The Arrhenius Equation

You should have done some advanced kinetics before reading this primer. If not, you can read the **Reaction Kinetics** primer on *CramNow*

The Arrhenius Equation is a very important relationship in chemistry. It is right at the heart of explaining the effect of temperature and catalysis on the rate of a chemical reaction. It is needed to explain why equilibrium position is affected by changes in temperature. It adds a quantitative nature to the more qualitative link between temperature and rate.

We have previously used a simplified form of kinetic theory and the Maxwell-Boltzmann Distribution of molecular energies to explain why reactions go faster at higher temperatures. It's time to find out about a more detailed relationship and mathematical link between temperature, activation energy and rate.

The equation was worked out by the Swedish chemist, Svante Arrhenius about 80 years ago. Arrhenius has given the world of chemistry, so much. His work on the study of acids won him the Nobel Prize. My personal view is that the work that led to this equation, is even more impressive as it explains so much fundamental chemistry.

Before we look at (and explain) the equation, let's remind ourselves of some basic kinetic theory so that we can understand what we need to explain.

For a reaction to proceed, the particles of reactants must:

1. collide with each other.
2. collide with at least a minimum combined energy for successful collisions to occur (the activation energy)
3. collide with the correct orientation to each other.

So, we need an equation to build in all these requirements.

One more thing which we also need to recall is the **rate law** and the **rate constant, k**

Consider the following simple reaction between solutions of reactants A and B.

$$A_{(aq)} + B_{(aq)} \rightarrow C_{(g)}$$

Let's say that we have found out the following rate equation, by experiment.

$$\text{rate} = \mathbf{k}\,[A]^1 \times [B]^1$$

Clearly, if we carry out two experiments where only the temperature is changed, then the increased rate must be a result of an increased value of k.

So, for fixed concentrations of A and B, $\text{rate} \propto k$.

If we can link k to **temperature** and **activation energy**, then we can also link temperature and activation energy to the **rate**. This is exactly what the Arrhenius Equation is going to do for us!

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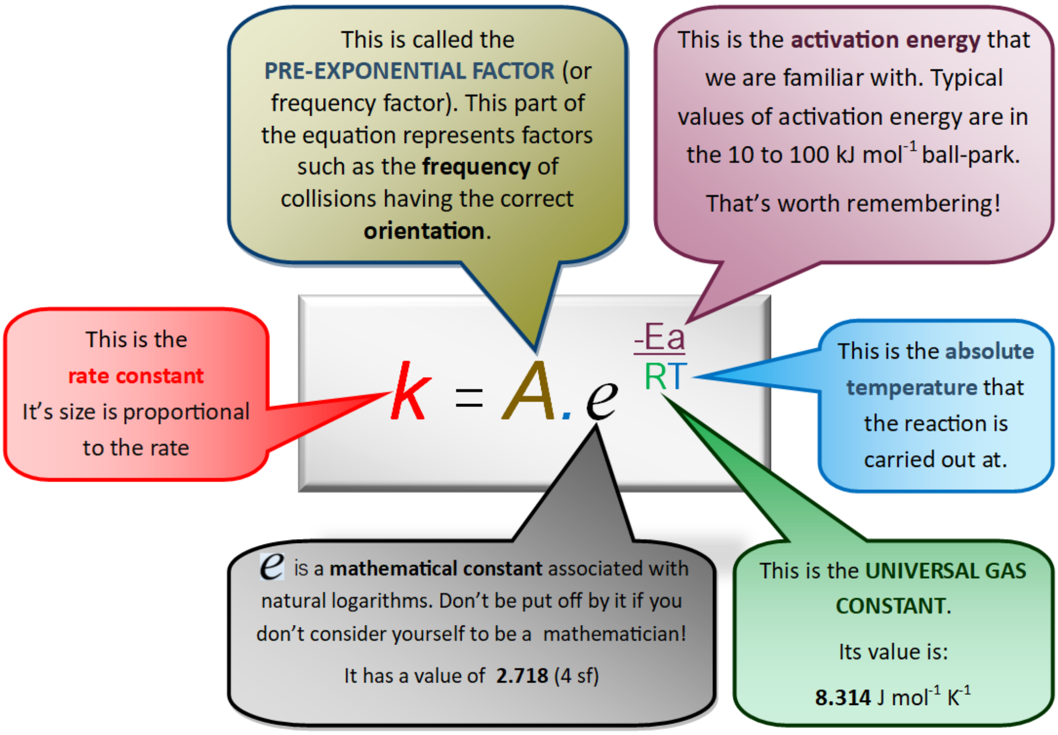
The Arrhenius Equation



Now we have this relationship, there is so much that we can do with it.

Things that we can do with the Arrhenius equation:

1. Calculate the Activation Energy for reactions using some simple experimental data.
2. Demonstrate quantitatively, the effect of temperature on the rate of reaction.
3. Demonstrate quantitatively, the effect of catalysis on the rate of reaction.
4. Explain the effect of changing temperature on the position of equilibrium in a chemical reaction.

Personally speaking, the most impressive thing that can be done with this equation is to use it to access values of Activation Energy by carrying out a small number of simple rates experiments. I never cease to be amazed that a handful of experiments done in a hour's work in the lab, using nothing elaborate, can give a pretty good value of the activation energy for a reaction.

I'm going to go through each of these uses of the Arrhenius Equation.

Using the Arrhenius Equation to Obtain and Activation Energy for a Reaction

The first thing we need to do is to write the equation in a slightly different form.

$$k = A.e^{-Ea/RT}$$

Taking natural logs of both sides $\quad \ln k = \ln (A.\, e^{-Ea/RT})$

$$\ln k = \ln A + \ln e^{-Ea/RT}$$

$$\ln k = \ln A + \frac{-Ea}{RT}$$

$$\ln k = \frac{-Ea}{RT} + \ln A$$

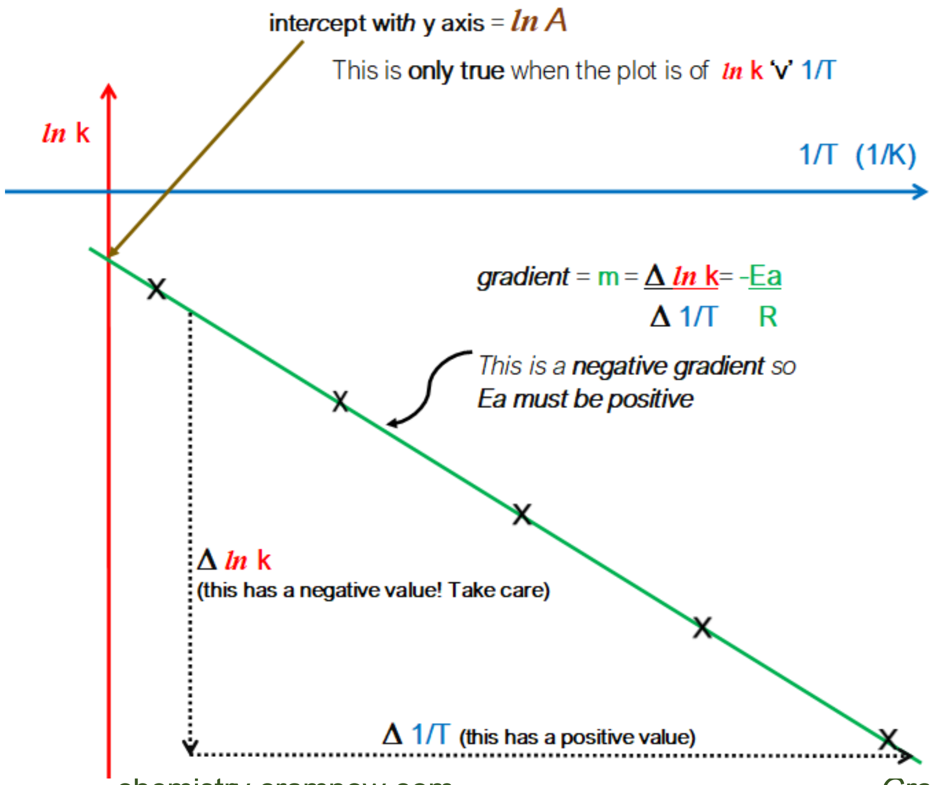
Pulling Ea away from temperature $\quad \ln k = -\frac{Ea}{R} \times \frac{1}{T} + \ln A$

Now that we have got this last equation, we can see that this maps nicely onto the equation for linear regression: $y = m\,x + c$

$$\ln k = -\frac{Ea}{R} \times \frac{1}{T} + \ln A$$

$$y = m \quad x + c$$

Arrhenius Plot



Theoretically, what one needs to do it obtain several values of rate constant, each one being obtained at a different temperature.

Once you have some k and T values, they can be converted into *ln* k and 1/T

These can then be plotted on axes like those above. The intercept of the plotted line with the y axis will give the value of *ln A.*

However, obtaining values of k can be long winded and require lots of experiments (using the initial rates method explained on the Reaction Kinetics on *CramNow*).

Here's where we can make our lives a little simpler and still be able to arrive at the Activation Energy, which is what we have set out to do.

Let's recall something about 'Clock Reactions'. If you aren't clear what Clock Reactions are, you really should read the Reaction Kinetics.

In brief, we can carry out a **clock reaction** at a given temperature and measure a time, **t** (for something specific to happen, *e.g.* a cross disappearing when we look at it through a solution. You'll probably have done one of these!).

We can state the following for a clock reaction:

$$\frac{1}{t} \; \alpha \; \text{rate} \; \alpha \; k$$

This doesn't say that: 1/t = rate = k

But, because there is the proportionality sign, we can still use 1/t in our Arrhenius Equation to 'stand in' for rate. The rules of maths allow us to do this, but there will be a small price to pay for this relative simplification. See below:

This equation is used if values of **k** have been worked out at different temperatures.

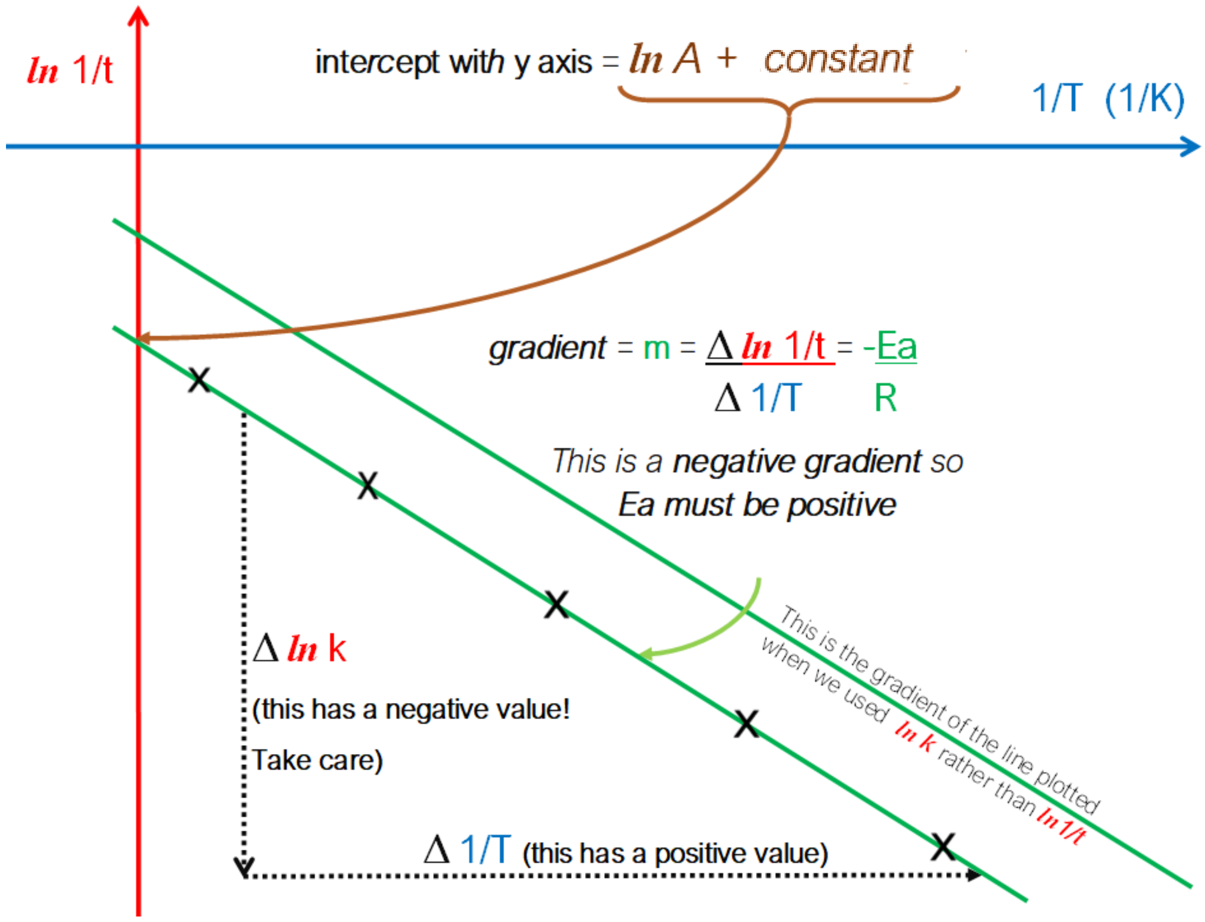
$$\ln k = -\frac{Ea}{R} \times \frac{1}{T} + \ln A$$

This equation is used if values of **1/t** or initial rate have been worked out at different temperatures.

$$\ln \frac{1}{t} = -\frac{Ea}{R} \times \frac{1}{T} + (\ln A + \text{constant})$$

$$y = m \quad x + c$$

A plot of *ln* 1/t 'v' 1/T is given below.



The important thing to notice is that the line generated from a plot of *ln* 1/t 'v' 1/T has exactly the same gradient as the line that is produced if we plot *ln* k 'v' 1/T.

However, I said that there would be a small price to pay. Here it is.

The intercept with the y axis is no longer equal to *ln A*. It is now qual to *ln A* + *ln* constant.

In summary:

1 Experiments that produce values of the rate constant k at different temperatures can be used produce graphs. The gradient of these graphs is used to find Ea (the -ve gradient x R) and *ln* A (the intercept with the y axis)

2 Experiments that produce values of the initial rates or 1/t at different temperatures can be used produce graphs. The gradient of these graphs is used to find Ea (the -ve gradient x R) but the intercept with the y axis is now longer equal to *ln* A

A worked example is given at the end of this primer.

A Useful Form of the Arrhenius Equation.

There is a way in which we can manipulate the Arrhenius equation which will allow us to determine the activation energy as long as we know the rate constants at 2 different temperatures

Here's how we get there:

Seen before:

$$k = A.e^{-Ea/RT}$$

$$\ln k = \frac{-Ea}{RT} + \ln A$$

Now let's consider a chemical reaction that is performed at 2 different temperatures T_1 and T_2 where $T_1 < T_2$.

Values of A and Ea are the same in both reactions.
Values of k_1 at T_1 and k_2 at T_2 could be looked up or worked out experimentally.

So, we have two equation for the different temperatures

$$\ln k_1 = \frac{-Ea}{RT_1} + \ln A \quad \text{and} \quad \ln k_2 = \frac{-Ea}{RT_2} + \ln A$$

$$\ln k_2 - \ln k_1 = \left[\frac{-Ea}{RT_2} + \ln A\right] - \left[\frac{-Ea}{RT_1} + \ln A\right]$$

$$\ln k_2 - \ln k_1 = \left[\frac{-Ea}{R} \times \frac{1}{T_2}\right] - \left[\frac{-Ea}{R} \times \frac{1}{T_1}\right] + \ln A - \ln A$$

$\ln A$ has disappeared:

$$\ln k_2 - \ln k_1 = \left[\frac{-Ea}{R} \times \frac{1}{T_2}\right] - \left[\frac{-Ea}{R} \times \frac{1}{T_1}\right]$$

$$\boxed{\ln\left(\frac{k_2}{k_1}\right) = \frac{-Ea}{R}\left[\frac{1}{T_2 - T_1}\right]}$$

The value of Ea can now be obtained. Essentially, you're doing nothing different than when you plot a graph and work out the gradient.

$\ln\left(\frac{k_2}{k_1}\right)$ Is the change on the y axis and $\left[\frac{1}{T_2 - T_1}\right]$ is the change in the x axis.

$\frac{-Ea}{R}$ is the gradient

Using the Arrhenius Equation to Show the Effect of Temperature on Reaction Rate

$$k = A.e^{-Ea/RT}$$

To see how temperature affects the rate in a quantitative way, we are going to use the Arrhenius equation.

I'm going to look at the **relative change** in the number of particles that possess the minimum required energy to react. This will be done by calculating two different values of the exponential factor. The value of *A* is a constant.

$$e^{-Ea/RT}$$

It is this part of the equation that will give us an idea of the proportion of particles that have sufficient energy to stand a chance of reacting. They still may not react upon their collision because of their not having the correct orientation. Only a very tiny proportion if collisions are successful due to the lack of correct orientation. (That aspect of collisions is dealt with in the pre-exponential factor, *A*. The value of *A* is a constant for a given reaction.)

We will compare values of $e^{-Ea/RT}$ at 2 different temperatures. A sensible temperature to start with could be a typical lab temperature (20°C, 293K). Then we'll raise the temperature by 10°C to 30°C, 303K.

We need to choose a value of activation energy. I think it's a good idea to remember that Activation Energies are often around 10-100kJ mol^{-1}. I will go for 50kJ mol^{-1}

@ 293K	Heating up the reaction →	@ 303K
Ea=50 000 J mol^{-1} R =8.314 J mol^{-1}K^{-1} T =20°C = 293K	$e^{-Ea/RT}$	Ea=50 000 J mol^{-1} R =8.314 J mol^{-1}K^{-1} T =30°C = 303K
$e^{-50\,000 / 8.314 \times 293}$		$e^{-50\,000 / 8.314 \times 303}$
$=1.22 \times 10^{-9}$		$=2.40 \times 10^{-9}$

This tells us that if we raise the temperature of a reaction by 10°C at temperatures typically found in lab experiments (between 0 and 100°C), we should see a doubling of rate for that 10°C rise.

So, a 20°C rise should increase the rate by 4 times. Remember, this is a broad rule that applies to typical lab temperatures and for reaction where Ea is around 30-70 kJ mol^{-1}

You may want to test this by checking how rate changes when there is a 10°C rise at temperatures around 1000 K and 100 K.

Using the Arrhenius Equation to Show the Effect of Catalysis on Reaction Rate

$$k = A.e^{-Ea/RT}$$

To see how catalysts affect the rate in a quantitative way, we are going to use the Arrhenius equation.

Like I did on the previous page, I'm going look at the relative change in the number of particles that possess the minimum required energy to react. This will be done by calculating two different values of the exponential factor. The value of *A* is a constant for a given reaction.)

$$e^{-Ea/RT}$$

It is this part of the equation that will give us an idea of the proportion of particles that have sufficient energy to stand a chance of reacting. They still may not react upon their collision because of their not having the correct orientation. Only a very tiny proportion if collisions are successful due to the lack of correct orientation. (That aspect of collisions is dealt with in the pre-exponential factor, *A*. The value of *A* is a constant for a given reaction.)

We'll compare values of $e^{-Ea/RT}$ with 2 different activation energies, Ea. We need to carry out both calculations with a constant temperature. We'll choose a typical lab temperature (20°C, 293K).

We will select a tyical value of activation energy of 75 kJ mol^{-1}. This is the Ea for the decomposition of hydrogen peroxide. We'll then repeat the calculation but with manganese (IV) oxide catalyst. You'll know that catalysts reduces the activation energy. MnO_2 reduces the activation energy to 58 kJ mol^{-1}

Ea=75 000 J mol^{-1} → adding a catalyst → Ea=58 000 J mol^{-1}

$$e^{-Ea/RT}$$

Without catalyst	With catalyst
Ea=75 000 J mol^{-1} R =8.314 J $mol^{-1}K^{-1}$ T =20°C = 293K	Ea=58 000 J mol^{-1} R =8.314 J $mol^{-1}K^{-1}$ T =20°C = 293K
$e^{-75\,000 / 8.314 \times 293}$	$e^{-58\,000 / 8.314 \times 293}$
$=4.25 \times 10^{-14}$	$=4.57 \times 10^{-11}$

This tells us that if we reduce the activation energy by adding a catalyst, the rate is increased by a very significant amount. The activation energy was reduced by around 25%, the rate increases over 1000 times.

The effectiveness of a catalyst varies with temperature. You can test this by repeating the calculations at 1000K and 100K.

Using Arrhenius to Explain How Temperature Changes affect the Position of Equilibrium in a Chemical Reaction

So far, when you have been asked to explain why an equilibrium shifts when the temperature is altered, you have probably used some 'explanation' that involves ***Le Châtelier's Principle*** (L.C.P.). Most students will correctly state that the equilibrium moves in the direction that leads to a minimising of the temperature change applied.

Consider the following simple exothermic reaction:

$$A_{(aq)} + B_{(aq)} \rightleftharpoons C_{(aq)} + D_{(aq)} \qquad \Delta H_r = -93 \text{ kJmol}^{-1}$$

Almost all students will be able to **predict** the shift in equilibrium caused by an increase in temperature.
L.C.P. predicts that the equilibrium position will move to the left. This is correct, it does.
However, when I ask for an explanation, I nearly always get an answer like this one.

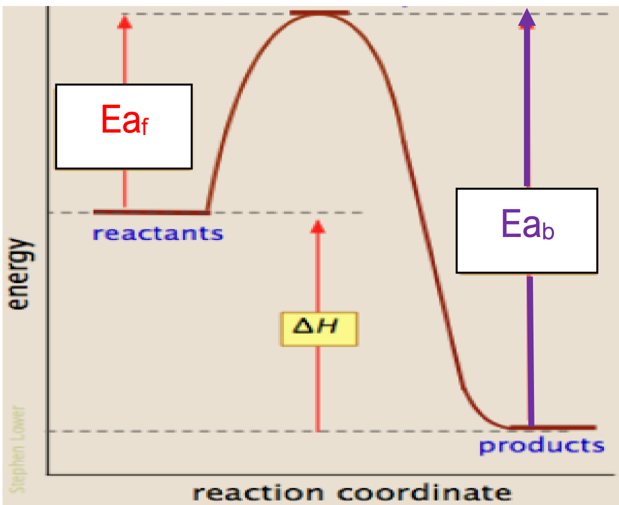
"*The equilibrium position moves in the endothermic direction **because** this causes the heat that was put into the system when the temperature was raised, to be absorbed*."

This is an incorrect answer to the question "*Why does the equilibrium shift*?"

Although Le Châtelier's principle is a very useful predicative tool, **it is not a scientific explanation.** There are textbooks and websites that suggest that this is an explanation.

To correctly explain this, we will need to apply the Arrhenius Equation. You probably aren't surprised!

The enthalpy profile is shown here:



The rate constant for the forward reaction could be written k_f

The rate constant for the backward reaction could be written k_b.

If we assume that this reaction is a **single step reaction**, then we assume the **rate equations** will be as follows. (It will be first order with respect to all the components. Orders are explained on the Reaction Kinetics on *CramNow*.)

Forward reaction — rate of forward reaction $r_f = k_f [A][B]$

Backward reaction — rate of forward reaction $r_b = k_b [C][D]$

Now we recall the definition of a system at equilibrium, *i.e.* ***a system that is in a closed system and where the rates of the forward and backward reactions are equal.***

So,

$$r_f = r_b$$

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

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

The values k_f and k_b are almost certainly going to have different values at a given temperature. Let's say that k_f is larger than k_b at this value of T.

If $k_f > k_b$ then it follows that $[A][B] < [C][D]$ (due to the equality above!)

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

We have already seen how and why rate constant k is affected by temperature using the Arrhenius Equation.

You have also seen that **the value of k always increases with the temperature.**

And you will recall that the size of the effect on rate constant k differs depending upon the size of the **activation energy, Ea.** We saw this when we were looking at the effect of adding a catalyst.

So, the reaction with lower activation energies (the Ea for the forwards reaction in this equilibrium), will have its rate constants increased by a smaller factor compared to the reaction with the higher Ea (the Ea_b for the backward reaction in this equilibrium).

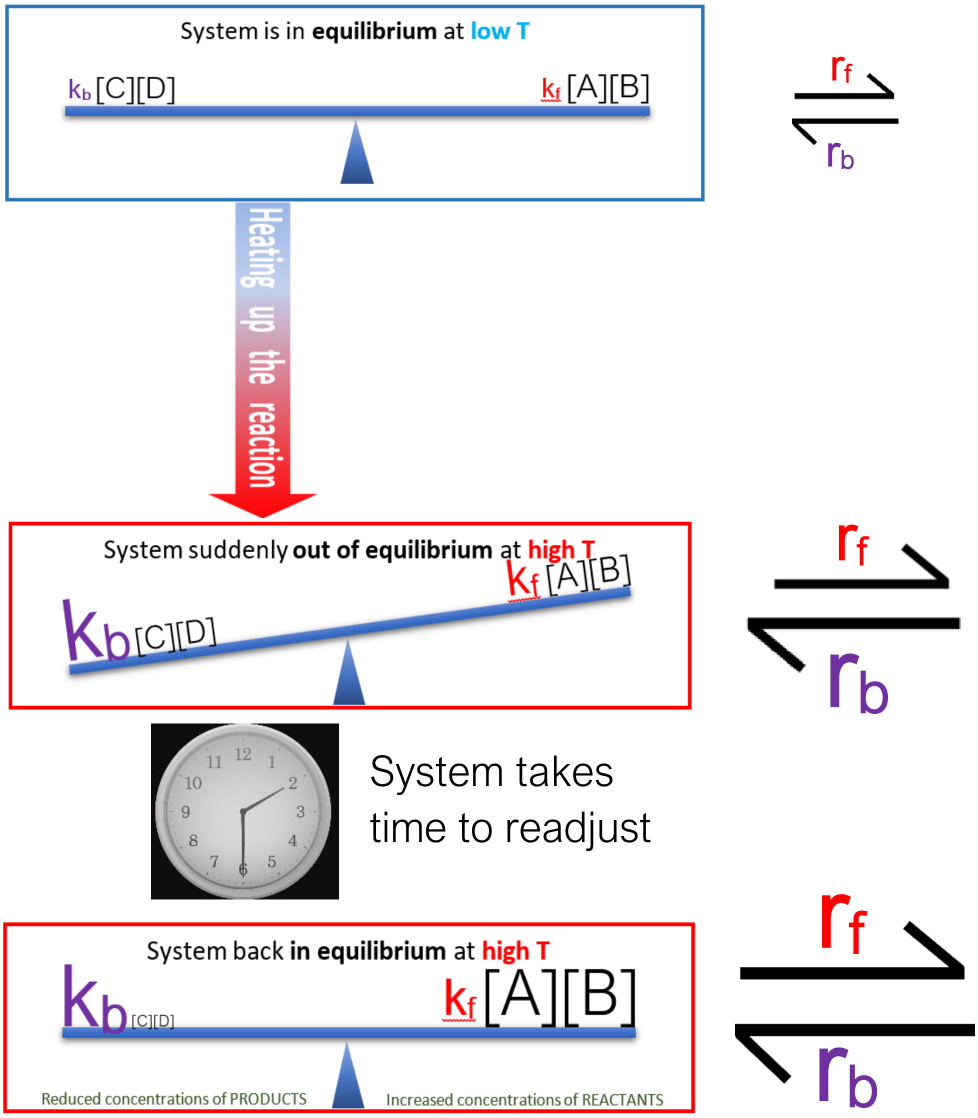
Putting this all together

1. The **temperature, T, is increased** on an equilibrium that is exothermic in the forward direction.
2. k_f is increased so r_f is increased. The reaction goes faster in the forwards direction.
3. k_b is increased so r_b is increased. The reaction goes faster in the backwards direction **but by a larger factor**.
4. Temporarily, $r_b > r_f$ so more reactants [A] and [B] are being made than are being used up. Conversely, [C] and [D] are being used up faster than they are being made. This means that the equilibrium position **moves to the left** when T increases in an exothermic process!

Here is a sequence of diagrams to help illustrate what is happening.

To make it simpler, I will suggest a reaction where k_f = k_b at low T.

In this case [A][B] = [C][D] at low T.



A new equilibrium position needs to be established and so this shifting position must stop moving to the left; r_b and r_f must become equal again **but in a new equilibrium position**.

The values of [A]x[B] and [C]x[D] must both adjust so that they can 'make up' for the changes in k_f and k_b.

The Link Between Rate Constant k and Equilibrium constant K

We saw earlier that, at equilibrium

$$\text{rate}_f = \text{rate}_b$$

Therefore

$$r_f = r_b$$

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

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

This can be rearranged to get

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

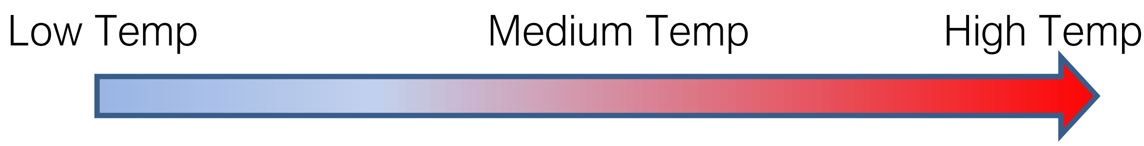
If you have done some advanced equilibrium study (probably in Y13) You should be able to recognize this expression!

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

So, we see that the equilibrium constant K_c **is simply a ratio of the rate constants.**
When temperature rises on a system at equilibrium, the position of equilibrium shifts in the endothermic direction, not because of anything to do with ***Le Châtelier's principle***, but because of the differential effects that temperature has on the rate constants for the forward and backwards reaction.

For the following example (exothermic in the forwards direction):

$$A_{(aq)} + B_{(aq)} \rightleftharpoons C_{(aq)} + D_{(aq)} \quad \Delta H_r = -93 \text{ kJmol}^{-1}$$



$$\frac{k_f}{k_b} = \frac{[C][D]}{[A][B]} = K_c \qquad \frac{k_f}{k_b} = \frac{[C][D]}{[A][B]} = K_c \qquad \frac{k_f}{k_b} = \frac{[C][D]}{[A][B]} = K_c$$

As T increases, k_f and k_b both increase but k_b increases by a greater factor than k_f. This leads to a change in the concentrations of reactants and products; K_c is reduced in value.
The equilibrium **shifts to the left when temperature increases** on this equilibrium.

A Worked Example

1. Consider the following reaction:

$$2N_2O_{5(g)} \rightarrow 2N_2O_{4(g)} + O_{2\,(g)}$$

The following data was obtained for this reaction.

Experimental data

Temperature/°C	327	527	727	827	1027
k/ mol s^{-1}	3.37×10^3	3.58×10^5	5.90×10^6	1.63×10^7	7.83×10^7

Complete the table and then plot an appropriate graph (using false origins if necessary!) that will allow you to calculate the activation energy, E_a for this reaction. Make sure that you **show clearly on your graph** how you have used it to achieve the activation energy. Give the units.

Value of E_a = ...

WORKED ANSWER:

You must first check that the temperatures that you were given are in units of **Kelvin**.

These are in °C so will first need converting to Kelvin.

temperature/°C	327	527	727	827	1027
temperature /K	600	800	1000	1100	1300
k/ mol s^{-1}	3.37×10^3	3.58×10^5	5.90×10^6	1.63×10^7	7.83×10^7

You must then convert the temperatures into 1/T.

temperature/°C	327	527	727	827	1027
temperature /K	600	800	1000	1100	1300
1/T (K^{-1})	1.67×10^{-3}	1.25×10^{-3}	1.00×10^{-3}	9.10×10^{-4}	7.69×10^{-4}
k/ mol s^{-1}	3.37×10^3	3.58×10^5	5.90×10^6	1.63×10^7	7.83×10^7

The values of k need to be converted into *ln* k

temperature/°C	327	527	727	827	1027
temperature /K	600	800	1000	1100	1300
1/T (K^{-1})	1.67×10^{-3}	1.25×10^{-3}	1.00×10^{-3}	9.10×10^{-4}	7.69×10^{-4}
k/ mol s^{-1}	3.37×10^3	3.58×10^5	5.90×10^6	1.63×10^7	7.83×10^7
ln k	8.12	12.79	15.59	16.61	18.17

You are now ready to plot your graph.

Take care with the numbers! There can often be negative values which can be carelessly plotted upside down on the y axis!