Rates and equilibria

Student worksheet: CDROM index 31SW

Discussion of answers: CDROM index 31DA

Topics

Equilibria (K_c, K_p, Le Chatelier's principle), the rate equation, the rate constant, the Arrhenius equation and activation energy.

Level

Able post-16 students.

Prior knowledge

Rates of reaction, rate equations and K_c (K_p would be helpful but it is explained in the worksheet).

Rationale

This activity demonstrates the links between the topics of rates of reaction and the equilibrium law. It provides students with an explanation of the equilibrium law and helps them explain why Le Chatelier's principle works for temperature, concentration and pressure.

The information card approach helps students develop their communication skills and their synthesis – higher order thinking.

Use

This is a group activity and groups of three or four students are ideal. Each group should have one set of the information cards which is dealt out between the members of the group. The cards are labelled with which part of the activity they are for; they can all be dealt out at the start and the students told to refer just to the cards for the part of the activity they are working on. They should not 'lay their cards out on the table' unless they

are stuck.

Cards which have an asterisk (*) can be held back by the teacher initially and given to the students when or if they need help.

The groups could produce one set of written answers which could be reviewed in the light of the *Discussion of answers* sheet by another group (with instructions to be positive in their comments).

If you want to reuse the information cards it is helpful to reproduce them on different coloured card or paper.

Chemistry for the gifted and talented

Rates and equilibria

You have been given some information cards. You can share this information with other members of the group (*ie* tell them about it), although you should not show other people in your group your cards. You will need to use the information cards for parts 1, 2 and 4. The cards are labelled according to which part of the activity they relate to.

Part 1

Use the information in the cards to help explain why K_c for a single step reaction
$A + B \rightleftharpoons C + D$ is equal to $[C][D]/[A][B]$.

Part 2

The cards contain information about a multi-step reaction.

Use the information in the cards to:
- write an overall equation for the equilibrium; and
- show that the ratio $[C][D]/[A]^2[B]$ has a constant value.

Part 3

a) Make up your own hypothetical multi-step reaction and show that at equilibrium K_c is a constant value.
b) Explain the effect of lowering the concentration of product on the position of equilibrium in terms of rate of reaction.
c) For the equilibrium $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$, write down the expression for K_p. (K_p is similar to K_c except that, instead of concentrations in mol dm^{-3} for K_c, the ratio is expressed in terms of the partial pressures of the gases involved for K_p.)
d) Use the fact that $P_A = X_A \times P_{Total}$ to explain why increasing the pressure (at constant T) favours the production of NH_3.

P_A is the partial pressure of gas A in a mixture of gases;
X_A is the mole fraction of A = moles of A/moles of all the gases in the mixture; and
P_{Total} is the total pressure (the sum of all the partial pressures).

Part 4

Use the information on the cards to account for the effect of temperature on the position of equilibrium (extra card to show rule about how $e^a/e^b = e^{a-b}$).

At equilibrium the forward rate equals the backward rate.

Part 1

For a single step reaction, each species involved in the step will appear in the rate equation.

Part 1

At equilibrium
$$\frac{k_f}{k_b} = \frac{[C][D]}{[A][B]}$$

Part 1*

K_c for a single step reaction equals k_f/k_b, where kf and kb are the rate constants for the forward and back reactions.

Part 1

The forward rate
$= k_f [A][B]$

Part 1*

The backward
rate $= k_b [C][D]$

Part 1*

The rate constant
for a particular step
is constant at a
given temperature.

Part 1

At equilibrium

$k_f[A][B] = k_b[C][D]$

Part 1*

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K_c is a constant value for an equilibrium system at constant temperature.

Part 1

The second step is the rate determining step for the forward reaction.

Part 2

Step 1 in the multi-step reaction is
$A + E \rightleftharpoons G$

Part 2

Step 2 in the multi-step reaction is
$A + G \rightleftharpoons H + E$

Part 2

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Step 3 in the multi-step reaction is
$H + B \rightleftharpoons C + D$

Part 2

The equilibrium constant for step 1 is k_1 and for step 2 is k_2 etc.

Part 2

If the overall reaction is at equilibrium, each step must be at equilibrium.

Part 2*

If K_1, K_2, and K_3 are constants, then K_1 x K_2 x K_3 is also a constant.

Part 2*

Overall equation
2A + B ⇌ C + D

Part 2

$$K_1 = \frac{[G]}{[A][E]}$$

$$K_2 = \frac{[H][E]}{[A][E]}$$

$$K_3 = \frac{[C][D]}{[H][B]}$$

Part 2

$$K_1 \times K_2 \times K_3 =$$
$$\frac{[G]}{[A][E]} \times \frac{[H][E]}{[A][G]} \times \frac{[C][D]}{[H][B]}$$

Part 2*

$$K_1 \times K_2 \times K_3 =$$
$$\frac{[C][D]}{[A]^2[B]} = K_c$$

Part 2*

Reagent *E* is acting as a catalyst.

Part 4

The value of K_c is not affected by which step is the rate determining step.

Part 4

Arrhenius found that the variation in the rate constant (*k*) with temperature for a reaction could be expressed by the equation

$k = Ae^{-E_a/RT}$

Part 4

K_c for a single step reaction equals k_f/k_b, where k_f and k_b are constants for the forward and back reactions.

Part 4

In the Arrhenius equation E_a can be interpreted as the activation energy.

Part 4*

In the Arrhenius equation A is called the pre-exponential factor and does not vary with temperature.

Part 4

The difference in energy between reactant and products is related to the activation energies
$$E_{a(f)} - E_{a(b)} = \Delta E$$

Part 4

For our purpose we can assume that $\Delta E = \Delta H$

Part 4
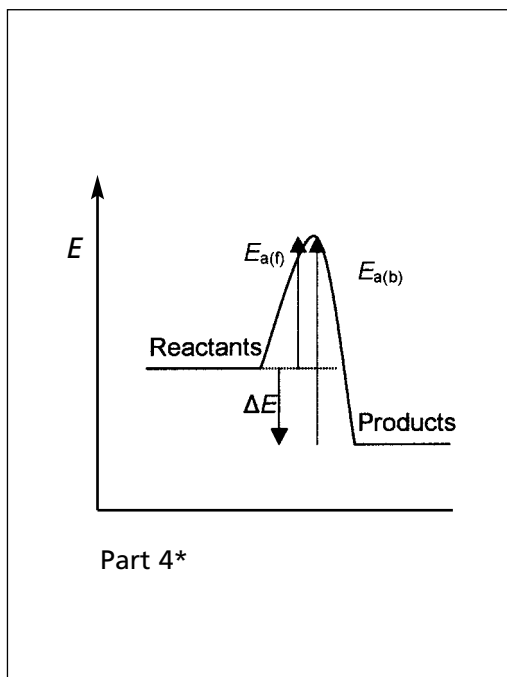
Part 4*

$$K_c = \frac{k_f}{k_b} = \frac{A_f}{A_b}\, e^{(E_{a(b)} - E_{a(f)})/RT}$$

Part 4*

For an endothermic reaction, increasing the temperature increases the value of K_c because an endothermic reaction has a positive ΔH and therefore the fraction $e^{-\Delta HR/T}$ gets *bigger* as T increases.

Part 4

$$K_c = \frac{k_f}{k_b} = \frac{A_f}{A_b}\, e^{-\Delta H/RT}$$

Part 4*

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Discussion of answers

Rates and equilibria

Part 1

*Use the information in the cards to explain why K_c for a single step reaction
$A + B \rightleftharpoons C + D$ is equal to the ratio $[C][D] / [A][B]$.*

At equilibrium the forward rate equals the backward rate.

For a single step reaction, each species involved in the step will appear in the rate equation.

The forward rate = $k_f[A][B]$	The backward rate = $k_b[C][D]$

At equilibrium $k_f[A][B] = k_b[C][D]$

The rate constant for a particular step is constant at a given temperature.	At equilibrium $\dfrac{k_f}{k_b} = \dfrac{[C][D]}{[A][B]}$

K_c for a single step reaction equals k_f/k_b, where k_f and k_b are the rate constants for the forward and back reactions.

K_c is a constant value for an equilibrium system at constant temperature.

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Part 2

The cards contain information about a multi-step reaction.

Use the information in the cards to:

- *write an overall equation for the equilibrium; and*
- *show that the [C][D]/[A]²[B] has a constant value.*

Step 1 A + E ⇌ G
Step 2 A + G ⇌ H + E
Step 3 H + B ⇌ C + D

If the overall reaction is at equilibrium, each step must be at equilibrium.

Overall equation
2A + B ⇌ C + D

The equilibrium constant for step 1 is K_1 and for step 2 is K_2 etc.
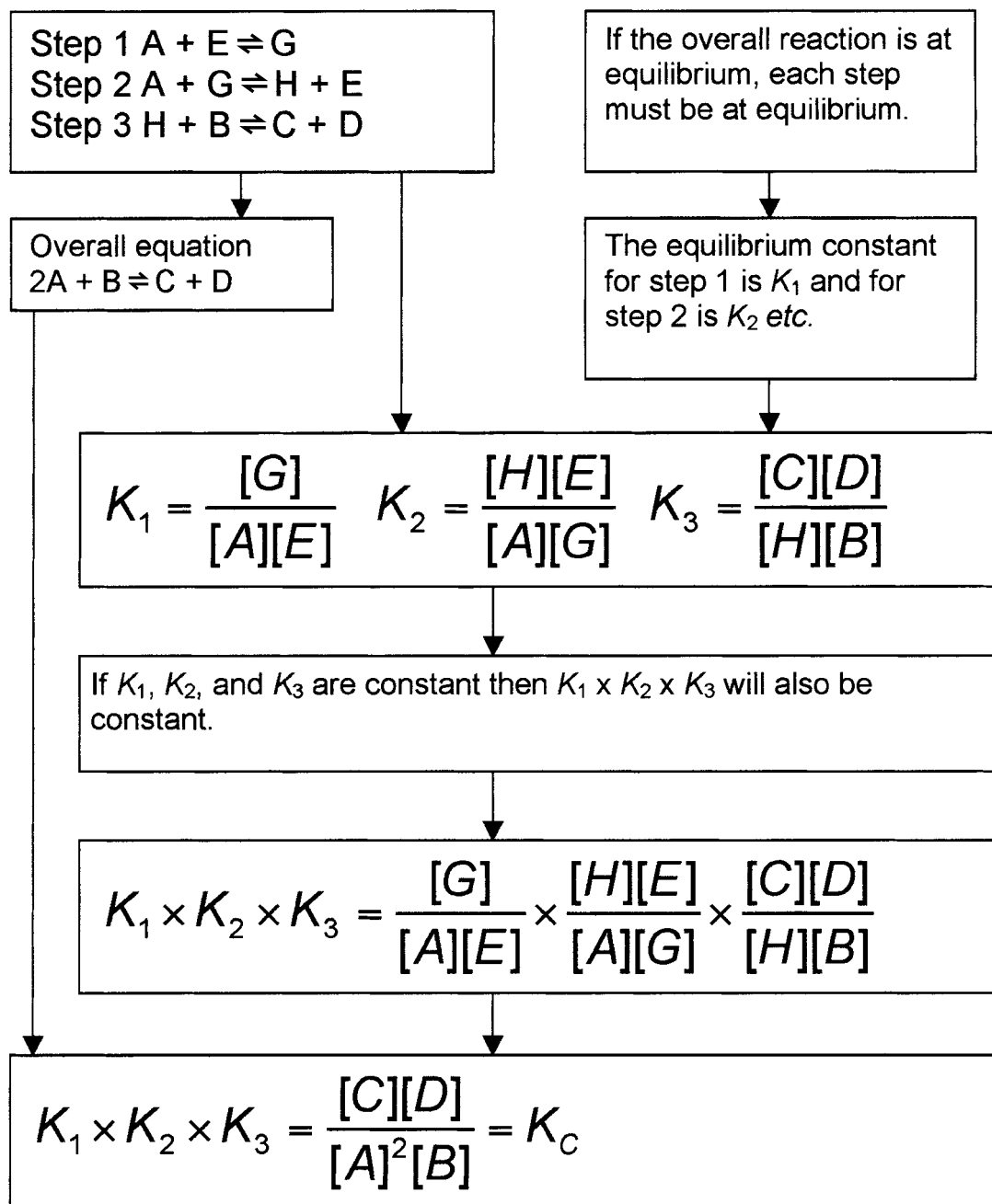
$$K_1 = \frac{[G]}{[A][E]} \quad K_2 = \frac{[H][E]}{[A][G]} \quad K_3 = \frac{[C][D]}{[H][B]}$$

If K_1, K_2, and K_3 are constant then $K_1 \times K_2 \times K_3$ will also be constant.

$$K_1 \times K_2 \times K_3 = \frac{[G]}{[A][E]} \times \frac{[H][E]}{[A][G]} \times \frac{[C][D]}{[H][B]}$$

$$K_1 \times K_2 \times K_3 = \frac{[C][D]}{[A]^2[B]} = K_c$$

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Part 3

a) *Make up your own hypothetical multi-step reaction and show that at equilibrium K_c will be a constant value.*

There are many different possibilities but one example would be

Step 1   A + B $\rightleftharpoons$ C + D

Step 2   C + B $\rightleftharpoons$ F

Overall   A + 2B $\rightleftharpoons$ D + F
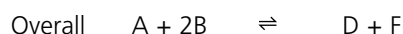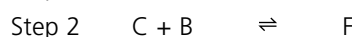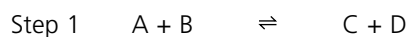
$$K_1 = \frac{[C][D]}{[A][B]} \qquad K_2 = \frac{[F]}{[C][B]}$$

$$K_1 \times K_2 = \frac{[F][D]}{[A][B]^2} = K_c$$

b) *Explain the effect of lowering the concentration of product on the position of equilibrium in terms of rate of reaction.*

The lowering of the concentration of the product decreases the rate of the back reaction so that it is temporarily less than the forward rate. The system is not now in equilibrium but will re-establish equilibrium after a period of time. Reactants are converted to product at a faster rate than the reverse reaction until the two rates are equal again. Because more product has formed we describe this as a shift to the right in the position of equilibrium.

c) For the equilibrium $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$, write down the expression for K_p.

$$K_p = \frac{P_{NH_3}^2}{P_{N_2} \times P_{H_2}^3}$$

d) *Use the fact that $P_A = X_A \times P_{Total}$ to explain why increasing the pressure (at constant T) favours the production of NH_3.*

$$K_p = \frac{P_{NH_3}^2}{P_{N_2} \times P_{H_2}^3} = \frac{X_{NH_3}^2 \times P_{Total}^2}{X_{N_2} \times X_{H_2}^3 \times P_{Total}^4}$$

$$K_p = \frac{X_{NH_3}^2}{X_{N_2} \times X_{H_2}^3} \times \frac{1}{P_{Total}^2}$$

So when P_{Total} is increased the mole fraction of NH_3 has to increase because K_p has to remain constant.

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Part 4

Use the information on the cards to help account for the effect of temperature on the position of equilibrium.

K_c for a single step reaction equals k_f/k_b, where k_f and k_b are the rate constants for the forward and back reactions.

Arrhenius found that the variation in the rate constant (k) with temperature for a reaction could be expressed by the equation $k = Ae^{-Ea/RT}$

In the Arrhenius equation A is called the pre-exponential factor and does not vary with temperature.

In the Arrhenius equation E_a can be interpreted as the activation energy.

$$K_c = \frac{k_f}{k_b} = \frac{A_f}{A_b}e^{(E_{a(b)}-E_{a(f)})/RT}$$

The difference in energy between reactants and products is related to the activation energies
$E_{a(f)} - E_{a(b)} = \Delta E$

For our purpose we can assume that $\Delta E = \Delta H$

$$K_c = \frac{k_f}{k_b} = \frac{A_f}{A_b}e^{-\Delta H/RT}$$

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