

Important Questions on Statistical Thermodynamics

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1. A system consists of non-interacting Fermi particles with Fermi energy E_F has the density of states proportional to \sqrt{E} , where E is the energy of a particle. Determine the average energy per particle at temperature $T = 0$.

- A. $1/5 E_F$ B. $1/6 E_F$
C. $3/5 E_F$ D. $2/5 E_F$

2. A system consists of N non-interacting and distinguishable particles of spin 1 which are present in thermodynamics equilibrium. Calculate the entropy of the system.

- A. $2k_B \ln N$ B. $Nk_B \ln 3$
C. $Nk_B \ln 2$ D. $3k_B \ln N$

3. A system of N particles has, among others, two energy levels with $g_1 = 2$, $g_2 = 3$, $U_1 = 41.84 \text{ kJ mol}^{-1}$ and $U_2 = 58.58 \text{ kJ mol}^{-1}$. Calculate the ratio of the number of particles in the two energy states at 1000 K.

- A. 0.51 B. 0.46
C. 0.92 D. 0.20

4. Calculate the molar residual entropy of an AX crystal in which the molecule can adopt 4 orientations of equal energy.

- A. $18.526 \text{ JK}^{-1} \text{ mol}^{-1}$ B. $11.526 \text{ JK}^{-1} \text{ mol}^{-1}$
C. $10.526 \text{ JK}^{-1} \text{ mol}^{-1}$ D. $14.526 \text{ JK}^{-1} \text{ mol}^{-1}$

5. In a system of two particles, each particle can be present in any one of three possible quantum states. Calculate the ratio of the probability that the two particles occupy the same state to the probability that the two particles occupy different states for M-B statistics.

- A. $1/3$ B. $1/2$
C. $3/2$ D. $2/3$

6. Six distinguishable particles can be distributed over three non-degenerate levels having energies 0, E and $2E$. Determine the total energy of the distribution for which the probability is a maximum.

- A. $4E$ B. $6E$
C. $3E$ D. None of the above

7. Consider N particles at temperature T , pressure P , Volume V and chemical potential μ having energy E . The parameters that are kept constant for a canonical ensemble are:

- A. N, V, T B. N, V, E
C. N, P, T D. μ, V, T

8. If the partition function of a harmonic oscillator with frequency ω at a temperature T is $\frac{kT}{\hbar\omega}$, then the free energy of N such independent oscillators is:

- A. $\frac{3}{2} NkT$ B. $kT \ln \frac{\hbar\omega}{kT}$
C. $NkT \ln \frac{\hbar\omega}{kT}$ D. $NkT \ln \frac{\hbar\omega}{2kT}$

9. The term symbol for the ground state of a metal ion is 3F_4 . The residual entropy of a crystal of a salt of this metal ion at 0 K is:

- A. $3k_B \ln 3$ B. $k_B \ln 4$
C. $2k_B \ln 2$ D. $4k_B \ln 9$

10. Calculate the characteristic rotational temperature and the rotational partition function for H_2 gas at 2727°C given that the moment of inertia of hydrogen gas molecule at this temperature is $4.6033 \times 10^{-48} \text{ kg m}^2$.

- A. 12.799 B. 17.144
C. 16.322 D. 18.432

ANSWER KEY

1. C	2. B	3. D	4. B	5. B	6. B
7. A	8. C	9. A	10. B		

SOLUTIONS

Solution 1. The relation between E and U is:

$$E = \frac{U}{N}$$

Here,

$$E = \frac{\pi}{5} \left[\frac{8ma^2}{n^2} \right]^{3/2} (E_F)^{5/2}$$

And,

$$N = \frac{\pi}{3} \left[\frac{8m}{n^2} \right]^{3/2} V(E_F)^{3/2}$$

$$E = \frac{3}{5} E_F$$

Solution 2. The formula to calculate entropy is:

Entropy is $S = k \ln \Omega$

Number of microstates can be calculated as:

$$\Omega = 3^N$$

$$\therefore S = Nk_B \ln 3$$

Solution 3. Since we know that-

$$\begin{aligned} \frac{n_2}{n_1} &= \frac{g_2}{g_1} \exp\left[-\frac{\epsilon_2 - \epsilon_1}{kT}\right] = \frac{g_2}{g_1} \exp\left[-\frac{U_2 - U_1}{RT}\right] \\ &= \frac{3}{2} \exp\left[-\frac{(58580 - 41840) \text{ J mol}^{-1}}{(8.314 \text{ JK}^{-1} \text{ mol}^{-1})(1000)}\right] = 0.201 \end{aligned}$$

Solution 4. The residual entropy is given by $S = Nk \ln W$

Here,

$W =$ Number of orientations = 4

$N =$ Number of Particles

For 1 mole,

$N = N_A$

$N_A k = R =$ gas constant = $8.314 \text{ JK}^{-1} \text{ mol}^{-1}$

$S = R \ln 4$

$S = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 2.303 \log 4$

$S = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 2.303 \times 0.602$

$S = 11.526 \text{ JK}^{-1} \text{ mol}^{-1}$

Solution 5. Let a be the desired ratio.

$W_1 \rightarrow$ the number of ways in which two particles occupy the same state.

$W_2 \rightarrow$ the state in which they occupy different states.

According to this,

$$a = \frac{W_1}{W_2}$$

For M-B statistics,

The particles are distinguishable and $W_1 = 3$.

Now, one particle can be present in any one of the 3 quantum states and the remaining particles can be in any one of the 2 quantum states that are available to it. So,

$$W_2 = 3 \times 2 = 6$$

Therefore,

$$a = \frac{W_1}{W_2} = \frac{3}{6} = \frac{1}{2}$$

Solution 6. As the levels are non-degenerate, there is only one state associated with each energy. Let the number of particles in the three energy states be N_1 , N_2 and N_3 respectively. Here,

$$N_1 + N_2 + N_3 = 6.$$

As the particles are distinguishable, the number of microstates that is the number of ways of choosing N_1 , N_2 and N_3 particles from 6 particles is:

$$W = \frac{6!}{N_1! N_2! N_3!}$$

Thermodynamic probability (W) is maximum when denominator is minimum, and it is true when $N_1 = N_2 = N_3 = 2$

The corresponding total energy of the distribution is:

$$0 \times N_1 + E N_2 + 2E \times N_3 = 2E + 4E = 6E$$

Solution 7. An ensemble is a collection of a very large number of assemblies, which are independent of each other and microscopically as identical as possible. Canonical ensemble is defined on the collection of independent assemblies having the same temperature T , volume V , and the number of system N . Hence, the parameters that are kept constant for a canonical ensemble are N , V and T .

Solution 8. Free energy is given by,

$$F = -kT \ln z^N \text{ [for } N \text{ independent systems]}$$

where z is the partition function of an independent system.

$$\text{Here, } z = \frac{kT}{\hbar\omega}$$

$$\therefore F = -NkT \ln \left(\frac{kT}{\hbar\omega} \right) = NkT \ln \left(\frac{kT}{\hbar\omega} \right)^{-1} = NkT \ln \frac{\hbar\omega}{kT}$$

Solution 9. For 3F_4 term degeneracy $\Rightarrow (2J + 1) \Rightarrow J = 4$

$$g_J = (2J + 1) \Rightarrow (2 \times 4 + 1) \Rightarrow 9$$

Entropy, $S = k_B \ln q_e$

For electron ground state $q_e = g_e$, $g_e = 9$

$$S = k_B \ln g_e = k_B \ln 9 = 3k_B \ln 3$$

Solution 10. $T = 2727^\circ\text{C} = 3000\text{ K}$; $s = 2$

From Eq., the characteristic rotational temperature is given by

$$\Theta_{\text{rot}} = \frac{h^2}{8\pi^2Ik} = \frac{(6.626 \times 10^{-34} \text{ Js})^2}{(8\pi^2)(4.6033 \times 10^{-48} \text{ kg m}^2)(1.38 \times 10^{-23} \text{ J K}^{-1})} = 87.49 \text{ K}$$

From Eq., the rotational partition function is given by

$$q_{\text{rot}} = \frac{T}{\sigma \Theta_{\text{rot}}} = \frac{3,000 \text{ K}}{2(87.49 \text{ K})} = 17.144$$



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