Reaction kinetics

The investigation of the factors that affect the rate of a chemical reaction is important in the study of physical chemistry. The temperature and the addition of a catalyst can both affect the progression of a chemical reaction.

a explain and use the term rate of reaction ☐

b explain qualitatively, in terms of collisions, the effect of concentration changes on the rate of a reaction ☐

c explain and use the term activation energy, including reference to the Boltzmann distribution ☐

d explain qualitatively, in terms both of the Boltzmann distribution and of collision frequency, the effect of temperature change on the rate of a reaction ☐

e

REACTION KINETICS

8 Reaction kinetics

The investigation of the factors that affect the rate of a chemical reaction is important in the study of physical chemistry. The temperature and the addition of a catalyst can both affect the progression of a chemical reaction.

Learning outcomes
Candidates should be able to:

8.1 Simple rate equations; orders of reaction; rate constants

a) explain and use the term *rate of reaction*

b) explain qualitatively, in terms of collisions, the effect of concentration changes on the rate of a reaction

c) explain and use the terms *rate equation, order of reaction, rate constant, half-life of a reaction, rate-determining step*

d) construct and use rate equations of the form rate = $k[A]^m[B]^n$ (for which *m* and *n* are 0, 1 or 2), including:

(i) deducing the order of a reaction, or the rate equation for a reaction, from concentration-time graphs or from experimental data relating to the initial rates method and half-life method

(ii) interpreting experimental data in graphical form, including concentration-time and rate-concentration graphs

(iii) calculating an initial rate using concentration data

(integrated forms of rate equations are not required)

e) (i) show understanding that the half-life of a first-order reaction is independent of concentration

(ii) use the half-life of a first-order reaction in calculations

f) calculate the numerical value of a rate constant, for example by using the initial rates or half-life method

g) for a multi-step reaction:

(i) suggest a reaction mechanism that is consistent with the rate equation and the equation for the overall reaction

(ii) predict the order that would result from a given reaction mechanism (and vice versa)

h) devise a suitable experimental technique for studying the rate of a reaction, from given information

8.2 Effect of temperature on reaction rates and rate constants; the concept of activation energy

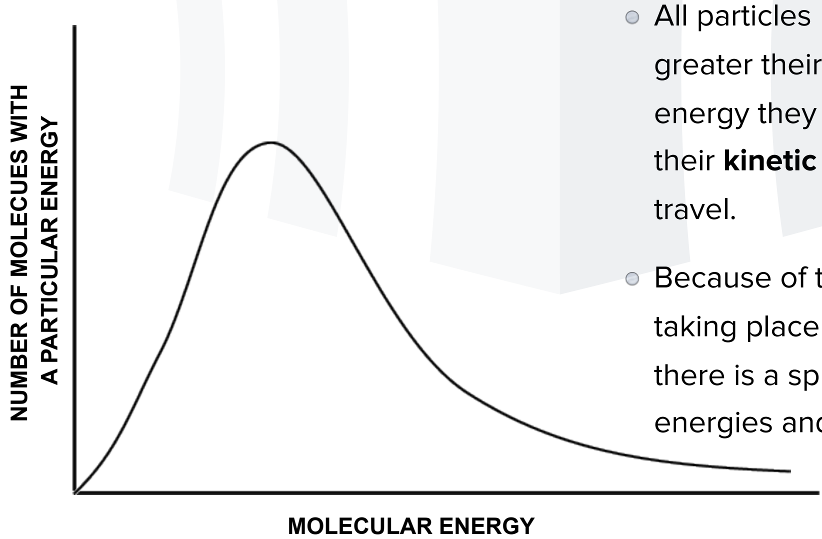
a) explain and use the term *activation energy*, including reference to the Boltzmann distribution

b) explain qualitatively, in terms both of the Boltzmann distribution and of collision frequency, the effect of temperature change on the rate of a reaction

c) explain qualitatively the effect of temperature change on a rate constant and hence the rate of a reaction

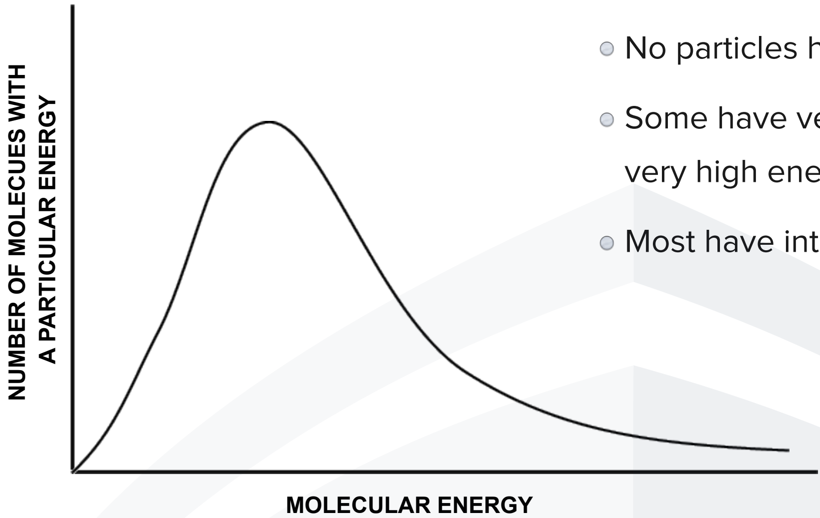
REACTION KINETICS

BOLTZMANN DISTRIBUTION OF MOLECULAR ENERGY



- All particles have energy - the greater their temperature, the more energy they possess. The greater their **kinetic energy** the faster they travel.
- Because of the many collisions taking place between molecules, there is a spread of molecular energies and velocities.

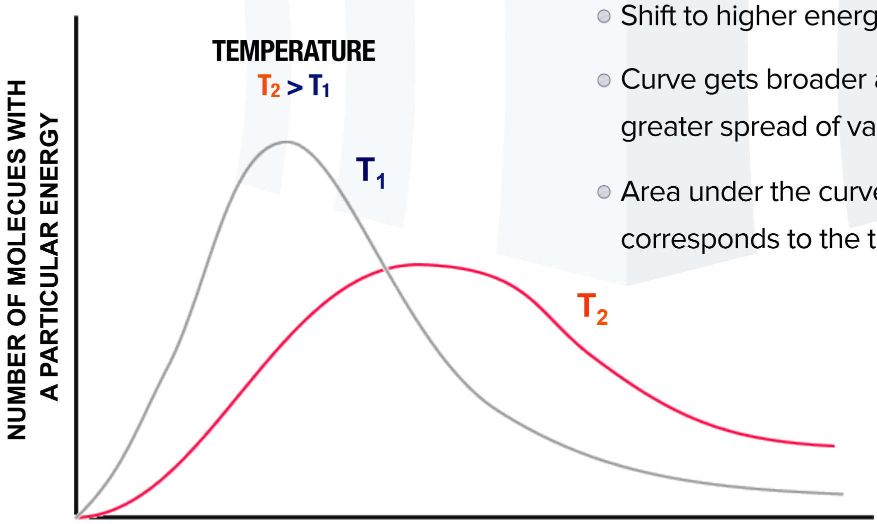
BOLTZMANN DISTRIBUTION OF MOLECULAR ENERGY



- No particles have zero energy/velocity
- Some have very low and some have very high energies/velocities
- Most have intermediate velocities.

3

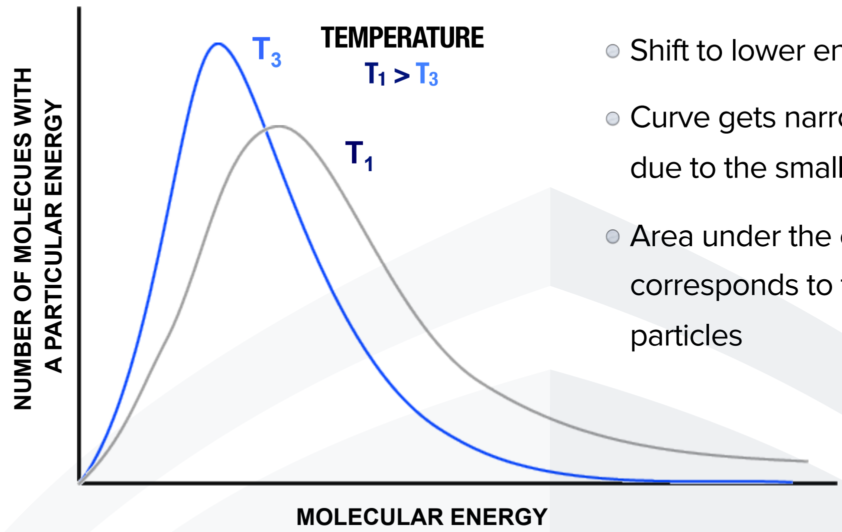
INCREASING TEMPERATURE



- Shift to higher energies/velocities
- Curve gets broader and flatter due to the greater spread of values
- Area under the curve stays constant - it corresponds to the total number of particles

4

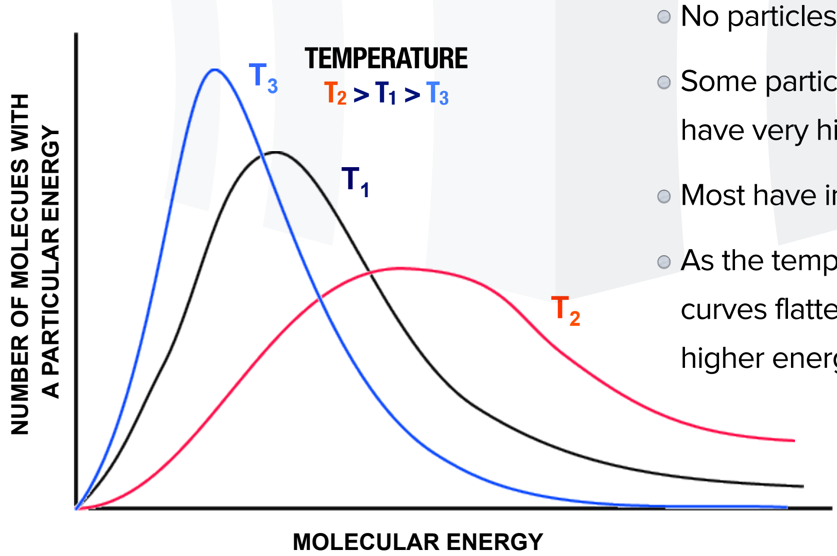
DECREASING TEMPERATURE



- Shift to lower energies/velocities
- Curve gets narrower and more pointed due to the smaller spread of values
- Area under the curve stays constant - it corresponds to the total number of particles

5

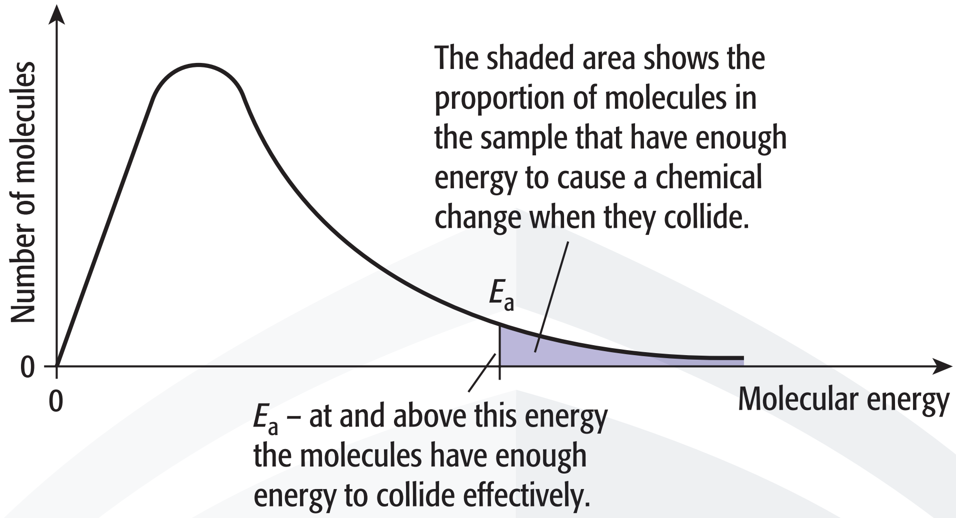
REVIEW



- No particles have zero energy/velocity
- Some particles have very low and some have very high energies/velocities
- Most have intermediate velocities
- As the temperature increases the curves flatten, broaden and shift to higher energies

6

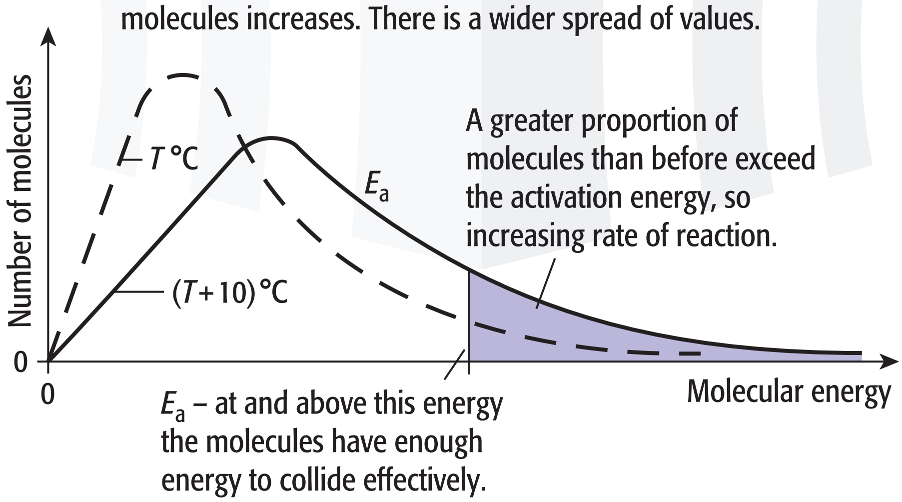
ACTIVATION ENERGY - E_A



7

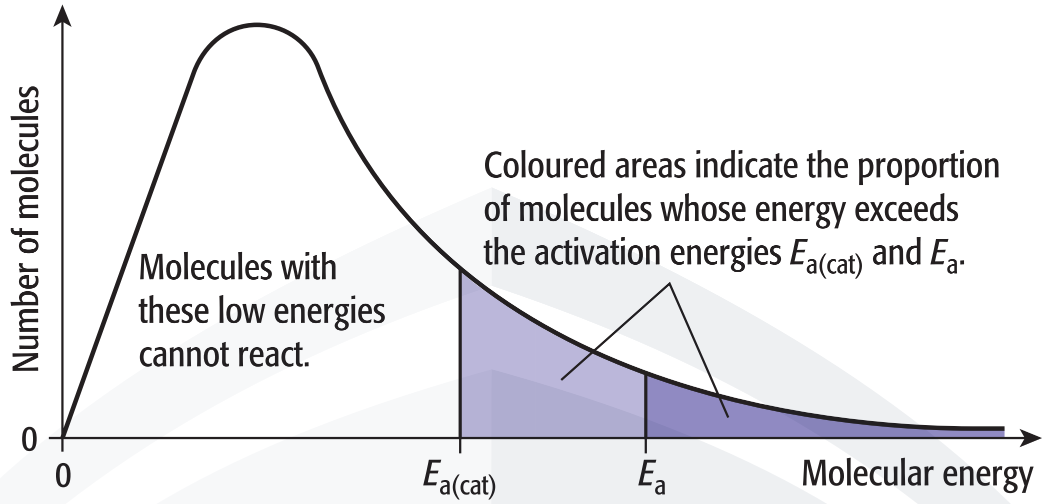
INCREASING TEMPERATURE

When the sample is heated, the mean energy of the molecules increases. There is a wider spread of values.



8

CATALYSTS



CATALYSIS

Catalysts increase the rate of a chemical reaction. They do this by providing an alternative pathway for the reaction with lower activation energy.

We can divide catalysts into two main classes.

Catalysis

Homogeneous Catalysis
Occurs when the catalyst is in the same phase as the reaction mixture. For example: hydrogen ions catalyse the hydrolysis of esters.

Heterogeneous Catalysis
Occurs when the catalyst is in a different phase to the reaction mixture. For example, decomposition of aqueous hydrogen peroxide catalysed by manganese(IV) oxide.

HOMOGENEOUS CATALYSIS

Homogeneous catalysis often involves changes in oxidation number of the ions involved in catalysis.

Ions of transition elements are often good catalysts because of their ability to change oxidation number.

Examples:

1. The catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric sulfur dioxide.
2. Catalytic role of Fe^{3+} in the $I^-/S_2O_8^{2-}$ reaction.

HETEROGENEOUS CATALYSIS

The mechanism of this catalysis can be explained using the theory of adsorption. Chemical adsorption (also called chemisorption) occurs when molecules become bonded to atoms on the surface of a solid.

You must be careful to distinguish between the words **adsorb** and **absorb**. Adsorb means to bond to the surface of a substance. Absorb means to move right into the substance – rather like a sponge absorbs water.

Examples:

1. Iron in the Haber Process
2. Transition elements in catalytic converters
3. Vanadium (V) oxide in the contact process