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Topic 7.5: Magnitude of the Equilibrium Constant

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UNIT 7 · EQUILIBRIUM

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K Is a Ratio, and Its Size Locates the Equilibrium

Topics 7.3 and 7.4 built the K expression and calculated it from equilibrium concentrations. Topic 7.5 reads the answer: the size of K states how the equilibrium mixture is divided between the two sides.

A large K means the product terms at equilibrium are large relative to the reactant terms; a small K means the reverse. The size of K describes the settled mixture only, not the route it took or how long it took to settle.

K Much Greater Than 1: Products Favoured

When K is much greater than 1, the numerator dwarfs the denominator, and the equilibrium mixture is almost entirely products. Started from reactants, the reaction runs forward until they are nearly used up: it goes essentially to completion.

Essentially is not literally: a trace of reactant always remains, because equilibrium is dynamic and the two rates are equal. Values like 10^{10} leave reactant amounts too small to measure, but they are not zero.

K Much Less Than 1: Reactants Favoured

When K is much less than 1, the denominator dominates, and the equilibrium mixture is almost entirely reactants. The forward reaction does occur, but the reverse rate catches up after only a little product has formed, so the mixture settles with very little product present.

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Very little is again not zero. For $K = 10^{-9}$ the equilibrium amount of product is minute but real: such reactions, for practical purposes, do not proceed, though the equilibrium is genuine.

K Near 1: Both Sides in Appreciable Amounts

When K is close to 1, the numerator and denominator are comparable and neither side dominates. The equilibrium mixture holds significant amounts of reactants and products alike.

Near 1 does not mean equal concentrations: K is the value of the whole expression, powers included. For A(g) ⇌ 2B(g), [A] = 0.25 and [B] = 0.50 mol L^{-1} gives $(0.50)^2$ / 0.25 = 1.0, with twice as much B as A present.

Comparing Reactions: Larger K, Further Toward Products

At the same temperature, the larger the K, the further the equilibrium lies toward products, and the greater the fraction of reactants converted. Ranking reactions by extent of reaction is therefore ranking them by K: 10^{-8} converts least, then 3.0, then 10^{10} most.

The comparison is cleanest for alike setups, because the exact percent converted also depends on stoichiometry and starting amounts.

Magnitude Says Nothing About Speed

K is a thermodynamic quantity: it fixes where equilibrium lies. Rate is a kinetic quantity, governed by activation energy, and the two are independent. A large K does not make a reaction fast, and a small K does not make one slow.

The standing counterexample is $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$. Its K at room temperature is enormous, so equilibrium lies overwhelmingly toward water, yet a mixture of hydrogen and oxygen can sit for years with no visible reaction, because the activation energy is high and the mixture needs a spark.

A catalyst changes neither K nor the position. It lowers the activation energy of both directions equally, so the same mixture is reached sooner.

Only Temperature Changes the Size of K

Changing amounts, volume, or pressure changes the equilibrium mixture, which then satisfies the same K as before (Topic 7.3's Q describes that readjustment). Only temperature produces a different constant.

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The change can be dramatic. One reaction has $K = 6.3 \times 10^{-2}$ at 500 K and $K = 4.1 \times 10^{2}$ at 800 K: reactant favoured when cold, product favoured when hot. Whether heating raises or lowers K depends on the reaction, so magnitudes are compared only at a stated temperature.

Worked Examples

Example 1: A small K priced out. For A(g) ⇌ B(g), K = 0.020. A flask that started with 1.0 mol L^{-1} of A settles with [A] = 0.980 and [B] = 0.0196 mol L^{-1}. Check: K = 0.0196 / 0.980 = 0.020, as stated. The B formed is 0.0196 of the 1.0 that started, so only 2.0% of the A was converted: reactant favoured, exactly as K << 1 promises.

Example 2: A moderately large K. For $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, Kc = 54. Starting with $[H_2] = [I_2] = 1.0$ mol L^{-1} and no HI, let x of each reactant be consumed: $K_c = (2x)^2 / (1.0 - x)^2 = 54$. Taking square roots, $2x / (1.0 - x) = 7.35$, so x = 0.786. The equilibrium row is $[H_2] = [I_2] = 0.214$ and [HI] = 1.57 mol L^{-1}, with about 79% converted: products clearly favoured, but appreciable reactants remain, unlike Example 1.

Example 3: An extremely small K. For $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, $K_c = 4.6 \times 10^{-31}$. Starting with 1.0 mol L^{-1} of each reactant, $(2x)^2 / (1.0 - x)^2 = 4.6 \times 10^{-31}$, and square roots give $2x / (1.0 - x) = 6.8 \times 10^{-16}$. Since x is minute, 1.0 − x is effectively 1.0, so $[NO] \approx 6.8 \times 10^{-16}$ mol L^{-1} and the fraction of N_2 converted is about 3.4×10^{-16}. Air at this temperature is, measurably, unreacted nitrogen and oxygen.

Example 4: Reading particle snapshots. Three flasks each hold an A(g) ⇌ B(g) equilibrium in the same volume, each beginning with 12 A particles. The snapshots show 1 A with 11 B, 6 A with 6 B, and 11 A with 1 B. Counts are proportional to concentrations in the same volume, so the K values are 11 / 1 = 11, 6 / 6 = 1.0, and 1 / 11 = 0.091. Ranked by extent: the 0.091 flask, then the 1.0 flask, then the 11 flask, and every snapshot conserves its 12 particles.

Traps That Cost Marks in Topic 7.5

"A large K means a fast reaction." K reports the equilibrium position, never a rate. The hydrogen and oxygen mixture has an enormous K and, without a spark, essentially no reaction at all.

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"With K >> 1, no reactants remain and the reverse reaction stops." Reactants are nearly consumed, not eliminated, and equilibrium is dynamic: both reactions continue at equal rates.

"With K << 1, no product forms." A very small amount forms before the rates equalize. K = 10^{-9} gives a minute equilibrium concentration of product, not a zero one.

"K = 1 means equal amounts of reactants and products." K = 1 means the expression equals 1. With powers in the expression, as in the [A] = 0.25, [B] = 0.50 mol L^{-1} case above, the amounts can differ by a factor of two while K stays exactly 1.

"K = 10^3 means products are present at 1000 times the reactant concentration." K is the whole expression, powers included. For 2A(g) ⇌ B(g), [A] = 0.10 and [B] = 10 mol L^{-1} gives K = 10 / $(0.10)^2$ = 1.0 × 10^3, yet B is present at only 100 times the concentration of A.

"Adding more reactant, or a catalyst, makes K larger." Neither touches K: more reactant changes the mixture, a catalyst changes only the time taken to settle, and temperature alone produces a new K.

Key Relationships to Remember

- K >> 1: the equilibrium mixture is almost all products; the reaction goes essentially to completion, with a trace of reactant remaining
- K << 1: the equilibrium mixture is almost all reactants; very little product forms, but the amount is not zero
- K near 1: appreciable amounts of reactants and products are both present at equilibrium
- At the same temperature, a larger K means an equilibrium further toward products and a greater fractional conversion, cleanest for alike setups
- K is the value of the full expression, powers included, not a simple ratio of amounts unless every coefficient is 1
- K measures extent, not speed: the time to reach equilibrium is set by activation energy, and a catalyst changes the time without changing K
- Only temperature changes K; concentrations, pressure, volume and catalysts change the mixture or the timing, never the constant
- Rewriting a reaction for a new K is Topic 7.6; solving a full equilibrium composition from K is Topic 7.7; the K and Gibbs energy link is Unit 9

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