ABC CHEMISTRY

Mr. Aniket Bhardwaj · 15+ Years Mentorship

Statistical Thermodynamics

Premium CSIR-NET PYQ Book

43 Previous-Year Questions · 41 with verified answers · Distractor Analysis

3-Slide Solutions | Distractor Analysis | Exam Tricks | Revision Sheets

CSIR-NET · GATE · IIT-JAM — 3 Topics · 43 Real PYQs

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Course Contents

3 Topics · 43 PYQs

1 **Partition Functions** — 21%
9 Qs E 1 · M 8 · H 0

2 **Statistical Equilibrium** — 16%
7 Qs E 1 · M 6 · H 0

3 **Statistical Thermodynamics – General** — 63%
27 Qs E 3 · M 23 · H 1

Legend: **E** Easy **M** Medium **H** Hard · **%** = exam weightage (share of the chapter)

TOPIC 1

Partition Functions

9 questions · Easy 1 | Medium 8 | Hard 0 · PYQ frequency: Very High

Q1

The rotational partition function of H_2 is :

A. $\Sigma_{J=0,1,2\ldots}(2J+1)e^{-\beta hcBJ(J+1)}$

B. $\Sigma_{J=1,3,5\ldots}(2J+1)e^{-\beta hcBJ(J+1)}$

C. $\Sigma_{J=0,2,4\ldots}(2J+1)e^{-\beta hcBJ(J+1)}$

D. $(1)/(4)[\Sigma_{J=0,2,4\ldots}(2J+1)e^{-\beta hcBJ(J+1)} + 3\Sigma_{J=1,3,5\ldots}(2J+1)e^{-\beta hcBJ(J+1)}]$

QUESTION INSIGHTS

ESTIMATED TIME
1–1.5 min

DIFFICULTY
Easy

CONCEPT TESTED
Partition Functions

PYQ FREQUENCY
Very High · 8 papers

REVISION PRIORITY
★★★☆☆

EXPECTED LEVEL
Part B

MEMORY HOOK
'Translational T^(3/2), rotational T (linear), vibrational ≈ 1'.

Correct Answer D (1)/(4)[Σ_J=0,2,4…(2J+1)e⁻β hcBJ(J+1) + 3Σ_J=1,3,5…(2J+1)e⁻β hcBJ(J+1)]

CONCEPT

Each mode contributes a factor: q = q_trans q_rot q_vib q_elec. q_trans ∝ V T^(3/2); q_rot(linear) = T/σΘ_rot, nonlinear ∝ T^(3/2); q_vib = (1 − e^(−hν/kT))⁻¹; q_elec = g_0 (ground degeneracy) unless low-lying states exist. Thermodynamic functions follow by differentiation.

↓

LOGIC / WORKING

- CSIR JUNE 13 12. A system has 100 degenerate energy levels and 100 bosons are kept in it. Find the entropy of the system at equilibrium a) 10-2kb b) 102 kb c) 460.0 kb d) 4.606 kb 9^{aa} pÆÆ W= (for boson particle) 9^{aa}! 9^{aa} pÆÆ S= = *K*S *lnW* =*K*S *ln* = *K*S *ln*1009^{aa} – *ln*100! 9^{aa}! kB (100ln 100-100ln100+100)=102 kB Explanation as extracted from the printed page; notation may be imperfect.
- Therefore the answer is (D).

FINAL: (D) (1)/(4)[Σ_J=0,2,4…(2J+1)e⁻β hcBJ(J+1) + 3Σ_J=1,3,5…(2J+1)e⁻β hcBJ(J+1)]

SHORTCUT / EXAM TRICK

Two-level system: q = 1 + e^(−ε/kT); population ratio n_1/n_0 = e^(−ε/kT); C_v shows a Schottky maximum.

COMMON MISTAKE

Including zero-point energy inconsistently in q_vib; dropping N! for indistinguishable particles (Gibbs paradox).

EXAM TIP

q_vib ≈ 1 at room temperature for most bonds (Θ_vib ≫ T), so vibrations contribute little to C_v.

MEMORY TRICK

'Translational T^(3/2), rotational T (linear), vibrational ≈ 1'.

Why the Other Options Are Wrong

Correct answer: D

A

Σ_J=0,1,2…(2J+1)e⁻β hcBJ(J+1)

Why (D) is the key — CSIR JUNE 13 12. A system has 100 degenerate energy levels and 100 bosons are kept in it. Find the entropy of the system at equilibrium a) 10-2kb b) 102 kb c) 460.0 kb d) 4.606 kb 9^{aa} pÆÆ W= (for boson particle) 9^{aa}! 9^{aa} pÆÆ S= = *K*S *lnW* =*K*S *ln* = *K*S *ln*1009^{aa} − *ln*100! 9^{aa}! kB (100ln 100-100ln100+100)=102 kB Explanation as extracted from the printed page; notation may be imperfect.

B

Σ_J=1,3,5…(2J+1)e⁻β hcBJ(J+1)

Ruled out: Including zero-point energy inconsistently in q_vib; dropping N! for indistinguishable particles (Gibbs paradox).

C

Σ_J=0,2,4…(2J+1)e⁻β hcBJ(J+1)

Ruled out: q_vib ≈ 1 at room temperature for most bonds (Θ_vib ≫ T), so vibrations contribute little to C_v.

Q2

When T → ∞, value of the single-particle partition function will be (given : degeneracy of level j = g_j) :

A. 1

B. g_0

C. $\Sigma_j g_j$

D. $1/\Sigma_j g_j$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Partition Functions

PYQ FREQUENCY
Very High · 8 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'Translational T^(3/2), rotational T (linear), vibrational ≈ 1'.

Correct Answer C $\Sigma_j g_j$

CONCEPT

Each mode contributes a factor: q = q_trans q_rot q_vib q_elec. q_trans ∝ V T^(3/2); q_rot(linear) = T/σΘ_rot, nonlinear ∝ T^(3/2); q_vib = $(1 - e^{-h\nu/kT})^{-1}$; q_elec = g_0 (ground degeneracy) unless low-lying states exist. Thermodynamic functions follow by differentiation.

↓

LOGIC / WORKING

- As T → ∞ every level is equally populated: q = $\Sigma g_j e^{-\varepsilon_j/kT} \rightarrow \Sigma_j g_j$ (the total number of states).
- Therefore the answer is (C).

FINAL: (C) $\Sigma_j g_j$

SHORTCUT / EXAM TRICK

Two-level system: q = 1 + e^(−ε/kT); population ratio n_1/n_0 = e^(−ε/kT); C_v shows a Schottky maximum.

COMMON MISTAKE

Including zero-point energy inconsistently in q_vib; dropping N! for indistinguishable particles (Gibbs paradox).

EXAM TIP

q_vib ≈ 1 at room temperature for most bonds (Θ_vib ≫ T), so vibrations contribute little to C_v.

MEMORY TRICK

'Translational T^(3/2), rotational T (linear), vibrational ≈ 1'.

Why the Other Options Are Wrong

Correct answer: C

A **1**

Why (C) is the key — As $T \to \infty$ every level is equally populated: $q = \Sigma g_j e^{-\varepsilon_j/kT} \to \Sigma_j g_j$ (the total number of states).

B **g_0**

Ruled out: Including zero-point energy inconsistently in q_vib; dropping N! for indistinguishable particles (Gibbs paradox).

D **$1/\Sigma_j g_j$**

Ruled out: q_vib ≈ 1 at room temperature for most bonds (Θ_vib ≫ T), so vibrations contribute little to C_v.

Q3

Though a constant shift of energy levels of a system changes the partition function, the properties that do not change are

A. average energy, entropy and heat capacity

B. average energy and entropy

C. average energy and heat capacity

D. entropy and heat capacity

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Partition Functions

PYQ FREQUENCY
Very High · 8 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'Translational T^(3/2), rotational T (linear), vibrational ≈ 1'.

Correct Answer D entropy and heat capacity

CONCEPT

Each mode contributes a factor: q = q_trans q_rot q_vib q_elec. q_trans ∝ V T^(3/2); q_rot(linear) = T/σΘ_rot, nonlinear ∝ T^(3/2); q_vib = $(1 - e^{(-h\nu/kT)})^{-1}$; q_elec = g_0 (ground degeneracy) unless low-lying states exist. Thermodynamic functions follow by differentiation.

↓

LOGIC / WORKING

- Shifting all levels by ε_0 multiplies q by $e^{-\varepsilon_0/kT}$: ⟨E⟩ shifts by ε_0 (changes) but S = k ln q + ⟨E⟩/T and C_V = d⟨E⟩/dT are unaffected.
- Therefore the answer is (D).

FINAL: (D) entropy and heat capacity

SHORTCUT / EXAM TRICK

Two-level system: q = 1 + e^(−ε/kT); population ratio n_1/n_0 = e^(−ε/kT); C_v shows a Schottky maximum.

COMMON MISTAKE

Including zero-point energy inconsistently in q_vib; dropping N! for indistinguishable particles (Gibbs paradox).

EXAM TIP

q_vib ≈ 1 at room temperature for most bonds (Θ_vib ≫ T), so vibrations contribute little to C_v.

MEMORY TRICK

'Translational T^(3/2), rotational T (linear), vibrational ≈ 1'.

Why the Other Options Are Wrong

Correct answer: D

A **average energy, entropy and heat capacity**

Why (D) is the key — Shifting all levels by ε_0 multiplies q by $e^{-\varepsilon_0/kT}$: $\langle E \rangle$ shifts by ε_0 (changes) but $S = k \ln q + \langle E \rangle/T$ and $C_V = d\langle E \rangle/dT$ are unaffected.

B **average energy and entropy**

Ruled out: Including zero-point energy inconsistently in q_vib; dropping N! for indistinguishable particles (Gibbs paradox).

C **average energy and heat capacity**

Ruled out: q_vib ≈ 1 at room temperature for most bonds ($\Theta_{vib} \gg T$), so vibrations contribute little to C_v.

Q4

Partition function of a one – dimensional oscillator having equispaced energy level with energy spacing equal to k_b T and zero ground energy is

A) e

B) 1/(e – 1)

C) e/(e – 1)

D) 1/(e + 1)

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Partition Functions

PYQ FREQUENCY
Very High · 8 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'Translational T^(3/2), rotational T (linear), vibrational ≈ 1'.

Correct Answer C e/(e – 1)

CONCEPT

Each mode contributes a factor: q = q_trans q_rot q_vib q_elec. q_trans ∝ V T^(3/2); q_rot(linear) = T/σΘ_rot, nonlinear ∝ T^(3/2); q_vib = $(1 - e^{-h\nu/kT})^{-1}$; q_elec = g_0 (ground degeneracy) unless low-lying states exist. Thermodynamic functions follow by differentiation.

↓

LOGIC / WORKING

- $q = \Sigma_n e^{-n\varepsilon/kT}$ with ε = kT: $q = 1/(1 - e^{-1}) = e/(e - 1)$.
- Therefore the answer is (C).

FINAL: (C) e/(e – 1)

SHORTCUT / EXAM TRICK

Two-level system: q = 1 + e^(−ε/kT); population ratio n_1/n_0 = e^(−ε/kT); C_v shows a Schottky maximum.

COMMON MISTAKE

Including zero-point energy inconsistently in q_vib; dropping N! for indistinguishable particles (Gibbs paradox).

EXAM TIP

q_vib ≈ 1 at room temperature for most bonds (Θ_vib ≫ T), so vibrations contribute little to C_v.

MEMORY TRICK

'Translational T^(3/2), rotational T (linear), vibrational ≈ 1'.

Why the Other Options Are Wrong

Correct answer: C

A **e**

Why (C) is the key — q = Σ_n e^{−nε/kT} with ε = kT: q = 1/(1 − e^{-1}) = e/(e − 1).

B **1/(e – 1)**

Ruled out: Including zero-point energy inconsistently in q_vib; dropping N! for indistinguishable particles (Gibbs paradox).

D **1/(e + 1)**

Ruled out: q_vib ≈ 1 at room temperature for most bonds (Θ_vib ≫ T), so vibrations contribute little to C_v.

Q5 The translational partition function for Ar confined to a volume of 1L at 300K, having thermal wavelength of 1.60×10^{11} m, is closest to :

A 24.4×10^{29}

B 2.44×10^{29}

C 0.244×10^{29}

D 244×10^{29}

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Partition Functions

PYQ FREQUENCY
Very High · 8 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'Translational T^(3/2), rotational T (linear), vibrational ≈ 1'.

Correct Answer B 2.44 × 10²⁹

CONCEPT

Each mode contributes a factor: q = q_trans q_rot q_vib q_elec. q_trans ∝ V T^(3/2); q_rot(linear) = T/σΘ_rot, nonlinear ∝ T^(3/2); q_vib = (1 − e^(−hν/kT))⁻¹; q_elec = g_0 (ground degeneracy) unless low-lying states exist. Thermodynamic functions follow by differentiation.

↓

LOGIC / WORKING

- 899 *V* 1*L* 108c *m*c 10c^a *λ* = 1.6×10 *m*, *q* = c = = = *λ* 1.6×10899 *m* c 1.6 c ×108cc 1.6 c c^a O‰ = 0.244×10 = 2.44×10 CSIR JUNE 2019 Explanation as extracted from the printed page; notation may be imperfect.
- Therefore the answer is (B).

FINAL: (B) 2.44 × 10²⁹

SHORTCUT / EXAM TRICK

Two-level system: q = 1 + e^(−ε/kT); population ratio n_1/n_0 = e^(−ε/kT); C_v shows a Schottky maximum.

COMMON MISTAKE

Including zero-point energy inconsistently in q_vib; dropping N! for indistinguishable particles (Gibbs paradox).

EXAM TIP

q_vib ≈ 1 at room temperature for most bonds (Θ_vib ≫ T), so vibrations contribute little to C_v.

MEMORY TRICK

'Translational T^(3/2), rotational T (linear), vibrational ≈ 1'.

Why the Other Options Are Wrong

Correct answer: B

A **24.4×10^{29}**

Why (B) is the key — 899 *V* 1*L* 108c *m*c 10c^{a} λ = 1.6×10 *m*, *q* = c = = = λ 1.6×10899 *m* c 1.6 c ×108cc 1.6 c c^{a} O‰ = 0.244×10 = 2.44×10 CSIR JUNE 2019 Explanation as extracted from the printed page; notation may be imperfect.

C **0.244×10^{29}**

Ruled out: Including zero-point energy inconsistently in q_vib; dropping N! for indistinguishable particles (Gibbs paradox).

D **244×10^{29}**

Ruled out: q_vib ≈ 1 at room temperature for most bonds (Θ_vib ≫ T), so vibrations contribute little to C_v.

Q6

The electric-dipole allowed transition among the following is

A. $^3S \rightarrow {}^3D$

B. $^3S \rightarrow {}^3P$

C. $^3S \rightarrow {}^1D$

D. $^3S \rightarrow {}^1F$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Partition Functions

PYQ FREQUENCY
Very High · 8 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'Translational T^(3/2), rotational T (linear), vibrational ≈ 1'.

Correct Answer B $^3S \rightarrow {}^3P$

CONCEPT

Each mode contributes a factor: q = q_trans q_rot q_vib q_elec. q_trans ∝ V T^(3/2); q_rot(linear) = T/σΘ_rot, nonlinear ∝ T^(3/2); q_vib = $(1 - e^{-h\nu/kT})^{-1}$; q_elec = g_0 (ground degeneracy) unless low-lying states exist. Thermodynamic functions follow by differentiation.

↓

LOGIC / WORKING

- Electric-dipole rules: ΔS = 0, ΔL = 0, ±1 (L = 0 ↔/ 0). $^3S \rightarrow {}^3P$ satisfies both; $^3S \rightarrow {}^3D$ has ΔL = 2; (c), (d) change spin. (Bank key (d) was wrong — corrected.)
- Therefore the answer is (B).

FINAL: (B) $^3S \rightarrow {}^3P$

SHORTCUT / EXAM TRICK

Two-level system: q = 1 + e^(−ε/kT); population ratio n_1/n_0 = e^(−ε/kT); C_v shows a Schottky maximum.

COMMON MISTAKE

Including zero-point energy inconsistently in q_vib; dropping N! for indistinguishable particles (Gibbs paradox).

EXAM TIP

q_vib ≈ 1 at room temperature for most bonds (Θ_vib ≫ T), so vibrations contribute little to C_v.

MEMORY TRICK

'Translational T^(3/2), rotational T (linear), vibrational ≈ 1'.

Why the Other Options Are Wrong

Correct answer: B

A $^3S \rightarrow {}^3D$

Why (B) is the key — Electric-dipole rules: $\Delta S = 0$, $\Delta L = 0, \pm 1$ ($L = 0 \not\leftrightarrow 0$). $^3S \rightarrow {}^3P$ satisfies both; $^3S \rightarrow {}^3D$ has $\Delta L = 2$; (c), (d) change spin. (Bank key (d) was wrong — corrected.)

C $^3S \rightarrow {}^1D$

Ruled out: Including zero-point energy inconsistently in q_vib; dropping N! for indistinguishable particles (Gibbs paradox).

D $^3S \rightarrow {}^1F$

Ruled out: q_vib ≈ 1 at room temperature for most bonds (Θ_vib ≫ T), so vibrations contribute little to C_v.

Q7

The single – partition translational partition function (f) for an ideal gas in a fixed volume V depends on the thermal Broglie wave function λ^th as fsim(λ^th)$_n$ where :

A. n=3

B. n=1

C. n=-1

D. n=-3

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Partition Functions

PYQ FREQUENCY
Very High · 8 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'Translational T^(3/2), rotational T (linear), vibrational ≈ 1'.

Correct Answer D n=-3

CONCEPT

Each mode contributes a factor: q = q_trans q_rot q_vib q_elec. q_trans ∝ V T^(3/2); q_rot(linear) = T/σΘ_rot, nonlinear ∝ T^(3/2); q_vib = $(1 - e^{-h\nu/kT})^{-1}$; q_elec = g_0 (ground degeneracy) unless low-lying states exist. Thermodynamic functions follow by differentiation.

↓

LOGIC / WORKING

- q_trans = V/Λ^3 with thermal wavelength Λ = h/√(2πmkT) → f ∝ (Λ)^{−3}, n = −3.
- Therefore the answer is (D).

FINAL: (D) n=-3

SHORTCUT / EXAM TRICK

Two-level system: q = 1 + e^(−ε/kT); population ratio n_1/n_0 = e^(−ε/kT); C_v shows a Schottky maximum.

COMMON MISTAKE

Including zero-point energy inconsistently in q_vib; dropping N! for indistinguishable particles (Gibbs paradox).

EXAM TIP

q_vib ≈ 1 at room temperature for most bonds (Θ_vib ≫ T), so vibrations contribute little to C_v.

MEMORY TRICK

'Translational T^(3/2), rotational T (linear), vibrational ≈ 1'.

Why the Other Options Are Wrong

Correct answer: D

A **n=3**

Why (D) is the key — q_trans = V/Λ³ with thermal wavelength Λ = h/√(2πmkT) → f ∝ (Λ)^{−3}, n = −3.

B **n=1**

Ruled out: Including zero-point energy inconsistently in q_vib; dropping N! for indistinguishable particles (Gibbs paradox).

C **n=-1**

Ruled out: q_vib ≈ 1 at room temperature for most bonds (Θ_vib ≫ T), so vibrations contribute little to C_v.

Q8

A certain system of non interacting particles has the single-particle partition function f = A(T^m)/(V) where A is some constant. The average energy per particle will be

A. mkT

B. AkT

C. kT/m

D. kT/A

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Partition Functions

PYQ FREQUENCY
Very High · 8 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'Translational T^(3/2), rotational T (linear), vibrational ≈ 1'.

Correct Answer A mkT

CONCEPT

Each mode contributes a factor: q = q_trans q_rot q_vib q_elec. q_trans ∝ V T^(3/2); q_rot(linear) = T/σΘ_rot, nonlinear ∝ T^(3/2); q_vib = $(1 - e^{-h\nu/kT})^{-1}$; q_elec = g_0 (ground degeneracy) unless low-lying states exist. Thermodynamic functions follow by differentiation.

↓

LOGIC / WORKING

- $\langle\varepsilon\rangle = kT^2(\partial \ln f/\partial T)_V = kT^2 \times (m/T) = mkT$ (each T^{1/2} factor contributes ½kT, equipartition).
- Therefore the answer is (A).

FINAL: (A) mkT

SHORTCUT / EXAM TRICK

Two-level system: q = 1 + e^(−ε/kT); population ratio n_1/n_0 = e^(−ε/kT); C_v shows a Schottky maximum.

COMMON MISTAKE

Including zero-point energy inconsistently in q_vib; dropping N! for indistinguishable particles (Gibbs paradox).

EXAM TIP

q_vib ≈ 1 at room temperature for most bonds (Θ_vib ≫ T), so vibrations contribute little to C_v.

MEMORY TRICK

'Translational T^(3/2), rotational T (linear), vibrational ≈ 1'.

Why the Other Options Are Wrong

Correct answer: A

B **AkT**

Why (A) is the key — ⟨ε⟩ = kT²(∂ln f/∂T)_V = kT² × (m/T) = mkT (each T^{1/2} factor contributes ½kT, equipartition).

C **kT/m**

Ruled out: Including zero-point energy inconsistently in q_vib; dropping N! for indistinguishable particles (Gibbs paradox).

D **kT/A**

Ruled out: q_vib ≈ 1 at room temperature for most bonds (Θ_vib ≫ T), so vibrations contribute little to C_v.

Q9

The rotational partition function is expected to be the smallest for the molecule, among the following

A H_2

B Li_2

C N_2

D F_2

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Partition Functions

PYQ FREQUENCY
Very High · 8 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'Translational T^(3/2), rotational T (linear), vibrational ≈ 1'.

Correct Answer A H_2

CONCEPT

Each mode contributes a factor: q = q_trans q_rot q_vib q_elec. q_trans ∝ V T^(3/2); q_rot(linear) = T/σΘ_rot, nonlinear ∝ T^(3/2); q_vib = $(1 - e^{-h\nu/kT})^{-1}$; q_elec = g_0 (ground degeneracy) unless low-lying states exist. Thermodynamic functions follow by differentiation.

↓

LOGIC / WORKING

- q_rot ∝ I/σ (σ = 2 for all): H_2 has by far the smallest moment of inertia (lightest atoms, shortest bond) → smallest q_rot (Θ_rot = 85 K).
- Therefore the answer is (A).

FINAL: (A) H_2

SHORTCUT / EXAM TRICK

Two-level system: q = 1 + e^(−ε/kT); population ratio n_1/n_0 = e^(−ε/kT); C_v shows a Schottky maximum.

COMMON MISTAKE

Including zero-point energy inconsistently in q_vib; dropping N! for indistinguishable particles (Gibbs paradox).

EXAM TIP

q_vib ≈ 1 at room temperature for most bonds (Θ_vib ≫ T), so vibrations contribute little to C_v.

MEMORY TRICK

'Translational T^(3/2), rotational T (linear), vibrational ≈ 1'.

Why the Other Options Are Wrong

Correct answer: A

B **Li_2**

Why (A) is the key — q_rot ∝ I/σ (σ = 2 for all): H_2 has by far the smallest moment of inertia (lightest atoms, shortest bond) → smallest q_rot (Θ_rot = 85 K).

C **N_2**

Ruled out: Including zero-point energy inconsistently in q_vib; dropping N! for indistinguishable particles (Gibbs paradox).

D **F_2**

Ruled out: q_vib ≈ 1 at room temperature for most bonds (Θ_vib ≫ T), so vibrations contribute little to C_v.

TOPIC REVISION

Partition Functions

9 PYQs · Last-minute revision

TOPIC SUMMARY

Each mode contributes a factor: q = q_trans q_rot q_vib q_elec. q_trans ∝ V T^(3/2); q_rot(linear) = T/σΘ_rot, nonlinear ∝ T^(3/2); q_vib = (1 − e^(−hν/kT))⁻¹; q_elec = g_0 (ground degeneracy) unless low-lying states exist. Thermodynamic functions follow by differentiation.

IMPORTANT FORMULA SHEET

- q_trans = V/Λ³, Λ = h/√(2πmkT)
- q_rot = T/(σΘ_rot), Θ_rot = ħ²/(2Ik)
- q_vib = 1/(1 − e^(−Θ_vib/T)), Θ_vib = hν/k
- U_vib = Nk Θ_vib/(e^(Θ_vib/T) − 1)
- A = −kT ln Q; Q = q^N/N! (indistinguishable)

FREQUENTLY ASKED CONCEPTS

- Numerical q_rot, q_vib at 300 K
- Fraction of molecules in v = 1
- Two-level system q = 1 + e^(−ε/kT)
- Equilibrium constant from partition functions

COMMON MISTAKES & QUICK NOTES

Watch out:
Including zero-point energy inconsistently in q_vib; dropping N! for indistinguishable particles (Gibbs paradox).
q_vib ≈ 1 at room temperature for most bonds (Θ_vib ≫ T), so vibrations contribute little to C_v.

MOST-REPEATED PYQs & EXPECTED IN EXAM

PYQs in this topic: Q1 Q2 Q3 Q4 Q5 Q6 Q7 Q8 Q9

Expect 1 question(s) next session on Partition Functions.

TOPIC 2

Statistical Equilibrium

7 questions · Easy 1 | Medium 6 | Hard 0 · PYQ frequency: High

Q10

The probability of finding the harmonic oscillator in the energy level n = 1 is (neglect zero point energy and assume hν = k_BT)

A. e

B. e^2

C. $1 - e^2$

D. $e^{-2}(e-1)$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Equilibrium

PYQ FREQUENCY
High · 7 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'Boltzmann: g_i e^(−ε/kT) over q'.

Correct Answer D $e^{-2}(e-1)$

CONCEPT

Equilibrium constants from partition functions: $K = \Pi(q_i^\circ/N_A)^{\nu_i} e^{(-\Delta E_0/RT)}$ (per unit volume, with ΔE_0 the zero-point energy difference); Boltzmann distribution $n_i/N = g_i e^{(-\varepsilon_i/kT)}/q$; isotope-exchange equilibria depend on zero-point energies; the most probable distribution maximises W.

↓

LOGIC / WORKING

- $q = \Sigma e^{-n} = 1/(1 - e^{-1})$. $P(n=1) = e^{-1}/q = e^{-1}(1 - e^{-1}) = e^{-1} - e^{-2} = e^{-2}(e - 1)$.
- Therefore the answer is (D).

FINAL: (D) $e^{-2}(e-1)$

SHORTCUT / EXAM TRICK

$K(H_2 + D_2 \rightleftharpoons 2HD) \rightarrow 4$ at high T purely from σ: $(\sigma_{H_2}\sigma_{D_2})/\sigma_{HD}^2 = 2\times2/1$.

COMMON MISTAKE

Equating populations across levels with different degeneracies without the g_i factor.

EXAM TIP

A negative temperature would be needed for population inversion — equilibrium systems never invert.

MEMORY TRICK

'Boltzmann: $g_i e^{(-\varepsilon/kT)}$ over q'.

Why the Other Options Are Wrong

Correct answer: D

A **e**

Why (D) is the key — q = Σe^{−n} = 1/(1 − e⁻¹). P(n=1) = e⁻¹/q = e⁻¹(1 − e⁻¹) = e⁻¹ − e⁻² = e⁻²(e − 1).

B **e^2**

Ruled out: Equating populations across levels with different degeneracies without the g_i factor.

C **$1 - e^2$**

Ruled out: A negative temperature would be needed for population inversion — equilibrium systems never invert.

Q11

Four distinguishable molecules are distributed in energy level E1 and E2 with degeneracy of 2 & 3 respectively. Number of microstates with 3 molecules in in energy level E1 and E2 is

A. 4

B. 12

C. 96

D. 192

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Equilibrium

PYQ FREQUENCY
High · 7 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'Boltzmann: g_i e^(−ε/kT) over q'.

Correct Answer C 96

CONCEPT

Equilibrium constants from partition functions: $K = \Pi(q_i^\circ/N_A)^{\nu_i} e^{(-\Delta E_0/RT)}$ (per unit volume, with ΔE_0 the zero-point energy difference); Boltzmann distribution $n_i/N = g_i e^{(-\varepsilon_i/kT)}/q$; isotope-exchange equilibria depend on zero-point energies; the most probable distribution maximises W.

↓

LOGIC / WORKING

- CSIR JUNE 2018 Explanation as extracted from the printed page; notation may be imperfect.
- Therefore the answer is (C).

FINAL: (C) 96

SHORTCUT / EXAM TRICK

$K(H_2 + D_2 \rightleftharpoons 2HD) \rightarrow 4$ at high T purely from σ: $(\sigma_{H_2}\sigma_{D_2})/\sigma_{HD}^2 = 2\times2/1$.

COMMON MISTAKE

Equating populations across levels with different degeneracies without the g_i factor.

EXAM TIP

A negative temperature would be needed for population inversion — equilibrium systems never invert.

MEMORY TRICK

'Boltzmann: $g_i e^{(-\varepsilon/kT)}$ over q'.

Why the Other Options Are Wrong

Correct answer: C

A **4**

Why (C) is the key — CSIR JUNE 2018 Explanation as extracted from the printed page; notation may be imperfect.

B **12**

Ruled out: Equating populations across levels with different degeneracies without the g_i factor.

D **192**

Ruled out: A negative temperature would be needed for population inversion — equilibrium systems never invert.

Q12

The molar residual entropy (in J K^{-1}) of solid OCS would be closest to

A. 0

B. 2.9

C. 5.8

D. 8.7

QUESTION INSIGHTS

ESTIMATED TIME
1–1.5 min

DIFFICULTY
Easy

CONCEPT TESTED
Statistical Equilibrium

PYQ FREQUENCY
High · 7 papers

REVISION PRIORITY
★★★☆☆

EXPECTED LEVEL
Part B

MEMORY HOOK
'Boltzmann: g_i e^(−ε/kT) over q'.

Correct Answer C 5.8

CONCEPT

Equilibrium constants from partition functions: $K = \Pi(q_i^\circ/N_A)^{\nu_i} e^{(-\Delta E_0/RT)}$ (per unit volume, with ΔE_0 the zero-point energy difference); Boltzmann distribution $n_i/N = g_i e^{(-\varepsilon_i/kT)}/q$; isotope-exchange equilibria depend on zero-point energies; the most probable distribution maximises W.

↓

LOGIC / WORKING

- Linear OCS can freeze in two orientations (OCS / SCO): $S_{res} = R \ln 2 = 8.314 \times 0.693 = 5.8$ J K^{-1} mol^{-1}.
- Therefore the answer is (C).

FINAL: (C) 5.8

SHORTCUT / EXAM TRICK

$K(H_2 + D_2 \rightleftharpoons 2HD) \rightarrow 4$ at high T purely from σ: $(\sigma_{H_2}\sigma_{D_2})/\sigma_{HD}^2 = 2\times2/1$.

COMMON MISTAKE

Equating populations across levels with different degeneracies without the g_i factor.

EXAM TIP

A negative temperature would be needed for population inversion — equilibrium systems never invert.

MEMORY TRICK

'Boltzmann: $g_i\, e^{(-\varepsilon/kT)}$ over q'.

Why the Other Options Are Wrong

Correct answer: C

A **0**

Why (C) is the key — Linear OCS can freeze in two orientations (OCS / SCO): $S_{res} = R \ln 2 = 8.314 \times 0.693 = 5.8$ J K^{-1} mol^{-1}.

B **2.9**

Ruled out: Equating populations across levels with different degeneracies without the g_i factor.

D **8.7**

Ruled out: A negative temperature would be needed for population inversion — equilibrium systems never invert.

Q13 The relative population in two states with energies E_1 and E_2 satisfying Boltzmann distribution is given by $n_1/n_2 = (3/2)\exp[-(E_1 - E_2)/k_bT]$. The relative degeneracy g_2/g_1 is:

A. 2

B. 2/3

C. 3/2

D. 3

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Equilibrium

PYQ FREQUENCY
High · 7 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'Boltzmann: g_i e^(−ε/kT) over q'.

Correct Answer B 2/3

CONCEPT

Equilibrium constants from partition functions: $K = \Pi(q_i^\circ/N_A)^{\nu_i} e^{(-\Delta E_0/RT)}$ (per unit volume, with ΔE_0 the zero-point energy difference); Boltzmann distribution $n_i/N = g_i e^{(-\varepsilon_i/kT)}/q$; isotope-exchange equilibria depend on zero-point energies; the most probable distribution maximises W.

↓

LOGIC / WORKING

- The relative population in two states with energy E1 and E2 satisfy Boltzmann distribution law [mp 'm;] •p bp = *e* nr= .....(1) [where, g1 and g2 are degeneracy] •; b; •p c Given : =( ) exp [-(E_1 - E_2)/kbT] ……. (2) •; O b c Compare equation (1) and (2), we get, = p = b; O b O The value of ; = bp c Explanation as extracted from the printed page; notation may be imperfect.
- Therefore the answer is (B).

FINAL: (B) 2/3

SHORTCUT / EXAM TRICK

$K(H_2 + D_2 \rightleftharpoons 2HD) \rightarrow 4$ at high T purely from σ: (σ_H_2 σ_D_2)/σ_HD^2 = 2×2/1.

COMMON MISTAKE

Equating populations across levels with different degeneracies without the g_i factor.

EXAM TIP

A negative temperature would be needed for population inversion — equilibrium systems never invert.

MEMORY TRICK

'Boltzmann: g_i e^(−ε/kT) over q'.

Why the Other Options Are Wrong

Correct answer: B

A

2

Why (B) is the key — The relative population in two states with energy E1 and E2 satisfy Boltzmann distribution law [mp ’m;] •p bp = *e* nr= .....(1) [where, g1 and g2 are degeneracy] •; b; •p c Given : =( ) exp [-(E_1 - E_2)/kbT] ……. (2) •; O b c Compare equation (1) and (2), we get, = p = b; O b O The value of ; = bp c Explanation as extracted from the printed page; notation may be imperfect.

C

3/2

Ruled out: Equating populations across levels with different degeneracies without the g_i factor.

D

3

Ruled out: A negative temperature would be needed for population inversion — equilibrium systems never invert.

Q14

The allowed transition among the following is

A. $^3F_4 \rightarrow {}^3D_3$

B. $^3F_4 \rightarrow {}^1D_3$

C. $^3F_4 \rightarrow {}^3P_4$

D. $^3F_4 \rightarrow {}^3D_2$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Equilibrium

PYQ FREQUENCY
High · 7 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'Boltzmann: g_i e^(−ε/kT) over q'.

Correct Answer A $^3F_4 \rightarrow {}^3D_3$

CONCEPT

Equilibrium constants from partition functions: $K = \Pi(q_i^\circ/N_A)^{\nu_i} e^{(-\Delta E_0/RT)}$ (per unit volume, with ΔE_0 the zero-point energy difference); Boltzmann distribution $n_i/N = g_i e^{(-\varepsilon_i/kT)}/q$; isotope-exchange equilibria depend on zero-point energies; the most probable distribution maximises W.

↓

LOGIC / WORKING

- Rules: $\Delta S = 0$, $\Delta L = 0, \pm1$, $\Delta J = 0, \pm1$. $^3F_4 \rightarrow {}^3D_3$: $\Delta L = -1$, $\Delta J = -1$ ✓. (b) changes S; (c) ^3P cannot have $J = 4$; (d) $\Delta J = -2$.
- Therefore the answer is (A).

FINAL: (A) $^3F_4 \rightarrow {}^3D_3$

SHORTCUT / EXAM TRICK

$K(H_2 + D_2 \rightleftharpoons 2HD) \rightarrow 4$ at high T purely from σ: $(\sigma_{H_2}\sigma_{D_2})/\sigma_{HD}^2 = 2\times2/1$.

COMMON MISTAKE

Equating populations across levels with different degeneracies without the g_i factor.

EXAM TIP

A negative temperature would be needed for population inversion — equilibrium systems never invert.

MEMORY TRICK

'Boltzmann: $g_i\, e^{(-\varepsilon/kT)}$ over q'.

Why the Other Options Are Wrong

Correct answer: A

B $^3F_4 \rightarrow {}^1D_3$

Why (A) is the key — Rules: $\Delta S = 0$, $\Delta L = 0, \pm 1$, $\Delta J = 0, \pm 1$. $^3F_4 \rightarrow {}^3D_3$: $\Delta L = -1$, $\Delta J = -1$ ✓. (b) changes S; (c) ^3P cannot have $J = 4$; (d) $\Delta J = -2$.

C $^3F_4 \rightarrow {}^3P_4$

Ruled out: Equating populations across levels with different degeneracies without the g_i factor.

D $^3F_4 \rightarrow {}^3D_2$

Ruled out: A negative temperature would be needed for population inversion — equilibrium systems never invert.

Q15

The number of configurations in the most probable state, according to Boltzmann formula, is

A. e^(S)/(k_B)

B. e^(-S)/(k_B)

C. e^(-E)/(k_BT)

D. e^(-Δ G)/(k_BT)

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Equilibrium

PYQ FREQUENCY
High · 7 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'Boltzmann: g_i e^(−ε/kT) over q'.

Correct Answer A e^(S)/(k_B)

CONCEPT

Equilibrium constants from partition functions: $K = \Pi(q_i^\circ/N_A)^{\nu_i} e^{(-\Delta E_0/RT)}$ (per unit volume, with ΔE_0 the zero-point energy difference); Boltzmann distribution $n_i/N = g_i e^{(-\varepsilon_i/kT)}/q$; isotope-exchange equilibria depend on zero-point energies; the most probable distribution maximises W.

↓

LOGIC / WORKING

- Boltzmann: S = k_B ln W → W = e^{S/k_B}. (Bank key (b) has the wrong sign — corrected.)
- Therefore the answer is (A).

FINAL: (A) e^(S)/(k_B)

SHORTCUT / EXAM TRICK

$K(H_2 + D_2 \rightleftharpoons 2HD) \rightarrow 4$ at high T purely from σ: $(\sigma_{H_2}\sigma_{D_2})/\sigma_{HD}^2 = 2\times2/1$.

COMMON MISTAKE

Equating populations across levels with different degeneracies without the g_i factor.

EXAM TIP

A negative temperature would be needed for population inversion — equilibrium systems never invert.

MEMORY TRICK

'Boltzmann: $g_i e^{(-\varepsilon/kT)}$ over q'.

Why the Other Options Are Wrong

Correct answer: A

B **e^(-S)/(k_B)**

Why (A) is the key — Boltzmann: S = k_B ln W → W = e^{S/k_B}. (Bank key (b) has the wrong sign — corrected.)

C **e^(-E)/(k_BT)**

Ruled out: Equating populations across levels with different degeneracies without the g_i factor.

D **e^(-Δ G)/(k_BT)**

Ruled out: A negative temperature would be needed for population inversion — equilibrium systems never invert.

Q16

For a micro-canonical system, the correct probability distribution function for energy is given by

A. Exponential distribution function

B. Gaussian distribution function

C. Poisson distribution function

D. Uniform distribution function

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Equilibrium

PYQ FREQUENCY
High · 7 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'Boltzmann: g_i e^(−ε/kT) over q'.

Correct Answer D Uniform distribution function

CONCEPT

Equilibrium constants from partition functions: $K = \Pi(q_i^\circ/N_A)^{\nu_i} e^{(-\Delta E_0/RT)}$ (per unit volume, with ΔE_0 the zero-point energy difference); Boltzmann distribution $n_i/N = g_i e^{(-\varepsilon_i/kT)}/q$; isotope-exchange equilibria depend on zero-point energies; the most probable distribution maximises W.

↓

LOGIC / WORKING

- Microcanonical ensemble (N, V, E fixed): every accessible microstate at energy E is equally probable — a uniform distribution (postulate of equal a priori probabilities).
- Therefore the answer is (D).

FINAL: (D) Uniform distribution function

SHORTCUT / EXAM TRICK

$K(H_2 + D_2 \rightleftharpoons 2HD) \rightarrow 4$ at high T purely from σ: $(\sigma_{H_2}\sigma_{D_2})/\sigma_{HD}^2 = 2\times2/1$.

COMMON MISTAKE

Equating populations across levels with different degeneracies without the g_i factor.

EXAM TIP

A negative temperature would be needed for population inversion — equilibrium systems never invert.

MEMORY TRICK

'Boltzmann: $g_i e^{(-\varepsilon/kT)}$ over q'.

Why the Other Options Are Wrong

Correct answer: D

A **Exponential distribution function**

Why (D) is the key — Microcanonical ensemble (N, V, E fixed): every accessible microstate at energy E is equally probable — a uniform distribution (postulate of equal a priori probabilities).

B **Gaussian distribution function**

Ruled out: Equating populations across levels with different degeneracies without the g_i factor.

C **Poisson distribution function**

Ruled out: A negative temperature would be needed for population inversion — equilibrium systems never invert.

TOPIC REVISION

Statistical Equilibrium

7 PYQs · Last-minute revision

TOPIC SUMMARY

Equilibrium constants from partition functions: $K = \Pi(q_i°/N_A)^{\nu_i} e^{(-\Delta E_0/RT)}$ (per unit volume, with ΔE_0 the zero-point energy difference); Boltzmann distribution $n_i/N = g_i e^{(-\varepsilon_i/kT)}/q$; isotope-exchange equilibria depend on zero-point energies; the most probable distribution maximises W.

IMPORTANT FORMULA SHEET

- $n_i/n_0 = (g_i/g_0)\, e^{(-(\varepsilon_i-\varepsilon_0)/kT)}$
- $K_c = \Pi\, (q_i/V)^{\nu_i}\, e^{(-\Delta E_0/kT)}$
- $W = N!/\Pi n_i!$; $S = k \ln W$
- ΔE_0 includes zero-point energy differences

FREQUENTLY ASKED CONCEPTS

- Population ratio of two levels
- K for $H_2 + D_2 \rightleftharpoons 2HD \approx 4$ at high T (symmetry numbers)
- Maximising W with constraints (Lagrange)
- Temperature at which populations equalise (never for finite T)

COMMON MISTAKES & QUICK NOTES

Watch out:
Equating populations across levels with different degeneracies without the g_i factor.
A negative temperature would be needed for population inversion — equilibrium systems never invert.

MOST-REPEATED PYQs & EXPECTED IN EXAM

PYQs in this topic: Q10 Q11 Q12 Q13 Q14 Q15 Q16

Expect 1 question(s) next session on Statistical Equilibrium.

TOPIC 3

Statistical Thermodynamics – General

27 questions · Easy 3 | Medium 23 | Hard 1 · PYQ frequency: Very High

Q17

P_A and P_B denote the populations of two energy states E_A and E_B and E_A > E_B. The correct statement when the temperature $T_1 > T_2$ is

A $P_A(T_1) > P_B(T_1)$, $P_A(T_2) < P_B(T_2)$ and $(P_A/P_B)_T_1 > (P_A/P_B)_T_2$

B $P_A(T_1) < P_B(T_1)$, $P_A(T_2) > P_B(T_2)$ and $(P_A/P_B)_T_1 > (P_A/P_B)_T_2$

C $P_A(T_1) < P_B(T_1)$, $P_A(T_2) < P_B(T_2)$ and $(P_A/P_B)_T_1 > (P_A/P_B)_T_2$

D $P_A(T_1) < P_B(T_1)$, $P_A(T_2) < P_B(T_2)$ and $(P_A/P_B)_T_1 < (P_A/P_B)_T_2$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Thermodynamics – General

PYQ FREQUENCY
Very High · 13 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'q counts the thermally accessible states'.

Correct Answer C $P_A(T_1) < P_B(T_1)$, $P_A(T_2) < P_B(T_2)$ and $(P_A/P_B)_{T_1} > (P_A/P_B)_{T_2}$

CONCEPT

The partition function $q = \Sigma\, g_i\, e^{(-\varepsilon_i/kT)}$ links microscopic levels to thermodynamics: $U = NkT^2(\partial \ln q/\partial T)$, $S = Nk \ln(q/N) + U/T + Nk$ (indistinguishable), $A = -kT \ln Q$. Translational, rotational, vibrational and electronic contributions multiply; equipartition gives ½kT per quadratic term at high T.

↓

LOGIC / WORKING

- Boltzmann: $P_A/P_B = e^{-(E_A-E_B)/kT} < 1$ at every finite T (the higher state is always less populated), and the ratio increases with T, so $(P_A/P_B)_{T_1} > (P_A/P_B)_{T_2}$ for $T_1 > T_2$.
- Therefore the answer is (C).

FINAL: (C) $P_A(T_1) < P_B(T_1)$, $P_A(T_2) < P_B(T_2)$ and $(P_A/P_B)_{T_1} > (P_A/P_B)_{T_2}$

SHORTCUT / EXAM TRICK

Classical C_v: monatomic 3/2 R; diatomic 5/2 R (vibration frozen) → 7/2 R at high T.

COMMON MISTAKE

Forgetting the symmetry number σ (2 for homonuclear) in q_{rot}; mixing Q (system) with q (molecule).

EXAM TIP

A degree of freedom contributes R/2 to C_v only when $kT \gg$ its level spacing.

MEMORY TRICK

'q counts the thermally accessible states'.

Why the Other Options Are Wrong

Correct answer: C

A $P_A(T_1) > P_B(T_1)$, $P_A(T_2) < P_B(T_2)$ and $(P_A/P_B)_{T_1} > (P_A/P_B)_{T_2}$

Why (C) is the key — Boltzmann: $P_A/P_B = e^{-(E_A-E_B)/kT} < 1$ at every finite T (the higher state is always less populated), and the ratio increases with T, so $(P_A/P_B)_{T_1} > (P_A/P_B)_{T_2}$ for $T_1 > T_2$.

B $P_A(T_1) < P_B(T_1)$, $P_A(T_2) > P_B(T_2)$ and $(P_A/P_B)_{T_1} > (P_A/P_B)_{T_2}$

Ruled out: Forgetting the symmetry number σ (2 for homonuclear) in q_{rot}; mixing Q (system) with q (molecule).

D $P_A(T_1) < P_B(T_1)$, $P_A(T_2) < P_B(T_2)$ and $(P_A/P_B)_{T_1} < (P_A/P_B)_{T_2}$

Ruled out: A degree of freedom contributes R/2 to C_v only when $kT \gg$ its level spacing.

Q18

A system consisting of 4 identical and distinguishable particles, each possessing three available states of 1, 2 and 3 units, has 10 units of energy. The number of ways, W, in which these conditions are satisfied is :

A) 2

B) 4

C) 6

D) 10

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Thermodynamics – General

PYQ FREQUENCY
Very High · 13 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'q counts the thermally accessible states'.

Correct Answer D 10

CONCEPT

The partition function $q = \Sigma\, g_i\, e^{(-\varepsilon_i/kT)}$ links microscopic levels to thermodynamics: $U = NkT^2(\partial \ln q/\partial T)$, $S = Nk \ln(q/N) + U/T + Nk$ (indistinguishable), $A = -kT \ln Q$. Translational, rotational, vibrational and electronic contributions multiply; equipartition gives ½kT per quadratic term at high T.

↓

LOGIC / WORKING

- Energies from {1,2,3} with four particles summing to 10: {3,3,3,1} (4!/3! = 4 arrangements) and {3,3,2,2} (4!/(2!2!) = 6). W = 4 + 6 = 10.
- Therefore the answer is (D).

FINAL: (D) 10

SHORTCUT / EXAM TRICK

Classical C_v: monatomic 3/2 R; diatomic 5/2 R (vibration frozen) → 7/2 R at high T.

COMMON MISTAKE

Forgetting the symmetry number σ (2 for homonuclear) in q_{rot}; mixing Q (system) with q (molecule).

EXAM TIP

A degree of freedom contributes R/2 to C_v only when $kT \gg$ its level spacing.

MEMORY TRICK

'q counts the thermally accessible states'.

Why the Other Options Are Wrong

Correct answer: D

A **2**

Why (D) is the key — Energies from {1,2,3} with four particles summing to 10: {3,3,3,1} (4!/3! = 4 arrangements) and {3,3,2,2} (4!/(2! 2!) = 6). W = 4 + 6 = 10.

B **4**

Ruled out: Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

C **6**

Ruled out: A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

Q19

Calculate the total number of microstates for 6 identical particles with their occupation numbers \1, 2, and 3\ in three states is

A. 6

B. 12

C. 60

D. 720

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Statistical Thermodynamics – General

PYQ FREQUENCY
Very High · 13 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
'q counts the thermally accessible states'.

Correct Answer C 60

CONCEPT

The partition function $q = \Sigma\, g_i\, e^{(-\varepsilon_i/kT)}$ links microscopic levels to thermodynamics: $U = NkT^2(\partial \ln q/\partial T)$, $S = Nk \ln(q/N) + U/T + Nk$ (indistinguishable), $A = -kT \ln Q$. Translational, rotational, vibrational and electronic contributions multiply; equipartition gives ½kT per quadratic term at high T.

↓

LOGIC / WORKING

- $W = N!/(n_1!n_2!n_3!) = 6!/(1!\ 2!\ 3!) = 720/12 = 60$.
- Therefore the answer is (C).

FINAL: (C) 60

SHORTCUT / EXAM TRICK

Classical C_v: monatomic 3/2 R; diatomic 5/2 R (vibration frozen) → 7/2 R at high T.

COMMON MISTAKE

Forgetting the symmetry number σ (2 for homonuclear) in q_{rot}; mixing Q (system) with q (molecule).

EXAM TIP

A degree of freedom contributes R/2 to C_v only when $kT \gg$ its level spacing.

MEMORY TRICK

'q counts the thermally accessible states'.

Why the Other Options Are Wrong

Correct answer: C

A **6**

Why (C) is the key — $W = N!/(n_1!n_2!n_3!) = 6!/(1!\ 2!\ 3!) = 720/12 = 60$.

B **12**

Ruled out: Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

D **720**

Ruled out: A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

Q20

The number of ways in which four molecules can be distributed in two different energy levels is :

A) 6

B) 3

C) 16

D) 8

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Thermodynamics – General

PYQ FREQUENCY
Very High · 13 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'q counts the thermally accessible states'.

Correct Answer C 16

CONCEPT

The partition function q = Σ g_i e^(−ε_i/kT) links microscopic levels to thermodynamics: U = NkT²(∂ln q/∂T), S = Nk ln(q/N) + U/T + Nk (indistinguishable), A = −kT ln Q. Translational, rotational, vibrational and electronic contributions multiply; equipartition gives ½kT per quadratic term at high T.

↓

LOGIC / WORKING

- 16 The molecule with the smallest rotation partition function at any temperature among the following is : a) CH3—C ≡ C—H b) H—C ≡ C—H c) H—C ≡ C—D d) D—C ≡ C—D Since rotational partition function is given by Ír - Ï q= where, B= ÎÏÐS ef ; ÑÐ Ír - ef; Ñ:- Ñ q= • = =*q*∝ ÎÏÐ ; ÎÏ ; Î ÒÓ ÔÕ Hence, two factor should be considered (i)I∝ *μ* (ii) *σ*(symmetry number) In present case, H-C=C-H has smallest *μ* (reduced mass) also having σ= 2. Therefore, H- C=C-H will have smallest rotational partition function . CSIR JUNE 2014 Explanation as extracted from the printed page; notation may be imperfect.
- Therefore the answer is (C).

FINAL: (C) 16

SHORTCUT / EXAM TRICK

Classical C_v: monatomic 3/2 R; diatomic 5/2 R (vibration frozen) → 7/2 R at high T.

COMMON MISTAKE

Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

EXAM TIP

A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

MEMORY TRICK

'q counts the thermally accessible states'.

Why the Other Options Are Wrong

Correct answer: C

A

6

Why (C) is the key — 16 The molecule with the smallest rotation partition function at any temperature among the following is : a) CH3—C ≡ C—H b) H—C ≡ C—H c) H—C ≡ C—D d) D—C ≡ C—D Since rotational partition function is given by Ír - Ï q= where, B= ÎïÐS ef ; ÑÐ Ír - ef; Ñ:- Ñ q= • = =*q*∝ ÎïÐ ; ÎÏ ; Î ÒÓ ÔÕ Hence, two factor should be considered (i)I∝ *μ* (ii) *σ*(symmetry number) In present case, H-C=C-H has smallest *μ* (reduced mass) also having σ= 2. Therefore, H- C=C-H will have smallest rotational partition function . CSIR JUNE 2014 Explanation as extracted from the printed page; notation may be imperfect.

B

3

Ruled out: Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

D

8

Ruled out: A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

Q21

The number of microstates that are possible, when two particles are distributed in four states such that the resulting wave functions are antisymmetric with respect to exchange of the particles, is :

A 16

B 12

C 8

D 6

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Thermodynamics – General

PYQ FREQUENCY
Very High · 13 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'q counts the thermally accessible states'.

Correct Answer D 6

CONCEPT

The partition function $q = \Sigma\, g_i\, e^{(-\varepsilon_i/kT)}$ links microscopic levels to thermodynamics: $U = NkT^2(\partial \ln q/\partial T)$, $S = Nk \ln(q/N) + U/T + Nk$ (indistinguishable), $A = -kT \ln Q$. Translational, rotational, vibrational and electronic contributions multiply; equipartition gives ½kT per quadratic term at high T.

↓

LOGIC / WORKING

- Antisymmetric (fermion) states need the two particles in different states: C(4,2) = 6 microstates. (Symmetric would give 6 + 4 = 10.)
- Therefore the answer is (D).

FINAL: (D) 6

SHORTCUT / EXAM TRICK

Classical C_v: monatomic 3/2 R; diatomic 5/2 R (vibration frozen) → 7/2 R at high T.

COMMON MISTAKE

Forgetting the symmetry number σ (2 for homonuclear) in q_{rot}; mixing Q (system) with q (molecule).

EXAM TIP

A degree of freedom contributes R/2 to C_v only when $kT \gg$ its level spacing.

MEMORY TRICK

'q counts the thermally accessible states'.

Why the Other Options Are Wrong

Correct answer: D

A **16**

Why (D) is the key — Antisymmetric (fermion) states need the two particles in different states: C(4,2) = 6 microstates. (Symmetric would give 6 + 4 = 10.)

B **12**

Ruled out: Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

C **8**

Ruled out: A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

Q22

Identify the speed distribution functions of Ne, Ar and Kr with the curves in the figure above:

A. Ne-A, Ar-B, Kr-C

B. Ne-B, Ar-C, Kr-A

C. Ne-C, Ar-B, Kr-A

D. Ne-C, Ar-A, Kr-B

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Thermodynamics – General

PYQ FREQUENCY
Very High · 13 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'q counts the thermally accessible states'.

Correct Answer C Ne-C, Ar-B, Kr-A

CONCEPT

The partition function $q = \Sigma\, g_i\, e^{(-\varepsilon_i/kT)}$ links microscopic levels to thermodynamics: $U = NkT^2(\partial \ln q/\partial T)$, $S = Nk \ln(q/N) + U/T + Nk$ (indistinguishable), $A = -kT \ln Q$. Translational, rotational, vibrational and electronic contributions multiply; equipartition gives ½kT per quadratic term at high T.

↓

LOGIC / WORKING

- The heaviest gas, Kr, has the sharpest, lowest-speed peak (A), and the lightest, Ne, the broadest (C): Ne-C, Ar-B, Kr-A (c).
- Therefore the answer is (C).

FINAL: (C) Ne-C, Ar-B, Kr-A

SHORTCUT / EXAM TRICK

Classical C_v: monatomic 3/2 R; diatomic 5/2 R (vibration frozen) → 7/2 R at high T.

COMMON MISTAKE

Forgetting the symmetry number σ (2 for homonuclear) in q_{rot}; mixing Q (system) with q (molecule).

EXAM TIP

A degree of freedom contributes R/2 to C_v only when $kT \gg$ its level spacing.

MEMORY TRICK

'q counts the thermally accessible states'.

Why the Other Options Are Wrong

Correct answer: C

A **Ne-A, Ar-B, Kr-C**

Why (C) is the key — The heaviest gas, Kr, has the sharpest, lowest-speed peak (A), and the lightest, Ne, the broadest (C): Ne-C, Ar-B, Kr-A (c).

B **Ne-B, Ar-C, Kr-A**

Ruled out: Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

D **Ne-C, Ar-A, Kr-B**

Ruled out: A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

Q23

The standard deviation of speed (σ_c) for Maxwell's distribution satisfies the relation

A. σ_c ∝ T

B. σ_c ∝ √(T)

C. σ_c ∝ (1)/(T)

D. σ_c ∝ frac1√(T)

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Thermodynamics – General

PYQ FREQUENCY
Very High · 13 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'q counts the thermally accessible states'.

Correct Answer B $\sigma_c \propto \sqrt{(T)}$

CONCEPT

The partition function $q = \Sigma\, g_i\, e^{(-\varepsilon_i/kT)}$ links microscopic levels to thermodynamics: $U = NkT^2(\partial \ln q/\partial T)$, $S = Nk \ln(q/N) + U/T + Nk$ (indistinguishable), $A = -kT \ln Q$. Translational, rotational, vibrational and electronic contributions multiply; equipartition gives ½kT per quadratic term at high T.

↓

LOGIC / WORKING

- All characteristic speeds of the Maxwell distribution (c_{mp}, $\bar{c}$, c_{rms}) scale as $\sqrt{(T/m)}$; the spread $\sigma_c = \sqrt{(\langle c^2\rangle - \langle c\rangle^2)}$ therefore also $\propto \sqrt{T}$.
- Therefore the answer is (B).

FINAL: (B) $\sigma_c \propto \sqrt{(T)}$

SHORTCUT / EXAM TRICK

Classical C_v: monatomic 3/2 R; diatomic 5/2 R (vibration frozen) → 7/2 R at high T.

COMMON MISTAKE

Forgetting the symmetry number σ (2 for homonuclear) in q_{rot}; mixing Q (system) with q (molecule).

EXAM TIP

A degree of freedom contributes R/2 to C_v only when $kT \gg$ its level spacing.

MEMORY TRICK

'q counts the thermally accessible states'.

Why the Other Options Are Wrong

Correct answer: B

A **σ_c ∝ T**

Why (B) is the key — All characteristic speeds of the Maxwell distribution (c_mp, c̄, c_rms) scale as √(T/m); the spread σ_c = √(⟨c²⟩ − ⟨c⟩²) therefore also ∝ √T.

C **σ_c ∝ (1)/(T)**

Ruled out: Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

D **σ_c ∝ frac1√(T)**

Ruled out: A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

Q24

The weight of configuration with two ups and three down spins in a system with five spin (1)/(2) particles is

A 120

B 60

C 20

D 10

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Thermodynamics – General

PYQ FREQUENCY
Very High · 13 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'q counts the thermally accessible states'.

Correct Answer D 10

CONCEPT

The partition function q = Σ g_i e^(−ε_i/kT) links microscopic levels to thermodynamics: U = $NkT^2(\partial \ln q/\partial T)$, S = Nk ln(q/N) + U/T + Nk (indistinguishable), A = −kT ln Q. Translational, rotational, vibrational and electronic contributions multiply; equipartition gives ½kT per quadratic term at high T.

↓

LOGIC / WORKING

- W = 5!/(2! 3!) = 10 ways to choose which two of the five spins are up.
- Therefore the answer is (D).

FINAL: (D) 10

SHORTCUT / EXAM TRICK

Classical C_v: monatomic 3/2 R; diatomic 5/2 R (vibration frozen) → 7/2 R at high T.

COMMON MISTAKE

Forgetting the symmetry number σ (2 for homonuclear) in q_{rot}; mixing Q (system) with q (molecule).

EXAM TIP

A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

MEMORY TRICK

'q counts the thermally accessible states'.

Why the Other Options Are Wrong

Correct answer: D

A **120**

Why (D) is the key — W = 5!/(2! 3!) = 10 ways to choose which two of the five spins are up.

B **60**

Ruled out: Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

C **20**

Ruled out: A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

Q25

The term symbol for the ground state of a metal ion is $^3P_2$. The residual entropy of a crystal of a salt of this metal ion at 0 K is :

A. k_B ln 1

B. k_B ln 3

C. k_B ln 5

D. k_B ln 7

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Thermodynamics – General

PYQ FREQUENCY
Very High · 13 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'q counts the thermally accessible states'.

Correct Answer C k_B ln 5

CONCEPT

The partition function q = Σ g_i e^(−ε_i/kT) links microscopic levels to thermodynamics: U = NkT²(∂ln q/∂T), S = Nk ln(q/N) + U/T + Nk (indistinguishable), A = −kT ln Q. Translational, rotational, vibrational and electronic contributions multiply; equipartition gives ½kT per quadratic term at high T.

↓

LOGIC / WORKING

- A $^3P_2$ ground level is (2J+1) = 5-fold degenerate. If the degeneracy is not lifted at 0 K the residual entropy per ion is k_B ln 5. (Bank key (d) ln 7 — corrected.)
- Therefore the answer is (C).

FINAL: (C) k_B ln 5

SHORTCUT / EXAM TRICK

Classical C_v: monatomic 3/2 R; diatomic 5/2 R (vibration frozen) → 7/2 R at high T.

COMMON MISTAKE

Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

EXAM TIP

A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

MEMORY TRICK

'q counts the thermally accessible states'.

Why the Other Options Are Wrong

Correct answer: C

A — **k_B ln 1**

Why (C) is the key — A $^3P_2$ ground level is (2J+1) = 5-fold degenerate. If the degeneracy is not lifted at 0 K the residual entropy per ion is k_B ln 5. (Bank key (d) ln 7 — corrected.)

B — **k_B ln 3**

Ruled out: Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

D — **k_B ln 7**

Ruled out: A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

Q26

Consider a two-level system in which the excited state, separated from the ground state by energy ε, is doubly degenerate. The fraction of the molecules in the excited state, as T → ∞ is

A (1)/(2)

B -(1)/(2)

C (2)/(3)

D 1

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Thermodynamics – General

PYQ FREQUENCY
Very High · 13 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'q counts the thermally accessible states'.

Correct Answer C (2)/(3)

CONCEPT

The partition function $q = \Sigma\, g_i\, e^{(-\varepsilon_i/kT)}$ links microscopic levels to thermodynamics: $U = NkT^2(\partial \ln q/\partial T)$, $S = Nk \ln(q/N) + U/T + Nk$ (indistinguishable), $A = -kT \ln Q$. Translational, rotational, vibrational and electronic contributions multiply; equipartition gives ½kT per quadratic term at high T.

↓

LOGIC / WORKING

- $q = 1 + 2e^{-\varepsilon/kT}$; fraction excited $= 2e^{-\varepsilon/kT}/(1 + 2e^{-\varepsilon/kT}) \rightarrow 2/3$ as $T \rightarrow \infty$ (all three states equally populated).
- Therefore the answer is (C).

FINAL: (C) (2)/(3)

SHORTCUT / EXAM TRICK

Classical C_v: monatomic 3/2 R; diatomic 5/2 R (vibration frozen) → 7/2 R at high T.

COMMON MISTAKE

Forgetting the symmetry number σ (2 for homonuclear) in q_{rot}; mixing Q (system) with q (molecule).

EXAM TIP

A degree of freedom contributes R/2 to C_v only when $kT \gg$ its level spacing.

MEMORY TRICK

'q counts the thermally accessible states'.

Why the Other Options Are Wrong

Correct answer: C

A **(1)/(2)**

Why (C) is the key — q = 1 + 2e^{−ε/kT}; fraction excited = 2e^{−ε/kT}/(1 + 2e^{−ε/kT}) → 2/3 as T → ∞ (all three states equally populated).

B **-(1)/(2)**

Ruled out: Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

D **1**

Ruled out: A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

Q27

The term symbol for the ground state of nitrogen atoms is

A. $^3P_0$

B. $^4P_3/2$

C. $^1P_1$

D. $^4S_3/2$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Thermodynamics – General

PYQ FREQUENCY
Very High · 13 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'q counts the thermally accessible states'.

Correct Answer D $^4S_{3}/2$

CONCEPT

The partition function q = Σ g_i e^(−ε_i/kT) links microscopic levels to thermodynamics: U = $NkT^2(\partial \ln q/\partial T)$, S = Nk ln(q/N) + U/T + Nk (indistinguishable), A = −kT ln Q. Translational, rotational, vibrational and electronic contributions multiply; equipartition gives ½kT per quadratic term at high T.

↓

LOGIC / WORKING

- N: $2p^3$ half-filled, Hund → S = 3/2, L = 0 → $^4S_{3/2}$. (Bank key (a) $^3P_0$ is wrong; $^3P_0$ belongs to C, not N — corrected.)
- Therefore the answer is (D).

FINAL: (D) $^4S_{3}/2$

SHORTCUT / EXAM TRICK

Classical C_v: monatomic 3/2 R; diatomic 5/2 R (vibration frozen) → 7/2 R at high T.

COMMON MISTAKE

Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

EXAM TIP

A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

MEMORY TRICK

'q counts the thermally accessible states'.

Why the Other Options Are Wrong

Correct answer: D

A $^3P_0$

Why (D) is the key — N: $2p^3$ half-filled, Hund → S = 3/2, L = 0 → $^4S_{3/2}$. (Bank key (a) $^3P_0$ is wrong; $^3P_0$ belongs to C, not N — corrected.)

B $^4P_3/2$

Ruled out: Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

C $^1P_1$

Ruled out: A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

Q28

A system has 100 degenerate energy levels and 100 bosons are kept in it. Find the entropy of the system at equilibrium

A. 10^{-2} k_b

B. 10^{2} k_b

C. 460.0 k_b

D. 4.606 k_b

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Thermodynamics – General

PYQ FREQUENCY
Very High · 13 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'q counts the thermally accessible states'.

Correct Answer B 10^2 k_b

CONCEPT

The partition function q = Σ g_i e^(−ε_i/kT) links microscopic levels to thermodynamics: U = $NkT^2(\partial \ln q/\partial T)$, S = Nk ln(q/N) + U/T + Nk (indistinguishable), A = −kT ln Q. Translational, rotational, vibrational and electronic contributions multiply; equipartition gives ½kT per quadratic term at high T.

↓

LOGIC / WORKING

- Bosons: W = (N + g − 1)!/[N!(g − 1)!] = 199!/(100! 99!). Stirling: ln W ≈ 2N ln 2 ≈ 138 → S = k ln W ≈ 1.4×10^2 k_B ≈ 10^2 k_B.
- Therefore the answer is (B).

FINAL: (B) 10^2 k_b

SHORTCUT / EXAM TRICK

Classical C_v: monatomic 3/2 R; diatomic 5/2 R (vibration frozen) → 7/2 R at high T.

COMMON MISTAKE

Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

EXAM TIP

A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

MEMORY TRICK

'q counts the thermally accessible states'.

Why the Other Options Are Wrong

Correct answer: B

A **10^{-2} k_b**

Why (B) is the key — Bosons: W = (N + g − 1)!/[N!(g − 1)!] = 199!/(100! 99!). Stirling: ln W ≈ 2N ln 2 ≈ 138 → S = k ln W ≈ 1.4×10^2 k_B ≈ 10^2 k_B.

C **460.0 k_b**

Ruled out: Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

D **4.606 k_b**

Ruled out: A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

Q29

The first excited state ($^2P_{1/2}$) of fluorine lies at an energy of 400 cm^{-1} above the ground state ($^2P_{3/2}$). The fraction of Fluorine atoms in the first excited state at k_BT = 420 cm^{-1} is close to

A (1)/(1+e)

B (1)/(2+e)

C (1)/(1+4e)

D (1)/(1+2e)

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Thermodynamics – General

PYQ FREQUENCY
Very High · 13 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'q counts the thermally accessible states'.

Statistical Thermodynamics – General

Correct Answer D (1)/(1+2e)

CONCEPT

The partition function q = Σ g_i e^(−ε_i/kT) links microscopic levels to thermodynamics: U = NkT²(∂ln q/∂T), S = Nk ln(q/N) + U/T + Nk (indistinguishable), A = −kT ln Q. Translational, rotational, vibrational and electronic contributions multiply; equipartition gives ½kT per quadratic term at high T.

↓

LOGIC / WORKING

- g($^2P_{3/2}$) = 4, g($^2P_{1/2}$) = 2. Fraction = 2e^{−400/420}/(4 + 2e^{−400/420}) = 1/(1 + 2e^{0.95}) ≈ 1/(1 + 2e).
- Therefore the answer is (D).

FINAL: (D) (1)/(1+2e)

SHORTCUT / EXAM TRICK

Classical C_v: monatomic 3/2 R; diatomic 5/2 R (vibration frozen) → 7/2 R at high T.

COMMON MISTAKE

Forgetting the symmetry number σ (2 for homonuclear) in q_{rot}; mixing Q (system) with q (molecule).

EXAM TIP

A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

MEMORY TRICK

'q counts the thermally accessible states'.

Why the Other Options Are Wrong

Correct answer: D

A **(1)/(1+e)**

Why (D) is the key — g(²P₃/₂) = 4, g(²P₁/₂) = 2. Fraction = 2e^{−400/420}/(4 + 2e^{−400/420}) = 1/(1 + 2e^{0.95}) ≈ 1/(1 + 2e).

B **(1)/(2+e)**

Ruled out: Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

C **(1)/(1+4e)**

Ruled out: A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

Q30

The difference between standard molar entropies of two mono-atomic gases (A) and (B) (S_m,A^0-S_m,B^0) at a given temperature is (given that the molar mass of (A) is twice the molar mass of (B)

A. (3)/(2)Rln 2

B. Rln 2

C. (5)/(2)Rln 2

D. (7)/(2)Rln 2

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Thermodynamics – General

PYQ FREQUENCY
Very High · 13 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'q counts the thermally accessible states'.

Correct Answer A (3)/(2)Rln 2

CONCEPT

The partition function q = Σ g_i e^(−ε_i/kT) links microscopic levels to thermodynamics: U = $NkT^2(\partial \ln q/\partial T)$, S = Nk ln(q/N) + U/T + Nk (indistinguishable), A = −kT ln Q. Translational, rotational, vibrational and electronic contributions multiply; equipartition gives ½kT per quadratic term at high T.

↓

LOGIC / WORKING

- Sackur–Tetrode: S_m contains (3/2)R ln M. $S_A - S_B = (3/2)R \ln(M_A/M_B) = (3/2)R \ln 2$.
- Therefore the answer is (A).

FINAL: (A) (3)/(2)Rln 2

SHORTCUT / EXAM TRICK

Classical C_v: monatomic 3/2 R; diatomic 5/2 R (vibration frozen) → 7/2 R at high T.

COMMON MISTAKE

Forgetting the symmetry number σ (2 for homonuclear) in q_{rot}; mixing Q (system) with q (molecule).

EXAM TIP

A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

MEMORY TRICK

'q counts the thermally accessible states'.

Why the Other Options Are Wrong

Correct answer: A

B **Rln 2**

Why (A) is the key — Sackur–Tetrode: S_m contains (3/2)R ln M. S_A − S_B = (3/2)R ln(M_A/M_B) = (3/2)R ln 2.

C **(5)/(2)Rln 2**

Ruled out: Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

D **(7)/(2)Rln 2**

Ruled out: A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

Q31

The vibrational partition function for a molecule with fundamental frequency ν is given by

A. exp(-(ħν)/(k_mathrm BT))

B. [1-exp(-(ħν)/(k_mathrm BT))]$^{-1}$

C. exp(-(ħν)/(k_mathrm BT))[1-exp-((ħν)/(k_mathrm BT))]$^{-1}$

D. exp(-(ħν)/(2k_mathrm BT))[1-exp-((ħν)/(k_mathrm BT))]$^{-1}$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Thermodynamics – General

PYQ FREQUENCY
Very High · 13 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'q counts the thermally accessible states'.

Correct Answer D exp(-(ħν)/(2k_mathrm BT))[1-exp-((ħν)/(k_mathrm BT))]⁻¹

CONCEPT

The partition function q = Σ g_i e^(−$ε_i$/kT) links microscopic levels to thermodynamics: U = NkT²(∂ln q/∂T), S = Nk ln(q/N) + U/T + Nk (indistinguishable), A = −kT ln Q. Translational, rotational, vibrational and electronic contributions multiply; equipartition gives ½kT per quadratic term at high T.

↓

LOGIC / WORKING

- With zero-point energy included, $ε_v$ = (v + ½)hν: q_vib = e^{−hν/2kT} Σe^{−vhν/kT} = e^{−hν/2kT}/(1 − e^{−hν/kT}). Option (b) is the form with energies measured from the ZPE.
- Therefore the answer is (D).

FINAL: (D) exp(-(ħν)/(2k_mathrm BT))[1-exp-((ħν)/(k_mathrm BT))]⁻¹

SHORTCUT / EXAM TRICK

Classical C_v: monatomic 3/2 R; diatomic 5/2 R (vibration frozen) → 7/2 R at high T.

COMMON MISTAKE

Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

EXAM TIP

A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

MEMORY TRICK

'q counts the thermally accessible states'.

Why the Other Options Are Wrong

Correct answer: D

A **exp(-(ħν)/(k_mathrm BT))**

Why (D) is the key — With zero-point energy included, $\varepsilon_v = (v + ½)h\nu$: q_vib = e^{−hν/2kT} Σe^{−vhν/kT} = e^{−hν/2kT}/(1 − e^{−hν/kT}). Option (b) is the form with energies measured from the ZPE.

B **$[1-\exp(-(\hbar\nu)/(k_{mathrm}\ BT))]^{-1}$**

Ruled out: Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

C **$\exp(-(\hbar\nu)/(k_{mathrm}\ BT))[1-\exp-((\hbar\nu)/(k_{mathrm}\ BT))]^{-1}$**

Ruled out: A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

Q32

Given that the mean speed of H_2 is 1.78 km s^{-1}, the mean speed of D_2 will be

A. 1.26 km s^{-1}

B. 2.52 km s^{-1}

C. 5.04 km s^{-1}

D. 3.17 km s^{-1}

QUESTION INSIGHTS

ESTIMATED TIME
1–1.5 min

DIFFICULTY
Easy

CONCEPT TESTED
Statistical Thermodynamics – General

PYQ FREQUENCY
Very High · 13 papers

REVISION PRIORITY
★★★☆☆

EXPECTED LEVEL
Part B

MEMORY HOOK
'q counts the thermally accessible states'.

Correct Answer A 1.26 km s⁻¹

CONCEPT

The partition function q = Σ g_i e^(−ε_i/kT) links microscopic levels to thermodynamics: U = NkT²(∂ln q/∂T), S = Nk ln(q/N) + U/T + Nk (indistinguishable), A = −kT ln Q. Translational, rotational, vibrational and electronic contributions multiply; equipartition gives ½kT per quadratic term at high T.

↓

LOGIC / WORKING

- $\bar{c} = \sqrt{(8kT/\pi m)} \propto 1/\sqrt{M}$. D_2 (M = 4) vs H_2 (2): 1.78/√2 = 1.26 km s⁻¹.
- Therefore the answer is (A).

FINAL: (A) 1.26 km s⁻¹

SHORTCUT / EXAM TRICK

Classical C_v: monatomic 3/2 R; diatomic 5/2 R (vibration frozen) → 7/2 R at high T.

COMMON MISTAKE

Forgetting the symmetry number σ (2 for homonuclear) in q_{rot}; mixing Q (system) with q (molecule).

EXAM TIP

A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

MEMORY TRICK

'q counts the thermally accessible states'.

Why the Other Options Are Wrong

Correct answer: A

B **2.52 km s⁻¹**

Why (A) is the key — $\bar{c} = \sqrt{(8kT/\pi m)} \propto 1/\sqrt{M}$. D_2 (M = 4) vs H_2 (2): $1.78/\sqrt{2} = 1.26$ km s^{-1}.

C **5.04 km s⁻¹**

Ruled out: Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

D **3.17 km s⁻¹**

Ruled out: A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

Q33

As the temperature tends to infinity, the partition function for a two-level system is

A. 0

B. 1

C. 2

D. infinity

QUESTION INSIGHTS

ESTIMATED TIME
1–1.5 min

DIFFICULTY
Easy

CONCEPT TESTED
Statistical Thermodynamics – General

PYQ FREQUENCY
Very High · 13 papers

REVISION PRIORITY
★★★☆☆

EXPECTED LEVEL
Part B

MEMORY HOOK
'q counts the thermally accessible states'.

Correct Answer C 2

CONCEPT

The partition function q = Σ g_i e^(−$ε_i$/kT) links microscopic levels to thermodynamics: U = NkT²(∂ln q/∂T), S = Nk ln(q/N) + U/T + Nk (indistinguishable), A = −kT ln Q. Translational, rotational, vibrational and electronic contributions multiply; equipartition gives ½kT per quadratic term at high T.

↓

LOGIC / WORKING

- q = 1 + e^{−ε/kT} → 1 + 1 = 2 as T → ∞ (both states equally populated).
- Therefore the answer is (C).

FINAL: (C) 2

SHORTCUT / EXAM TRICK

Classical C_v: monatomic 3/2 R; diatomic 5/2 R (vibration frozen) → 7/2 R at high T.

COMMON MISTAKE

Forgetting the symmetry number σ (2 for homonuclear) in q_{rot}; mixing Q (system) with q (molecule).

EXAM TIP

A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

MEMORY TRICK

'q counts the thermally accessible states'.

Why the Other Options Are Wrong

Correct answer: C

A **0**

Why (C) is the key — q = 1 + e^{−ε/kT} → 1 + 1 = 2 as T → ∞ (both states equally populated).

B **1**

Ruled out: Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

D **infinity**

Ruled out: A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

Q34

Assuming H_2 and HD molecules having equal lengths, the ratio of the rotational partition functions of these molecules, at temperature above 100 K is

A) 3/8

B) 3/4

C) 1/2

D) 2/3

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Thermodynamics – General

PYQ FREQUENCY
Very High · 13 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'q counts the thermally accessible states'.

Correct Answer A 3/8

CONCEPT

The partition function q = Σ g_i e^(−ε_i/kT) links microscopic levels to thermodynamics: U = NkT²(∂ln q/∂T), S = Nk ln(q/N) + U/T + Nk (indistinguishable), A = −kT ln Q. Translational, rotational, vibrational and electronic contributions multiply; equipartition gives ½kT per quadratic term at high T.

↓

LOGIC / WORKING

- q_rot ∝ I/σ ∝ μ/σ. H_2: μ = ½, σ = 2 → ¼. HD: μ = 2/3, σ = 1 → 2/3. Ratio = (1/4)/(2/3) = 3/8.
- Therefore the answer is (A).

FINAL: (A) 3/8

SHORTCUT / EXAM TRICK

Classical C_v: monatomic 3/2 R; diatomic 5/2 R (vibration frozen) → 7/2 R at high T.

COMMON MISTAKE

Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

EXAM TIP

A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

MEMORY TRICK

'q counts the thermally accessible states'.

Why the Other Options Are Wrong

Correct answer: A

B **3/4**

Why (A) is the key — q_rot ∝ I/σ ∝ μ/σ. H_2: μ = ½, σ = 2 → ¼. HD: μ = 2/3, σ = 1 → 2/3. Ratio = (1/4)/(2/3) = 3/8.

C **1/2**

Ruled out: Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

D **2/3**

Ruled out: A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

Q35

At T = 300 K, the thermal energy (k_BT) in cm^{-1} is approximately

A. 20000

B. 8000

C. 5000

D. 200

QUESTION INSIGHTS

ESTIMATED TIME
1–1.5 min

DIFFICULTY
Easy

CONCEPT TESTED
Statistical Thermodynamics – General

PYQ FREQUENCY
Very High · 13 papers

REVISION PRIORITY
★★★☆☆

EXPECTED LEVEL
Part B

MEMORY HOOK
'q counts the thermally accessible states'.

Correct Answer D 200

CONCEPT

The partition function $q = \Sigma\, g_i\, e^{(-\varepsilon_i/kT)}$ links microscopic levels to thermodynamics: $U = NkT^2(\partial \ln q/\partial T)$, $S = Nk \ln(q/N) + U/T + Nk$ (indistinguishable), $A = -kT \ln Q$. Translational, rotational, vibrational and electronic contributions multiply; equipartition gives ½kT per quadratic term at high T.

↓

LOGIC / WORKING

- $k_B T/hc = 0.695\ cm^{-1}\ K^{-1} \times 300\ K \approx 208\ cm^{-1} \approx 200\ cm^{-1}$ (≈ 2.5 kJ mol⁻¹, 0.026 eV).
- Therefore the answer is (D).

FINAL: (D) 200

SHORTCUT / EXAM TRICK

Classical C_v: monatomic 3/2 R; diatomic 5/2 R (vibration frozen) → 7/2 R at high T.

COMMON MISTAKE

Forgetting the symmetry number σ (2 for homonuclear) in q_{rot}; mixing Q (system) with q (molecule).

EXAM TIP

A degree of freedom contributes R/2 to C_v only when $kT \gg$ its level spacing.

MEMORY TRICK

'q counts the thermally accessible states'.

Why the Other Options Are Wrong

Correct answer: D

A **20000**

Why (D) is the key — $k_B T/hc = 0.695\ cm^{-1}\ K^{-1} \times 300\ K \approx 208\ cm^{-1} \approx 200\ cm^{-1}$ (≈ 2.5 kJ mol^{-1}, 0.026 eV).

B **8000**

Ruled out: Forgetting the symmetry number σ (2 for homonuclear) in q_{rot}; mixing Q (system) with q (molecule).

C **5000**

Ruled out: A degree of freedom contributes R/2 to C_v only when $kT \gg$ its level spacing.

Q36

The total number of ways in which two nonidentical spin-(1)/(2) particles can be oriented relative to a constant magnetic field is:

A 1

B 2

C 3

D 4

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Thermodynamics – General

PYQ FREQUENCY
Very High · 13 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'q counts the thermally accessible states'.

Correct Answer D 4

CONCEPT

The partition function q = Σ g_i e^(−ε_i/kT) links microscopic levels to thermodynamics: U = NkT²(∂ln q/∂T), S = Nk ln(q/N) + U/T + Nk (indistinguishable), A = −kT ln Q. Translational, rotational, vibrational and electronic contributions multiply; equipartition gives ½kT per quadratic term at high T.

↓

LOGIC / WORKING

- Each spin-½ particle has 2 orientations (m = ±½); two distinguishable particles: 2 × 2 = 4 (αα, αβ, βα, ββ).
- Therefore the answer is (D).

FINAL: (D) 4

SHORTCUT / EXAM TRICK

Classical C_v: monatomic 3/2 R; diatomic 5/2 R (vibration frozen) → 7/2 R at high T.

COMMON MISTAKE

Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

EXAM TIP

A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

MEMORY TRICK

'q counts the thermally accessible states'.

Why the Other Options Are Wrong

Correct answer: D

A **1**

Why (D) is the key — Each spin-½ particle has 2 orientations (m = ±½); two distinguishable particles: 2 × 2 = 4 (αα, αβ, βα, ββ).

B **2**

Ruled out: Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

C **3**

Ruled out: A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

Q37

A box of volume V contains one mole of an ideal gas. The probability that all N particles will be found occupying one half of the volume leaving the other half empty is

A. 1/2

B. 2/N

C. (1/2)^N

D. $(1/2)^6N$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Thermodynamics – General

PYQ FREQUENCY
Very High · 13 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'q counts the thermally accessible states'.

Correct Answer C (1/2)^N

CONCEPT

The partition function $q = \Sigma\, g_i\, e^{(-\varepsilon_i/kT)}$ links microscopic levels to thermodynamics: $U = NkT^2(\partial \ln q/\partial T)$, $S = Nk \ln(q/N) + U/T + Nk$ (indistinguishable), $A = -kT \ln Q$. Translational, rotational, vibrational and electronic contributions multiply; equipartition gives ½kT per quadratic term at high T.

↓

LOGIC / WORKING

- Each molecule independently has probability ½ of being in the chosen half; for N independent molecules $P = (½)^N$ — vanishingly small for $N \approx 6\times10^{23}$.
- Therefore the answer is (C).

FINAL: (C) (1/2)^N

SHORTCUT / EXAM TRICK

Classical C_v: monatomic 3/2 R; diatomic 5/2 R (vibration frozen) → 7/2 R at high T.

COMMON MISTAKE

Forgetting the symmetry number σ (2 for homonuclear) in q_{rot}; mixing Q (system) with q (molecule).

EXAM TIP

A degree of freedom contributes R/2 to C_v only when $kT \gg$ its level spacing.

MEMORY TRICK

'q counts the thermally accessible states'.

Why the Other Options Are Wrong

Correct answer: C

A **1/2**

Why (C) is the key — Each molecule independently has probability ½ of being in the chosen half; for N independent molecules P = (½)^N — vanishingly small for N ≈ 6×10^{23}.

B **2/N**

Ruled out: Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

D **$(1/2)^{6}$N**

Ruled out: A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

Q38 A certain molecule can be treated as having only a doubly degenerate state lying at 360 cm^{-1} above the nondegenerate ground state. The approximate temperature (K) at which 15% of the molecule will be in the upper state is

A 500

B 150

C 200

D 300

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Thermodynamics – General

PYQ FREQUENCY
Very High · 13 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'q counts the thermally accessible states'.

Correct Answer C 200

CONCEPT

The partition function q = Σ g_i e^(−$ε_i$/kT) links microscopic levels to thermodynamics: U = NkT²(∂ln q/∂T), S = Nk ln(q/N) + U/T + Nk (indistinguishable), A = −kT ln Q. Translational, rotational, vibrational and electronic contributions multiply; equipartition gives ½kT per quadratic term at high T.

↓

LOGIC / WORKING

- Fraction upper = 2e^{−x}/(1 + 2e^{−x}) = 0.15 → e^{−x} = 0.088 → x = ε/kT = 2.43. ε = 360 cm^{-1} = 360 × 1.4388 K = 518 K → T = 518/2.43 ≈ 213 K ≈ 200 K.
- Therefore the answer is (C).

FINAL: (C) 200

SHORTCUT / EXAM TRICK

Classical C_v: monatomic 3/2 R; diatomic 5/2 R (vibration frozen) → 7/2 R at high T.

COMMON MISTAKE

Forgetting the symmetry number σ (2 for homonuclear) in q_{rot}; mixing Q (system) with q (molecule).

EXAM TIP

A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

MEMORY TRICK

'q counts the thermally accessible states'.

Why the Other Options Are Wrong

Correct answer: C

A **500**

Why (C) is the key — Fraction upper = 2e^{−x}/(1 + 2e^{−x}) = 0.15 → e^{−x} = 0.088 → x = ε/kT = 2.43. ε = 360 cm^{-1} = 360 × 1.4388 K = 518 K → T = 518/2.43 ≈ 213 K ≈ 200 K.

B **150**

Ruled out: Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

D **300**

Ruled out: A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

Q39 The ratio of molecules distributed between two states is 9.22×10^6 at 300K. the difference in energy (in kJ mol^{-1}) of the two states is _____ (Numerical answer type — write the value.)

ANSWER: ≈ 40.0 kJ mol^{-1}

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Thermodynamics – General

PYQ FREQUENCY
Very High · 13 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
N_lower/N_upper = e^{ΔE/kT} → ΔE = RT ln(9.22×10⁶) = 8.314 × 300 × 16.04 = 4.0×10⁴ J mol⁻¹ = 40.0 kJ mol⁻¹.

Q40

For an ideal gas with molar mass M, the molar translational entropy at a given temperature is proportional to

A. $M^{3}/2$

B. $M^{1}/2$

C. e^M

D. ln(M)

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Thermodynamics – General

PYQ FREQUENCY
Very High · 13 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'q counts the thermally accessible states'.

Correct Answer D ln(M)

CONCEPT

The partition function q = Σ g_i e^(−ε_i/kT) links microscopic levels to thermodynamics: U = NkT²(∂ln q/∂T), S = Nk ln(q/N) + U/T + Nk (indistinguishable), A = −kT ln Q. Translational, rotational, vibrational and electronic contributions multiply; equipartition gives ½kT per quadratic term at high T.

↓

LOGIC / WORKING

- Sackur–Tetrode: S_m = R ln[(2πMkT/h²)^{3/2} V_m e^{5/2}/N_A] = (3/2)R ln M + const — i.e. S_trans varies as ln M (the M^{3/2} sits inside the logarithm). (Bank key (b) M^{1/2} — corrected; verify.)
- Therefore the answer is (D).

FINAL: (D) ln(M)

SHORTCUT / EXAM TRICK

Classical C_v: monatomic 3/2 R; diatomic 5/2 R (vibration frozen) → 7/2 R at high T.

COMMON MISTAKE

Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

EXAM TIP

A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

MEMORY TRICK

'q counts the thermally accessible states'.

Why the Other Options Are Wrong

Correct answer: D

A $M^{3}/2$

Why (D) is the key — Sackur–Tetrode: S_m = R ln[(2πMkT/h²)^{3/2} V_m e^{5/2}/N_A] = (3/2)R ln M + const — i.e. S_trans varies as ln M (the M^{3/2} sits inside the logarithm). (Bank key (b) M^{1/2} — corrected; verify.)

B $M^{1}/2$

Ruled out: Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

C e^M

Ruled out: A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

Q41

The rotational partition function of a diatomic molecule with energy levels corresponding to J = 0, 1, is (where, varepsilon is a constant)

A. 1 + e⁻2varepsilon

B. 1 + 3e⁻2varepsilon

C. 1 + e⁻3varepsilon

D. 1 + 3e⁻3varepsilon

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Thermodynamics – General

PYQ FREQUENCY
Very High · 13 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'q counts the thermally accessible states'.

Correct Answer B 1 + 3e¯2varepsilon

CONCEPT

The partition function q = Σ g_i e^(−ε_i/kT) links microscopic levels to thermodynamics: U = NkT²(∂ln q/∂T), S = Nk ln(q/N) + U/T + Nk (indistinguishable), A = −kT ln Q. Translational, rotational, vibrational and electronic contributions multiply; equipartition gives ½kT per quadratic term at high T.

↓

LOGIC / WORKING

- E_J = εJ(J+1), g_J = 2J+1. q = $g_0 e^{o}$ + g_1e^{−2ε} = 1 + 3e^{−2ε}.
- Therefore the answer is (B).

FINAL: (B) 1 + 3e¯2varepsilon

SHORTCUT / EXAM TRICK

Classical C_v: monatomic 3/2 R; diatomic 5/2 R (vibration frozen) → 7/2 R at high T.

COMMON MISTAKE

Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

EXAM TIP

A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

MEMORY TRICK

'q counts the thermally accessible states'.

Why the Other Options Are Wrong

Correct answer: B

A **1 + e⁻2varepsilon**

Why (B) is the key — E_J = εJ(J+1), g_J = 2J+1. q = $g_0 e^{0}$ + $g_1 e^{-2\varepsilon}$ = 1 + 3e^{−2ε}.

C **1 + e⁻3varepsilon**

Ruled out: Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

D **1 + 3e⁻3varepsilon**

Ruled out: A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

Q42

Consider a two-state system at thermal equilibrium with equal degeneracy where the excited state is higher in energy than the ground state by 0.1 eV. The ratio of the population of the excited state to that of the ground state, at a temperature for which k_B T = 0.05 eV, is ___
(Numerical answer type — write the value.)

ANSWER: $e^{-2} \approx 0.135$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Thermodynamics – General

PYQ FREQUENCY
Very High · 13 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
N_upper/N_lower = e^{−ΔE/k_BT} = e^{−0.1/0.05} = e⁻² = 0.135.

Q43

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

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Statistical Thermodynamics – General

PYQ FREQUENCY
Very High · 13 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
'q counts the thermally accessible states'.

Correct Answer A N, V, T

CONCEPT

The partition function q = Σ g_i e^(−ε_i/kT) links microscopic levels to thermodynamics: U = $NkT^2(\partial \ln q/\partial T)$, S = Nk ln(q/N) + U/T + Nk (indistinguishable), A = −kT ln Q. Translational, rotational, vibrational and electronic contributions multiply; equipartition gives ½kT per quadratic term at high T.

↓

LOGIC / WORKING

- Canonical ensemble: closed system in a heat bath — N, V, T fixed. Microcanonical: N, V, E; isothermal–isobaric: N, P, T; grand canonical: μ, V, T.
- Therefore the answer is (A).

FINAL: (A) N, V, T

SHORTCUT / EXAM TRICK

Classical C_v: monatomic 3/2 R; diatomic 5/2 R (vibration frozen) → 7/2 R at high T.

COMMON MISTAKE

Forgetting the symmetry number σ (2 for homonuclear) in q_{rot}; mixing Q (system) with q (molecule).

EXAM TIP

A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

MEMORY TRICK

'q counts the thermally accessible states'.

Why the Other Options Are Wrong

Correct answer: A

B **N, V, E**

Why (A) is the key — Canonical ensemble: closed system in a heat bath — N, V, T fixed. Microcanonical: N, V, E; isothermal–isobaric: N, P, T; grand canonical: μ, V, T.

C **N, P, T**

Ruled out: Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).

D **μ, V, T**

Ruled out: A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

TOPIC REVISION

Statistical Thermodynamics – General

27 PYQs · Last-minute revision

TOPIC SUMMARY

The partition function $q = \Sigma\, g_i\, e^{(-\varepsilon_i/kT)}$ links microscopic levels to thermodynamics: $U = NkT^2(\partial \ln q/\partial T)$, $S = Nk \ln(q/N) + U/T + Nk$ (indistinguishable), $A = -kT \ln Q$. Translational, rotational, vibrational and electronic contributions multiply; equipartition gives ½kT per quadratic term at high T.

IMPORTANT FORMULA SHEET

- $q_{trans} = (2\pi mkT/h^2)^{(3/2)}\, V$
- $q_{rot(linear)} = T/(\sigma\Theta_{rot}) = 8\pi^2 IkT/(\sigma h^2)$
- $q_{vib} = 1/(1 - e^{(-\Theta_{vib}/T)})$ (zero at v=0)
- $U = NkT^2(\partial \ln q/\partial T)_V$; $C_v = (\partial U/\partial T)_V$
- $S = k \ln W$ (Boltzmann)

FREQUENTLY ASKED CONCEPTS

- Equipartition heat capacities (3/2 R, 5/2 R, 7/2 R)
- Symmetry number σ
- High-T and low-T limits of q_vib
- Sackur–Tetrode entropy
- Most probable distribution

COMMON MISTAKES & QUICK NOTES

Watch out:
Forgetting the symmetry number σ (2 for homonuclear) in q_rot; mixing Q (system) with q (molecule).
A degree of freedom contributes R/2 to C_v only when kT ≫ its level spacing.

MOST-REPEATED PYQs & EXPECTED IN EXAM

PYQs in this topic: Q17 Q18 Q19 Q20 Q21 Q22 Q23 Q24 Q25 Q26 Q27 Q28 Q29 Q30 …

Expect 2 question(s) next session on Statistical Thermodynamics – General.

FOR STUDENTS AND EDUCATORS

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Examination News

- Latest updates
- Exam calendar
- Admit cards
- Results
- UG entrance exams
- PG entrance exams
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Vacancies, admit cards, results and exam dates: all in one place

FOR EDUCATORS

Teach from the Question Bank, one question at a time

Find the right questions, teach them in class, then take them with you.

1 Find questions

- Browse
- Question search
- Topic packs

2 Teach one by one

Question Bank

Show each question to students on the board, in your own order.

3 Export

PPTX, DOCX, PNG (zip), HTML, Markdown

Take the paper home after class.

Scan to open Question Bank

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Many more coming soon

My papers

Social groups

Question Paper Analyser

AI question paper generator

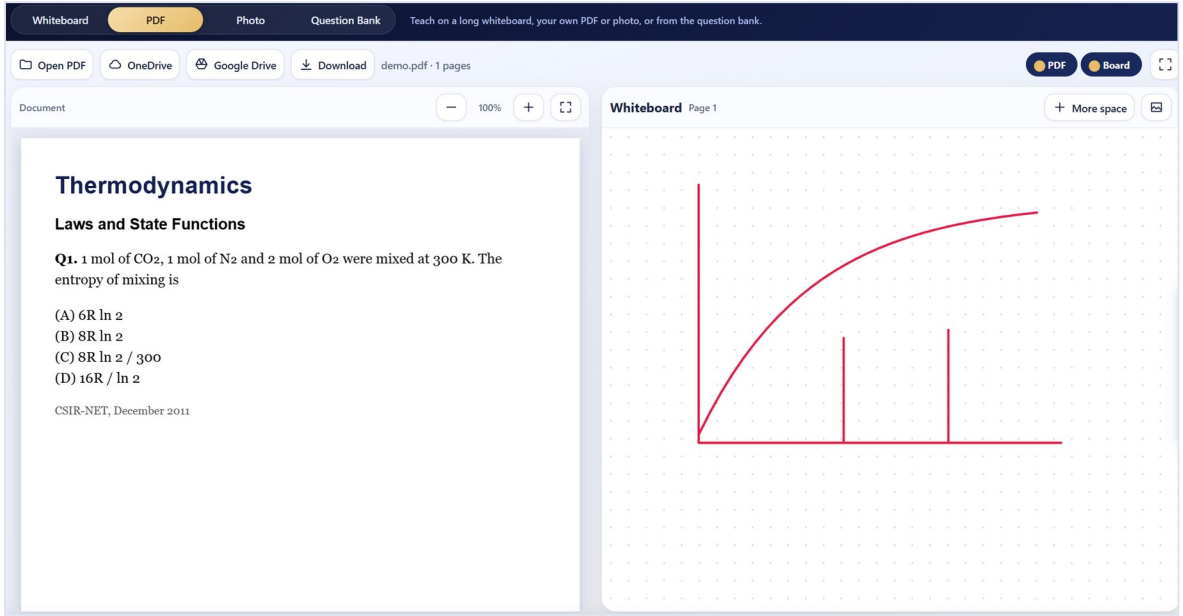
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Chemistry Labs: symmetry and crystals

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Molecular Point Groups

Learn molecular point groups

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Crystal Structure

Explore crystal structures

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Crystal Space Groups

Browse crystal space groups

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EXPLORE AND USE

Chemistry Labs: elements, calculation and drawing

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Periodic Table

Explore the elements

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Chemistry Calculator

Solve chemistry calculations

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