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Topic 7.8: Representations of Equilibrium

Revision Notes · AP Chemistry

UNIT 7 · EQUILIBRIUM

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Two Representations of the Same Mixture

A particulate diagram is a snapshot: a box of counted particles at one instant. The box has a fixed volume, so counts are proportional to concentrations, and counts substitute directly into the K or Q expression, exactly as concentrations do.

On a concentration-time graph, concentrations are read off the vertical axis, and the curve shapes show whether the mixture has settled.

The snapshot gives amounts at one instant, so it yields Q, or K if the mixture is at equilibrium. The graph gives amounts plus history, so it also shows whether equilibrium has been reached.

Reading K and Q from Particle Counts

Write the equilibrium expression first, then substitute the counts directly. Coefficients become powers of the counts exactly as they are powers of concentrations: for $2A(g) \rightleftharpoons B(g)$ the expression is $[B] / [A]^2$, and the A count is squared, not doubled.

A diagram of a mixture not known to be at equilibrium gives Q, not K. Compute Q with the same ratio method, then compare it with the given K: Q below K means the reaction shifts right toward products, Q above K means it shifts left toward reactants. When comparing a before and after pair of diagrams, the species that gained particles is on the side the reaction shifted toward.

Flat Lines on a Concentration-Time Graph

Reactant curves fall and product curves rise, steeply at first, then more gently, and as equilibrium approaches every slope eases toward zero.

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Equilibrium begins when every curve becomes horizontal, all at the same time. The flat values are the equilibrium concentrations, and they go straight into the K expression.

Two curves crossing only means the two concentrations are equal at that instant; both may still be changing. Equal concentrations are not the test; unchanging concentrations are.

Rate-Time Graphs and Equal Rates

On a rate-time graph the forward rate starts high and falls as reactants are used up, while the reverse rate starts at zero and rises as product builds up. Equilibrium is where the two curves meet and run together: the rates are equal, so concentrations stop changing, though the reactions continue. Equal rates say nothing about the concentrations themselves; those are set by K.

One Snapshot Cannot Prove Equilibrium

A single box shows amounts only. It carries no information about rates or about what the counts were a minute earlier, so the same picture could be a system at equilibrium or one passing through those counts on its way elsewhere.

Proof comes from comparison: two snapshots at different times with identical counts, or a graph whose curves have gone flat.

Equilibrium counts need not be equal on the two sides: a box heavy with products suits a large K, and a box heavy with reactants suits a small K.

The Same Equilibrium from Either Side

Start a closed vessel from reactants only, from products only, or from any mixture with the same totals, and at the same temperature it settles to the same equilibrium composition. From the reactant side the product count climbs, from the product side it falls, and both stop at the values whose ratio gives K. An equilibrium snapshot can be checked against K without knowing where the vessel started.

Volume Changes in Diagrams

Halving the volume doubles every concentration, which changes Q unless the moles of gas are equal on both sides. For $A(g) \rightleftharpoons B(g) + C(g)$, halving the volume raises Q above K, so the new diagram shows more A and fewer B and C. For $A(g) + B(g) \rightleftharpoons 2C(g)$, the moles are equal, so the counts stay the same.

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After a volume change, the curves on a concentration-time graph bend toward new flat levels. The first flattening marks the original equilibrium; the second flattening marks the new one.

Worked Examples

Example 1: A sequence of snapshots. For A(g) ⇌ B(g), a box shows 10 A and 0 B, then later 7 A and 3 B, then 6 A and 4 B, then 6 A and 4 B again. The last two snapshots are identical, so the system is at equilibrium there. The gas count is the same on both sides, so counts go directly into the expression: Kc = 4 / 6 = 0.67. The changes are one for one, as the equation requires.

Example 2: Equal counts, K far from 1. For 2A(g) ⇌ B(g), a vessel starts with 12 A particles and no B, and the equilibrium snapshot shows 4 A and 4 B. Substituting the counts directly gives Kc = 4 / 4^2 = 4 / 16 = 0.25. The particle units balance: 12 at the start, and 4 + 2 × 4 = 12 at equilibrium. Equal counts did not give K = 1, because the A count is squared.

Example 3: Reading a graph. For $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, a concentration-time graph shows $[N_2O_4]$ falling from 0.60 to 0.40 mol L^{-1} while $[NO_2]$ rises from 0 to 0.40 mol L^{-1}, both curves flat from t = 8 min onward. The plateau values give Kc = $(0.40)^2$ / 0.40 = 0.40. N_2O_4 fell by 0.20 and NO_2 rose by exactly twice that, 0.40.

Example 4: The same picture from both sides. For $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, Kc = 36, and counts substitute directly. One vessel starts with 8 H_2, 8 I_2 and no HI; another starts with 16 HI and nothing else. Both settle at 2 H_2, 2 I_2 and 12 HI particles. Check: 12^2 / (2 × 2) = 36. Halfway there the first vessel shows 4, 4 and 8 particles, where Q = 8^2 / (4 × 4) = 4, below Kc, so it is still moving forward.

Traps That Cost Marks in Topic 7.8

"Equilibrium is where the two curves cross." Crossing means the two concentrations are momentarily equal, nothing more. On a graph for A(g) ⇌ B(g) the curves cross at 0.50 mol L^{-1} each while both are still sloping; they flatten later at 0.25 and 0.75 mol L^{-1}, and that flattening is the equilibrium.

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"Equal particle counts at equilibrium mean Kc = 1." Only when the expression is a simple one-to-one ratio. For A(g) ⇌ 2B(g) with 4 A and 4 B particles, Kc = 4^2 / 4 = 4, not 1. The powers in the expression decide, not the headcount.

"This diagram shows the system at equilibrium." A single diagram cannot show that: it might equally be a mixture photographed mid-change. Ask for the next diagram or the flat graph before accepting the claim.

"The box with the most particles has the largest K." K depends on the ratio, not the total. For A(g) ⇌ B(g), a box with 12 A and 3 B gives K = 0.25, while a sparse box with 2 A and 4 B gives K = 2.0.

"The vertical jump on the graph is the reaction shifting." A sudden vertical jump in one curve, with the other curves unmoved, records a species being added or removed. The shift is the smooth bending that follows, toward new flat levels.

"Counts go into the expression as they stand." Coefficients become powers of counts too. For 2A(g) ⇌ B(g) with 8 A and 2 B particles, the correct value is 2 / 8^2 = 0.031. Leaving the A count unsquared gives 2 / 8 = 0.25 instead.

Key Relationships to Remember

- Particle counts in a fixed-volume box are proportional to concentrations, and counts substitute directly into the K or Q expression
- Write the K or Q expression first, then substitute counts, with each coefficient applied as a power
- When the gas particle total is the same on both sides of the equation, a volume change leaves Q unchanged and no shift occurs
- A snapshot of a mixture not known to be at equilibrium gives Q; only an equilibrium snapshot gives K
- On a concentration-time graph, equilibrium begins when every curve becomes horizontal at the same time
- On a rate-time graph, equilibrium is where the forward and reverse rate curves meet and stay equal
- Equilibrium counts and concentrations need not be equal on the two sides; K fixes their ratio, not their equality
- The same total contents at the same temperature reach the same equilibrium picture from either side

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