2B28 Problem sheet 1 – 2005 Solutions

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) 1 litre water (mass = 1 kg) heated from 10^oC to 90^oC
heat capacity of water = 4184 J kg^{-1}

(i) entropy change of water $\Delta S_{water} = \int_1^2 (dQ)/T = 4184 \int_1^2 (dT)/T$
$= 4184\ ln\ (T_2/T_1)$
$T_1 = 283K$, $T_2 = 363$ 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 $\Delta S_{res} = Q/T$, $T = T_{res} = 363$ 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)

$S(E,V,N) = k\, ln\, \Omega\, (E,V,N)$
Valid for isolated system with energy E, volume V, number of particles N.
k = Boltzmann's constant = 1.38×10^{-23} J K^{-1}
Ω = statistical weight of macrostate with (E,V,N) = number of microstates compatible with this macrostate. [2]

$\Omega = N! / \{n! (N-n)!\}$ [1]

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

$S = k\, ln\, \{(50!) / 15!\, 35!\}$
Using Stirling's formula $S = k \{ 50\, ln 50 - 15\, ln 15 - 35\, ln\, 35\}$
$= k \{195.6 - 40.62 - 124.44\} = 4.21 \times 10^{-22}$ 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) = 4.21×10^{-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 $S = k \{ 50\, ln 50 - 2 \times 25\, ln 25\}$
$= k \{195.6 - 2 \times 80.47\} = 4.78 \times 10^{-22}$ J K^{-1} [2]

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

Qu 3. (15 marks)
Schottky defect – statistical weight of *n* defects on *N* lattice sites
$\Omega (n) = N! / \{n! (N-n)!\}$
entropy $S(n) = k\, ln\, \Omega (n) = k [\, ln\, N! - ln\, n! - ln\, (N-n)!\,]$
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 $1/T = (\partial S/\partial E)$ where $E = n\, \varepsilon$
We have $1/T = [dS(n)/dn]\, [dn/dE] = (1/\varepsilon)\, dS(n)/dn$ [2]

From above eqn for S(n)

$dS(n)/dn = k \{- ln\, n - 1 + ln\, (N-n) + 1 \} = k\, ln\, \{(N-n)/n\}$

In equilibrium $1/T = (1/\varepsilon)\, k\, ln\, \{(N-n)/n\}$

$\exp(\varepsilon/kT) = \{(N-n)/n\} = (N/n) - 1 = N/n$ since $N \gg n$

$n = N \exp(-\varepsilon/kT)$ [2]

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 $(N-n) = n$, $N=2n$,

S is maximum when $n = N/2$, [2]
and minimum (perfect order) when $n=0$ [1]

We consider the temperature for which $n/N = 0.01\% = 1 \times 10^{-4}$
$1 \times 10^{-4} = \exp(-\varepsilon/kT)$
$(-\varepsilon/kT) = ln\,(1 \times 10^{-4}) = -9.210$

For Cu, $\varepsilon = 1.07$ eV $= 1.07 \times 1.6 \times 10^{-19}$ 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]