Chem Factsheet

www.curriculum-press.co.uk Number 184

Rate vs Yield I

To succeed in this topic you need to:-
- Be able to write balanced equations for reactions
- Be familiar with basic concepts related to equilibria and le Chatelier's Principle (Factsheet 9)
- Be familiar with basic concepts related to reaction kinetics (rates of reaction) (Factsheet 10)

After working through this Factsheet you will:-
- Have revisited the key concepts associated with kinetics
- Have had the opportunity to see some worked examples of typical exam questions on this topic.

This is the first of two linked Factsheets dealing with the confusion that can arise when you are asked questions about either reaction rates or yield and equilibria, both because there are areas of overlap between the two concepts and also because they are both affected in some way by a similar list of variables, such as concent!ation, temperature and pressure.

This first Factsheet will start by considering the ideas specifically related to the rates topic while the second will move on to look at equilibria and the areas of overlap and potential confusion.

Reaction Kinetics

The study of reaction rates at A-level comes under the heading of *chemical kinetics*. An understanding of the factors affecting the rates of chemical reactions depends on an appreciation of the *collision theory*, which essentially states that for a reaction to occur the reactant particles must collide with each other. Only a certain proportion of the total collisions actually result in chemical change; these are called *successful collisions*. The successful collisions are those that have sufficient energy (*activation energy*) at the moment of impact to break the existing bonds and form new bonds, resulting in the formation of the products of the reaction.

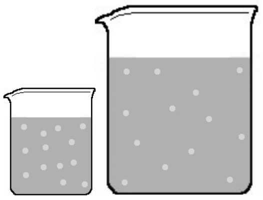
The effect of any variable on the rate of a reaction can therefore be explained in terms of its effect on either or both of the *collision frequency* and/or the proportion of *successful collisions*. In accordance with the collision theory, an increase in either of these will result in an overall increase in the reaction rate.

Successful collision
A molecular collision that **DOES** result in chemical change

Make sure that you can write definitions for each of the terms in italics above. When revising a good way to get to grips with this sort of basic recall learning is to use index cards. Write a key-word or phrase in big letters on the front of the card and then the definition and a few key, related bullet points on the back.

You can then test yourself in the future by trying to write out what's on the back just by looking at the word or phrase on the front.

Concentration



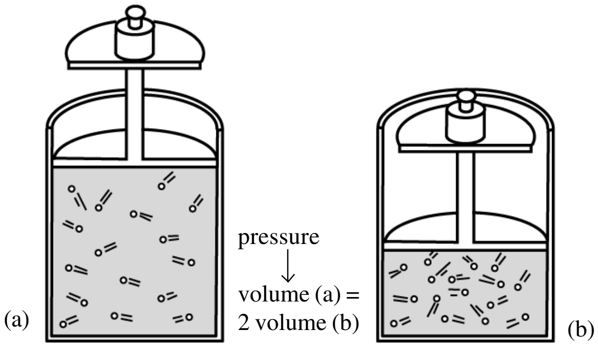
This concept is most usually applied to solutions but can also be used to describe gases in sealed containers. The concentration of a substance refers to the number of particles (i.e. the *amount* of substance) per unit volume – usually measured in mol dm^{-3}.

If reactant concentration is increased then the number of particles (moving around) in any given volume increases, which, in turn, increases the chance of collisions occurring between them. If the chance of collisions occurring increases then, inevitably, the frequency of successful collisions will also increase, so increasing the rate of reaction.

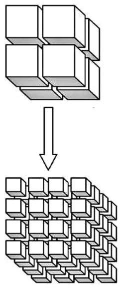
It is worth noting that the *proportion* of successful collisions stays the same if only the concentration changes but, if the overall collision frequency increases, then so too will the frequency of successful collisions.

Pressure

Increasing the pressure of a gas is the equivalent of increasing the concentration of a solution as the end result will be an increase in the number of gas particles in any given volume. The fact that increasing gas pressure increases reaction rate is therefore also explained in terms of increasing chance of collision leading to a greater successful collision frequency.



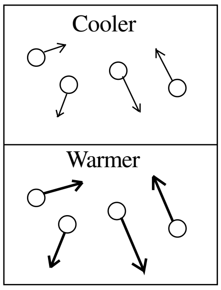
Surface Area (of solid reactants)



If a solid reactant is ground up into fine pieces then, by comparison with larger pieces, more of the fundamental particles are exposed at the surface (i.e. the surface area to volume ratio increases). The corresponding increase in reaction rate is therefore again explained by an increase in the chance and therefore the frequency of successful collisions between reacting particles.

Temperature

As temperature increases, molecules gain thermal energy and will move around more quickly. This will increase the collision frequency and so increase the rate – but this only explains a tiny fraction of the observed increase in rate with increasing temperature (it is possible to calculate that, for a typical reaction occurring near room temperature, with an activation energy of +50 kJ mol^{-1}, a 10 K increase in temperature will only cause the collision frequency to increase by about 1.7%, but the rate will approximately double – i.e. a 100% increase!) – there must be another, much more important, factor at work to explain the magnitude of the effect of temperature on rate.



The Arrhenius Equation is an expression that shows the relationship between the rate constant (and therefore the rate) of a reaction, the temperature and activation energy of the reaction: $k = Ae^{-Ea/RT}$ and, within this expression, the term $e^{-Ea/RT}$ gives a 'count' of the number of molecules with energy greater than the activation energy, E_a, for the reaction. Substituting typical values into this term allows the effect of temperature to be illustrated mathematically (although this 'proof' is not required at A level)

$\underline{\text{at 298 K:}}$ $e^{-Ea/RT} = e^{-50000/8.31 \times 298} = 1.7 \times 10^{-9}$

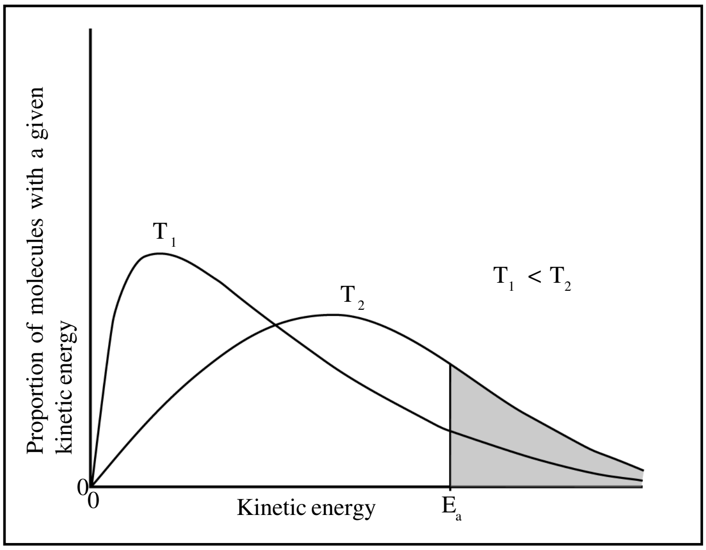
$\underline{\text{at 308 K:}}$ $e^{-Ea/RT} = e^{-50000/8.31 \times 308} = 3.3 \times 10^{-9}$

i.e. the value, and therefore the number of molecules whose energy is greater than the activation energy, has nearly doubled.

N.B. It is a common misconception that a temperature increase of 10 K always causes a doubling of rate – but this is only approximately true when the activation energy is around +50 kJ mol^{-1} and the temperature is close to room temperature. The increase needed to cause a doubling of rate will vary considerably for different values of activation energy and at temperatures well above room temperature.

This argument can be summarised and explained by reference to the Maxwell-Boltzmann distribution of molecular energies

Kinetic energy distribution of the particles in a substance at different temperatures



The shaded areas to the right of E_a represent the numbers of molecules with $E > E_a$ and it can clearly be seen that this area is much greater at the higher temperature, T_2, than at the lower temperature, T_1. This means that, at the higher temperature, as a much greater proportion of the molecules have $E > E_a$ then a correspondingly much greater proportion of the collisions between them will be successful collisions.

Catalysis

A catalyst is a substance that increases the rate of a chemical reaction, without itself being used up in the process. It acts by somehow allowing the reaction to occur by a different mechanism, with a lower activation energy. If the activation energy is lowered then the energy of the molecules, and therefore the collision frequency, are unaffected, but a larger proportion of the molecules will have $E > E_a$ and so the proportion of successful collisions is increased, thus increasing the rate.

Practice Questions

1. State what is meant by the term *rate of reaction*
2. The gas-phase reaction between hydrogen and chlorine is very slow at room temperature. $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$
   (a) Define the term *activation energy*
   (b) Give **one** reason why the reaction between hydrogen and chlorine is very slow at room temperature.
   (c) Explain why an increase in pressure, at constant temperature, increases the rate of reaction between hydrogen and chlorine.
   (d) Explain why a small increase in temperature can lead to a large increase in the rate of reaction between hydrogen and chlorine.
   (e) Give the meaning of the term *catalyst*.
   (f) Suggest **one** reason why a solid catalyst for a gas-phase reaction is often in the form of a powder.

Answers

1. *Rate of reaction* : Change in <u>concentration</u> **(1)** <u>per unit time</u> / per second / per minute **(1)**

2. (a) Minimum collision energy **(1)** to start a reaction / for a reaction to occur/ for a successful collision **(1)**]
   (b) Activation energy is high / few molecules/particles have sufficient energy to react/few molecules/particles have the required activation energy **(1)** *(or breaking bonds needs much energy)*
   (c) Molecules are closer together/ more particles in a given volume **(1)** therefore collide more often **(1)**
   (d) Many **(1)** more molecules have energy greater than activation energy **(1)**
   (e) Speeds up a reaction but is chemically unchanged at the end **(1)**
   (f) Increases the surface area **(1)**

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