Chemical Kinetics

DPP-4 (Order & Molecularity) — SOLUTIONS

"I don't rush. I don't panic. I understand... step by step. Clarity is my strength"

TYPE–1 : Order & Molecularity — Conceptual MCQs

Q.1 Which of the following statements is not correct about order of a reaction?

Explanation

The **order of a reaction** is defined as the sum of the powers of concentration terms in the experimentally determined rate law expression.

Let's check each statement:

- **(1) Correct:** Order can indeed be fractional (e.g., order = 1/2 for decomposition of acetaldehyde).
- **(2) Correct:** Order is always determined experimentally, never from the balanced equation.
- **(3) Incorrect:** Order is *NOT* equal to sum of stoichiometric coefficients. This is true only for elementary reactions (and even then, it's a coincidence, not a rule).
- **(4) Correct:** This is the exact definition of order from the rate law.

Approach & Analogy

Analogy: Imagine you're judging a cooking competition. The **recipe** (balanced equation) tells you the ingredients, but it doesn't tell you which ingredient actually *decides* the final taste. You only know that by *tasting* (experimenting). Similarly, the balanced equation tells you "what reacts," but only experiments reveal the *order*.

Key trick: Whenever you see "always equal to stoichiometric coefficients" — red flag! Order comes from the lab bench, not the blackboard.

Answer

Option (3) is NOT correct. Order is determined experimentally, not from stoichiometric coefficients.

Q.2 Rate law cannot be determined from balanced chemical equation if ______.

Explanation

Rate law can be directly written from the balanced equation **ONLY** for a pure, single-step elementary reaction. In all other cases, experimental determination is required.

Analysis of each option:

- **(1) Correct:** If a reverse reaction is involved, the net rate law has both forward and reverse terms. The balanced equation alone does NOT reveal this — we must experimentally find the contribution of the reverse step.
- **(2) Wrong:** For an elementary reaction, rate law CAN be written directly from the balanced equation. So this is NOT a case where we fail.
- **(3) Correct:** A sequence of elementary reactions (complex reaction) hides the mechanism. Rate depends on the rate-determining step, invisible in the overall balanced equation.
- **(4) Correct:** When any reactant is in excess, its concentration effectively stays constant, giving rise to *pseudo-order* behaviour. The balanced equation doesn't tell us which reactant is in excess — only the experiment does.

Approach & Analogy

Analogy: Think of a multi-stage factory assembly line. The *overall output rate* depends only on the *slowest machine* in the line, not on the average of all machines. If you just look at the factory's "final product equation" (balanced equation), you can't tell which machine is the bottleneck — you need to observe each stage (experiment).

Similarly, a **reverse reaction** adds a "backflow" in the pipeline, and an **excess reactant** is like one machine running so fast it's effectively invisible in the rate — both invisible from the balanced equation alone.

Key insight: The only time balanced equation gives rate law directly = pure elementary reaction. So (2) is the odd one out.

Answer

Options (1), (3), and (4) are all correct — in each of these cases, rate law cannot be determined from the balanced equation alone.

Q.3 Which of the following statements are applicable to a balanced chemical equation of an elementary reaction?

Explanation

For an **elementary reaction** (single-step):

$$\text{Order} = \text{Molecularity} = \text{Sum of stoichiometric coefficients of reactants}$$

This equality holds *only* for elementary reactions because the reaction occurs in one step, so the molecules that collide (molecularity) directly match the concentration dependence (order).

Also, molecularity represents the number of colliding species — this must always be a positive integer (≥ 1). It can never be zero or fractional.

Checking options:

- **(1) Correct:** Order = Molecularity for elementary reactions. ✓
- **(2)** Wrong — they're equal, not less.
- **(3)** Wrong — same reasoning, not greater either.

- **(4) Correct:** Molecularity of an elementary reaction represents real colliding species, so it must be ≥ 1. It can never be zero. ✓

Both (1) and (4) are universally true statements for elementary reactions.

Approach & Analogy

Analogy for (1): In a **one-shot movie scene** (elementary reaction), what you *plan* (molecularity) and what you *shoot* (order) are exactly the same — no editing, no retakes.

Analogy for (4): Can you have a meeting with *zero* people? No — at least one person must be present. Similarly, a reaction needs at least one colliding species (molecularity ≥ 1).

Memory hook: "Elementary = Equal AND non-zero molecularity."

Answer

Options (1) and (4) are both correct — Order equals Molecularity for elementary reactions, and molecularity can never be zero.

Q.4 In any unimolecular reaction ________.

Explanation

A **unimolecular reaction** means molecularity = 1, i.e., only ONE species is involved in the rate-determining step (the slowest step).

Key fact: Since a unimolecular *elementary step* is the rate-determining step, and for such an elementary step:

$$\text{Order of the step} = \text{Molecularity of the step} = 1$$

Checking options:

- **(1) Correct:** By definition, unimolecular = 1 species in the rate-determining step. ✓
- **(2) Correct:** Since the rate-determining step is a unimolecular elementary step, both its order and molecularity equal 1. ✓
- **(3)** Wrong — unimolecular means molecularity = 1, not order = 0.
- **(4)** Only true if the *overall reaction* is also elementary. For a complex reaction whose RDS is unimolecular, the overall order = 1 but the "molecularity of the reaction" as a whole is not defined. So this statement is not universally true for "any" unimolecular reaction.

Options (1) and (2) both describe the same rate-determining step from slightly different angles — both are correct.

Approach & Analogy

Analogy: Think of a **solo performance on stage**. "Unimolecular" is the actor count in the spotlight moment (rate-determining step) — there's just ONE species doing the critical work.

Why (1) and (2) both work: Option (1) says "only one species in RDS" (the physical picture), Option (2) says "order & molecularity of slowest step = 1" (the kinetic consequence). These are two sides of the same coin — both true for any unimolecular reaction.

Why (4) fails: The phrase "molecularity of the reaction" (not of the step) is tricky — for complex reactions, overall molecularity isn't even defined.

Answer

Options (1) and (2) are both correct — only one species is involved in the RDS, and its order & molecularity are both equal to one.

Q.5 For a complex reaction ________.

Explanation

For a **complex reaction** (multi-step), the rate is governed by the *slowest step* (rate-determining step, RDS).

Golden rule:

$$\text{Overall order of complex reaction} = \text{Molecularity of the slowest (RDS) step}$$

Two fundamental truths apply here:

- The slowest step controls the overall rate, and its molecularity (number of species colliding) becomes the order of the overall reaction.
- The slowest step is itself an *elementary step* — and for any elementary step, molecularity is a positive integer (1, 2, or 3). It can NEVER be zero or fractional.
- **(1) Correct:** Order of overall reaction = Molecularity of slowest step. ✓
- **(2)** Wrong — they're equal, not less.
- **(3)** Wrong — same reasoning, not greater either.
- **(4) Correct:** Since the slowest (RDS) is an elementary step, its molecularity must be a positive integer (≥ 1). It is never zero or non-integer. ✓

Both (1) and (4) are true universal statements about complex reactions.

Approach & Analogy

Analogy for (1): Imagine a **relay race where one runner has a broken leg**. No matter how fast the others run, the overall team time is dictated by that slowest runner. The slowest runner's "speed profile" (molecularity of RDS) becomes the team's effective performance (overall order).

Analogy for (4): You can have 1, 2, or 3 people in a "huddle" (elementary step molecularity) — but you can't have 0 people or 1.5 people in a huddle. Physical reality forces molecularity to be a positive whole number.

Mantra: "Order of complex = Molecularity of slowest AND molecularity is always a positive integer."

Answer

Options (1) and (4) are both correct — overall order equals molecularity of the slowest step, AND the slowest step's molecularity is never zero or non-integer.

Q.6 How can the rate law of the reaction $2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$ be determined?

Explanation

Even though the reaction *looks* simple (3 molecules reacting), we cannot assume it's elementary. The reaction could proceed through intermediates.

Rate laws are ALWAYS determined experimentally, regardless of how the balanced equation appears. Scientists do this by:
- Keeping concentration of one reactant constant and varying the other
- Measuring how the initial rate changes
- Using the method of initial rates to find the order with respect to each reactant

Checking options:
- **(1)** Wrong — stoichiometric coefficients do not give rate law.
- **(2) Correct:** This is exactly how rate laws are determined in the lab.
- **(3)** Wrong — assumption without verification is unscientific.
- **(4)** Molecularity ≠ Rate law for complex reactions.

Approach & Analogy

Analogy: Imagine you want to know "how much does a car's speed depend on fuel injection rate?" You wouldn't guess from the car's blueprint (balanced equation). You'd put it on a dyno and *measure* (experiment).

Rule of thumb: Unless explicitly stated "elementary reaction," always go with experimental determination.

Answer

Option (2) — By experimentally measuring how the rate changes with the concentration of each reactant.

Q.7 For which type of reactions do order and molecularity have the same value?

Explanation

Order = Molecularity **ONLY** for **simple, single-step elementary reactions**.

Reasoning:
- In an elementary reaction, the reaction happens in one collision, so the species that collide (molecularity) exactly determine the rate dependence (order).
- For complex reactions, the overall balanced equation hides multiple steps, so order (from experiment) generally differs from the sum of stoichiometric coefficients.

Checking options:
- **(1)** Wrong — complex reactions have mismatch between order and molecularity.
- **(2)** Catalyst affects rate but not this equality condition.
- **(3) Correct:** Single-step elementary reactions are the only place where both coincide.
- **(4)** Zero-order reactions have order = 0 but molecularity ≥ 1 — they're NOT equal.

Approach & Analogy

Analogy: In a **quick snapshot photo**, what you frame (molecularity) and what you capture (order) are identical — one click, one image. But in a **time-lapse video** (complex reaction), you plan many frames but the final output depends on editing (rate-determining step).

Remember: Simple one-step = both equal. Multi-step = they diverge.

Answer

Option (3) — Simple (single-step) elementary reactions.

Q.8 For a zero order reaction, will the molecularity be equal to zero?

Explanation

No! Order and molecularity are fundamentally different concepts:
- **Order** = experimental power of concentration in rate law → CAN be zero.
- **Molecularity** = number of species colliding → CANNOT be zero (at least 1 species must be present for any reaction).

Example: Photochemical decomposition of HI on a gold surface is zero-order, but molecularly, HI molecules are still involved (molecularity ≥ 1).

Checking options:
- **(1)** Wrong — order and molecularity are not always equal.
- **(2)** The reasoning about rate independence is true, but that doesn't make molecularity zero.
- **(3) Correct:** Perfect justification — at least one species must collide.
- **(4)** "Equal to two" is arbitrary — no rule forces this.

Approach & Analogy

Analogy: Imagine a **restaurant that serves food at a fixed rate regardless of how many customers come** (zero order — rate independent of concentration). But does that mean **zero chefs** are cooking? Of course not! At least one chef must be in the kitchen (molecularity ≥ 1).

Key distinction: Zero *rate dependence* ≠ Zero *participants*.

Answer

Option (3) — No, because molecularity cannot be zero; at least one species must collide.

Q.9 Why can the molecularity of any reaction never be equal to zero?

Explanation

Molecularity = number of reacting species (atoms, ions, molecules) that collide *simultaneously* in an elementary reaction.

Logic: If molecularity = 0, it means zero species are colliding → no collision → no reaction. So, by definition, molecularity must be at least 1 (a unimolecular decomposition is the minimum).

Checking options:
- **(1)** Wrong — molecularity is a *theoretical* quantity, not experimental.
- **(2) Correct:** Exactly the right reasoning based on the definition.
- **(3)** Confuses order and molecularity.
- **(4)** Partially true but weak reasoning — this is about balanced equations, not collision theory.

Approach & Analogy

Analogy: Can you have a **handshake with zero hands**? No — at least one hand (one species) must be there. Similarly, a reaction needs at least one species to transform.

Core definition lock-in: Molecularity counts real physical participants. Zero participants = no event.

Answer

Option (2) — Because molecularity is the number of species colliding, and at least one species must be present for a reaction to occur.

Q.10 Why is molecularity applicable only to elementary reactions, while order is applicable to both elementary and complex reactions?

Explanation

The fundamental difference:

- **Molecularity** is a *theoretical* concept based on the *mechanism* of a single elementary step. If a reaction has multiple steps (complex), there's no single "molecularity" for the overall reaction — each step has its own.
- **Order** is an *experimental* quantity derived from the rate law, which can be measured for ANY reaction (simple or complex) by observing how rate varies with concentration.

So, for a complex reaction, we can't assign a single molecularity, but we CAN experimentally determine an overall order.

Checking options:

- **(1) Correct:** Captures both the theoretical vs. experimental distinction perfectly.
- **(2)** Nonsense — complex reactions absolutely have reactants.
- **(3)** Wrong — molecularity is integer, order can be fractional (opposite claim).
- **(4)** Neither depends primarily on temperature in this distinction.

Approach & Analogy

Analogy: Molecularity is like the *screenplay's written cast list* for one scene (single step) — only meaningful if you're looking at one scene. **Order** is like the *audience's overall rating* of the whole movie — you can rate any movie (any reaction), simple or complex.

Theoretical (on paper, single step) vs. Experimental (in the audience, any movie).

Answer

Option (1) — Because molecularity is theoretical (defined for a single step), whereas order is experimentally determined from the rate law of any reaction.

Q.11 Why can we not determine the order of a reaction by taking into consideration the balanced chemical equation?

Explanation

Two strong reasons:

1. The balanced equation shows the *net overall stoichiometry*, but doesn't reveal the actual step-by-step mechanism. Without knowing the rate-determining step, you can't write the rate law.
2. The balanced equation at best tells us about molecularity (if elementary), but order is a fundamentally *experimental* quantity.

Both reasons (1) and (3) in the options are correct and complementary.

Checking options:

- **(1) Correct:** Mechanism is hidden in the balanced equation.
- **(2)** Wrong — stoichiometric coefficients often do NOT equal the order.

- **(3) Correct:** Order must be experimental; balanced equation gives molecularity info at best.
- **(4) Most Correct:** Both (1) and (3) together give the full picture.

Approach & Analogy

Analogy: Think of a **restaurant menu**. The menu tells you *what ingredients go into the final dish* (balanced equation), but it doesn't tell you *the exact cooking sequence* (mechanism) or *how long each step takes* (rate-determining step). To know which step is slowest (and thus controls the total time), you'd have to actually watch the chef cook (experiment).

Both reasons combined = complete answer.

Answer

Option (4) — Both (1) and (3).

TYPE–2 : Assertion & Reason

Q.12 **Assertion:** Order of the reaction can be zero or fractional.
Reason: We cannot determine order from balanced chemical equation.

Explanation

Assertion analysis: TRUE. Order can be:
- Zero (e.g., decomposition of HI on a gold surface)
- Fractional (e.g., decomposition of acetaldehyde, order = 3/2)
- Negative in some inhibition reactions

Reason analysis: TRUE. Order is strictly an experimental quantity; the balanced equation only gives stoichiometry, not kinetics.

Does Reason explain Assertion?
The reason ("cannot determine from balanced equation") tells us *why* we need experiments, but doesn't specifically explain *why* order can be zero or fractional. Those unusual values arise from the actual reaction mechanism, not just from the unavailability of the balanced equation route.

So: Both are true, but reason does NOT correctly explain the assertion.

Approach & Analogy

Analogy: Assertion: "The weather can be freezing or scorching." True.
Reason: "We can't predict weather from a calendar alone." Also true.
But does "can't use calendar" *explain* why weather varies so wildly? No — weather variability comes from atmospheric physics, not from calendar limitations.

Both statements are independently true, but the reason doesn't logically cause the assertion.

Answer

Option (2) — Both assertion and reason are correct, but reason does NOT explain assertion.

Q.13 **Assertion:** Order and molecularity are same.

Reason: Order is determined experimentally and molecularity is the sum of the stoichiometric coefficient of rate determining elementary step.

Explanation

Assertion analysis: FALSE (in general).
Order and molecularity are equal *only* for single-step elementary reactions. For complex reactions, they can differ. The assertion states them as universally same, which is incorrect.

Reason analysis: TRUE.

- Order is indeed determined experimentally. ✓
- Molecularity of the rate-determining elementary step equals the sum of the stoichiometric coefficients of the reactants in that step. ✓

So: Assertion is wrong, Reason is correct.

Approach & Analogy

Analogy: Assertion: "Dogs and wolves are the same animal." FALSE — they're related but distinct species.
Reason: "Dogs are domesticated through generations, and wolves are wild canines descended from a common ancestor." TRUE — this is correct biological fact.

The reason is factually correct but the assertion's broad equality claim is wrong.

Key trap: Students often assume "order = molecularity" universally — but that holds *only* for elementary reactions. Complex reactions break this equality.

Answer

Option (5) — Assertion is incorrect, but reason is correct.

— End of DPP-4 Solutions —

Samjho, apply karo, repeat karo! — Weird Chemist