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**THE USE OF THE ARRHENIUS EQUATION IN THE STUDY OF
DETERIORATION AND OF COOKING OF FOODS –
SOME SCIENTIFIC AND PEDAGOGIC ASPECTS**

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ABSTRACT: Conservation and cooking of foods can be used by students and instructors to demonstrate a fundamental relation of chemical kinetics, the Arrhenius equation. By plotting the logarithms of available conservation and cooking times versus the corresponding inverse temperatures, apparent activation energies for both the deterioration and the cooking of foods of various compositions can be obtained. Such simple applications lead to meaningful results. Examples of deviation from the Arrhenius equation are given by plotting data (shelf-life of certain frozen food at various temperatures) given on the food package. A better fit is obtained by applying a second order polynomial regression to the data. Cooking time ($\ln t$) vs. the inverse of temperature for five categories of foods is also examined and for each category there appears to be a common rate-determining step. Detailed results are presented for the meat category. The pedagogic aspects of the use of Arrhenius equation in the study of deterioration and of cooking of foods are also presented. [*Chem. Educ. Res. Pract. Eur.*: 2002, 3, 87-97]

KEY WORDS: *Chemical kinetics; deterioration of foods; cooking of foods; Arrhenius law (equation); deviation from the Arrhenius equation*

INTRODUCTION – THE ARRHENIUS LAW AND ITS APPLICATION

Chemical kinetics can be applied in food science for the prediction of the change in quality of a food as a function of time and environmental conditions (Labuza, 1984). The Arrhenius equation (Espenson, 1981; Katakis & Gordon, 1987) expresses the temperature dependence of the rate constant for an elementary chemical reaction

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (1)$$

where $R = 8.31 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, the parameter A is the frequency factor which is taken as independent of temperature and E_a is the Arrhenius activation energy. If the value of E_a is greater than about $20 \text{ kJ}\cdot\text{mol}^{-1}$, it is possible that processes that involve the breaking of primary chemical bonds may occur (Laidler, 1972). Even complex processes (such as those that take place in foods during storage and cooking), may under certain conditions, obey the Arrhenius law within the experimental error.

Based on the value of E_a , one can derive information about a reaction mechanism or, in some cases, extrapolate the data to new conditions. Extrapolation or interpolation to other values of temperature can be done judiciously. If, in a series of elementary processes, one step is much slower than the rest, E_a is the average thermal energy required to initiate the

rate-determining step of the reaction. On the other hand, there are some limitations (Labuza, 1984) to the Arrhenius model when applied to complex systems, such as food, since at higher temperatures the chemical transformations may be of a different kind than those occurring at lower temperatures. Apart from this, there are a number of other sources of non-linearity of the Arrhenius plot of $\ln k$ or $\log k$ versus $1/T$ (Hunlett, 1964).

In the process of preparation of food, it is certain that many chemical changes take place during the thermal procedure. For example, when meat is heated at around 50°C , breaking of intramolecular bonds occurs because of the increased molecular motion, resulting in the change of the folded structure of the proteins, which are thus denatured (Price & Schweigert, 1971; Forrest, Aberle, Hedrick, Judge & Merkel, 1975). Reactive regions of the molecules are consequently exposed and can participate in various intermolecular interactions. At around 60°C , the connective tissue sheaths collapse and shrink, pressing the free water in the cells, which then flows out. At temperature much higher than 70°C , the meat becomes very dry (Price & Schweigert, 1971; Forrest, Aberle, Hedrick, Judge & Merkel, 1975).

The goal of the present paper was:

I. To check whether the Arrhenius or shelf-life plot for various categories of frozen food is linear and, if so, if it can provide reasonable conclusions when it is applied to food storage at various temperatures. Our study was motivated by an article (Leenson, 1999), whose assumption that the storage data presented on the cover of a pizza followed the Arrhenius equation, led to the “conclusion” that there was “*a mistake in the information on the package*” since not all the points fall on a straight line ($\ln t$ vs. $1/T$). A valuable review of general approaches to the kinetics of food deterioration is the article by Labuza (1984), providing an extensive coverage of this topic.

II. To describe the use of the Arrhenius equation in order to obtain the apparent activation energies for cooking foods of various compositions in an oven. Moreover we wish to deduce information about cooking at lower temperatures, where disintegration of useful molecules such as vitamins is less likely. Though we present detailed analysis for meat containing food, additional results are included for four other food categories: fish, cakes, biscuits and vegetables – pastry.

III. To present the pedagogic aspects of using subjects of everyday life activities in order to introduce students to fundamental chemical principles. We have found that such simple applications, the experimental parts of which can be carried out in anyone’s kitchen (fridge, oven) while having fun, lead to meaningful results. The classroom topics presented here are most appropriate for introducing general chemistry students in chemical kinetics.

I. THE USE OF ARRHENIUS-TYPE PLOTS IN THE STUDY OF THE DETERIORATION OF FOODS

On the cover of the boxes containing frozen foods there is nutrition and storage information (Figure 1). We have used and examined seven categories of frozen foods: vegetables (artichoke, beans, peas, corn, carrot, onion, spinach, mixed salad, brussels sprouts, potatoes), fish (octopus, mullet, prawns, lobster, fish sticks, squib, sliced squib), meat [chicken, chicken balls, chicken liver (entrails), meatballs, chicken fillet], pies (cheese pie, sausage pie, spinach pie, cheese cakes, Greek cheese pie), sweet pies (Greek sweet cake, baklava, apple pie, cherry pie), dough (dough for pies, sweet pies, pizza dough, thin paste), pizzas (Italian pizza). In Table 1 data are presented (storage time and temperature) for some frozen foods (pizza dough, fish sticks, vegetables and chicken balls).

If we assume that the deterioration of the foods follows the Arrhenius equation and treat the storage data accordingly, we find that *approximately* straight lines can be drawn. The “deterioration rate”, *u*, must be constant at a given temperature *T* and inversely proportional to the storage time *t*, if ordinary kinetics are followed. Therefore we apply the equation

$$t \cong \frac{1}{u} \cong \text{const} \cdot \exp \frac{E_a}{RT} \quad (2)$$

to the data, i.e. storage time versus temperature of storage (Table 1). By taking the logarithms of both sides of the above equation, we get

$$\ln t = c' + \frac{E_a}{R} \cdot \left(\frac{1}{T} \right) \quad (3)$$

From this, a linear relation between $\ln t$ and $1/T$ follows. Figure 2 presents plots of $\ln t$ vs. $1/T$ for the data in Table 1. A linear regression ($y = A_0 + A_1 \cdot x$) has been applied to the data (Figure 2). The slope of the line gives E_a/R , from which an *apparent activation energy* E_a for the “deterioration” process is calculated (see Table 1, column 6).

Given the straight line, predictions can be made about the shelf-life of the various foods, which are reliable only within the experimental temperature range, whereas extrapolation or interpolation to other values of temperature could be made judiciously. The apparent activation energies deduced from Table 1, column 6th, are:

$$E_{a \text{ pizza dough}} = 101 \text{ kJ/mol} \quad E_{a \text{ squib}} = 86 \text{ kJ/mol} \quad E_{a \text{ fish sticks}} = 122 \text{ kJ/mol}$$

$$E_{a \text{ vegetables}} = 164 \text{ kJ/mol} \quad E_{a \text{ chicken balls}} = 131 \text{ kJ/mol}$$

$E_{a \text{ pizza}} = 170 \text{ kJ/mol}$ (using Leenson’s data; note that in the paper by Leenson an apparent E_a value of 180 kJ/mol is reported)

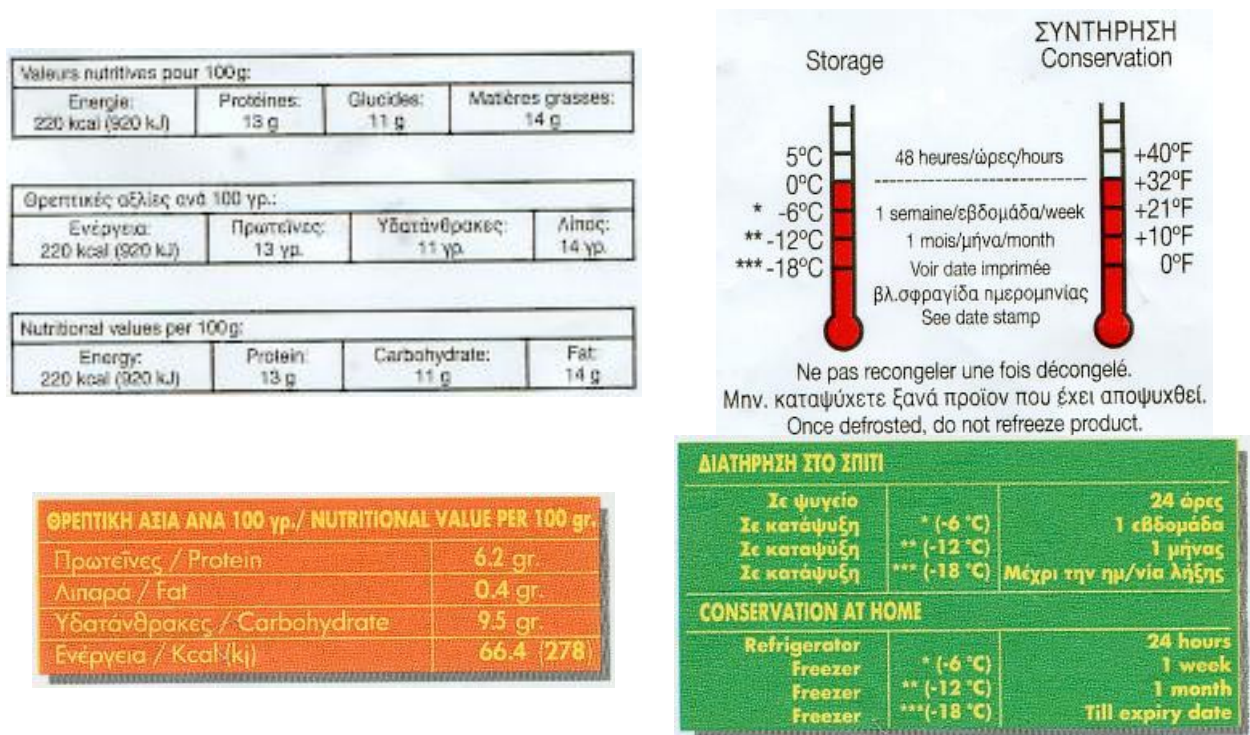


FIGURE 1. Nutrition and storage information for two types of frozen foods used in this work (up: chicken meatballs, down: peas).

TABLE 1. Storage data (time and temperature) for some kinds of examined food (R: correlation coefficient; SD: standard deviation).

t / days	$\ln t$	θ / °C	T / K	$1000T^{-1} / K^{-1}$	$A_1 = E_a/R$	R	SD
Pizza dough							
7	1.95	+5	278	3.60	12.17	0.9832	0.3729
30	3.4	-8	265	3.77			
3x30	4.5	-12	261	3.83			
12x30	5.89	-18	255	3.92			
Squib							
1	0.0	+5	278	3.6	10.36	0.9804	0.3463
3	1.1	-6	267	3.75			
14	1.95	-12	261	3.83			
12x30	3.4	-18	255	3.92			
Fish sticks							
2	0.69	+5	278	3.6	14.69	0.9694	0.6186
7	1.95	-6	267	3.75			
30	3.4	-12	261	3.83			
8x30	5.48	-18	255	3.92			
Vegetables							
1	0.0	+5	278	3.6	19.78	0.9667	0.8704
7	1.95	-6	267	3.75			
30	3.4	-12	261	3.83			
2x365	6.59	-18	255	3.92			
Chicken balls							
2	0.69	+5	278	3.6	15.76	0.9586	0.7789
7	1.95	-6	267	3.75			
30	3.4	-12	261	3.83			
12x30	5.89	-18	255	3.92			
Pizza (Leenson, 1999)							
1	0	0	273	3.66	20.49	0.9764	0.6158
7	1.95	-6	267	3.75			
14	2.64	-12	261	3.83			
275	5.62	-18	255	3.92			

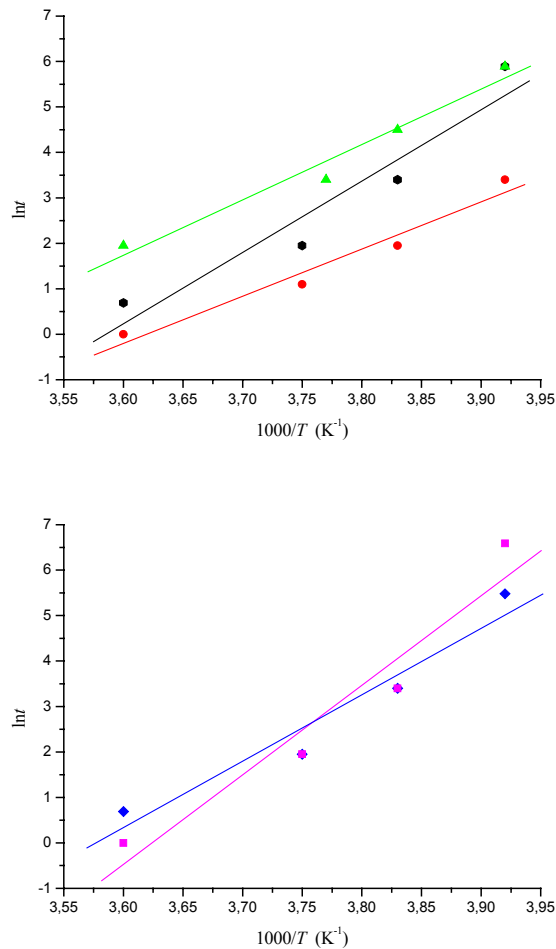


FIGURE 2. Plot of $\ln t$ vs. $1000/T$ for the data of Table 1 and their linear regression (hexagon: chicken balls, circle: squib, triangle: pizza dough, rhomb: fish sticks, square: vegetables).

AN ALTERNATIVE INTERPRETATION

By plotting the “experimental data” ($\ln t$ vs. $1/T$) and applying a second order polynomial regression ($y = A_0 + A_1 \cdot x + A_2 \cdot x^2$) a better fit results, showing a clear deviation from the Arrhenius equation (Figure 3, Table 2). The data for all kinds of foods examined give Arrhenius – type plots ($\ln t$ vs. $1/T$) which are concave upwards and thus the Arrhenius plots ($\ln k$ vs. $1/T$) should be concave downwards. In Figure 4 the data obtained from the paper by Leenson (1999) are also plotted.

It is thus concluded that the experimental data, i.e. the shelf - life of all the examined kinds of food at various temperatures, do not strictly vary linearly according to the Arrhenius equation. Note that in the article by Leenson (1999), in which the Arrhenius law was applied in the case of storage of a pizza in a freezer, the deviation from the straight line was interpreted as a “mistake”, whereas our alternative interpretation shows simply deviation from the Arrhenius law.

TABLE 2. Correlation coefficients of the linear (R) and second order (R , R^2) polynomial regressions of the data of Table 1.

Food	$y = A_0 + A_1 \cdot x$	$y = A_0 + A_1 \cdot x + A_2 \cdot x^2$	
	R	R	R^2
Pizza dough	0.9832	0.9980	0.9961
Squib	0.9804	0.9996	0.9992
Fish sticks	0.9694	0.9999	0.9998
Vegetables	0.9667	0.9979	0.9959
Chicken balls	0.9586	0.9999	0.9998
Pizza (Leenson, 1999)	0.9764	0.9847	0.9697

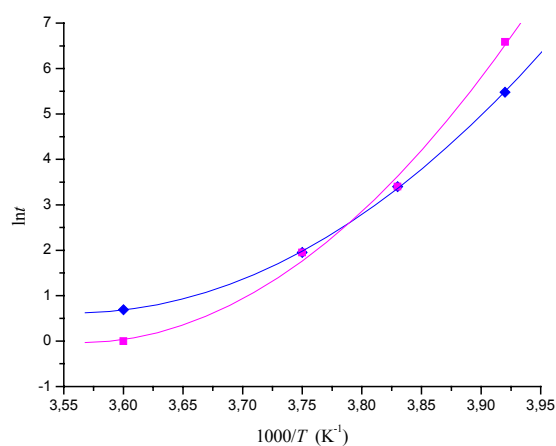
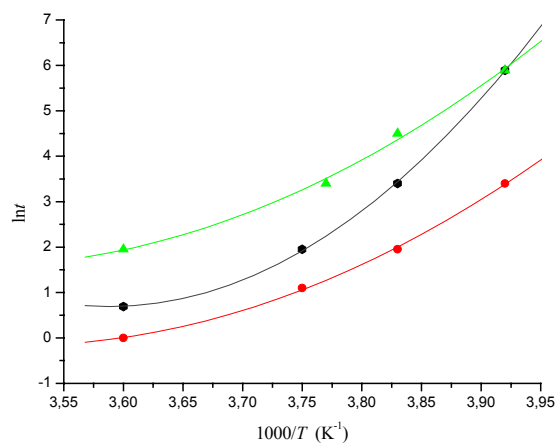


FIGURE 3. Plot of $\ln\tau$ vs. $1000/T$ for the data of Table 1 and their second order polynomial regression (hexagon: chicken balls, circle: squib, triangle: pizza dough, rhomb: fish sticks, square: vegetables).

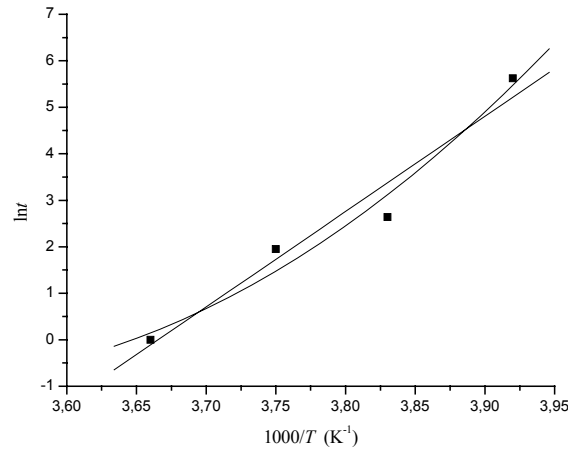


FIGURE 4. Plot of $\ln r$ vs. $1000/T$ for the data taken from the paper by Leenson (1999) (included in Table 1) and their linear and second order polynomial regressions.

II. THE ARRHENIUS LAW AND ITS APPLICATION TO COOKING OF FOODS

In cases where the Arrhenius law is applicable, since the rate of food preparation, v , is inversely proportional to the cooking time, t , one can also apply equations (2) and (3) to the (cooking) “experimental” data. It is expected that a straight line will be obtained from the plot of $\ln t$ vs. $1/T$, with the slope (E_a/R) giving an apparent activation energy E_a for the process, whatever its mechanism may be. Table 3 presents data (book and booklets) for the thermal cooking of meats of various kinds. The amount of food considered in each case was 1 kg.

TABLE 3. Cooking data (time and temperature) for meats of various kinds in a kitchen oven.

Food	t / min	$\ln t$	T / K	$1000/T / \text{K}^{-1}$
Beef steaks	30	3.4	523	1.91
(Stuffed) duck	40	3.68	523	1.91
Roast pork	60	4.09	503	1.99
Pork steak (chops)	60	4.09	503	1.99
Chicken	60	4.09	498	2.01
Roast pork	70	4.23	498	2.01
Poultry	60	4.09	473	2.11
Roast goat	90	4.5	473	2.11
Roast pork	120	4.79	473	2.11
Roast lamb	120	4.79	453	2.21
Beef with bacon	120	4.79	453	2.21
Roast beef	125	4.83	453	2.21
Duck	180	5.19	453	2.21
Lamb (greek style)	120	4.79	450	2.22
Duck	180	5.19	435	2.3
Pork (pieces) with vegetables	20	3.0	473	2.11
Ribs	35	3.56	473	2.11
Meatballs	35	3.56	473	2.11
Chicken (pieces) with mushrooms	30	3.4	453	2.21

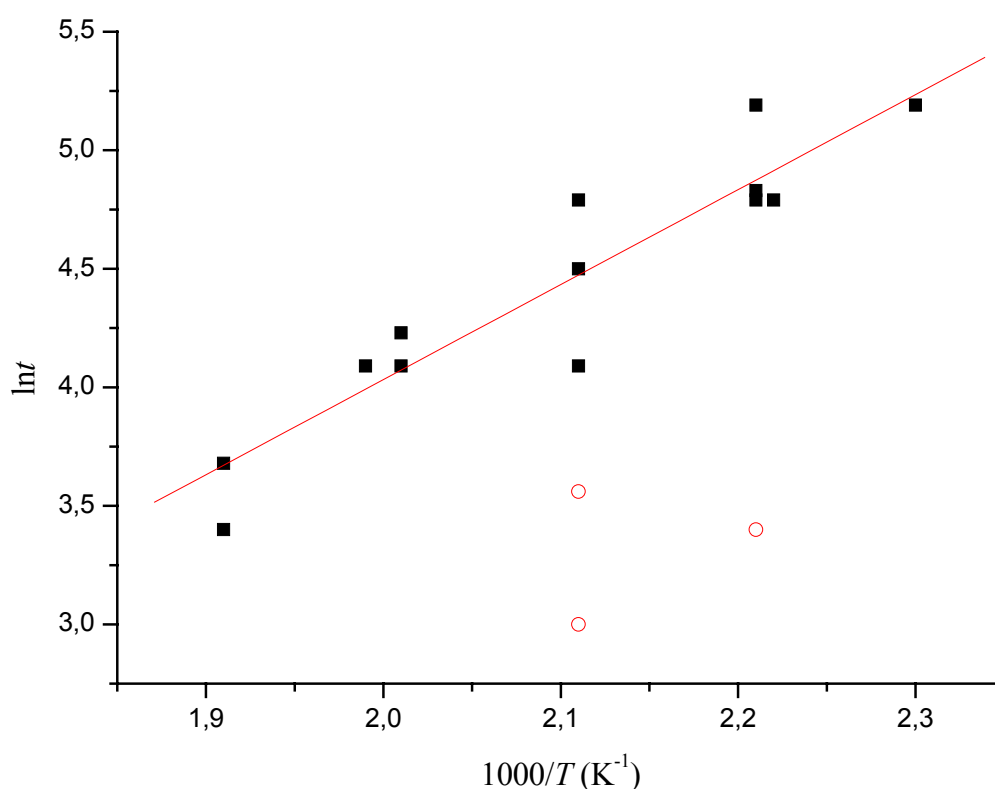


FIGURE 5. Plot of the logarithm of cooking time vs. the inverse of temperature for various meats. Squares: protein-containing foods (meats). Open circles: pieces of pork, chicken, ribs and meatballs.

In Figure 5 the plot of the logarithm of cooking time vs. the inverse of temperature is presented for various meats (protein-containing foods) (see Table 3). It is observed that the Arrhenius model is approximately valid (protein-containing foods: meats). The plot of $\ln t$ vs. $1/T$ gives a straight line with slope E_a/R . The slope of the line established by linear regression of the data is found to be $E_a/R = 4.019$ giving $E_a = 33 \text{ kJ}\cdot\text{mol}^{-1}$.

The important thing is that the data refer to meat of various kinds, i.e. chicken, beef, pork, goat, duck and lamb. The cuts of meat can be thought of as a matrix of protein molecules and water (Ledward, Johnston & Knight, 1992). The open circles (Figure 5) refer to meat in pieces, such as small pieces of pork, pieces of chicken, ribs and meatballs. The greater the surface of the pieces of meat is, the greater the rate is, and consequently the cooking time decreases. There are also data (book and booklets) referring to food with small surface (the opposite effect, for example whole potatoes, apples, etc.), which show greater cooking time than one would expect from the corresponding graph, i.e. smaller rate due to smaller surface. Thus, the big difference in surface causes different behaviour. According to a recent article (Mc Gree, Mc Inerney, & Harrus, 1999, which discusses the physics of cooking of steak, the rate-determining step in cooking is often the penetration of heat from the cooking medium through the meat to the centre, especially if the meat is thick; this behaviour also has to do with the volume of the pieces of meat and the heat transfer to the centre.

Data (book and booklets) are also available for the preparation of fish of various kinds, cakes, biscuits and vegetables-pastry, which result in $E_{a \text{ fish}} = 27 \text{ kJ}\cdot\text{mol}^{-1}$, $E_{a \text{ cakes}} = 26 \text{ kJ}\cdot\text{mol}^{-1}$, $E_{a \text{ biscuits}} = 24 \text{ kJ}\cdot\text{mol}^{-1}$, $E_{a \text{ vegetables-pastry}} = 20 \text{ kJ}\cdot\text{mol}^{-1}$. Fish has lower activation energy than a roast; it should perhaps be compared to the smaller pieces of meat, mammal

and fowl. E_a should be quite similar if we are correct about all animal protein being chemically approximately the same.

DISCUSSION

We find it important to stress that the Arrhenius model and its limitations apply to both our studies, that is, deterioration and cooking of foods. Despite this common behaviour, the two treatments differ, since for each conserved food four different temperatures are given for four different storage times (Figure 1, Table 1); that is, for the same food, four pairs of values (t , T) are given and we check if these data for each distinct food obey the Arrhenius law, i.e. the deterioration of the certain food follows the Arrhenius law. On the other hand, only one temperature and the corresponding time needed for cooking is given for each food; that is we have to combine those pairs of (t , T) for different kinds of food to check if there is a common rate-determining step in the thermal behaviour of food.

Deterioration of foods - Explanation

It is difficult to draw conclusions about a mechanism (or mechanisms) of the deterioration of frozen food on storage from the shape of the curves corresponding to the data (t , T) presented on the back cover of the boxes containing frozen foods. The curves show a concave upwards behaviour, which means that the $\ln k$ vs. $1/T$ plots should show a concave downwards behaviour. According to Labuza's review (Labuza, 1984) the most probable mechanism is enzymatic and microbial degradation. This could actually lead to the observed behaviour.

Other reasons leading to curvature of the Arrhenius plot are (Hunlett, 1964): consecutive reactions with similar rate constants, consecutive steps with different activation energies, the occurrence of a third order reaction, alternative paths (parallel reactions) with different activation energies, the existence of non-chemical control (i.e. reactions involving systems in two or more phases which are limited at high temperatures by the rate at which the reactants can come together; in these cases diffusion could be the rate determining step).

In biological reactions, another important source of non-linearity of the Arrhenius plot is the thermal inactivation of enzymes (Laidler, 1958). Many biological reactions (e.g. enzyme-catalysed reactions) have an optimum temperature at which the rate reaches a maximum; in these, the reaction rate increases steadily with temperature in an Arrhenius manner, until the thermal inactivation of the enzyme becomes more important.

In the cases where the curvature of the Arrhenius plot is concave downwards (as in the cases presented here), the deterioration process could be caused by consecutive reactions and/or non-chemical reasons, such as the concentration of all reactants in the unfrozen water during freezing, since the diffusion in the solid phase is not favoured, especially at low temperatures. General modes of food deterioration include, according to Labuza (1984), microbial decay, enzymatic and non-enzymatic chemical change (lipid oxidation, vitamin loss, etc.). The growth of microorganisms is also of great importance in the deterioration of food (Leenson, 1999).

Cooking of foods - Main chemical changes and variables affecting the data

Although such a simple study cannot point to the mechanism, there appears to be a more or less common rate determining step in each category of the examined food, since the results for corresponding members fall approximately on the same line (established by linear regression of the data). In the protein-containing foods (meat – fish), the main chemical

change is the denaturation of proteins (Price & Schweigert, 1971; Forrest, Aberle, Hedrick, Judge & Merkel, 1975), whilst in vegetables the main change is the modification of the (plant) cell architecture (Hulme, 1970).

It is important that students must be informed about the variables that can affect the data. Although we are dealing with an approximation, all following variables must be considered and evaluated:

- a) Oven thermostats may not be accurate and temperatures may fluctuate in the course of cooking. The effective cooking temperature at the surface of food (meat in the case of the discussed data) is the temperature of the cooking medium. Within the food, and especially in the case of meat, the effective cooking temperature cannot be higher than the boiling point of water because of the water content of meat. Meat is about 75% water by weight (Price & Schweigert, 1971; Forrest, Aberle, Hedrick, Judge, & Merkel, 1975).
- b) Meat is considered “properly done” when it is heated to the temperature range 55-70°C (130 –160°F) (Mc Gree, Mc Inerney & Harrus, 1999).
- c) Heating causes meat to lose fluid and shrink, and therefore the quantities change.
- d) A number of factors involved in cooking (i.e. portion size and shape, determining “doneness”, cooking temperature etc.) make this type of analysis approximate.
- e) The listed cooking times (Table 3) correspond to a certain amount of material: 1 kg (In Figure 5, squares: 1 kg piece, open circles: 1 kg of small pieces).

CONCLUSIONS AND PEDAGOGIC ASPECTS

The following conclusions can be drawn from this study:

- i) The Arrhenius equation can only approximately be applied to the storage of food. An alternative interpretation described in this article could lead to more reliable conclusions. The best way to obtain a shelf life for a given kind of food would be to do studies at the desired temperatures. This is usually not possible because it is costly and time-consuming (Labuza, 1984), though it is necessary due to the limitations of the Arrhenius model.
- ii) For all kinds of frozen food included in the category “vegetables”, the data (t , T) are identical, implying similar behaviour and thus similar mechanism of deterioration. Also the values of the E_a are in a reasonable order, i.e. $E_{a \text{ fish}} < E_{a \text{ meat}} < E_{a \text{ vegetables}}$.
- iii) Given the variability of meats, heat sources, surface of the cuts, it is not possible to generalise and deduce reliable general rules. However this phenomenological treatment significantly simplifies the problem and allows us to recognize some of the aspects in the cooking of food, such as the order of magnitude of the activation energy. Thus, the Arrhenius equation can be approximately applied to the thermal cooking of food.
- iv) This application of the Arrhenius equation suggests that by extrapolation we can find the appropriate time, t , for cooking food at low temperatures, within the limitations discussed above. This can be useful in cases where at low temperatures certain components are not destroyed, for example vitamins.

Chemistry and everyday life

Both the above applications of the Arrhenius equation can be used in the teaching of basic chemical concepts. One can teach the temperature dependence of the rate ($v \cong 1/t$) by explaining the plots $\ln t$ vs. $1000/T$ and pointing out the effect of surface (“concentration”) on the rate (Figure 5).

Students are encouraged to use different kinds of food, in order to understand basic chemical concepts, and in this way their work becomes interesting and enjoyable, while they realise that chemistry is useful in their everyday life. In such activities they can work in groups of 2-4, and thus develop skills for cooperative work. In addition, students can be encouraged to analyse and discuss the results, an activity that promotes constructivist learning and critical thinking.

NOTE ON SOURCES OF DATA: Data were collected from the covers of the boxes containing frozen foods. Also from various cooking books, such as “*Cooking, a commonsense guide*” (family circle), and booklets with instructions for the use of kitchen ovens.

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