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Topic 7.4: Calculating the Equilibrium Constant

Revision Notes · AP Chemistry

UNIT 7 · EQUILIBRIUM

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Only Equilibrium Values Give K

Calculating K means evaluating the Topic 7.3 expression with the concentrations the mixture has at equilibrium, at that temperature. Nothing about the expression changes; the discipline is entirely in which numbers are allowed into it.

In the data, equilibrium values announce themselves by standing still: a mixture sampled at two different times returns the same concentrations. Values that are still drifting belong to a mixture on its way to equilibrium, and they belong in Q.

The same substitution with starting concentrations gives Q. This is the most common way these calculations are lost: the powers are right, the arithmetic is right, and the values are from the wrong moment.

K is a pure number, without units. Each concentration is understood relative to a standard concentration of 1 mol L^{-1}, so the units cancel out of the ratio whatever the coefficients are.

The Haber reaction shows the rule in action.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$Kc = [NH_3]^2 / ([N_2][H_2]^3)$

The 3 on H_2 becomes a cube and the 2 on NH_3 becomes a square.

Pure Solids and Liquids Are Omitted

Pure solids and pure liquids never appear in a K expression. Their concentrations stay constant as the reaction proceeds, so they are folded into the constant itself. Gases and aqueous species are always included, so check every species before writing the expression.

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$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$K_c = [CO_2]$

For the Boudouard reaction, solid carbon is omitted and the CO term is squared.

$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$

$K_p = P(CO)^2 / P(CO_2)$

The AP exam tests this rule constantly: a solid left in the expression is one of the most common lost marks in this topic.

Building the Equilibrium Row From a Measured Change

Data often arrive as a starting mixture plus one measured equilibrium value. The bridge between them is the change row: the coefficients fix the ratios in which species are consumed and formed, so one measured change determines every change.

Work in three rows: initial, change, equilibrium. Let the change for a species with coefficient 1 be x. Every other species changes by its own coefficient times x, falling for reactants and rising for products, and each equilibrium value is the initial value plus or minus its change.

The rows work identically when the measured change runs the other way. If a product's equilibrium value is lower than its starting value, the reaction has run net in reverse: products fall and reactants rise, and the same coefficient ratios turn that one measured fall into every other change.

The finished row must conserve atoms: the total of each element is the same in the initial row and in the equilibrium row. A row that fails that check has a scaling error in it, and no value of K calculated from it can be trusted.

Moles Are Not Concentrations

The expression is built from concentrations, in mol L^{-1}. When the data are given as amounts in moles, divide every amount by the vessel volume first, and only then build the equilibrium row.

Skipping the division is invisible when the volume is 1.0 L. At any other volume every substituted number is off by a factor of the volume, and because the terms carry powers, the calculated K is wrong by more than that factor.

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Working Backwards: One Missing Equilibrium Value

Sometimes K is given and one equilibrium value is missing. Rearrange the expression to isolate the missing concentration, substitute the known equilibrium values, and solve.

If the missing species carries a coefficient of 2, it sits squared in the expression, and the final step is a square root. Take the positive root: a concentration cannot be negative, so the negative root is discarded.

Everything in this section applies to Kp unchanged, with partial pressures in place of concentrations: a missing pressure is isolated by the same rearrangement, and a squared pressure, such as the CO pressure over a carbon and carbon dioxide mixture, ends in the same square root.

The Same K From Any Starting Mixture

At a fixed temperature, every mixture that reaches equilibrium for the same reaction gives the same value of K, whatever it started from: reactants only, products only, or any blend.

Two careful determinations that land close together, such as 52 and 51, agree within experimental error and confirm the constant. Only a change of temperature gives a different K. Changing the starting amounts, the volume, or adding a catalyst changes the equilibrium mixture itself, never the constant that the mixture satisfies.

Worked Examples

Example 1: Direct substitution. At equilibrium for $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$, $[NO] = 0.040$, $[O_2] = 0.020$ and $[NO_2] = 0.16$ mol L^{-1}. $K_c = [NO_2]^2 / ([NO]^2[O_2]) = (0.16)^2 / ((0.040)^2 \times 0.020) = 0.0256 / (0.0016 \times 0.020) = 0.0256 / 0.000032 = 8.0 \times 10^2$.

Example 2: Initial amounts plus one measured value. A flask for $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ starts with $[N_2] = 0.90$, $[O_2] = 0.50$ and no NO. At equilibrium $[NO] = 0.20$ mol L^{-1}. Forming 0.20 of NO is a change of $2x$, so $x = 0.10$, and each reactant falls by 0.10: the equilibrium row is $[N_2] = 0.80$, $[O_2] = 0.40$, $[NO] = 0.20$. $K_c = (0.20)^2 / (0.80 \times 0.40) = 0.040 / 0.32 = 0.125$. The row conserves atoms: nitrogen totals 1.80 on both sides of the change, oxygen 1.00.

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Example 3: Moles in a vessel. A 5.0 L vessel for $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ starts with 1.00 mol of SO_2Cl_2 only. At equilibrium 0.40 mol of SO_2Cl_2 remains, so 0.60 mol reacted and 0.60 mol of each product formed. Converting first: $[SO_2Cl_2] = 0.40 / 5.0 = 0.080$, $[SO_2] = [Cl_2] = 0.60 / 5.0 = 0.12$ mol L^{-1}. $K_c = (0.12 \times 0.12) / 0.080 = 0.0144 / 0.080 = 0.18$.

Example 4: Finding a missing value. For $Br_2(g) + Cl_2(g) \rightleftharpoons 2BrCl(g)$, $K_c = 6.0$. An equilibrium mixture has $[Br_2] = 0.020$ and $[Cl_2] = 0.030$ mol L^{-1}. Rearranging, $[BrCl]^2 = K_c \times [Br_2] \times [Cl_2] = 6.0 \times 0.020 \times 0.030 = 0.0036$, so $[BrCl] = 0.060$ mol L^{-1}, taking the positive square root.

Traps That Cost Marks in Topic 7.4

"The starting concentrations go into the expression." They give Q, not K. Only the equilibrium row may be substituted, however complete the starting data look.

"Amounts in moles can be substituted directly." Only a 1.0 L vessel makes moles and concentrations numerically equal. Convert every amount with the stated volume before anything is substituted.

"Every species changes by the same amount." Changes follow the coefficients. A species with coefficient 3 changes three times as much as the species whose change defined x.

"A bigger starting mixture gives a bigger K." At a fixed temperature K is the same from any starting mixture. Starting amounts move the equilibrium row, not the constant.

"Two trials giving 52 and 51 mean one mixture never reached equilibrium." Small disagreements between careful determinations are experimental error. Values that agree closely confirm K; they do not undermine it.

"K carries whatever units the substitution leaves over." K is dimensionless. An answer quoted with units is wrong even when the number is right.

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Key Relationships to Remember

- K is the Topic 7.3 expression evaluated with equilibrium concentrations, or with equilibrium partial pressures for Kp, at the stated temperature
- Non-equilibrium values in the same expression give Q, never K
- One measured change fixes every change through the coefficients: equilibrium value = initial value plus or minus the coefficient share of the change
- The equilibrium row must conserve atoms element by element; a row that does not is wrong before K is calculated
- Concentrations are moles divided by vessel volume; convert first whenever amounts are given in moles
- A missing equilibrium value is found by rearranging the K expression; a squared unknown ends in a square root, and only the positive root is physical
- At a fixed temperature the same K comes from any starting mixture; only a temperature change alters K
- What the size of K says about how far a reaction goes is Topic 7.5, and solving for a whole equilibrium composition from K alone is Topic 7.7

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