Chem Factsheet

www.curriculum-press.co.uk Number 190

Rate vs Yield II

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 (Factsheet 10)

After working through this Factsheet you will:-
- Have revisited the key concepts associated with equilibria
- Understand the overlap between the ideas of rates and equilibria as well as the separate nature of each
- Have had the opportunity to see some worked examples of typical exam questions on these topics.

This is the second of two linked Factsheets dealing with the confusion that can arise when you are asked questions about either reaction rates or yield and equilibria (or 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 concentration, temperature and pressure.

The first factsheet started by considering the ideas specifically related to the rates topic while this second one will move on to look at equilibria and the areas of overlap and potential confusion.

Yield

There are three possible reasons why the total mass of the desired product (called the yield) is not always the same as suggested by the balanced equation for the reaction.

1. You might lose some of the products when you try to separate them from the mixture after the reaction has finished.
2. Some of the reactants may form different products from the ones you want. An example would be the preparation of a primary amine by reaction of ammonia with a halogenoalkane; when further substitutions lead to a mixture of the primary amine with secondary and tertiary amines as well as quaternary ammonium salts.
3. The reaction may be reversible, leading to an equilibrium mixture.

We will focus here on the third possibility.

Equilibria

A *dynamic equilibrium* occurs when a *reversible reaction* takes place in a *closed system*. A *closed* system is a system that allows the transfer of energy with the surroundings but NOT the transfer of matter.

At equilibrium, the quantities of everything present in the mixture remain constant, although the forward and reverse reactions are both still continuing. This is because the rates of the forward and the reverse reactions are equal, so that the reactants and products are used up and made at the same rate.

A typical equilibrium can be represented as: $A + B \rightleftharpoons C + D$

In this case A and B are called the "reactants", C and D are called the "products". The reaction between A and B to form C and D is called the *forward reaction* and the reaction between C and D to form A and B is called the *reverse reaction*.

If the reaction conditions were somehow changed, so that a new equilibrium is established, containing more C and D than the original equilibrium mixture, then we can say that the *position of equilibrium* has shifted (moved) to the right. Alternatively, we could say that the *yield* of product(s) has increased.

On the other hand, if the changes led to a new equilibrium with less C and D than the original mixture then we say that the position of equilibrium has shifted to the left and the yield of product(s) has decreased.

Le Chatelier's Principle

It is important to remember that, although you may well be asked to give a definition of Le Chatelier's Principle, it does not actually explain anything. It simply provides a summary of the outcomes of any change in reaction conditions made.

The principle can be quoted as:
"If any constraint is applied to a system in equilibrium then the system will adjust itself in such a manner as to counteract the effect of this constraint as far as is possible"

Or, if that is a bit 'old school' then think of it as simply:
"If any of the conditions are changed then an equilibrium will move to oppose the change"

The principle can be used to work out what will happen to an equilibrium mixture if any of the key conditions such as concentration, temperature or pressure are changed. The outcomes are summarised in the table below, for the generalised equilibrium: $aA + bB \rightleftharpoons cC + dD$

Note : [X] represents the concentration of X in mol dm^{-3}

Changes imposed on equilibrium system	**Shift in equilibrium position**
Increase [A] and/or [B] or Decrease [C] and/or [D]	To the right (increased yield)
Decrease [A] and/or [B] or Increase [C] and/or [D]	To the left (decreased yield)
Increase temperature	In the endothermic direction i.e. to the right if forward reaction is endothermic and to the left if forward reaction is exothermic
Decrease temperature	In the exothermic direction i.e. to the right if forward reaction is exothermic and to the left if forward reaction is endothermic
Increase pressure (or decrease volume)	*NB only affects gaseous systems:* To the right if (a + b) > (c + d) i.e. if more moles of gas on the left of the equation To the left if (c + d) > (a + b) i.e. if more moles of gas on the right of the equation
Decrease pressure (or increase volume)	*NB only affects gaseous systems:* To the right if (c + d) > (a + b) i.e. if more moles of gas on the right of the equation To the left if (a + b) > (c + d) i.e. if more moles of gas on the left of the equation
Adding a catalyst	None

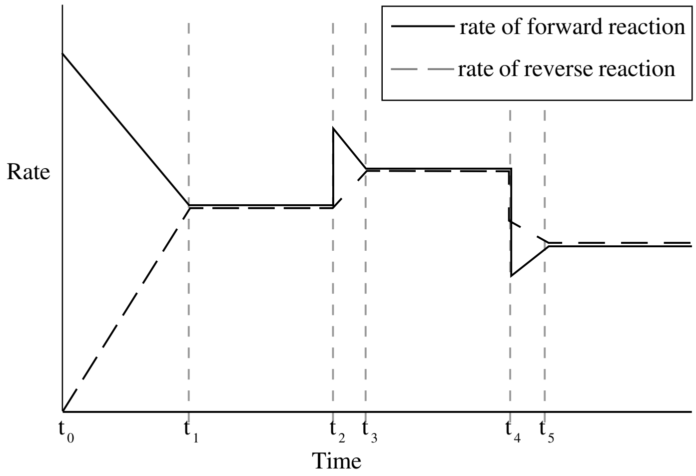
Overlap and Confusions

Apart from the fact that both topics often involve discussion of a similar list of variables, confusion can often arise because:

1. A more detailed discussion and explanation of *equilibria* inevitably involves mention of *rate*, because dynamic equilibria depend on the rates of the forward and reverse reactions being equal. Any 'response' to a change in the conditions arises from this equality of rates being disrupted.
2. Both topics (at A2 level!) involve mention of a term expressed as the letter 'k'. *k* is used to represent the rate constant in a rate equation, *K* is used to represent the equilibrium constant.

Explaining equilibria in terms of rate

A graph of rate vs time can be used to represent how an equilibrium is established and then how it 'responds' to changes in conditions.



1. $t_0 - t_1$: assuming the process is started by mixing the reactants together under suitable conditions then the rate of the forward reaction is initially high and of the reverse reaction is initially low because the reactant concentrations start relatively high and the product concentrations relatively low. Reactants are therefore being used up more quickly than they are being made so their concentrations will fall and the forward rate will also therefore fall. Products are being made more quickly than they are being used up so their concentrations will rise and the reverse rate will also therefore rise.
2. $t_1 - t_2$: the forward and reverse rates have become equal so both products and reactants are being used up and made at the same rate so their concentrations remain constant. The reaction is at equilibrium here!
3. at t_2: a reactant concentration is increased so the forward rate increases with no immediate impact on the reverse rate. The forward rate has therefore become greater than the reverse rate.
4. $t_2 - t_3$: Reactants are again being used up more quickly than they are being made so their concentrations will fall and the forward rate will also therefore fall. Products are being made more quickly than they are being used up so their concentrations will rise and the reverse rate will also therefore rise, until they again become equal and a 'new' equilibrium is established.
5. $t_3 - t_4$: the forward and reverse rates have become equal so both products and reactants are being used up and made at the same rate so their concentrations remain constant. As, for a while, the forward rate has been greater than the reverse rate there will have been a net production of product so this new equilibrium will contain higher product concentrations than the original equilibrium so we say that the position of equilibrium has shifted to the right or that the yield of product has increased.
6. at t_4: assuming that the forward reaction is endothermic (hence the reverse reaction is exothermic) this represents the 'response' following a reduction in temperature. Both rates will be decreased but the rate of the endothermic reaction will be affected to a greater extent (this can be proved using the Arrhenius equation but this goes beyond the scope of any A level syllabus). The rate of the reverse reaction will therefore be temporarily greater than the rate of the forward reaction.
7. $t_4 - t_5$: products are being used up more quickly than they are made so their concentrations will fall and the reverse rate will also therefore fall. Reactants are being made more quickly than they are being used up so their concentrations will rise and the forward rate will also therefore rise, until they again become equal and a 'new' equilibrium has been established. As, for a while the reverse rate has been greater than the forward rate there will have been a net production of reactant so this new equilibrium will contain higher reactant concentrations than the original equilibrium so we say that the position of equilibrium has shifted to the left or that the yield of product has decreased.

k vs *K* (A2 only)

Changes imposed	rate constant, *k*	Effect on equilibrium constant, *K*
Changing concentration	No change	None
Changing pressure	No change	None
Increasing temperature	Increases	Increases if forward reaction is exothermic Decreases if forward reaction is endothermic
Decreasing temperature	Decreases	Decreases if forward reaction endothermic Increases if forward reaction is exothermic
Adding a catalyst	Increases	None

Practice Questions

When ammonia gas is heated, a homogeneous, dynamic equilibrium is established between ammonia and its constituent elements. This decomposition is endothermic.

(a) Explain the terms *homogeneous, dynamic* and *equilibrium*. Write an equation for this decomposition and give an expression for the equilibrium constant, *K*c (5)

(b) State and explain the conditions under which a high equilibrium concentration of hydrogen would be obtained.(4)

(c) The decomposition of ammonia might be used as an industrial method for making hydrogen. Explain why an industrial chemist might decide to use conditions different from those you have given in part (b) if large quantities of hydrogen were to be produced by this decomposition. Discuss the effect that using a catalyst would have on the equilibrium yield and on the amount of hydrogen which could be produced in a given time. (6)

Answers

(a). Homogeneous; All reactants in the same phase or state **(1)**
Dynamic; Continuous or 'on-going' **(1)**
Equilibrium: Concentrations of reactants and products constant or rates of forward and reverse reactions equal **(1)**
Equation; $2NH_3 \rightleftharpoons N_2 + 3H_2$ (Must be decomposition) **(1)**
*K*c; $[N_2][H_2]^3/[NH_3]^2$ **(1)**]

(b). Decomposition favoured by high temp **(1)** since the reaction endothermic or logical application of Le Chatelier's principle **(1)**. Decomposition favoured by low pressure **(1)** 2 mole gas giving 4 moles gas or more gas moles on right **(1)**

(c) In practice low pressure means low yiel**d (1)**
Low pressure means low rat**e (1)**
High temperature means high rat**e (1)**
High temperature expensive in terms of the cost of energy requirements **(1)**
Catalyst: equilibrium yield unaffecte**d (1)**
Rates of forward and backwards reactions increased by an equal amoun**t (1)**
more hydrogen produced in a given tim**e (1)**

Acknowledgements: *This Factsheet was researched and written by Tony Tooth.* ***Curriculum Press, Bank House, 105 King Street, Wellington, Shropshire, TF1 1NU. ISSN 1351-5136***