2B28 Statistical Thermodynamics - Problem Sheet 1 (2005)

Answers should be handed in on Monday 31 January 2005

1 (a) Give the Kelvin and the Clausius statements of the Second Law of Thermodynamics.

(b) Show that if the Clausius statement is untrue, then the Kelvin statement is also untrue.

(c) One litre of water is heated from 10^oC to 90^oC by placing it in contact with a large reservoir at 90^oC. Calculate the entropy changes of:

(i) the water;

(ii) the reservoir;

(iii) the universe.

(d) One litre of water is heated from 10^oC to 90^oC by operating a *reversible heat engine* between it and a reservoir at 90^oC. Calculate the entropy changes of:

(i) the water;

(ii) the reservoir;

(iii) the universe.

(e) Explain briefly why the answers to c (iii) and d (iii) differ.

2. State Boltzmann's definition of entropy, explaining the symbols used, and the conditions under which the definition is valid.

Brass is an alloy of 70% copper and 30% zinc. If all the lattice sites are occupied by an atom, determine the configurational entropy of the system when the total number of atoms (N) is (i) 50 and (ii) 500. What are the corresponding values of the entropy for an alloy of 50% copper and 50% zinc?

You may use Stirling's formula for large N: $\ln N! = N \ln N - N$

3. A Schottky defect is formed when an atom leaves a perfect crystal and migrates to the surface. If the energy of formation of a single defect is ε, derive an expression for the concentration of defects at a temperature T.

For what concentration of defects does the entropy of the crystal reach (i) its maximum value, and (ii) its minimum value?

According to one theory, melting occurs when a substance contains 0.01% of vacancy defects. Consider whether this theory can satisfactorily explain the temperatures T_m at which Cu and Pt melt, given that:

for Cu, ε = 1.07 eV and T_m = 1356 K;

for Pt, ε = 1.3 eV and T_m = 2046 K.

2B28 Problem Sheet 2 . Answers to be handed in by Monday 14 February 2005

1. Derive the Boltzmann distribution for a system in equilibrium with a heat bath at temperature T. Explain the symbols used, and the conditions under which the distribution is valid.

A certain atom has 3 possible energy levels. These energies are $E_1 = 1.3 \times 10^{-22}$ J, $E_2 = 2.3 \times 10^{-22}$ J, and $E_3 = 3.2 \times 10^{-22}$ J. The first level is non-degenerate (g_1=1), whereas the other levels are degenerate : g_2=3 and g_3=5. If the atom is in equilibrium at (i) T=5 K, and (ii) T=10 K, calculate:

(a) the partition function Z(1,V,T);

(b) the probability that the atom has energy E_2;

(c) the mean energy of the atom.

2. A paramagnetic material has non-interacting magnetic dipoles with spin S=$^1/_2$, and magnetic moment μ. It is in contact with a heat bath at temperature T, and a magnetic field **B** is applied.

Show that the partition function of a single magnetic dipole Z(1,V,T) is 2 *cosh x*, where $x = \mu B / kT$.

Show that the average energy of a dipole is $E = - \mu B \tanh x$, and sketch E as a function of x.

By considering the possible states of a system of *two* dipoles, find an expression for Z(2,V,T).

If the magnetic moment $\mu = 0.93 \times 10^{-23}$ Am^2, T = 4.2 K, and the applied field B = 5 T, calculate Z(1,V,T) and Z(2,V,T). Deduce the temperature at which the probability of the moment being aligned parallel to the applied magnetic field is 0.8.

3.State the general definition of entropy in terms of the probabilities P_j of the accessible microstates. From this definition, show that the entropy of a system in contact with a heat bath at temperature T can be written as

S(N,V,T) = k *ln* Z(N,V,T) + E/T.

Use this expression to obtain a definition of thermal equilibrium for a system in contact with a heat bath at temperature *T*.

A particular system can exist in two energy levels. The ground level has energy 3.0×10^{-19} J, and has a degeneracy of 2. The excited level has energy 7.0×10^{-19} J, and a degeneracy of 4.

If the system is in equilibrium at T = 300 K, calculate (a) the entropy, and (b) the Helmholtz free energy. Give the units in each case.

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2B28 Problem Sheet 3 Answers should be handed in by *Monday 7 March 2005*.

1. Derive Planck's law for the energy density of radiation in a black-body cavity at a temperature T. Explain any assumptions or approximations that you use.

[11 marks]

Sketch the radiation spectra emitted by stars with surface temperatures of 6000 K and 8000 K, marking the visible and ultraviolet regions on your graphs. What is the

frequency of the maximum in the spectrum, in each case? What does the area under the curve represent, and how does it vary with temperature?

[6 marks]

Measurements of the cosmic microwave background suggest that the Universe has an effective temperature of about 3 K. Calculate the wavelength of the maximum in the radiation spectrum in this case, and the energy (in meV) of the corresponding photons.

[3 marks]

2. For an ideal gas comprised of N identical non-interacting *fermions*, explain the meaning of the Fermi energy, ε_F, and Fermi temperature T_F.

Draw the Fermi-Dirac distribution for the average occupation number of single-particle states as a function of energy, at T=0 K. Mark ε_F on your diagram.

[6 marks]

Consider N free electrons in a volume V as an ideal Fermi-Dirac gas. Show that the Fermi energy is given by $\varepsilon_F = (h^2/2m)(3N/8\pi V)^{2/3}$.

[8 marks]

Calculate the Fermi temperature and the average Fermi-Dirac pressure for:

(a) ^{3}He atoms in liquid ^{3}He, where the number density is 2.2×10^{28} m^{-3},

(b) conduction electrons in copper, where the number density is 8.45×10^{28} m^{-3},

(c) neutrons in a neutron star, for which the *mass* density is 10^{15} kg m^{-3}.

[6 marks]

2B28 Problem sheet 1 – 2005 Solutions 1

Qu 1. (20 marks)

(a) Second law : **Kelvin statement** : No process is possible whose sole result is the complete conversion of heat into work.

[1]

Clausius statement: No process is possible whose sole result is the transfer of heat from a cooler to a hotter body.

[1]

(b) to demonstrate equivalence show that if Clausius statement is untrue, then so is the Kelvin statement.

If Clausius statement is untrue, then this engine is possible.

Imagine the engine to be a composite engine in which engine 1 drives engine 2

Engine 2 is compatible with the First Law, but engine 1 is not, and violates the Kelvin statement.

Thus, if Clausius statement is untrue, then so is the Kelvin statement.

[8]

(c) For 1 litre water (mass = 1 kg) heated from 10^{o}C to 90^{o}C :

Heat capacity of water = 4184 J kg^{-1}

(i) Entropy change of water ΔS_{water} = (dQ)/T = 4184 = (dT)/T

= 4184 *ln* (T_2/T_1)

T_1 = 283K, T_2 = 363 K

$\therefore$ **ΔS_{water} = 4184 *ln* (363/283) = 1041.6 J K^{-1}**

[3]

(ii) Heat supplied by reservoir Q = (-) 1 x 4184 x 80 J

and entropy change of reservoir ΔS_{res} = Q/T, T = T_{res} = 363 K

$\therefore$ **ΔS_{res} = -922.1 J K^{-1}**

[2]

(iii**) Net increase in entropy of universe $\Delta S_{universe}$ = 119.5 J K^{-1}** (because process is *irreversible*)

[1]

(d) with a *reversible* heat engine

ΔS_{water} is unchanged at **1041.6 J K^{-1}**

[1]

but ΔS_{res} is now the same magnitude as this: **ΔS_{res} = - 1041.6 J K^{-1}**

[1]

so that **$\Delta S_{universe}$ = 0**

[1]

(e) because process is *reversible* [1]

Qu 2. (10 marks)

S(E,V,N) = k *ln* Ω (E,V,N)

Valid for isolated system with energy E, volume V, number of particles N.

k = Boltzmann's constant = 1.38 x10^{-23} J K^{-1}

Ω = statistical weight of macrostate with (E,V,N) = number of microstates compatible with this macrostate.

[2]

Ω = N! / {n! (N-n)!} [1]

(i) we have **N = 50, n = 15, (N-n) = 35**

S = k *ln* {(50!) / 15! 35!}

Using Stirling's formula: S = k { 50 *ln*50 � 15 *ln*15 �35 *ln* 35}

= k {195.6 �40.62 �124.44}� = 4.21 x 10^{-22} J K^{-1}

[2]

for N=500 since entropy scales with system size (strictly only true for macroscopic systems)
S (N=500) = 10 S(50) = 4.21 x 10^{-21} J K^{-1}

[2]

(ii) we have **N = 50, n = 25, (N-n) = 25**

S = k *ln* {(50!) / 25! 25!}

Using Stirling's formula: S = k { 50 *ln*50 � 2 x25 *ln*25}

= k {195.6 � 2 x 80.47}� = 4.78 x 10^{-22} J K^{-1}

[2]

and for **N = 500**, *S* = 4.78 x 10^{-21} J K^{-1}

[1]

Qu 3. (15 marks)

Schottky defect : statistical weight of *n* defects on *N* lattice sites

Ω (n) = N! / [n! (N-n)!]

Entropy S(n) = k *ln* Ω (n) = k [*ln* N! � *ln* n! � *ln* (N-n)!]

using *ln* N! = N *ln* N � N

S(n) = k {[N *ln* N � N] � [n *ln* N � n] � [(N-n) *ln* (N-n) � (N-n)]}

= k { N *ln* N � n *ln* n � (N-n) *ln* (N-n)}

[3]

Using 1/T = (∂S/∂E) where E = n ε

We have 1/T = [dS(n)/dn] [dn/dE] = (1/ε) �dS(n)/dn

[2]

From the above Eqn for S(n)

dS(n)/dn = k {- *ln* n �1 + *ln* (N-n) +1 } = k *ln* {(N-n)/n}

In equilibrium: 1/T = (1/ε) �k *ln* {(N-n)/n}

exp (ε /kT) = {(N-n)/n} = (N/n) � 1 = N/n since N >> n

n = N exp (-ε /kT)

[2]

□

S is max when dS(n)/dn = 0, i.e. when k *ln* {(N-n)/n} = 0

this is when {(N-n)/n} = 1, - i.e. when (N-n) = n, N=2*n*,

S is maximum when *n* = N/2,

[2]

and minimum (perfect order) when n = 0

[1]

We consider the temperature for which n/N = 0.01% = 1 x 10^{-4}

1 x 10^{-4} = exp (-ε /kT)

(-ε /kT) = *ln* (1 x 10^{-4}) = - 9.210

For Cu, ε = 1.07 eV = 1.07 x 1.6 x 10^{-19} J

T when $(n/N) = 1 \times 10^{-4}$ is $(1.07 \times 1.6 \times 10^{-19}) / (1.38 \times 10^{-23} \times 9.210)$

$= 1347$ K. This is in very good agreement with $T_m = 1356$ K [3]

For Pt, $\varepsilon = 1.3$ eV

T when $(n/N) = 1 \times 10^{-4}$ is $(1.3 \times 1.6 \times 10^{-19}) / (1.38 \times 10^{-23} \times 9.210)$

$= 1636$ K.

This is only 80% of the actual value of $T_m = 2046$ K, so this simple model is not very satisfactory for Pt.

[2]

(Problems rendering some of the equations in Solutions 1)