

GATE Chemistry Revision Notes

Physical Chemistry Formula and Problem Solving Book

QUANTUM MODEL SELECTION

Definition :-

Match each problem to box, oscillator, rotor, hydrogenic atom or approximation method before using equations.

Deciding rule :-

Test energy sign, zero-point value and degeneracy.

Key relation :-

box n^2 ; oscillator $v+1/2$; rotor $J(J+1)$; hydrogen $-Z^2/n^2$

GATE clue :-

Keywords about boundaries, vibration, rotation or Coulomb attraction identify the model.

Common mistake :-

Mixing quantum-number rules between models causes fast errors.

Worked cue :-

Use the recognition clue first. Begin with box n^2 ; oscillator $v+1/2$; rotor $J(J+1)$; hydrogen $-Z^2/n^2$, then apply the deciding rule and reject the stated common mistake.

→ Rapid recall: Quantum model selection: T...

→ Mistake repair: Mixing quantum-number ru...

QUANTUM MODEL SELECTION : EXAM ROUTE

Recognize the pattern :-

Keywords about boundaries, vibration, rotation or Coulomb attraction identify the model.

Start from the concept :-

Match each problem to box, oscillator, rotor, hydrogenic atom or approximation method before using equations.

Working relation :-

box n^2 ; oscillator $v+1/2$; rotor $J(J+1)$; hydrogen $-2/n^2$

Solve in this order :

- write the species, state or model clearly
- mark symmetry, charge, spin and conditions
- use the relation before inserting numbers
- test dimensions and the extreme limit

Common mistake :-

Mixing quantum-number rules between models causes fast errors.

One-line decision :-

Test energy sign, zero-point value and degeneracy.

Bottom-line check :-

Verify the relation, condition and trend before accepting the answer.

→ Mini application: Quantum model selectio...

→ Correction cue: Mixing quantum-number ru...

OPERATOR AND EXPECTATION TOOLKIT

Definition :-

Operators represent observables; normalization, eigenvalue equations and expectation values control measurement predictions.

Deciding rule :-

Hermitian observables give real expectation values.

Key relation :-

$$A \psi = a \psi; \text{ average } A = \text{bracket } \psi | A | \psi$$

GATE clue :-

Check whether the state is an eigenstate before claiming zero uncertainty.

Common mistake :-

An average value need not be one measurement outcome.

Final check :-

Confirm the result against the defining assumption, then test the sign, symmetry, charge or limiting chemical trend.

Worked cue :-

Use the recognition clue first. Begin with $A \psi = a \psi$; average $A = \text{bracket } \psi | A | \psi$, then apply the deciding rule and reject the stated common mistake.

Rapid recall :-

Operator and expectation toolkit: Hermitian observables give real expectation values.

OPERATOR AND EXPECTATION TOOLKIT : EXAM ROUTE

Recognize the pattern :-

Check whether the state is an eigenstate before claiming zero uncertainty.

Start from the concept :-

Operators represent observables; normalization, eigenvalue equations and expectation values control measurement predictions.

Working relation :-

$$A \psi = a \psi; \text{ average } A = \langle \psi | A | \psi \rangle$$

Solve in this order :

- write the species, state or model clearly
- mark symmetry, charge, spin and conditions
- use the relation before inserting numbers
- test dimensions and the extreme limit

Common mistake :-

An average value need not be one measurement outcome.

One-line decision :-

Hermitian observables give real expectation values.

Bottom-line check :-

Verify the relation, condition and trend before accepting the answer.

- Mini application: Operator and expectati...
- Correction cue: An average value need no...

SPECTROSCOPY FORMULAS

Definition :-

Rotational, vibrational and electronic spectra use energy gaps, selection rules and transition moments.

Deciding rule :-

Heavier isotopes lower rotational and vibrational spacings.

Key relation :-

rotational spacing $2B$; vibration frequency proportional $\sqrt{k/\mu}$

GATE clue :-

Use symmetry and dipole change before calculating frequency.

Common mistake :-

An existing mode can be spectroscopically inactive.

Final check :-

Confirm the result against the defining assumption, then test the sign, symmetry, charge or limiting chemical trend.

Worked cue :-

Use the recognition clue first. Begin with rotational spacing $2B$; vibration frequency proportional $\sqrt{k/\mu}$, then apply the deciding rule and reject the stated common mistake.

Rapid recall :-

Spectroscopy formulas: Heavier isotopes lower rotational and vibrational spacings.

→ Rapid recall: Spectroscopy formulas: Hea...

SPECTROSCOPY FORMULAS : EXAM ROUTE

Recognize the pattern :-

Use symmetry and dipole change before calculating frequency.

Start from the concept :-

Rotational, vibrational and electronic spectra use energy gaps, selection rules and transition moments.

Working relation :-

rotational spacing $2B$; vibration frequency proportional $\sqrt{k/\mu}$

Solve in this order :

- write the species, state or model clearly
- mark symmetry, charge, spin and conditions
- use the relation before inserting numbers
- test dimensions and the extreme limit

Common mistake :-

An existing mode can be spectroscopically inactive.

One-line decision :-

Heavier isotopes lower rotational and vibrational spacings.

Bottom-line check :-

Verify the relation, condition and trend before accepting the answer.

Mini application :-

Spectroscopy formulas: start from rotational spacing $2B$; vibration frequency proportional $\sqrt{k/\mu}$.

THERMODYNAMIC IDENTITIES

Definition :-

Choose the potential whose natural variables match the process and use exact relations consistently.

Deciding rule :-

At equilibrium the appropriate potential is minimized.

Key relation :-

$$dG = VdP - SdT; \Delta G = \Delta H - T \Delta S$$

GATE clue :-

Mark T , P , V and composition constraints first.

Common mistake :-

A negative ΔG says nothing about rate.

Final check :-

Confirm the result against the defining assumption, then test the sign, symmetry, charge or limiting chemical trend.

Worked cue :-

Use the recognition clue first. Begin with $dG = VdP - SdT$; $\Delta G = \Delta H - T \Delta S$, then apply the deciding rule and reject the stated common mistake.

Rapid recall :-

Thermodynamic identities: At equilibrium the appropriate potential is minimized.

→ Rapid recall: Thermodynamic identities:...

→ Mistake repair: A negative ΔG says...

THERMODYNAMIC IDENTITIES : EXAM ROUTE

Recognize the pattern :-

Mark T , P , V and composition constraints first.

Start from the concept :-

Choose the potential whose natural variables match the process and use exact relations consistently.

Working relation :-

$$dG = VdP - SdT; \Delta G = \Delta H - T \Delta S$$

Solve in this order :

- write the species, state or model clearly
- mark symmetry, charge, spin and conditions
- use the relation before inserting numbers
- test dimensions and the extreme limit

Common mistake :-

A negative ΔG says nothing about rate.

One-line decision :-

At equilibrium the appropriate potential is minimized.

Bottom-line check :-

Verify the relation, condition and trend before accepting the answer.

Mini application :-

Thermodynamic identities: start from $dG = VdP - SdT$;
 $\Delta G = \Delta H - T \Delta S$.

→ Mini application: Thermodynamic identiti...

SOLUTION AND EQUILIBRIUM FORMULAS

Definition :-

Chemical potential, activity, fugacity and reaction quotient extend ideal equations to real mixtures.

Deciding rule :-

Compare Q with K for reaction direction.

Key relation :-

$$\mu = \mu_{\text{standard}} + RT \ln a; \Delta G = \Delta G_{\text{standard}} + RT \ln Q$$

GATE clue :-

Define the standard state before inserting activity.

Common mistake :-

Raw concentration is not automatically a dimensionless activity.

Final check :-

Confirm the result against the defining assumption, then test the sign, symmetry, charge or limiting chemical trend.

Worked cue :-

Use the recognition clue first. Begin with $\mu = \mu_{\text{standard}} + RT \ln a$; $\Delta G = \Delta G_{\text{standard}} + RT \ln Q$, then apply the deciding rule and reject the stated common mistake.

Rapid recall :-

Solution and equilibrium formulas: Compare Q with K for reaction direction.

SOLUTION AND EQUILIBRIUM FORMULAS : EXAM ROUTE

Recognize the pattern :-

Define the standard state before inserting activity.

Start from the concept :-

Chemical potential, activity, fugacity and reaction quotient extend ideal equations to real mixtures.

Working relation :-

$$\mu = \mu_{\text{standard}} + RT \ln a; \Delta G = \Delta G_{\text{standard}} + RT \ln Q$$

Solve in this order :

- write the species, state or model clearly
- mark symmetry, charge, spin and conditions
- use the relation before inserting numbers
- test dimensions and the extreme limit

Common mistake :-

Raw concentration is not automatically a dimensionless activity.

One-line decision :-

Compare Q with K for reaction direction.

Bottom-line check :-

Verify the relation, condition and trend before accepting the answer.

Correction cue :-

Raw concentration is not automatically a dimensionless activity. Instead, Compare Q with K for reaction direction.

ELECTROCHEMISTRY TOOLKIT

Definition :-

Cell potential, free energy, equilibrium and composition are connected through electron transfer number.

Deciding rule :-

At equilibrium E cell is zero and Q equals K .

Key relation :-

$$\Delta G = -nFE; E = E_{\text{standard}} - \frac{RT}{nF} \ln Q/nF$$

GATE clue :-

Balance the redox reaction before forming Q .

Common mistake :-

Do not multiply E standard by stoichiometric coefficients.

Final check :-

Confirm the result against the defining assumption, then test the sign, symmetry, charge or limiting chemical trend.

Worked cue :-

Use the recognition clue first. Begin with $\Delta G = -nFE$; $E = E_{\text{standard}} - \frac{RT}{nF} \ln Q/nF$, then apply the deciding rule and reject the stated common mistake.

Rapid recall :-

Electrochemistry toolkit: At equilibrium E cell is zero and Q equals K .

→ Rapid recall: Electrochemistry toolkit:...

→ Mistake repair: Do not multiply E standa...

ELECTROCHEMISTRY TOOLKIT : EXAM ROUTE

Recognize the pattern :-

Balance the redox reaction before forming Q.

Start from the concept :-

Cell potential, free energy, equilibrium and composition are connected through electron transfer number.

Working relation :-

$$\Delta G = -nFE; E = E_{\text{standard}} - \frac{RT}{nF} \ln Q$$

Solve in this order :

- write the species, state or model clearly
- mark symmetry, charge, spin and conditions
- use the relation before inserting numbers
- test dimensions and the extreme limit

Common mistake :-

Do not multiply E_{standard} by stoichiometric coefficients.

One-line decision :-

At equilibrium E_{cell} is zero and Q equals K.

Bottom-line check :-

Verify the relation, condition and trend before accepting the answer.

Mini application :-

Electrochemistry toolkit: start from $\Delta G = -nFE; E = E_{\text{standard}} - \frac{RT}{nF} \ln Q$.

→ Mini application: Electrochemistry toolk...

PHASE EQUILIBRIUM TOOLKIT

Definition :-

Phase rule, Clapeyron slope, tie lines and lever rule organize phase-diagram questions.

Deciding rule :-

Use the opposite tie-line segment for phase fraction.

Key relation :-

$$F = C - P + 2; dP/dT = \Delta H / (T \Delta V)$$

GATE clue :-

Identify components and phases at the chosen point.

Common mistake :-

Species count is not component count.

Final check :-

Confirm the result against the defining assumption, then test the sign, symmetry, charge or limiting chemical trend.

Worked cue :-

Use the recognition clue first. Begin with $F = C - P + 2$; $dP/dT = \Delta H / (T \Delta V)$, then apply the deciding rule and reject the stated common mistake.

Rapid recall :-

Phase equilibrium toolkit: Use the opposite tie-line segment for phase fraction.

→ Rapid recall: Phase equilibrium toolkit:...

→ Mistake repair: Species count is not com...

PHASE EQUILIBRIUM TOOLKIT : EXAM ROUTE

Recognize the pattern :-

Identify components and phases at the chosen point.

Start from the concept :-

Phase rule, Clapeyron slope, tie lines and lever rule organize phase-diagram questions.

Working relation :-

$$F = C - P + 2; \quad dP/dT = \Delta H / (T \Delta V)$$

Solve in this order :

- write the species, state or model clearly
- mark symmetry, charge, spin and conditions
- use the relation before inserting numbers
- test dimensions and the extreme limit

Common mistake :-

Species count is not component count.

One-line decision :-

Use the opposite tie-line segment for phase fraction.

Bottom-line check :-

Verify the relation, condition and trend before accepting the answer..

Mini application :-

Phase equilibrium toolkit: start from $F = C - P + 2$;
 $dP/dT = \Delta H / (T \Delta V)$.

→ Mini application: Phase equilibrium tool...

KINETIC RATE TOOLKIT

Definition :-

Integrated laws, steady state, Arrhenius and transition-state relations connect concentration and activation parameters to rate.

Deciding rule :-

Units of k reveal overall order.

Key relation :-

$$\ln k = \ln A - E_a/RT; k = \kappa k_B T/h \exp(-\Delta G^\ddagger/RT)$$

GATE clue :-

Determine reaction order from evidence, not overall stoichiometry.

Common mistake :-

The slowest-looking equation is not always rate determining.

Final check :-

Confirm the result against the defining assumption, then test the sign, symmetry, charge or limiting chemical trend.

Worked cue :-

Use the recognition clue first. Begin with $\ln k = \ln A - E_a/RT; k = \kappa k_B T/h \exp(-\Delta G^\ddagger/RT)$, then apply the deciding rule and reject the stated common mistake.

Rapid recall :-

Kinetic rate toolkit: Units of k reveal overall order.

KINETIC RATE TOOLKIT : EXAM ROUTE

Recognize the pattern :-

Determine reaction order from evidence, not overall stoichiometry.

Start from the concept :-

Integrated laws, steady state, Arrhenius and transition-state relations connect concentration and activation parameters to rate.

Working relation :-

$$\ln k = \ln A - E_a/RT; k = \kappa k_B T/h \exp(-\Delta G^\ddagger/RT)$$

Solve in this order :

- write the species, state or model clearly
- mark symmetry, charge, spin and conditions
- use the relation before inserting numbers
- test dimensions and the extreme limit

Common mistake :-

The slowest-looking equation is not always rate determining.

One-line decision :-

Units of k reveal overall order.

Bottom-line check :-

Verify the relation, condition and trend before accepting the answer.

- Mini application: Kinetic rate toolkit:...
- Correction cue: The slowest-looking equa...

STATISTICAL MECHANICS TOOLKIT

Definition :-

Partition functions generate populations and thermodynamic quantities from microscopic energy levels.

Deciding rule :-

Low temperature emphasizes the ground manifold.

Key relation :-

$$q = \sum g \exp(-E/kT); U = kT^2 \frac{d \ln q}{dT}$$

GATE clue :-

Separate independent translational, rotational, vibrational and electronic factors.

Common mistake :-

Degeneracy must be included in population ratios.

Final check :-

Confirm the result against the defining assumption, then test the sign, symmetry, charge or limiting chemical trend.

Worked cue :-

Use the recognition clue first. Begin with $q = \sum g \exp(-E/kT); U = kT^2 \frac{d \ln q}{dT}$, then apply the deciding rule and reject the stated common mistake.

Rapid recall :-

Statistical mechanics toolkit: Low temperature emphasizes the ground manifold.

→ Rapid recall: Statistical mechanics tool...

STATISTICAL MECHANICS TOOLKIT : EXAM ROUTE

Recognize the pattern :-

Separate independent translational, rotational, vibrational and electronic factors.

Start from the concept :-

Partition functions generate populations and thermodynamic quantities from microscopic energy levels.

Working relation :-

$$q = \sum g \exp(-E/kT); U = kT^2 \frac{d \ln q}{dT}$$

Solve in this order :

- write the species, state or model clearly
- mark symmetry, charge, spin and conditions
- use the relation before inserting numbers
- test dimensions and the extreme limit

Common mistake :-

Degeneracy must be included in population ratios.

One-line decision :-

Low temperature emphasizes the ground manifold.

Bottom-line check :-

Verify the relation, condition and trend before accepting the answer.

Mini application :-

Statistical mechanics toolkit: start from $q = \sum g \exp(-E/kT); U = kT^2 \frac{d \ln q}{dT}$.

SURFACE AND COLLOID TOOLKIT

Definition :-

Adsorption, capillarity, micelles and colloidal stability rely on coverage, interfaces and competing interactions.

Deciding rule :-

Strong adsorption can inhibit catalysis by site blocking.

Key relation :-

$$\text{Langmuir theta} = KP/(1+KP); \Delta P = 2 \gamma a/r$$

GATE clue :-

Check low- and high-pressure or concentration limits.

Common mistake :-

Empirical Freundlich behavior cannot predict saturation.

Final check :-

Confirm the result against the defining assumption, then test the sign, symmetry, charge or limiting chemical trend.

Worked cue :-

Use the recognition clue first. Begin with $\text{Langmuir theta} = KP/(1+KP)$; $\Delta P = 2 \gamma a/r$, then apply the deciding rule and reject the stated common mistake.

Rapid recall :-

Surface and colloid toolkit: Strong adsorption can inhibit catalysis by site blocking.

→ Rapid recall: Surface and colloid toolki...

→ Mistake repair: Empirical Freundlich beh...

SURFACE AND COLLOID TOOLKIT : EXAM ROUTE

Recognize the pattern :-

Check low- and high-pressure or concentration limits.

Start from the concept :-

Adsorption, capillarity, micelles and colloidal stability rely on coverage, interfaces and competing interactions.

Working relation :-

$$\text{Langmuir } \theta = \frac{KP}{1+KP}; \Delta P = 2 \gamma a/r$$

Solve in this order :

- write the species, state or model clearly
- mark symmetry, charge, spin and conditions
- use the relation before inserting numbers
- test dimensions and the extreme limit

Common mistake :-

Empirical Freundlich behavior cannot predict saturation.

One-line decision :-

Strong adsorption can inhibit catalysis by site blocking.

Bottom-line check :-

Verify the relation, condition and trend before accepting the answer.

Mini application :-

Surface and colloid toolkit: start from Langmuir $\theta = \frac{KP}{1+KP}$; $\Delta P = 2 \gamma a/r$.

→ Mini application: Surface and colloid to...

CK RECALL : PHYSICAL CHEMISTRY FORMULA AND PROBLEM SOLVING

- Quantum model selection : box n squared; oscillator $v+1/2$; ro...
- Operator and expectati... : $A \psi = a \psi$; average $A = \text{bracket}...$
- Spectroscopy formulas : rotational spacing $2B$; vibration fr...
- Thermodynamic identities : $dG = VdP - SdT$; $\Delta G = \Delta H - ...$
- Solution and equilibri... : $\mu = \mu_{\text{standard}} + RT \ln a$; $\Delta G...$
- Electrochemistry toolkit : $\Delta G = -nFE$; $E = E_{\text{standard}} - RT...$
- Phase equilibrium toolkit : $F = C - P + 2$; $dP/dT = \Delta H / (T \Delta ...)$
- Kinetic rate toolkit : $\ln k = \ln A - E_a/RT$; $k = k_B T / h \exp(...)$
- Statistical mechanics... : $q = \sum g \exp(-E/kT)$; $U = kT \text{ square}...$
- Surface and colloid to... : Langmuir $\theta = KP/(1+KP)$; $\Delta P...$

Recall method :-

Cover the right side, say the relation or deciding rule aloud, then verify it. Repeat weak rows after one hour.

Three-way recall :

- say the definition without looking
- write the relation and assumptions
- name the most likely exam mistake

Final recall pair :-

Quantum model selection and Surface and colloid toolkit:
connect both to their deciding relations.

Self-test :-

Explain Solution and equilibrium formulas in two lines, then state its common mistake.

GATE MISTAKES & FINAL CHECK

Physical Chemistry Formula and Problem Solving Book :-

- Quantum model s... : Mixing quantum-number ru...
- Operator and ex... : An average value need no...
- Spectroscopy fo... : An existing mode can be...
- Thermodynamic i... : A negative ΔG says...
- Solution and eq... : Raw concentration is not...
- Electrochemistr... : Do not multiply E standa...
- Phase equilibri... : Species count is not com...
- Kinetic rate to... : The slowest-looking equa...
- Statistical mec... : Degeneracy must be inclu...
- Surface and col... : Empirical Freundlich beh...

Before selecting the answer :-

- check sign, units and order of magnitude
- check charge, electron count and symmetry
- separate kinetic from thermodynamic claims
- verify whether an approximation is allowed

Final habit :-

Use the quickest decisive rule first. Calculate only when two options survive the conceptual checks.

Repair drill :-

The slowest-looking equation is not always rate determining. Correct rule: Units of k reveal overall order.

- Repair drill: The slowest-looking equati...