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The Arrhenius Equation is Still a Useful Tool in Chemical Engineering

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KEYWORDS: Activation energy, Cellulose, Hemicellulose, Kinetics, Kraft pulping, Lignin, Sulfite pulping

SUMMARY: The Arrhenius equation correlates the rate of a chemical reaction with the corresponding activation energy, reaction time and reaction temperature, where the latter is measured in Kelvin. Although the equation is rather simple it can be used to summarize the kinetics of most chemical reactions in a surprisingly good manner. The activation energy is an interesting parameter that can be seen as an energy barrier which the reacting chemicals have to pass before a chemical reaction is initiated. Thus, the higher the activation energy, the lower is the rate of the chemical reaction. Moreover, the equation can also be used, for example, to forecast the influence of a higher temperature on the composition of a product consisting of components with different activation energies. In such a case, a component with higher activation energy will increase its rate of reaction more than a component with lower activation energy. The composition of the original product will thus obtain a shrinking fraction of the fast reacting component. The report gives some guidelines of how to calculate the activation energy for a given case in a pulp mill.

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The Arrhenius equation was presented by the Swedish professor Svante Arrhenius in 1889 and it has been used in numerous studies since then. It can be written as shown in Eq 1, where k is the rate constant, B is a constant, E is the activation energy, R is the universal gas constant and T is the absolute temperature.

$$k = B \cdot e^{-E/RT} \quad [1]$$

The constant E is called the activation energy and it can be considered as an energy barrier over which the reacting chemicals have to pass before a chemical reaction is initiated, Fig 1. Thus, in the figure the component A is ready to climb over the hill, which height is E , and if this is successful A will react to B. The new product B will be on a lower and more stable energy level than A. If the activation energy increases the rate constant will decrease and fewer moles of A will be able to climb the hill.

The Arrhenius equation shows how the reaction rate is influenced by time and temperature. It can also be used to estimate the amount by which one of these variables has to be adjusted to compensate for a variation in the other parameter to keep the rate of reaction constant. This equation is applied, in many cases, to chemical reactions of the first order mainly because the mathematics required to solve the equation is not too complicated. In pulp and paper research, the Arrhenius equation has been used in

numerous publications concerning kraft cooking (Vroom 1957; Wilder, Daleski, 1965; Kleinert 1966; Lémon, Teder 1973; Axegård et al. 1979; Schöön 1982; Andersson 2003), sulphite cooking (Schöön 1962, Deshpande et al. 2016), oxygen delignification (Olm, Teder 1979), removal of shives in different bleaching stages (Axegård 1979), pulp bleaching with chlorine dioxide (Edwards et al. 1973; Teder, Tormund 1977; Germgård, Teder 1980) etc. Sometimes detailed chemical mechanisms with specific activation energies have been suggested but, in most cases, the exact chemical reaction is not stated and the equation is therefore only used for the overall reaction.

The way the activation energy is determined for a chemical reaction is usually numeric or graphic, although specific computer software is also available.

The numerical value of the activation energy is interesting as it can be used to determine whether the rate-controlling step of a certain reaction is the chemical reaction or the rate of the transport of reactants to and from the reactive site. A few examples are shown in Table 1 where it is indicated that the rate controlling stage changes from diffusion control to chemical reaction control somewhere between an activation energy of 30-50 kJ/mol. Thus, kraft pulping of chips and bleaching of chemical pulps are rate controlled by the chemical reaction while chemical bleaching of shives is controlled by the transport rate to the reaction site.

This report summarizes a few issues concerning the determination of the numerical values of the constants in the equation for a specific case, and how the equation can be used in the comparison of parallel reactions.

Fig 1- Component A must have sufficient energy to pass the energy hill (i.e. the activation energy E) if it shall be able to react to component B.

Table 1 -. Activation energy of different types of rate-controlling steps.

Stage	Activation energy, kJ/mol	Rate-controlling step
Kraft pulping	120-150	The chemical reaction
Bleaching of fibres in the D 0- stage	50-70	The chemical reaction
Bleaching of shives in the D1 -stage	20-30	Diffusion to the site of reaction

Results

In the Arrhenius equation the activation energy (E) is a very important parameter and it can be determined in the following way for a first order reaction, indicated here by compound A that reacts to form compound B, Eq 2. In reality the first step in this process involves experiments that are carried out at different temperatures. The results are then plotted in a figure where the remaining amount of A is on the y-axis and the reaction time on the x-axis. The time needed to reach a certain value of A is then recorded.

Table 2 shows a case in which three temperatures were examined. If the experimental results are good and if they have a relatively low scatter, it is then possible to plot, for example, the amount of A versus reaction time t . The next step is to determine the time required to reach a given value of A here defined as a concentration of "a" in Table 2.

As the time needed to reach the A value "a" at different temperatures now is determined, we can calculate the average reaction rate at different temperatures using $dA/dt \sim \Delta A/\Delta t$, Table 3.

If it is assumed that the chemical reaction is of first order with respect to A, a kinetic equation can be written according to Eq 3, where B is a constant. This is shown to the left in Eq 3. The rate constant k is then replaced with the corresponding k in Eq 1 as shown to the right in Eq 3.

$$-dA/dt = k \cdot A = B \cdot e^{-E/RT} \cdot A \quad [3]$$

Eq 3 can be rearranged slightly to obtain Eq 4.

$$-dA/A = B \cdot e^{-E/RT} dt \quad [4]$$

Table 2 - Remaining amount of A versus reaction time.

Remaining amount of A	Time, h	Temperature, K
a	2	323 (50°C)
a	1	333 (60°C)
a	1/2	343 (70°C)

Table 3 - The reaction rate ($\Delta A/\Delta t$) for the degradation of A at three temperatures according to Table 2.

Reaction rate ($\Delta A/\Delta t$)	Time, h	Temperature, K
$\Delta A/2$	2	323 (50°C)
$\Delta A/1$	1	333 (60°C)
$\Delta A/0.5$	1/2	343 (70°C)

The equation can now be integrated from time zero to time t for a certain temperature T , thus giving us Eq 5. After integrating this equation, Eq 6 is finally obtained:

$$-\int dA/A = \int B \cdot e^{-E/RT} dt \quad [5]$$

$$\ln A_0 - \ln A_t = B \cdot e^{-E/RT} \cdot t \quad [6]$$

If $\ln A_t$ is plotted versus the reaction time taken from Table 1, a straight line with the slope $B \cdot e^{-E/RT}$ is obtained. The experiments have, however, been carried out at different temperatures so there is one data point, or slope, per temperature. The new constant Y can now be defined according to Eq 7, which can be rewritten as Eq 8.

$$Y = B \cdot e^{-E/RT} \quad [7]$$

$$\ln Y = \ln B - E/RT \quad [8]$$

Finally, plotting $\ln Y$ versus $1/T$, where T is the absolute temperature, provides a correlation with the slope $-E/R$. As R is the general gas constant and its numerical value is thus well known, the activation energy of the initial reaction in Eq 1 can now be calculated. Using the numbers in Table 2, the activation energy can be determined to be 64 kJ/mol. Thus, we have a reaction that is rate controlled by the chemistry of the reaction and not by the diffusion of A to its final reaction site in the fiber wall.

The calculation above contains some simplifications to make it easier to solve the equation and one is that the concentrations of the various reactants included in the reaction of A to B are assumed to be the same throughout the stage. The experiments therefore have to be adjusted by, for example, ensuring that there is a high surplus of all active chemicals throughout the stage to ensure that their concentrations are constant during the experiment. However, an over-charge of chemicals will, in some cases, result in a different reaction pattern compared with the conventional case, in which the concentration of chemicals decreases significantly during the reaction. In such a case a different experimental method can be used i.e. one that mainly uses the very first part of the reaction in the evaluation of the experiment. Thus, at the beginning of the reaction, all chemical concentrations can be assumed to be more or less unchanged and their actual concentration can be calculated from the amount charged at time zero. The downside of this method is that only the very first data points can be used in the determination of the various constants, so the scatter in the results will increase.

The activation energy in chemical pulping

In the chemical pulping process, the Arrhenius equation has been used by a large number of researchers as an important tool in the interpretation of the chemical reaction steps that take place during the cook. Two examples are given here below. In the first case, (Andersson N. (2003)) the researchers have studied kraft pulping of spruce. The activation energies obtained for the bulk and final phases are given in Table 4.

As the table shows, the activation energy of the lignin reaction differs to those of the corresponding values of the three polysaccharides glucomannan, xylan and cellulose.

Note that in this study all poly-saccharides had the same activation energies. The Arrhenius equation can now be employed to analyze the reaction rate for example if the temperature is increased from 160 to 165 °C. It is here assumed that the cooking result with respect to lignin remained unchanged. Labelling the reference temperature T_1 and the new and higher temperature T_2 , the reaction rate of lignin is thus increased by k_2/k_1 . The ln function of this equation is given in Eq 9.

$$\ln(k_2/k_1) = (E_{\text{lignin}}/R)(1/T_1 - 1/T_2) \quad [9]$$

In the same way, the rate of degradation of the polysaccharides (i.e. the hemicelluloses and cellulose) is increased according to Eq 10 by:

$$\ln(k_2/k_1) = (E_{\text{polysaccharide}}/R)(1/T_1 - 1/T_2) \quad [10]$$

Thus, using Eq 10 above, and the temperatures in Kelvin, the new lignin reaction rate can be determined. We then find that the reaction rate (k_2/k_1) for the lignin reaction was increased by 50% as shown in Eq 11.

$$\ln(k_2/k_1) = (127000/8.314)((1/(273+160) - 1/(273+165))) = 0.40327 \text{ or } k_2/k_1 = 1.50 \quad [11]$$

The rate of the polysaccharide reactions, which had a higher activation energy as shown in Table 5, increased by 56% as shown in Eq. 12.

$$\ln(k_2/k_1) = (140000/8.314)((1/(273+160) - 1/(273+165))) = 0.4445 \text{ or } k_2/k_1 = 1.56 \quad [12]$$

This means that when comparing pulps which have been pulped at a certain temperature with pulps that have been pulped at higher temperature more cellulose and hemicellulose have reacted in the experiment that was carried out at the higher temperature. Thus, the pulp yield at a given lignin content will be lower if the cooking temperature is increased.

It is also clear that the compound that has the highest activation energy also has the highest relative rate at higher temperature.

The activation energies reported in Table 5 were obtained recently by Deshpande et al. (Deshpande 2016), who studied bisulphite and acid sulphite pulping of spruce focusing on the initial phase of the cook (> 60% pulp yield).

Table 4 Activation energies of the kraft pulping of spruce (Andersson 2003)

Wood component	Activation energy kJ/mol
Lignin	127
Glucomanan	140
Xylan	140
Cellulose	140

In the initial phase of a sulphite cook, it can be noted that the cellulose in the pulp is totally intact due to its high crystallinity. This means that the degradation rate of cellulose in the initial part of the cook can be written as –

$dC/dt = 0$. The system can be analyzed further using Eq 13 giving:

$$-dC/dt = 0 = B \cdot e^{E/RT} \cdot C = 0 \quad [13]$$

However, knowing that $B > 0$ and $C > 0$, it can be concluded that $e^{E/RT} = 0$. The only solution to this equation is that the activation energy E of the initial phase of a sulphite cook must be infinite. As stated earlier, the activation energy can be seen as an energy barrier for a chemical reaction, and the higher the activation energy, the lower the reaction rate. Thus, if the barrier is so high that no molecules can pass it, the reaction rate can be claimed to be zero and the activation energy is thus infinite.

How will the sulfite cook behave if we increase the temperature by 5 °C in the same way as the in the earlier example for the kraft cook? To solve this problem we can then use the data in Table 5 and the corresponding Eq 11 and 12.

The result is shown in Table 6. Thus, the reaction rates for the four components have increased by 24–47% and we can easily see that the pulp will lose more lignin and less xylan in a relative comparison at the higher temperature. We can also understand that as the cellulose is not reacting at all the pulp will after the stage have a higher fraction of cellulose and lower fraction of hemicellulose than if the comparison was done at the lower temperature.

Final remarks.

The Arrhenius equation is a simple equation that correlates the time and the temperature of a given chemical reaction. In chemical engineering it is often used as a first estimation of the kinetics of a given reaction and in the pulp and paper industry it has been used in studies of for example kraft and sulfite pulping, oxygen and chlorine dioxide bleaching, removal of shives

Table 5 - Activation energies of the initial phase of bisulphite pulping of spruce (Deshpande et al., 2016).

Wood component	Activation energy kJ/mol
Lignin	130
Glucomanan	101
Xylan	69
Cellulose (initially totally intact)	Infinite

Table 6 - Result of bisulphite pulping of spruce where the temperature has been raised from 160 to 165 °C. Only the initial phase of the cook was studied.

Wood component	Rate at 160 °C	Rate at 165 C
Lignin	1.0	1.47
Glucomanan	1.0	1.38
Xylan	1.0	1.24
Cellulose	None	None

etc. It can also be used to compare for example the pulp composition before and after the temperature has been raised during pulping or bleaching or be used for estimation of the type of rate controlling step that is active in a given process stage in a pulp mill.

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