Topic 7.1: Introduction to Equilibrium

Revision Notes · AP Chemistry

UNIT 7 · EQUILIBRIUM

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Reversible Reactions

A reversible reaction can run in both directions in the same mixture: the products can react to re-form the reactants while reactants are still forming products.

Such a reaction is written with a double arrow, ⇌: read left to right it is the forward reaction; read right to left it is the reverse reaction.

Colorless $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is the standard picture: N_2O_4 molecules split into brown NO_2, and NO_2 molecules pair back up into N_2O_4, both in the same sealed flask at the same time.

A single arrow claims the reaction goes essentially to completion. The ⇌ arrow claims something different: neither direction wins outright, and both keep happening.

The Approach to Equilibrium

Start a reversible reaction with reactants only. The forward rate starts at its maximum, because reactant concentration is at its highest, and the reverse rate starts at zero, because there is no product yet to react back.

As the forward reaction runs, reactant concentration falls, so the forward rate falls with it. Product concentration climbs from zero, so the reverse rate climbs: the more product there is, the more often product particles react.

The net change is the gap between the two rates, and it narrows steadily: product still builds up, but more and more slowly, as the reverse rate catches up.

That slowing, flattening change is the signature of an approach to equilibrium: the concentrations themselves drag the two rates toward each other until they meet.

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Dynamic Equilibrium

Equilibrium is reached when the forward and reverse rates become equal.

forward rate / reverse rate = 1

At equilibrium the concentration of every species stops changing, but not at an equal value: reactants and products generally sit at different concentrations, fixed by reaction and temperature.

The reactions themselves do not stop: reactant particles keep turning into product particles, and product particles keep turning back, at the same rate, so every conversion is balanced by one the other way.

This is why equilibrium is called dynamic: bonds keep breaking and forming continuously. Isotopic tracers prove it: label added to a reactant at equilibrium appears in the products, even though the bulk composition never changes.

Conditions Equilibrium Needs

A closed system. No matter may enter or leave. If a gaseous product can escape, it is removed before it can react back, starving the reverse rate, and the system can never settle.

Constant temperature. Both rates, and the composition the system settles at, depend on temperature, so comparisons are only fair at the same temperature.

Time, and nothing else. No catalyst is required: a catalyst makes both rates larger and shortens the journey, but changes neither the equality the rates reach nor the composition.

The Same Equilibrium From Either Side

A system can be set up from reactants only, from products only, or from any mixture of the two. Provided the totals sealed in the flask and the temperature are the same, every version ends at the same equilibrium composition.

Approaching from the products side runs the same story in mirror image: the reverse rate starts at its maximum, the forward rate at zero, and the two converge on the same meeting point.

This is a strong check: if two flasks at the same temperature, holding the same total contents, are said to finish with different compositions, at least one cannot be at equilibrium.

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Reading Equilibrium Graphs

On a concentration-time graph, the reactant curve falls steeply at first and then flattens, and the product curve rises and flattens in mirror image. Equilibrium begins where both curves become horizontal plateaus.

The plateau values are the equilibrium concentrations: constant, and generally not equal, because the two plateaus sit at different heights.

On a rate-time graph, the forward rate curve falls from its starting maximum while the reverse rate curve rises from zero. Equilibrium begins where the two curves meet and run together as one level line.

After the curves meet, the shared rate is not zero: both reactions continue at that common rate, which is why the concentration plateaus stay flat instead of the system freezing.

Worked Examples

Example 1: Equilibrium concentrations from a table. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ starts with $[N_2O_4] = 0.80$ mol L^{-1} and no NO_2. Readings each minute: $[N_2O_4] = 0.80, 0.50, 0.30, 0.22, 0.20, 0.20, 0.20$ mol L^{-1}, while $[NO_2] = 0.00, 0.60, 1.00, 1.16, 1.20, 1.20, 1.20$ mol L^{-1}. Each fall in $[N_2O_4]$ is matched by a rise in $[NO_2]$ exactly twice as large, as the coefficients demand: the first minute converts 0.30 mol L^{-1} of N_2O_4 into 0.60 mol L^{-1} of NO_2. Both concentrations are constant from 4 minutes on, so equilibrium is reached by 4 minutes, at $[N_2O_4] = 0.20$ mol L^{-1} and $[NO_2] = 1.20$ mol L^{-1}: constant plateaus, nowhere near equal.

Example 2: The same flask filled from the other side. A second flask at the same temperature starts with $[NO_2] = 1.60$ mol L^{-1} and no N_2O_4, the same totals as Example 1. Here the reverse reaction runs first: NO_2 pairs up, $[NO_2]$ falls, $[N_2O_4]$ rises. By equilibrium, 0.40 mol L^{-1} of NO_2 has been consumed, forming 0.20 mol L^{-1} of N_2O_4. The flask settles at $[N_2O_4] = 0.20$ mol L^{-1} and $[NO_2] = 1.20$ mol L^{-1}, identical to Example 1.

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Example 3: Unequal concentrations, equal rates. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ starts with $[H_2] = [I_2] = 1.00$ mol L^{-1} and no HI. At equilibrium $[H_2] = [I_2] = 0.22$ mol L^{-1} and $[HI] = 1.56$ mol L^{-1}: 0.78 mol L^{-1} of each reactant was consumed, forming $2 \times 0.78 = 1.56$ mol L^{-1} of HI. The forward rate fell from 0.085 mol L^{-1} s^{-1} at the start to 0.012 mol L^{-1} s^{-1}, while the reverse rate climbed from zero to the same 0.012 mol L^{-1} s^{-1}. Products outweigh reactants sevenfold, yet the system is at equilibrium, because the rates match.

Example 4: The rate ratio test. A mixture has a forward rate of 0.060 mol L^{-1} s^{-1} and a reverse rate of 0.020 mol L^{-1} s^{-1}. The ratio is 0.060 / 0.020 = 3, not one, so the system is not at equilibrium and products accumulate. Later the forward rate has fallen to 0.030 mol L^{-1} s^{-1} while the reverse rate has risen to 0.030 mol L^{-1} s^{-1}. The ratio is now 0.030 / 0.030 = 1 and the net rate is zero, so the system is at equilibrium even though both rates are still 0.030 mol L^{-1} s^{-1}.

Traps That Cost Marks in Topic 7.1

"Equilibrium means equal concentrations." Equilibrium means constant concentrations and equal rates. Examples 1 and 3 settle at products 1.20 and 1.56 mol L^{-1} against reactants 0.20 and 0.22 mol L^{-1}.

"The reaction stops at equilibrium." Nothing stops. Both reactions continue at equal rates, which is why tracers keep exchanging and the state is called dynamic, not static.

"The reverse reaction starts once the forward reaction finishes." The reverse reaction starts the moment any product exists. It runs alongside the forward reaction throughout, growing from zero as product accumulates.

"An open beaker reaches equilibrium too." In an open system, escaping gas or vapor removes a species before it can react back. Equilibrium requires a system closed to matter.

"A catalyst shifts the equilibrium toward products." A catalyst raises the forward and reverse rates together, so the system arrives sooner at the same composition, with no shift.

"A mixture that has stopped changing must be finished reacting." A flat concentration trace with both species present is the fingerprint of equilibrium, not completion: completion would leave no reactant behind.

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Key Relationships to Remember

- A reversible reaction is written with ⇌ and runs in both directions at the same time
- Equilibrium: forward rate = reverse rate, so the ratio of the two rates is exactly one
- At equilibrium, concentrations are constant over time, not necessarily equal to each other
- Equilibrium requires a closed system, held at constant temperature
- The same equilibrium composition is reached from either side, given the same total contents and temperature
- Concentration-time curves level into plateaus at equilibrium; rate-time curves meet and run together
- A catalyst shortens the approach to equilibrium and changes neither the position nor the composition
- How far the position sits toward products is measured by the equilibrium constant, K, in Topic 7.3

Continue Revising

Topic 7.1 Quiz: Introduction to Equilibrium

Topic 7.1 Worksheet

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