exchange is internal to the system). Note that, in the first law as stated, W is the work done on the system.

The total change in the internal energy of the combined system is

$$\Delta U = \Delta U_h + \Delta U_c + \Delta U_{engine} = C\Delta T_h + C\Delta T_c + 0$$

$$= C(T_f - T_1) + C(T_f - T_2) = C(2T_f - T_1 - T_2)$$

Therefore, work done by the engine becomes $-\Delta U = C(T_1 + T_2 - 2T_f)$

(d) As in part (b), use entropy considerations to derive an inequality relating T_f to the initial temperatures T_1 and T_2 .

Once again, $\Delta S_h + \Delta S_c + \Delta S_{engine} \geq 0$

However, unlike in part (b), the temperature of the two bodies is now changing.

Therefore, $\Delta S_h = \int_{T_1}^{T_f} \frac{-dQ_h}{T_h} = \int_{T_1}^{T_f} \frac{CdT_h}{T_h} = C \ln\left(\frac{T_f}{T_1}\right)$, where $-dQ_h$ is the heat absorbed by the hot body in each infinitesimal step of a reversible path that takes the hot body from an initial temperature T_1 to a final temperature T_f .

Similarly, $\Delta S_c = \int_{T_2}^{T_f} \frac{dQ_c}{T_c} = \int_{T_2}^{T_f} \frac{CdT_c}{T_c} = C \ln\left(\frac{T_f}{T_2}\right)$.

As before, $\Delta S_{engine} = 0$

Note that, since entropy is a function of state, we can pick any reversible path to calculate the entropy change between the initial and the final states of each of the bodies, even if the engine operates irreversibly between them.

The condition $\Delta S_h + \Delta S_c + \Delta S_{engine} \geq 0$ leads to:

$$C \ln\left(\frac{T_f}{T_1}\right) + C \ln\left(\frac{T_f}{T_2}\right) \geq 0 \Rightarrow C \ln\left(\frac{T_f^2}{T_1 T_2}\right) \geq 0 \Rightarrow T_f \geq \sqrt{T_1 T_2}$$

(e) For given initial temperatures T_1 and T_2 , what is the maximum amount of work obtainable by operating an engine between these two bodies?

The maximum amount of work is done by a reversible engine, for which $T_f = \sqrt{T_1 T_2}$, which, from part (c) is: $W = C(T_1 + T_2 - \sqrt{T_1 T_2})$.

Problem 3

Consider a paramagnetic material consisting of N non-interacting spin-1 particles (with magnetic dipole moment $\vec{\mu} = \frac{\mu}{\hbar} \vec{S}$, $S_z = m\hbar$, $m = 0, \pm 1$). Suppose that these spins reside in (and are in thermal equilibrium with) a crystal lattice, which is in good thermal contact with a reservoir at temperature T . We apply a magnetic field of magnitude B in the z -direction.

(a) Write the partition function of the paramagnetic system in terms of $k_B T$ and μB .

In the presence of a magnetic field, the allowed energy states of a single spin are: $\varepsilon = -\mu B, 0, +\mu B$

The partition function of a single spin becomes:

$$Z_1 = \exp(\mu B / k_B T) + 1 + \exp(-\mu B / k_B T) = 1 + 2 \cosh(\beta \mu B)$$

(b) How does the average energy of the N spins vary with temperature T ?

The average energy of a single spin is given by

$$\langle E \rangle = -\frac{1}{Z} \left(\frac{\partial Z}{\partial \beta} \right) = -\frac{2\mu B \sinh(\beta\mu B)}{1 + 2 \cosh(\beta\mu B)}$$

(c) Calculate the spin contribution to the entropy of the crystal and show that it is only a function of $\mu B / k_B T$.

$$F = U - TS, \text{ where } U = N\langle E \rangle \text{ and } F = -Nk_B T \ln(Z_1)$$

$$\text{Therefore, } S = \frac{U}{T} - \frac{F}{T} = -2Nk_B \frac{(\beta\mu B) \sinh(\beta\mu B)}{1 + 2 \cosh(\beta\mu B)} + Nk_B \ln(1 + 2 \cosh(\beta\mu B))$$

(d) What are the limiting values of the entropy as $T \rightarrow 0$ and as $T \rightarrow \infty$? How would your results change if it was a spin-1/2 particle?

In the limit $T \rightarrow 0$ (or $B \rightarrow \infty$), only the lowest (ground) state is occupied. The multiplicity of the ground state is $\Omega = 1$. Therefore, $S = k_B \ln \Omega \rightarrow 0$

In the limit $T \rightarrow \infty$ (or $B \rightarrow 0$), all accessible states of the system are equally likely. Each spin has three allowed orientations. The total number of accessible states in the high temperature limit is $\Omega = 3^N$, and hence $S = k_B \ln \Omega \rightarrow Nk_B \ln 3$

For a spin-1/2 particle, the entropy as $T \rightarrow 0$ would still be 0. As $T \rightarrow \infty$, the total number of accessible states in the high temperature limit would be $\Omega = 2^N$, and hence $S = k_B \ln \Omega \rightarrow Nk_B \ln 2$

(e) The crystal is initially in contact with a reservoir at $T = T_1$ and the magnetic field has a magnitude B_1 . The crystal is now thermally isolated, and the magnetic field strength is slowly turned down to a value B_2 . Calculate the final temperature T_2 of the spins (and therefore the temperature of the crystal lattice).

In a quasistatic, adiabatic process, the entropy of the system remains unchanged. Since the entropy of the spin system is a function of the dimensionless parameter $\mu B / k_B T$, constant entropy in this adiabatic

demagnetization process implies $\frac{B_1}{T_1} = \frac{B_2}{T_2} \Rightarrow T_2 = T_1 \left(\frac{B_2}{B_1} \right)$.

Problem 4

(a) Consider a spinless quantum mechanical particle of mass m in a simple harmonic oscillator potential in one dimension of frequency ν and at temperature T . The energy levels for this particle are given by $E_n = (n+1/2)h\nu$. Write down the partition function, Z_1 , of a single such particle in the oscillator. Express your result in terms of the dimensionless quantity $\alpha = h\nu/k_B T$

$$Z_1 = \sum_n \exp(-E_n / k_B T) = \exp(-h\nu / 2k_B T) \sum_n \exp(-nh\nu / k_B T)$$

$$Z_1 = \frac{\exp(-\alpha/2)}{1 - \exp(-\alpha)} = \frac{1}{\exp(\alpha/2) - \exp(-\alpha/2)}$$

(b) Consider N spinless, distinguishable particles placed in this oscillator. Write down the partition function Z_N for N such particles.

$$\text{For } N \text{ distinguishable particles, } Z_N = Z_1^N = \frac{1}{(\exp(\alpha/2) - \exp(-\alpha/2))^N}$$

(c) Now consider two identical spinless particles placed in this oscillator. Write down the partition function Z_2 for the two particles at temperature T as an expansion in $\xi = e^{-\alpha}$ up to and including order ξ^4 .

The energy levels are given by $E_n = (n_1 + n_2 + 1)h\nu$,
where $n_1 = 0, 1, 2, \dots$ and $n_2 = 0, 1, 2, \dots$

The lowest five energy levels are $E_n = h\nu, 2h\nu, 3h\nu, 4h\nu, 5h\nu, \dots$ with degeneracy $g_n = 1, 1, 2, 2, 3, \dots$, respectively, for identical bosons.

The partition function becomes

$$Z_2 = e^{-\alpha} + e^{-2\alpha} + 2e^{-3\alpha} + 2e^{-4\alpha} + 3e^{-5\alpha} + \dots$$

(d) Repeat part (c) for two identical Fermi particles, of spin 1/2, put in such an oscillator, one with spin up and the other with spin down.

For two distinguishable fermions, the energy levels are the same as in part (c), but now the degeneracy of each level becomes $g_n = 1, 2, 3, 4, 5, \dots$

Thus, the partition function becomes

$$Z_2 = e^{-\alpha} + 2e^{-2\alpha} + 3e^{-3\alpha} + 4e^{-4\alpha} + 5e^{-5\alpha} + \dots$$

(e) How does the partition function from part (d) change if the two fermions are both in spin-up states in the oscillator.

For two indistinguishable fermions, all double-occupancy states are forbidden as a result of the Pauli-exclusion principle, so the lowest five energy levels are given by $E_n = 2h\nu, 3h\nu, 4h\nu, 5h\nu, 6h\nu, \dots$, with degeneracy $g_n = 1, 1, 2, 2, 3, \dots$, and the partition function becomes $Z_2 = e^{-2\alpha} + e^{-3\alpha} + 2e^{-4\alpha} + 2e^{-5\alpha} + 3e^{-6\alpha} + \dots$.

Problem 5

The internal energy U and entropy S of an ideal monatomic gas at temperature T are, respectively:

$$U = 3Nk_B T / 2; \quad S = Nk_B [\ln(n_o / n) + 5/2]$$

Here k_B is the Boltzmann constant, N is the number of atoms, $n = N/V$ is the average concentration, and $n_o = (Mk_B T / 2\pi\hbar^2)^{3/2}$, with M the atomic mass.

(a) Show that the chemical potential μ of the gas is related to the pressure P of the gas by $\mu = -k_B T \ln(n_o k_B T / P)$.

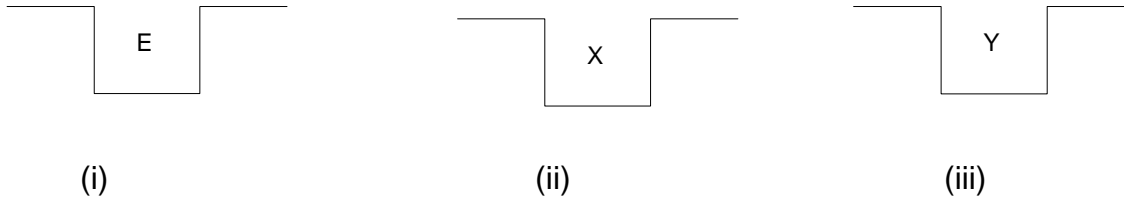
Since $F = U - TS$ and $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$,

we have $\mu = \left(\frac{\partial U}{\partial N}\right)_{T,V} - T \left(\frac{\partial S}{\partial N}\right)_{T,V}$, where $S = Nk_B \left[\ln\left(\frac{V}{N} n_o\right) + 5/2 \right]$

Therefore

$$\mu = \frac{3k_B T}{2} - k_B T \left[\ln\left(\frac{V}{N} n_o\right) + \frac{5}{2} \right] - Nk_B T \left(\frac{N}{V n_o} \right) \left(-\frac{V}{N^2} n_o \right) = -k_B T \ln\left(\frac{V}{N} n_o\right) = -k_B T \ln\left(\frac{n_o k_B T}{P}\right)$$

Two such gases, X and Y, are in equilibrium with surface sites at which the gases bind to a metal surface. In the presence of X and Y simultaneously there are just three possible configurations of each surface site: (i) the surface site is empty (denoted by E below); (ii) the surface site is occupied by one X atom, with energy ϵ_x relative to the empty site; (iii) the surface site is occupied by one Y atom, with energy ϵ_y relative to the empty site. Excited configurations at the site are not bound, and multiple occupancy is forbidden.



(b) The metal surface is at equilibrium with gases X and Y simultaneously at temperature T . In terms of the parameters defined above, and chemical potentials μ_x and μ_y , write down the grand partition function for the configurations of one site.

For the empty site $\varepsilon = 0$, $n = 0$, and the Gibbs factor is $\exp(0) = 1$;

For the site occupied by an X atom, $\varepsilon = \varepsilon_x$, $n = 1$, and the Gibbs factor is $\exp(-(\varepsilon_x - \mu_x)/k_B T)$;

Similarly, for the site occupied by a Y atom, $\varepsilon = \varepsilon_y$, $n = 1$, and the Gibbs factor is $\exp(-(\varepsilon_y - \mu_y)/k_B T)$;

Therefore, the grand partition function can be written as:

$$\Xi = 1 + \exp(-(\varepsilon_x - \mu_x)/k_B T) + \exp(-(\varepsilon_y - \mu_y)/k_B T)$$

$$= 1 + \lambda_x \exp(-\varepsilon_x/k_B T) + \lambda_y \exp(-\varepsilon_y/k_B T)$$

where $\lambda = \exp(\mu/k_B T)$

(c) Calculate the probability that the site is (i) empty, (ii) occupied by X, (iii) occupied by Y.

The probabilities for (i), (ii), and (iii), are:

$$\wp_E = \frac{1}{\Xi}$$

$$\wp_x = \frac{\lambda_x \exp(-\varepsilon_x/k_B T)}{\Xi}$$

$$\wp_y = \frac{\lambda_y \exp(-\varepsilon_y/k_B T)}{\Xi}$$

(d) At room temperature, and fixed partial pressures of $P_x = P_y = 0.5$ atm, the sites are occupied in the ratio $n_E:n_X:n_Y = 1:1:2$. What is the energy difference $\Delta\varepsilon = \varepsilon_X - \varepsilon_Y$? Ignore any differences in the atomic masses M_x and M_y . Express your answer in units of $k_B T$.

$$\frac{n_x}{n_y} = \frac{\rho_x}{\rho_y} = \frac{\lambda_x}{\lambda_y} \exp(-\Delta\varepsilon/k_B T)$$

From part (a), λ can be expressed in terms of the partial pressure P and temperature T as: $\lambda = \exp(\mu/k_B T) = \frac{P}{n_0 k_B T}$.

Assuming that the atomic masses M_x and M_y are approximately equal, we have $\frac{\lambda_x}{\lambda_y} = \frac{P_x}{P_y} = 1$, which gives $\exp(-\Delta\varepsilon/k_B T) = \frac{n_x}{n_y} = \frac{1}{2} \Rightarrow \Delta\varepsilon = k_B T \ln 2$.

(e) The partial pressures are now doubled to 1 atm each. What is the new value of the ratio $n_E:n_X:n_Y$?

The probability that a state is occupied is proportional to its Gibbs factor. Under conditions of 0.5 atm partial pressure for X and Y, the Gibbs factors for the 3 states are in the ratio 1:1:2. When the partial pressure of each gas is doubled, the Gibbs factor for the state with the empty site is unchanged, whereas the Gibbs factors for the states with the site occupied by X or Y are doubled. Therefore, the ratio $n_E:n_X:n_Y$ is now 1:2:4.

Equations and constants:

$$k_B = 1.381 \times 10^{-23} \text{ J/K}; \quad N_A = 6.022 \times 10^{23}; \quad R = 8.315 \text{ J/mol/K}; \quad 1 \text{ atm} = 1.013 \times 10^5 \text{ N/m}^2$$

Hyperbolic functions

$$\sinh x = \frac{e^x - e^{-x}}{2} \quad \cosh x = \frac{e^x + e^{-x}}{2} \quad \tanh x = \frac{\sinh x}{\cosh x}$$

Maxwell's relations

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V; \quad \left(\frac{\partial T}{\partial V} \right)_P = - \left(\frac{\partial P}{\partial S} \right)_T; \quad \left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P;$$
$$\left(\frac{\partial T}{\partial P} \right)_V = \left(\frac{\partial V}{\partial S} \right)_T$$