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Topic 5.5: Collision Model

Revision Notes · AP Chemistry

UNIT 5 · KINETICS

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Reactions Happen in Collisions

The collision model explains rates at the particle level. Reactant particles move constantly, and a reaction can only happen when the particles whose bonds must rearrange actually meet: a collision.

The rate is set by how many collisions per second succeed, not by the total collisions. Three things decide that count: collision frequency, the fraction of collisions with enough energy, and the fraction correctly oriented. A collision meeting both conditions is an effective collision; all others are ineffective and the particles bounce apart unchanged.

Two Conditions for an Effective Collision

The energy condition. Colliding particles must bring at least the activation energy into the collision. Below it they cannot cross the barrier and separate as reactants again.

The orientation condition. The particles must meet in the correct geometric alignment, so the atoms that must form new bonds are the atoms that touch. This is the steric factor, or orientation factor. In Cl + NOCl → NO + Cl_2, the incoming Cl atom must strike the Cl atom of NOCl, the atom it will bond with; a hit at the nitrogen end fails, however energetic it is.

Both must hold in the same collision: an energetic collision at the wrong angle fails, and a well aligned one with too little energy fails.

Activation Energy: The Threshold

Activation energy, E_a, is the minimum energy colliding particles need to react. It is fixed by the reaction and its pathway.

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The barrier exists because existing bonds must begin to break before new bonds can form, and breaking bonds costs energy up front, before any energy is released later. So even strongly exothermic reactions need activation energy: methane releases much energy overall, $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$, yet the mixture needs a spark.

A large E_a means a tiny reactive fraction and a slow reaction; a small E_a means the opposite. Temperature and concentration never change E_a, only how many particles exceed it.

The Maxwell-Boltzmann Distribution of Energies

Particles in a sample do not share one energy. A few have very little, most cluster near the average, and a few sit in a long tail of high energies. Plotting number of particles against energy gives the Maxwell-Boltzmann distribution. The area under the whole curve represents all the particles in the sample, and for a sealed sample it cannot change, whatever happens to the shape.

E_a is drawn as a vertical line at the threshold. The area to its right is the fraction of particles with enough energy to react, if they also collide correctly oriented.

Average kinetic energy per mole is (3/2)RT: about 3.74 kJ/mol at 300 K and 7.48 kJ/mol at 600 K. A typical E_a of 60 kJ/mol lies far above both, so reaction depends on the small tail of energetic particles, not the average particle.

Temperature: Shifting the Distribution

Heating raises the average kinetic energy in proportion to the kelvin temperature. The curve spreads out: the peak shifts right, lower and broader, while the total area stays the same and the E_a line does not move.

The area to the right of the line, the fraction able to react, therefore grows steeply. This is the main reason rates rise so sharply with temperature: speeds grow only with the square root of temperature, a factor of about 1.41 between 300 K and 600 K, but the reactive fraction can multiply several times over. Heated particles also collide slightly more often, but that effect is small beside it.

Concentration, Pressure and Surface Area

Raising concentration puts more particles in the same volume, so collisions per second rise. At fixed temperature the energy and orientation fractions stay the same, so a larger collision count gives proportionally more effective collisions per second. Compressing a gas raises pressure by crowding particles into less volume, the same change as raising concentration.

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Only a solid's surface particles can collide with anything. Grinding exposes far more of them, so powdered magnesium reacts with hydrochloric acid, $Mg + 2HCl \rightarrow MgCl_2 + H_2$, far faster than one lump of the same mass.

Catalysts in Collision Terms

A catalyst provides an alternative pathway with a lower activation energy. On the same distribution, its E_a line sits further left, so a much larger fraction of particles can react.

The catalyst does not heat the mixture or give particles more energy. It lowers the barrier itself, the one thing temperature and concentration cannot do.

Worked Examples

Example 1: Reading a distribution in bins. A sample of 1,000 particles is counted in energy bins of 20 kJ/mol. At 300 K the counts from the lowest bin up are 520, 310, 120, 38 and 12. With E_a = 60 kJ/mol, the particles above the threshold fill the top two bins: 38 + 12 = 50, or 5.0%. At 400 K the counts are 280, 300, 220, 120 and 80, again totalling 1,000, and the top two bins hold 120 + 80 = 200, or 20.0%. Heating multiplied the reactive fraction by 4, while the total area stayed at 1,000 particles.

Example 2: Counting effective collisions. A mixture produces 2.0×10^6 collisions per second. At 300 K, 5.0% have enough energy and 1 in 20 has the correct orientation, a fraction of 0.050, so effective collisions per second = $2.0 \times 10^6 \times 0.050 \times 0.050$ = 5,000. At 400 K the energy fraction is 20.0%; holding the other factors fixed gives $2.0 \times 10^6 \times 0.20 \times 0.050$ = 20,000 per second, four times as many.

Example 3: Doubling concentrations. A mixture of A and B has 4.0×10^5 collisions per second, of which 0.10%, a fraction of 0.0010, are effective: 400 per second. Doubling [A] alone doubles collisions to 8.0×10^5 and effective collisions to 800 per second. Doubling both multiplies collisions by 2 × 2 = 4, giving 1,600 effective collisions per second. E_a and the effective fraction never move, because temperature is unchanged.

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Example 4: A catalyst moves the line, not the curve. Using the Example 1 distribution at 300 K, a catalysed pathway with E_a = 40 kJ/mol places the top three bins above the threshold: 120 + 38 + 12 = 170 particles, or 17.0%, instead of 5.0%. With 5.0 × 10^5 collisions per second and 1 in 10 correctly oriented, the uncatalysed count is 5.0 × 10^5 × 0.050 × 0.10 = 2,500 per second and the catalysed count is 5.0 × 10^5 × 0.17 × 0.10 = 8,500 per second, a factor of 3.4 at the same temperature.

Traps That Cost Marks in Topic 5.5

Heating lowers the activation energy. It never does: E_a is fixed by the pathway, and heating only moves more particles past the unchanged threshold.

More collisions automatically means more reaction. Only effective collisions count. A huge collision rate still gives a slow reaction if almost no collision clears E_a or arrives correctly oriented.

The area under the curve grows on heating. The area counts the particles and is conserved. The hotter curve is lower and broader precisely because the same area spreads wider.

Doubling concentration makes particles more energetic. At fixed temperature the distribution and the fraction above E_a are unchanged; concentration changes only how often particles meet.

A catalyst heats the mixture or energises particles. It does neither: it offers a lower E_a, so a larger fraction of ordinary collisions succeeds.

Orientation always takes care of itself. Single atoms have no wrong end, but large, complex molecules must align specific atoms, so the steric factor cuts their effective fraction sharply.

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Key Relationships to Remember

- Effective collision: energy at or above E_a and the correct orientation in the same collision, so products form
- Activation energy E_a: the minimum energy colliding particles need to react; fixed by the pathway
- Rate is set by collisions per second, times the fraction with energy at or above E_a, times the fraction correctly oriented
- Maxwell-Boltzmann energy plot: total area is the total number of particles and never changes; E_a is a vertical line, and the area to its right is the fraction with enough energy
- Heating: curve shifts right, lower and broader; E_a stays put and the fraction above it grows steeply
- Concentration, gas pressure and surface area change collisions per second only: the energy fraction and E_a stay the same
- Catalyst: an alternative pathway with lower E_a, so more particles react at the same temperature

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