Rate vs. Temperature: the Arrhenius Equation

The rate at which a chemical reaction proceeds depends on:

(a) the nature of the reaction	- reactions between oppositely charged ions or between smaller molecules tend to be faster.
(b) the concentrations of the reactants	- reactions tend to get faster as concentrations increase.
(c) the temperature of the reaction mixture	- reactions tend to get faster as the temperature increases.
(d) the presence of a catalyst	- a catalyst increases the rate of reaction without being consumed in the reaction.
(e) the surface area of any solid reactant or catalyst	- for a fixed mass of solid, smaller solid particles increase the total surface area and increase the rate of reaction.

The Collision Theory of rates of reaction states that a reaction will occur between chemical particles only if:
(1) the particles collide with each other.
(2) the colliding particles possess a minimum kinetic energy to initiate the reaction – this is the *activation energy* (E_a) for the reaction.
(3) the colliding particles collide with the correct orientation.

This means that the more *frequently* molecules collide with energy greater than or equal to the activation energy, the faster the reaction will be.

Rate vs. temperature – qualitative
This Factsheet is concerned with the effects of *temperature changes* on rate of reaction. The general relationship stated in (c) can be explained in terms of the collision theory by making use of how the distribution of molecular energies varies as temperature changes. This distribution of molecular energies is best shown by the Maxwell-Boltzmann distribution of molecular energies, as shown in Fig. 1 and Fig. 2.
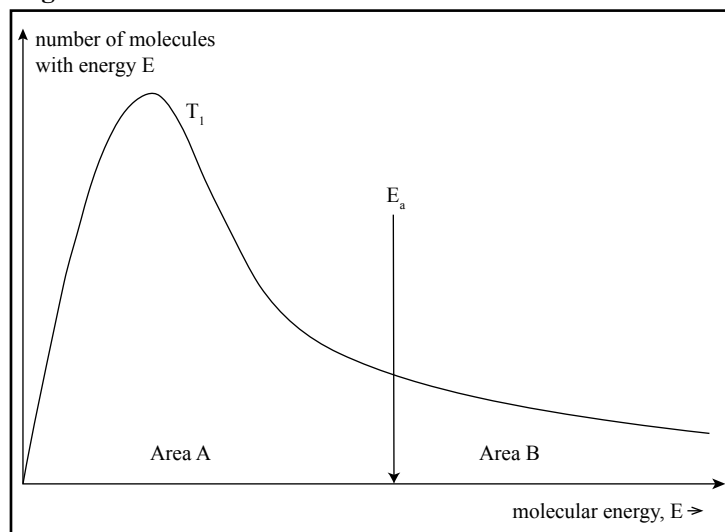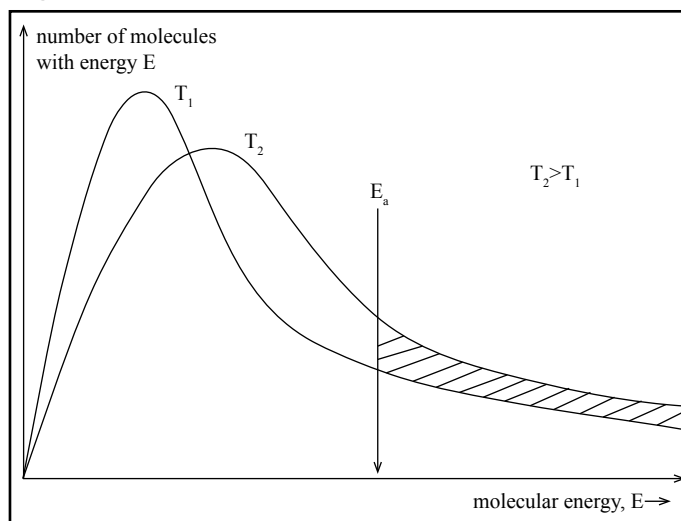
Fig. 1

Fig. 2

It is important to note that the area under each distribution corresponds to the total number of molecules in the system. Hence, area B of Fig. 1 represents the number of molecules with energy greater than, or equal to, the activation energy (E_a). These molecules have sufficient energy to react if they collide with the appropriate orientation. Conversely, area A represents the number of molecules that will not react when they collide.

As shown in Fig. 2, when the temperature is increased (T_1 to T_2), the distribution shifts to the right but maintains the total area under the curve. Consequently, the number of molecules with energy greater than or equal to E_a increases by the amount represented by the shaded area. Hence, the *frequency of collisions* at energy greater or equal to E_a ("successful collisions") increases, resulting in an increase in rate of reaction.

Rate vs. temperature – quantitative
The dependence of rate on reactant concentrations is represented by an experimentally determined *rate equation*.
For example, if   R1 + R2 + R3 → products
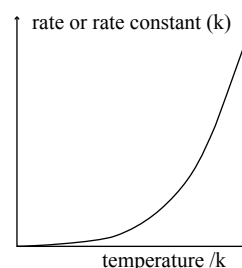Experiment may show that: Rate = $k[R1]^a[R2]^b[R3]^c$
where rate is the rate of reaction measured in mol dm^{-3} s^{-1}
    k is the rate constant for the reaction
    [R1], [R2] and [R3] are the concentrations of reactants R1-3 in mol dm^{-3}
    and a, b and c are the orders of reaction (typically 0, 1 or 2) for reactants R1, R2 and R3 respectively.

Fig. 3

This shows that, *at fixed concentrations*, rate depends on the value of the rate constant. Consequently, since rate increases with increasing temperature, the value of the rate constant must also increase with increasing temperature as shown in Fig. 3.

Note that k does not increase linearly with temperature and its value is zero when the temperature is zero because, at this point, the molecules all have zero kinetic energy.

During the latter part of the nineteenth century, the Swedish scientist Svante August Arrhenius noticed this general experimental relationship between k and T, and suggested that there must be a more specific mathematical relationship. Subsequently, he formulated the Arrhenius Equation which relates k to T:

Svante August
Arrhenius
1859-1927

$$k = A^{-\left(\frac{E_a}{RT}\right)}$$

where A is the pre-exponential or frequency factor (sometimes called the Arrhenius constant),
E_a is the activation energy for the reaction, in J mol^{-1}
R is the Universal Gas Constant (8.314 J mol^{-1} K^{-1})
and T is the reaction temperature (in Kelvin).

The frequency factor can be thought of as the total number of collisions per second occurring with the proper orientation for reaction to occur whether they lead to a reaction or not. The exponential term, $e^{-E_a/RT}$ represents the fraction of these collisions that will result in a reaction.

The equation shows that either increasing the temperature or decreasing the activation energy (for example through the use of a catalyst) will result in an increase in the value of k and, thus, the rate of reaction.

In practice, the Arrhenius equation is usually linearised to a more convenient form by taking the natural logarithm (ln) of each side of the equation.

This gives: $$ln\,k = ln\,A - \frac{E_a}{RT}$$

Note that this assumes that A and E_a are independent of temperature. Provided the range of temperatures studied is not too large, this assumption is found to be valid within experimental error.

Using the Arrhenius equation in calculations
Example 1
Consider the decomposition of NO_2: $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$
At 650K, the rate constant is 1.65 s^{-1}.
At 700K, the rate constant is 7.34 s^{-1}.
Calculate the activation energy for the reaction.

Answer 1
Note that the temperatures are in Kelvin. Hence, these values can be used directly. Any data given in centigrade must first be converted to K. Substituting the data into the modified Arrhenius equation gives:

At 650K, $ln\,1.65 = lnA - \dfrac{E_a}{8.314 \times 650}$ ------------------(1)

At 700K, $ln\,7.34 = lnA - \dfrac{E_a}{8.314 \times 700}$ ------------------(2)

Subtracting equation (1) from (2) eliminates ln A and gives:

$$ln\,7.34 - ln\,1.65 = -\frac{E_a}{8.314}\left(\frac{1}{700} - \frac{1}{650}\right)$$

Hence $1.993 - 0.501 = -\dfrac{E_a}{8.314}(-0.0001099)$

Note that the two minus signs make both sides of the equation positive resulting in a positive value for E_a. This must always occur because E_a represents an input of energy to initiate the reaction.

Hence $E_a = (1.993 - 0.501) \times \dfrac{8.314}{0.0001099}$

Hence $E_a = +112871$ J mol^{-1}

Traditionally this will be in kJ mol^{-1} giving $E_a = +112.9$ kJ mol^{-1} (1dp). Alternatively, the Arrhenius equation can be applied at 2 different temperatures (T_1 and T_2 in Kelvin) with the corresponding rate constants k_1 and k_2.

This gives: $ln\,k_1 = ln\,A - \dfrac{E_a}{RT_1}$

At T_1, $ln\,k_1 = ln\,A - \dfrac{E_a}{RT_1}$ ------------------(3)

At T_2, $ln\,k_2 = ln\,A - \dfrac{E_a}{RT_2}$ ------------------(4)

Subtracting equation (4) from (3) again eliminates ln A and gives a general equation relating the different k values at the different temperatures. i.e.,

$$ln\,k_1 - ln\,k_2 = -\frac{E_a}{RT_1} - -\frac{E_a}{RT_2}$$

$$ln\,k_1 - ln\,k_2 = -\frac{E_a}{RT_2} - -\frac{E_a}{RT_1}$$

Taking E_a/R out as a common factor on the right-hand side and remembering that the difference of two logs is the log of the quotient (ln a – ln b = ln a/b) finally gives:

$$ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

This can then be applied directly to questions like example 1 where, at 650K, the rate constant was 1.65 s^{-1} and, at 700K, the rate constant is 7.34 s^{-1}.

Hence $ln\,\dfrac{1.65}{7.34} = \dfrac{E_a}{8.314}\left(\dfrac{1}{700} - \dfrac{1}{650}\right)$

Giving $-1.4926 \times 8.314 = E_a \times (-1.0989 \times 10^{-4})$
and hence $E_a = 1.4926 \times 8.314 / 1.0989 \times 10^{-4} = +112924$ J mol^{-1}
$= +112.9$ kJ mol^{-1} (1dp)

Graphical treatment
In example 1, only two sets of data are available. Small errors in any of these can lead to large errors in the calculated value of E_a. It is better to have a range of k vs T data that can be analysed graphically, allowing erroneous data to be highlighted and consequently ignored.

This is done by noting that the modified Arrhenius equation is of the form "y = mx +c", which is the general equation of a straight line.

$$ln\,k = ln\,A - \frac{E_a}{R}\left(\frac{1}{T}\right)$$

Compare y = c + m x

plot lnk
on y-axis

plot $1/T$
on x-axis

Hence, a plot of *ln* k against 1/T gives a straight line which has y-intercept (c) equal to *ln* A and gradient (m) equal to $-E_a/R$. The line will always show a *negative* gradient and, typically, has a magnitude of several thousand.

Example 2

The rate constants for a particular reaction at various temperatures are presented in the table. Determine the activation energy for the reaction by an appropriate graphical method.

Rate constant, k /s⁻¹	Temperature /°C
3.715×10^{-5}	27.3
8.128×10^{-5}	32.8
4.074×10^{-4}	44.5
3.888×10^{-5}	50.2
1.995×10^{-3}	57.0

This data must be processed appropriately before plotting a graph:
1. The temperature must be converted to K by adding 273.
2. 1/T must then be calculated making sure that at least 3 significant figures are used. This is appropriate because the data is given to 3 s.f. and without it the graph will be very difficult to interpret.
3. *ln* k must be calculated, again using the same number of significant figure as the data.

Rate constant, k /s⁻¹	Temperature, T /°C	Temperature, T/K	*ln* k (no units)	1/T /K⁻¹
3.715×10^{-5}	27.3	300.3	-10.20	3.33×10^{-3}
8.128×10^{-5}	32.8	305.8	-9.418	3.27×10^{-3}
4.074×10^{-4}	44.5	317.5	-7.806	3.15×10^{-3}
3.888×10^{-4}	50.2	323.2	-7.852	3.09×10^{-3}
1.995×10^{-3}	57.0	330.0	-6.217	3.03×10^{-3}

Remembering to maximise the two scales by not including the origin on either scale, this gives:
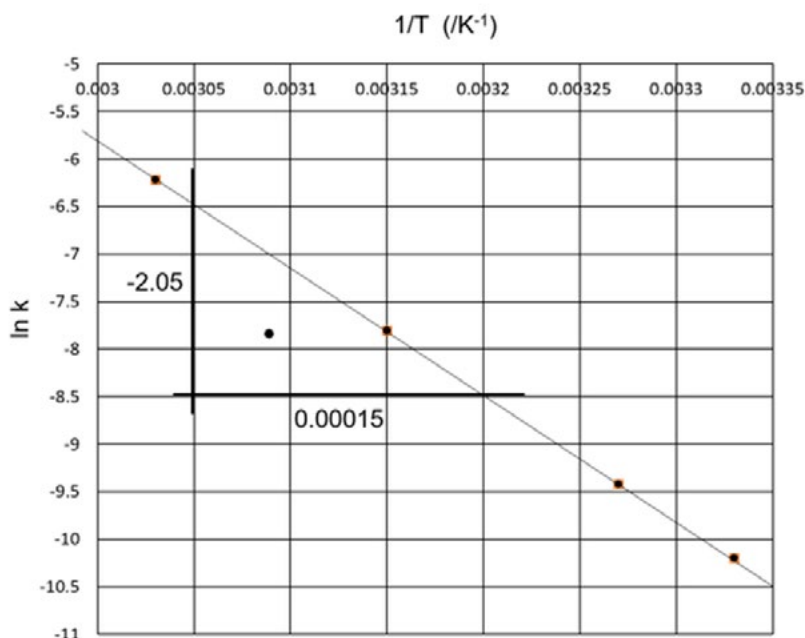
There is clearly an erroneous result which is ignored when fitting the best straight line.
The gradient is given by -2.05/0.00015 = -13667K.

Hence E_a = -8.314 × (-13667) = +113627 J mol⁻¹ = +114 kJ mol⁻¹ (3 s.f.).

Of course, the data could be analysed using an Excel spreadsheet. This gives a gradient of -13301K which leads to a value for E_a of +112 kJ mol⁻¹ (3 s.f.). It also gives a value for *ln* A (the y-intercept) of 34.1, making A equal to 6.5×10^{14} s⁻¹.

Obtaining a value for *ln* A from the *manual* plot is unreliable because the scale on the x-axis has to be extended to 1/T = 0 and the maximum value on the y-axis also has to be increased considerably to include the y-intercept. This means the data points become very clustered in a very small region of the overall range, making the choice of best fit difficult. This can be seen in question 3. The value of A is typically determined by substituting the values calculated using the graphical method back into one of the forms of the Arrhenius equation.

Questions

1. The rate of a reaction doubles when the temperature is increased from 25 °C to 35 °C. Calculate the activation energy, E_a, for the reaction. Hint: see example 1.

2. The activation energy for the isomerisation of cyclopropane to propene is +274 kJ mol^{-1}. By what factor does the rate of reaction increase if the temperature is raised from 500 °C to 600 °C and all other factors are kept constant? Hint: also see example 1.

3. Experiments were carried out to investigate the effect of temperature on the rate of reaction when glucose is oxidised in acid solution by manganate (VII) solution. The results are presented below.

Rate constant, k	Temperature, T /K	ln k	1/T /K^{-1}
2.88 x 10^{-3}	295	-5.85	3.39 x 10^{-3}
1.01 x 10^{-2}	305	-4.60	3.28 x 10^{-3}
1.83 x 10^{-2}	311		
4.98 x 10^{-2}	320	-3.00	3.13 x 10^{-3}
2.02 x 10^{-1}	333	-1.60	3.00 x 10^{-3}

Complete the data table and then use a graphical method to determine the activation energy, E_a, for the reaction and the frequency factor A (ignore its units). Hint: see example 2.

4. If a reaction has a rate constant of 7.24 x 10^{-2} s^{-1} and pre-exponential factor of 2.88 x 10^{14} s^{-1}, calculate a value for the activation energy, E_a, at 30 °C.

Answers

1. $ln\frac{1}{2} = \frac{E_a}{8.314} \left(\frac{1}{308} - \frac{1}{298} \right)$

  $= +52900$ J mol^{-1} = +52.9 kJ mol^{-1}

2. E_a must be converted to J mol^{-1}.

  $ln\frac{\text{Rate 1}}{\text{Rate 2}} = \frac{274000}{8.314} \left(\frac{1}{873} - \frac{1}{773} \right) = -4.88$

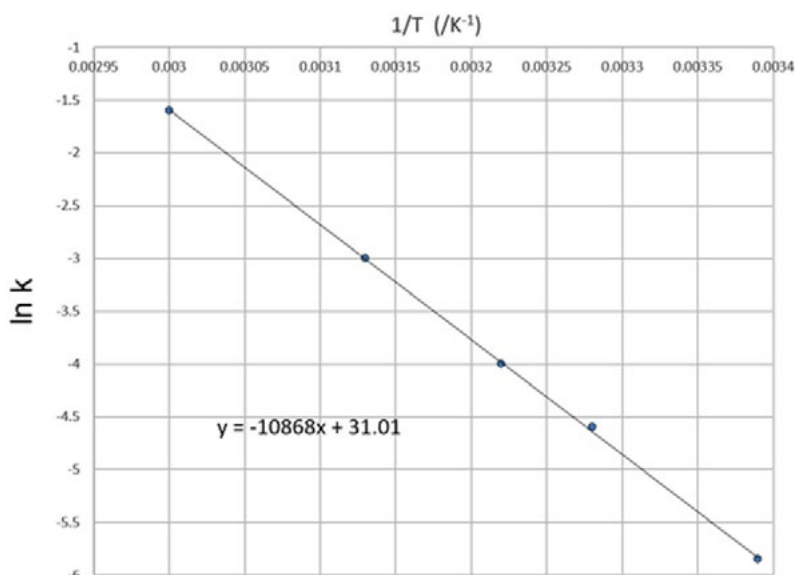 $\frac{\text{Rate 1}}{\text{Rate 2}} = e-4.88 = 0.00757$

  $\frac{\text{Rate 2}}{\text{Rate 1}} = 132$ fold increase

  therefore $\frac{\text{Rate 2}}{\text{Rate 1}} = 132$ fold increase

3.

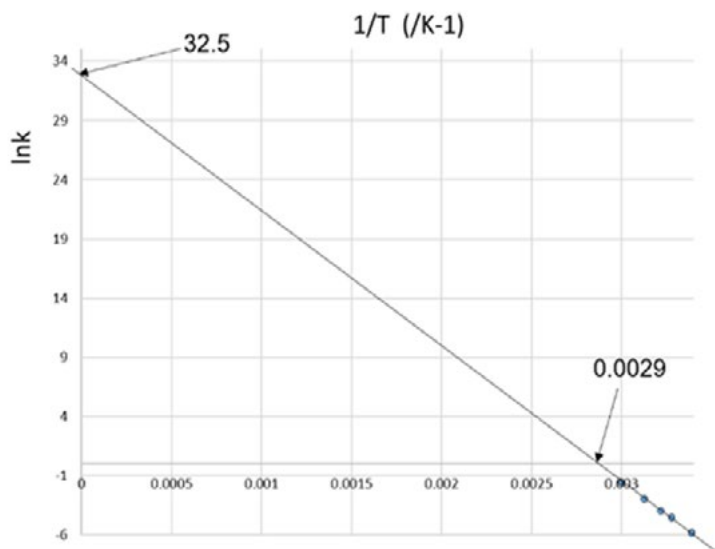| Rate constant, k	Temperature, T /K	ln k	1/T /K^{-1}
1.83 x 10^{-2}	311	-4.00	3.22 × 10^{-3}

Plotting *ln k* vs 1/T gives

Excel gives the gradient as -10868 K
→ E_a = -(-10868) × 8.314
= +90356 J mol^{-1}
= +90.4 kJ mol^{-1} (3 s.f.)

Using Excel the y-intercept is seen to be 31.01
Hence, *ln* A = 31.01
Hence A = $e^{31.01}$ = 2.93 ×10^{13}

Manually. the plot would look as follows:

The gradient is approximately -32.5/0.0029 = -11207K.
This gives E_a = -(-11207) × 8.314 = +93175 J mol⁻¹ = +93.2 kJ mol⁻¹ (3 s.f.)

Also the y-intercept is approximately 32.5 giving A = $e^{32.5}$ = 1.3 × 10¹⁴

4. Substituting directly into the Arrhenius equation ($k = Ae^{-Ea/RT}$) gives:
   7.24x 10⁻² = 2.88 × 10¹⁴ × $e^{-Ea/8.314 \times 303}$
   $e^{-Ea/2519}$ = 0.0724/2.88 × 10¹⁴ = 2.514 ×10⁻¹⁶

   Taking *ln* of both sides,
   $-E_a/2519 = ln$ 2.514 ×10⁻¹⁶ = -35.92

   E_a = 35.92 × 2519 = +90483 J mol⁻¹ = +90.5 kJmol⁻¹