2. PRODUCT CHANGES DURING PROCESSING

2.1 Introduction

Processing converts the food raw material into the food product. The process must be designed to ensure that, in the final product, the composition and the levels of the other product attributes are as demanded in the specification. Processing moves in steps towards this end product. The final qualities are therefore created through the processing steps, by reactions causing changes in the food materials. These changes have to be instigated; they have to be continued at rates that are as fast as can be operated industrially, yet they must be kept under control. Then they must be stopped, when the necessary qualities in the final product have been reached but before they are exceeded. To do all these things, the best attainable understanding is needed of the:

- raw materials – composition and other attributes inherent in the food raw materials;
- reactions – causing changes in composition and other attributes of food raw materials during processing;
- processing conditions – external factors which instigate and modify these changes;
- final product – composition and other attributes specified in the final product.

The composition and the attributes of the raw materials and the possible changes are basically a matter of chemistry. But foods are complex chemical systems, and, in reaction technology, other physical, sensory and biological changes are followed as well as chemical changes. The rates of changes, their inception, modification and control, need to be studied and understood so that they can be implemented in manufacturing practice. This chapter takes an initial look into the rates of individual food processing reactions and the effects of some controllable variables, particularly processing temperature, and constituent concentration, on them.

The rates at which changes occur can be understood, predicted and controlled, and this knowledge can be applied to design and control the process to give the specified final product quality. A general scheme for the use of reaction technology in processing is shown in Fig. 2.1.

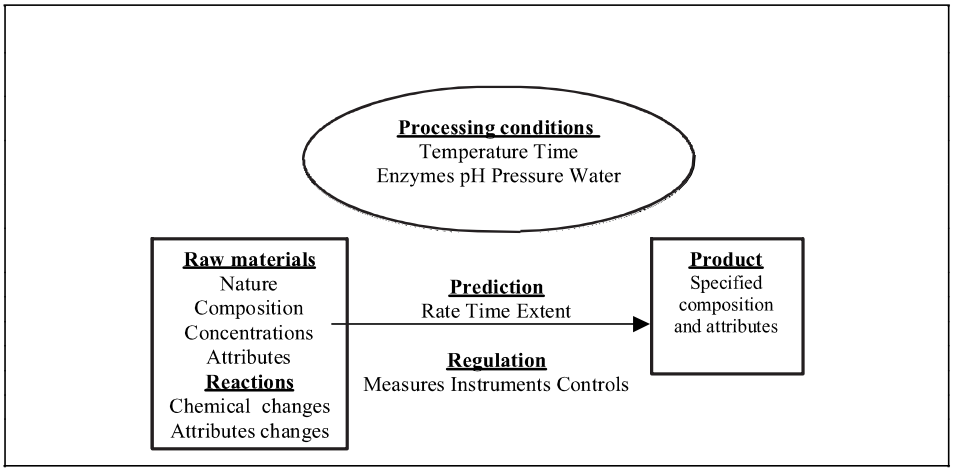


Fig. 2.1. Reaction technology in processing

2.2 Reactions in Food Materials During Processing

An immediate impact can come from focusing on a practical example of processing, preferably a simple one. One common and relatively uncomplicated process is the manufacture of jam by boiling fruit and sugar. It is a simple and straightforward process, encountered domestically as well as industrially, and yet one that illustrates very many of the important principles that arise in processing and which have to be taken into account to arrive at a good-quality product. In jam processing, many reactions have to take place before the ingredients are changed into the food product.

The ingredients are generally only fruit pulp and sugar, to which pectin and acid may have to be added if not present in sufficient concentration in the fruit, and perhaps additional water for handling. The reactions start on heating the pulp and sugar mixture; effectively, they do not occur without this heat. So the first point emerging is that reactions are initiated and speeded by higher temperatures. Some reactions in jam making are shown in Table 2.I.

TABLE 2.I
Some reactions in jam making

Reactions		Products
Sucrose hydrolysis catalysed by acid	→	glucose and fructose
Sucrose hydrolysis catalysed by enzymes	→	glucose and fructose
Caramelisation/burning of sugars	→	darkening and caramel/burnt flavours
Browning, sugar/protein (Maillard) reactions	→	darkening, bitter flavours
Colour bleaching	→	colourless compounds
Pectin polymerisation	→	gelation
Pectin breakdown catalysed by enzymes	→	simpler carbohydrates
Enzyme activation/inactivation	→	increase or stopping of reactions

Sugar hydrolysis, where the acid and enzymes in the fruit cause the sugar (sucrose) to undergo hydrolysis (inversion) into glucose and fructose (invert sugar). High concentrations of dissolved solids in the jam are needed (65-70% total solids content) to create high osmotic pressures and reduce water activity so that potential spoilage organisms can no longer grow. Therefore, total sugar concentrations need to be high, but, if high enough in sucrose, its crystallisation can occur. So some inversion of the sucrose, in fact about 50%, is used to prevent its crystals from forming in the final product. The invert sugar contributes to the high concentrations but does not crystallise.

Pectin changes, in which carbohydrate polymers present mostly in the peel of the fruit polymerise further to give gels that solidify the jam. But enzymes, pectinesterases, may also break down the pectins and interfere with the gelling needed to give substance to the product. So there are enzymes that are helpful in aiding the sugar hydrolysis, and enzymes that are unhelpful in destroying pectin functionality.

Sugar caramelisation, where the sugars caramelise or in more extreme circumstances start to burn, forming dark colours and unwanted flavours. The reducing sugars can react with proteins that are present, through the browning (Maillard) reaction.

Complex flavour and aroma constituents in the fruit can evaporate and be lost, but they can also react, generally to form less desirable products. Colour constituents can bleach and change.

So there are reactions, occurring simultaneously, in parallel, and in sequence. There may be interaction – for example, the pH may change, and the enzymes may be inactivated by internal reaction to a greater or lesser extent, and caramelisation can be affected by the degree of sucrose hydrolysis.

Think break

Choose a food manufacturing system, e.g. bread baking, or blanching and freezing vegetables.

* Identify the critical and important constituents and attributes of the raw materials
* List the reactions that are being induced in the processing, the constituents involved both as reactants and as products, and the attributes being changed
* Identify the processing conditions causing the changes
* Identify the critical and important constituents and attributes in the final product.

2.3 Time and Temperature in Food Processing

Time is a critical variable in food processing. At this point it may be helpful to look at the range of time spans that are encountered in food processing, to put time scales into perspective. Food processing occurs on a time scale from a few seconds in a rapid heating process to years in shelf lives on storage. The rates of the important reactions in the process vary, respectively, from very fast to very slow. In using reaction technology, times are easier to compare with all of them in the same units, usually minutes, even though the numbers can commonly vary from 10^{-1} to 10^{6} min. Because we shall be looking at processing rates, the average rates can be compared by looking at the reciprocal of the time needed for the process to be completed. Thus for the short time scale for manufacturing/ processing, of between 0.1 and 100 min duration, rates vary from 10^{1} to 10^{-2} min^{-1}; for preservation lasting from a few days to a few months, average rates vary from 10^{-4} to 10^{-6} min^{-1}. And so the corresponding practical 'half-life' range, the time needed for 'concentrations' to halve, is a wide one, from around 10^{-1} to around 10^{6} min. Times and the equivalent rates of reaction are shown in Table 2.II.

TABLE 2.II
Processing times and rates of reactions

Time (min)	Rate of reaction (min^{-1})
0.01 (0.6 s)	10^{2}
0.10 (6 s)	10^{1}
1.0	10^{0}
10	10^{-1}
100 (1.7 h)	10^{-2}
1,000 (17 h)	10^{-3}
10,000 (7 days)	10^{-4}
100,000 (70 days)	10^{-5}

Some practical examples are:

- Seconds to 1 min: very short-time flow heat sterilisations, rates 10^{1} to 10^{0} min^{-1}
- 10 min to 1 hour: heating, cooking, canning, baking, rates 10^{-1} to 1.6×10^{-2} min^{-1}
- 2 hours to a day: curing meat, rates 8.3×10^{-3} to 6.9×10^{-4} min^{-1}
- 10 days to 2 years: ambient, chilled and frozen storage, maturation, rates 7×10^{-5} to 1×10^{-6} min^{-1}

Reactions such as denaturation of proteins, gelation and hydrolysis can have rates varying from 10^{-1} to 10^{-3} min^{-1} depending on process conditions.

Temperature is another critical variable. Temperatures lie over limited ranges, running from approximately 250 °C (or about 523 K) at the high end, briefly on

the surface of foods in an oven, down to -25 °C (or about 248 K) in freezer stores. There are a few and substantially more expensive cold storage temperatures down to as low as -70 °C (200 K) for very special food situations but these are rare. So the working range for most food reactions is essentially from +250 °C to -25 °C, or from 523 K to 248 K, i.e. a range of 275 degrees. For many purposes, Celsius units (°C) are convenient and widely understood, but sometimes (although the unit intervals stay the same) it is necessary to move to the Kelvin scale (K) based from absolute zero (-273 °C), and therefore with K = (°C + 273). Processing and storage temperature ranges are shown in Table 2.III.

TABLE 2.III
Processing and storage temperatures: ranges for typical food processing reactions

Process/storage	Temperatures (°C)	Temperatures (K)
Frozen storage	(-70)-1	203-272
Chill storage	0-5	273-278
Ambient processing	10-30	283-303
Warm processing	40-80	313-353
Hot processing	80-150	353-423

2.4 Concentration Sensitivity

The rate at which a food material is changed in a reaction, in terms of its mass transforming with time, has been found to relate to the mass itself that is present and so to its concentration. Concentration measures the closeness of the molecules together and thus their potential to react with each other. One reaction system that can be used to study the effect of concentration on rate of reaction is the hydrolysis of sucrose to invert sugar. Sucrose hydrolysis is a simple chemical reaction, and shows how the effect of concentration on rate of reaction can be quantified.

2.4.1 Rate of change proportional to concentration

The rate of change in sucrose has been found experimentally to depend directly on the sucrose level present, that is on the sucrose concentration. Therefore, as the reaction proceeds and the sugar concentration drops, so does the rate of the reaction.

The rate of change of sucrose to invert sugar is:

Rate of reaction $(r) = dC/dt$

where C is the concentration, t is increasing time; and dC is the decrease in concentration during the time interval of dt.

Because the rate of the reaction is proportional to the concentration of sucrose, an equation can be written:

$$r = dC/dt = - k C$$

where r is the rate of the reaction, k is a proportionality called a reaction rate constant, and C is the concentration of sucrose, the quantity of sucrose present in a unit of volume. The negative sign arises because the concentration of the reactant C decreases as time t increases. In this case the concentration of the sucrose could for example be measured in grams per litre, g/l.

This form of dependence is called a ***first order reaction***, and is one that is encountered commonly throughout food processing. The dependence of rate of reaction on concentration can more generally be expressed by proportionality to some power of the concentration,

$$r = dC/dt = - kC^n$$

but in the case of sucrose inversion it has been found to be linear, that is concentration (C) is raised to the first power. Other orders, zero and second order, are described in Theory 2.1. Many food processing reactions only approximately follow such simple equations over the full range of the reaction, but this particular reaction follows it throughout. It has been very extensively studied and it also just happens to be needed in making jam. It is a classical chemical reaction, and it has been experimentally found to fit the equation very well.

2.4.2 Time needed to reach a particular concentration

To predict the time needed to move from the concentration of sucrose in the raw materials to that of the final jam, the equation is integrated. The reaction rate constant can be determined experimentally, or in some cases the data can be found in published reports. In Example 2.1, the results for sucrose hydrolysis are taken from an old data handbook (1), which makes the additional point that information useful in the food industry is often available from a wide variety of sources. It is worth noting that the range over which the concentrations have been measured (1,000-fold ratio) is wider than might normally be determined in an industrial study.

Having arrived at the rate equation, then the integration, which is just summation over time, allows either the time to be found knowing end concentrations, or the end concentration to be found for a given time of reaction. The mathematics of the integration is shown in Theory 2.1, where results are also given for reactions of other orders.

Theory 2.1: Integration of rate equations

The equations can be integrated formally, keeping to one component.

General equation $dC/dt = - kC^n$ where n is the order

First order n = 1 $dC/dt = - kC$
and so $dC/C = - k\,dt$
and integrating $\ln C/C_0 = - k(t-t_0) = - k\,t$ if $C=C_0$ when $t = t_0 = 0$
i.e. $\ln C/C_0 = - kt$

General order n ($n \neq 1$) $dC/dt = - kC^n$
and so $dC/C^n = - k\,dt$
and integrating $\{C^{1-n}-C_0^{1-n}\} = (n-1)\,k\,t$

For zero order when n = 0, then
$C - C_0 = - k\,t$

For second order when n = 2
$C^{-1} - C_0^{-1} = 1/C - 1/C_0 = k\,t$

Many practical purposes can be covered by zero and first order, and sometimes second order is added. The addition of other and fractional orders, especially over two, is rarely needed. Further information on the analysis of reaction rates can be found in Levenspiel (2).

This leads to the integrated equation for *first order*:

$$t = (-1/k_T) \ln (C/C_O)$$

In this equation, t is the time needed for the concentration of the sucrose in the jam, in for example g per litre, to move from its initial value C_O to a final value of C, and k_T is the reaction rate constant at temperature T. The reaction rate constant, k_T has units of inverse time (commonly min^{-1}) subscripted T to indicate the temperature at which it applies, and ln indicates taking the logarithm to base e (found in practice by keying in the number and then pushing the ln button on the hand calculator). The negative sign comes in from the integration (you will find a problem if it is not included as C/C_0 is less than 1 and so $\ln(C/C_0)$ is negative). The equation may look a little formidable, but it can be worked through using a hand calculator or on a computer spreadsheet. This is shown in Example 2.1, illustrating hydrolysis (inversion) of sucrose.

Example 2.1: Sucrose: change of concentration with time (hydrolysis)

The times needed for inversion of sucrose in N/100 HCl at 80 °C, are given as 50% inverted after 9.1 min, 90% after 30.3 min and 99.9% after 90 min (1).

These values are plotted in Fig. 2.2(a). Figure 2.2(a) shows the direct plot of C/C_0 against time and on to this a computer-generated trend line has also been added.

Then the logarithms of C/C_0 are calculated.

Time (min)	9.1	30.3	90
C/C_0	0.5	0.1	0.001
$-\ln(C/C_0)$	0.693	2.303	6.91

C/C_0 are plotted on a logarithmic scale against time in Fig. 2.2(b).

Figure 2.2(b) gives a logarithmic plot showing an excellent straight line, and so giving positive confirmation to a first order reaction.

The reaction rate constant at 80 °C (k_{80}) can then be found from the equation:

$$t = (-1/k_{80})ln(C/C_0)$$

as it is the slope of the line on the logarithmic graph.

$$k_{80} = 0.076 \text{ min}^{-1} = 7.6 \times 10^{-2} \text{ min}^{-1}$$

The equation can be used to determine the time for any ratio of C/C_0 and also the concentration ratio for any time at 80 °C.

This example shows how once the rate of reaction is determined from sufficient experimental results, the equation can be used to determine the time for any specified concentration of sucrose. This time is obviously a key aspect for the jam manufacturer, determining the time needed for the processing and, amongst other things, the throughput of the equipment and the output from a particular process line. It can also provide a time signal for the operator to move from general to close supervision as the desired end point is approached. This may not explicitly be needed by a skilled operator but is a help for the less skilled and can be worked into the control strategy as the process control moves towards automation.

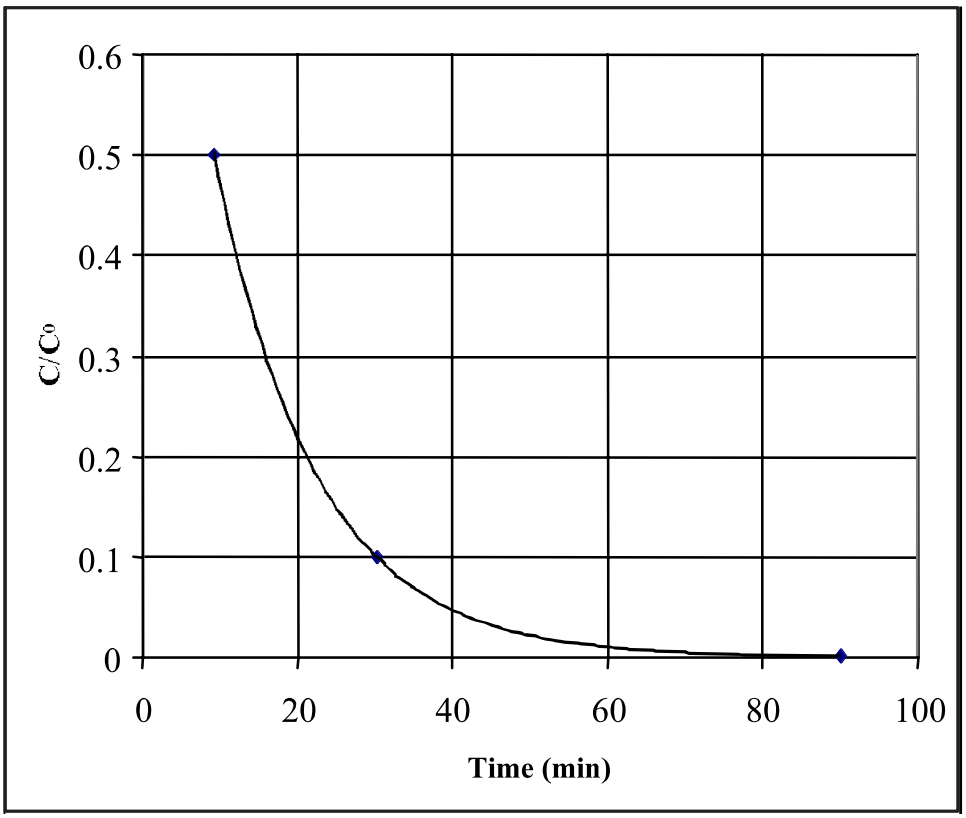
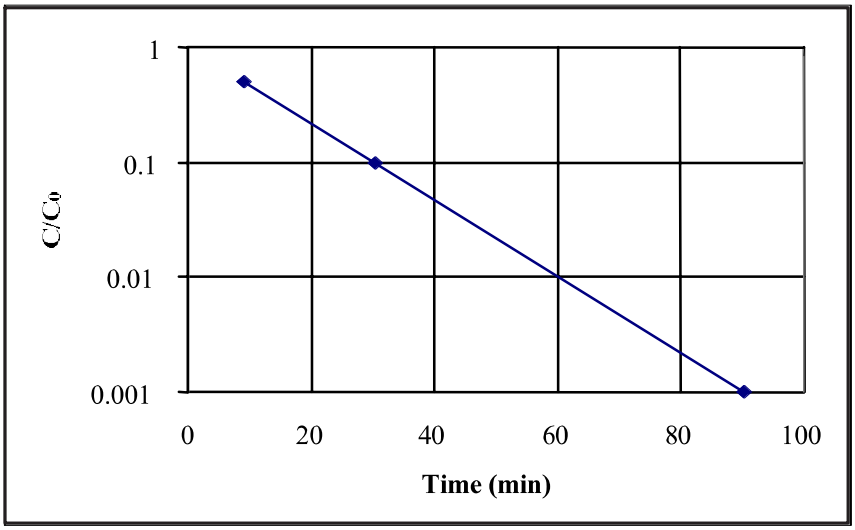


Fig. 2.2(a). Sucrose hydrolysis at 80 °C – natural scale



Data from: International Critical Tables (1)

Fig. 2.2(b). Sucrose hydrolysis at 80 °C – logarithmic scale

Think break

Using the information in Example 2.1:

* work out intermediate sucrose concentrations at times: 10, 20, 50, 70 min.
* work out the times for different concentrations: 60, 70, 80, 90%.

For example, after 30.3 min, C/C_0 = 0.1 so ln (C/C_0) = -2.303 and therefore

$$k_{80} = -(1/t)x \ln (C/C_0) = -(1/30.3) \times (-2.303) = 0.076 \text{ min}^{-1}$$

Using the equation

$$t = (-1/k_T) \ln (C/C_O)$$

After 15 min, the sucrose concentration can be calculated:

$$C/C_0 = \exp (-0.076 \times 15) = 0.32$$

that is concentration has dropped to 32% of the original concentration. The time taken to reach 50% of the original concentration, C/C_0 = 0.5

then $t = -(1/0.076) \times \ln(0.5) = -13.2 \times (-0.693) = 9.1$ min.

2.4.3 Rate equations

It may be appropriate to notice here the ways in which measures of concentration in food processing can take many forms, and these include mg/ml, g/l, kg/tonne, g/100 g, mol/l, microorganisms/cm^2 surface or per cm^3 volume, and so on. Similar reaction rate equations have also been found to fit some measures of consumer acceptance. This diversity of measures conforms to kinetic rate equations so long as the measures are quantitative. With only a change in numerical constants to make the differing numbers fit consistently, the pattern stays the same.

The rate may also be proportional to the concentrations of other components, C_B, C_C, and so on, but for the moment it is best to concentrate on one only, just $C_A = C$, in our example sucrose. The others will follow similarly.

When looking at rate equations it is always worth remembering that, from the present point of view, that of the process technologist, rate equations are simply descriptive. It is a matter of finding an equation that fits the experimental data, and then using it only so long as it continues to fit closely enough for the technical purpose in hand. There may also be further systematic and theoretical ways of looking at the systems that may be helpful, but they are not necessary for

technological calculations and predictions, so we need not worry about them here in order to reach the required end product satisfactorily.

Think break

* Using a hand calculator, arbitrarily select a value for the reaction rate constant k (perhaps 1 min^{-1}) and an initial food constituent concentration (perhaps 300 g/l), and, assuming a first order reaction, calculate progressive concentration/time values until the concentration reduces to 1% of its initial value.
* Plot the concentrations linearly and logarithmically, against time.

As an example for $t = 0.5$ min and $C_0 = 100$ g/l, with $k = 1$ min^{-1} then

$$t = (-1/k_T)\ \ln (C/C_O)$$

$$0.5 = (-\ 1/1)\ln (C/100) = -1\ \ln(C/100)$$

therefore $C = 100 \exp(-0.5) = 100\ e^{-0.5} = 61$ g/l

(If unfamiliar with exponentials, run these numbers back and forth a few times on a calculator to convince yourself that they all fit together and make sense.)

The integrated first order equation can be applied under any concentration circumstances. For example, when the concentration halves C becomes $C_0/2$ and so

$$\mathbf{-\ln(C/C_0) = -\ln(½) = 0.693}$$

$$= k \text{ x (time for concentration to halve)} = k \text{ x } (\textit{half-life}) = k\ t_{0.5}$$

This *half-life* gives some feeling for the magnitude of the reaction rate constant because k for these first order reactions equals {0.693/(the half-life)}. With the logarithmic nature of the first order reaction, in a further time interval of a half-life the concentration will halve again, and so on. So, for example, if our sucrose hydrolysis has a half-life of 9.1 min, in a further 9.1 min it will halve again, that is to ¼ of its original concentration, and for the reaction discussed in Example 2.1 at 80 °C, the reaction rate constant is 0.693 $(1/t_{0,5})$ = 0.693 (1/9.1) = 0.076 min^{-1} as set out in the Example.

The concept of a reaction rate that is linearly related to the present concentration, and which therefore generates constant fractional, first order reaction rates, is in fact a rather fundamental one. What it says for the hydrolysis in the jam is that the initial rate at which the sucrose that was added to the fruit starts to invert, that is to change into glucose and fructose, is proportional to the

actual amount of the sucrose that was added. And further, as the sucrose reacts and its concentration decreases, so the reaction rate in terms of, say, grammes of sucrose inverting per minute decreases proportionately. This seems a rather probable and intuitive behaviour. So it is hardly surprising that it has many wide-ranging applications.

Processing times are critically important in food processing. We have already encountered times for concentration changes. Another very common instance arises in both the growth and the death of microorganisms. In growth patterns in biology, the concept of a doubling time is well known. It is just another example of increase being based on present numbers (concentrations), applied in this case to cell division. Microorganism growth is important in food processing for two broad reasons: for the building up of desired cultures to establish flavours and textures, and in the unwanted proliferation of pathogens and spoilage organisms creating toxins, potential infections, off-flavours, less desirable textures, colours and slimes. The death/inactivation of microorganisms follows a similar pattern during processing, at least over limited ranges. Numbers of microorganisms can be reduced dramatically, thus decreasing deterioration in the food. Heating is one way of deliberately inducing death by increasing local energy intensity. Other methods of increasing local energy intensity are irradiation, much elevated pressures, and electric fields. After such treatment, the number of live organisms, or their ability to metabolise and reproduce, decreases and it has been found to do so systematically.

2.5 Temperature Sensitivity

As well as having concentration sensitivity, reaction rates are also sensitive to temperature. A problem in processing is that the temperature may be not constant. In our continuing example, during processing, the jam has to be heated up and cooled down. If steam pressures are not steady, then heating jacket temperatures can vary accordingly, and also as the jam is boiled its solid content rises and so does its boiling temperature. Changes in temperature are implicit in most of processing. Reaction rates generally increase with increasing temperature, and the reaction rate constant is only constant as long as the temperature is also. So the reaction rate constant has also to be predictable in terms of the working temperature for it to be useful in processing. This can be done.

2.5.1 Relationship between reaction rate and temperature

Much experimentation has shown the rate/temperature relationship for a simple irreversible reaction to be an exponential one in which the basic rate equation is expanded and of the form:

$$- r = k_T C^n = (\mathrm{A}\, e^{-E/RT})\, \mathrm{C}^{\mathrm{n}}$$

and, on cancelling the concentration terms:

$$k_T = \mathbf{A}\ e^{-E/RT} = \mathbf{A}\ \exp\{-E/RT\}$$

This is a fundamental equation connecting reaction rate constants with absolute temperature. Here *r* is the rate of the reaction, k_T *is* the reaction rate constant and subscripted *T* to indicate that it is a function of temperature, A is called the ***frequency factor*** and is a constant for a particular reaction, *E* is called the ***activation energy*** of the reaction (in Joules/mol.), *T* is the temperature (absolute, in degrees Kelvin, K = 273 + C) at which the reaction takes place, *C* is the concentration of the reacting component, and *R* is a constant (called the 'universal gas constant' and numerically 8.314 Joule/mol. K).This shows that rates and temperatures are connected through an exponential (exp), and further that the temperature occurs in the exponent (the term in the {} brackets) as the reciprocal (1/T) of the temperature measured in degrees K.

This is commonly named the ***Arrhenius equation*** after its originator, who, well over 100 years ago and working as it happens on the sucrose hydrolysis system, advanced the idea. His choice must have been sound as it has remained the best for many purposes ever since. An enormous amount of work has been done on it, and, while never definitively proven, no simple experimental reaction has ever been found that departs from it (3). Its form may look complicated, but once more the hand calculator comes to the rescue when working in practice.

The Arrhenius equation can also be written:

$$\ln k_T = \ln A - (E/R) \bullet (1/T)$$

In the ***Arrhenius plot***, the natural logarithms of the reaction rate constants at different temperatures are graphed against the reciprocal of temperature(1/T). If the data conform to the equation, then the graph is a straight line and the value of E/R is the slope of the line. As R is constant, the activation energy, E, can be found. This is shown in Example 2.3 for the hydrolysis of sugar.

The Arrhenius equation and its implications are at the heart of food processing reaction technology because so often temperature is the primary agent in initiating and controlling the actual processing. It contains two terms, one a multiplier, A, and the second an exponential, $e^{-E/RT}$, which can also and perhaps more conveniently be written $\exp\{-E/RT\}$. The magnitudes of the terms A and E once known, for any particular reaction, allow calculation of the rates at different temperatures, T_1, T_2, and so on. The first, A, the frequency factor, in effect sets the general level of the rate and is often found to be numerically very large (for example of the order of 10^{10}). Everyday manageable processing levels of the rates (from about 10^{-3} min^{-1} to about 10 min^{-1}, implying half-lives from about 10 hours to a few seconds) emerge only after it has been multiplied by the second term. The second term has a negative exponent, and is often in real circumstances found to be extremely small (for example of the order of 10^{-10}). It contains in the exponent the quantity *E*, the activation energy, and this characterises classes of reactions. It has the effect of setting the sensitivity of a reaction to (absolute) temperature *T*. The term *R* is there for thermodynamic reasons only; it is a constant. Working with

this equation, the changes in reaction rates consequent upon a given change in temperature can be calculated. Also sensitivities, which are the percentage change in reaction rate due to unit change in temperature, can be calculated. These can be so useful when considering rates in practice.

Reaction rate constants at different temperatures are connected by:

$$k_{T1} / k_{T2} = \exp \{E/R(1/T_2 - 1/T_1)\}$$

found by dividing the Arrhenius equation for the one temperature by that for the other.

The time for 50% hydrolysis at temperature T can be determined by using:

$$t = (1/k_T) \ln \tfrac{1}{2} = 0.693\ (1/k_T)$$

Example 2.2 illustrates the effects of temperature on reaction rate constants in hydrolysis of sucrose.

Example 2.2: Sucrose hydrolysis: reaction rate constants at different temperatures

The reaction rates at different temperatures for the hydrolysis of 50% sucrose solution in 0.1N HCl are given in the International Critical Tables (1).

Temperature (T)						
	(°C)	0	15	30	40	50
	(K)	273	288	303	313	323
1/T	(1/K)	3.67×10^{-3}	3.47×10^{-3}	3.30×10^{-3}	3.19×10^{-3}	3.10×10^{-3}
Reaction rate (k)						
k	(min^{-1})	7.7×10^{-6}	9.2×10^{-5}	8.7×10^{-4}	3.3×10^{-3}	1.2×10^{-2}
ln k		-11.77	-9.29	-7.05	-5.71	-4.42

ln k is plotted against 1/K in Fig. 2.3, the Arrhenius plot for sugar hydrolysis.

Contd..

Example 2.2 (contd)

This is a straight-line relationship, so the slope gives the value of:

$E/R = (11.77 - 4.42)/(3.67 \times 10^{-3} - 3.1 \times 10^{-3}) = 7.35/0.57 \times 10^{-3}$
$= 12.9 \times 10^{3}$ K

R, the gas constant, is 8.314 joules/mol K

so $E = 107 \times 10^{3}$ J/mol
$= 107$ kJ/mol

To estimate the reaction rate at 110 °C, that is 383 K,

$k_{383} / k_{323} = exp\{-E/RT_{383}\} / exp\{-E/RT_{323}\}$

so $k_{383} / 1.2 \times 10^{-2} = exp\{E/R\ (1/323 - 1/383)\}$
$= exp\ (12.99 \times 10^{3}(3.096 \times 10^{-3} - 2.611 \times 10^{-3})$
$= exp\ (6.30)$
$= 545$

and so $k_{383} = 545 \times 1.2 \times 10^{-2}$
$= 6.54\ min^{-1}$

To estimate the time for 50% hydrolysis at 110 °C, that is 383 K

$-t_{0.5} = (1/6.54)(\ln ½)$
$= 0.153 \times -0.693$
$= 0.11$ min

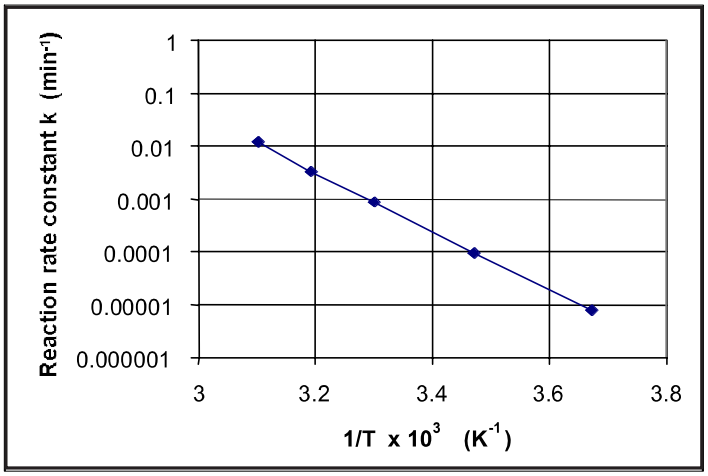


Fig. 2.3. Sucrose hydrolysis – Arrhenius plot for reaction rate against temperature

Think break

The reaction rate constants, k, for the hydrolysis of sucrose at temperatures from 60 to 91 °C using 0.1NHCl are:

Temperature T (°C)	59.90	69.97	80.13	90.29	90.32
Reaction rate constant k (min^{-1})	0.4000	0.1236	0.3687	1.033	1.020

* Draw the Arrhenius graph from these data for the hydrolysis of sucrose between 50 and 90 °C
* Determine the activation energy E
* Predict the reaction rate constant, k, at 100 °C
* Determine the time for 50% hydrolysis at 90 and 100 °C
* How do the reaction rate constants vary with increasing temperatures?
* What does this mean for process control?

2.5.2 Sensitivity to processing temperature

The sensitivity of processing to temperature can be worked out very straightforwardly by remembering that it is from $(k_{T+1})/(k_T) = (1 + \text{sensitivity})$ or it can be related to the activation energy, as shown in Theory 2.2.

Theory 2.2: Temperature sensitivity calculation

The Arrhenius equation is

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

Taking the derivative $dk/dT = (Ae^{-E/RT}) \bullet E/(RT^2) = k\,[E/(RT^2)]$

Therefore $dk/kd(T) \doteq d(\ln k)/dT = E/RT^2$

And since $d(\ln k)/dT \doteq \ln[(k_{T+1}) / (k_T)]$

Therefore $E/(RT^2) \doteq \ln[(k_{T+1}) / (k_T)]$

$$\exp(E/RT^2) \doteq (k_{T+1}) / (k_T) = 1 + \text{sensitivity}$$

or $$\exp(E/RT^2) - 1 \doteq \text{sensitivity}$$

Because:

$$\mathbf{(k_{T+1})/(k_T) = \exp\{E/RT^2\} = 1 + sensitivity}$$

R is a constant and 8.314 J/mol K, for a reaction with an activation energy of, say, 100,000 J/mol, the sensitivity at 100 °C or 373 K, can be found from:

$$\exp\{100{,}000/(8.314.373.373)\} = 1.09 = 1 + (9/100)$$

This (9/100) can be thought of as a temperature sensitivity of the reaction rate amounting to 9% per degree C and written 9%/°C. Experimentally, 9%/°C is found to be close to the temperature sensitivity of the sucrose hydrolysis reaction. In case you are not familiar with exponentials, it is salutary to consider their power in these ratios, as shown in Example 2.3.

Example 2.3: Demonstrating the power of logarithmic temperature sensitivities

Sensitivities seem at first sight to be rather innocuous, but their "logarithmic" force gives them great power. For example, with a 26% per degree sensitivity:

- a 3 °C shift upward doubles the rate of the reaction (1.26^3) = 2;
- a 5 °C shift increases the rate (1.26^5) = 3.2 times, and
- a 20 °C shift multiplies it (1.26^{20}) = 102 times.

While a 20 °C shift may seem large around 100 °C, it is not an altogether remote possibility in the fluctuations of an oven at 200 °C.

Think break

For three activation energies: 100, 200 and 400 kJ/mol

* Work out the sensitivities at temperatures of 100 °C and 110 °C.
* Determine the ratio of reaction rate constants, k_{110}/k_{100}.
* Reflect on the magnitudes of these numbers and of their significance in a food process in which they might occur.

For example, for E = 200,000 J/mol at 100 °C = 373 K,

$$E/RT^2 = 0.173$$

so $\exp\{E/RT^2\} = 1.19 = (1 + \text{sensitivity})$, so the sensitivity is 19%/ °C.

Over a 10 degree temperature range

$$k_{383}/k_{373} = A\exp(-E/R.383)/ A\exp(-E/R.373) = \exp\{E/R(1/373-1/383)\}$$
$$= \exp\{ (200{,}000/8.314) (1/373 - 1/383)\} = \exp\{ 1.684\} = 5.4$$

so this reaction moves over five times faster at 110 than at 100 °C.

2.6 Reaction Rate/Temperature Relationships: Activation Energies

Food processing predictions can be made using the ranges of concentration and temperature found in food processing combined with the levels of activation energies calculated from experimental observations. The activation energies broadly lie between those of many chemical reactions, with a minimum of about 50 kJ/mol and an average probably nearer to 100 kJ/mol, and those of protein denaturations (and bacterial deaths that may be caused by somewhat the same basic molecular rearrangements) with a maximum of about 500 kJ/mol the activation energies of many enzyme reactions lie in between these. The total range is about tenfold, 50-500 kJ/mol.

Activation energies for particular reactions have to be determined experimentally. This is normally done by measuring rates over a range of temperatures and then constructing the so-called Arrhenius plot of the logarithm of the measured reaction rate constants against the reciprocal of the absolute temperature, ($\ln k$) against (1/T) as illustrated in Fig. 2.3. Table 2.IV gives a general picture of the expected magnitudes, together with the calculated sensitivities at two temperatures, using the higher of the activation energy ranges.

TABLE 2.IV
Activation energies for typical food processing reactions

	E	Sensitivity*	
	kJ/mol	(40 °C)	(120 °C)
Chemical reactions			
General chemical reactions	40-100	13%/ °C	8%/ °C
Hydrolysis reactions	60-120	16%/ °C	10%/ °C
Lipid oxidations	40-100	13%/ °C	8%/ °C
Browning (non-enzymic) reactions	100-200	28%/ °C	17%/ °C
Vitamin destruction	70-150	18%/ °C	12%/ °C
Protein denaturation/coagulation	200-500	84%/ °C	47%/ °C
Enzyme reactions	100-200	28%/ °C	17%/ °C
Microbiological changes			
Microorganism growth	100-150	18%/ °C	na
Vegetative microorganism death	300-500	84%/ °C	47%/ °C
Spore death	250-350	53%/ °C	31%/ °C

* (The sensitivities are calculated using the highest activation energy in the range and at the temperatures quoted. Notice that they are temperature-dependent, which the Arrhenius equation requires.)

The sensitivities were calculated for the highest activation energy and at two temperatures: 40 °C and 120 °C. For example, taking general chemical reactions and the highest activation energy of 100 kJ/mol:

Sensitivity at 40 °C

E = 100,000 J/mol at 40 °C = 313 K, R = 8.314 Joules/mol. K

$E/RT^2 = 0.123$

$\exp\{E/RT^2\} = 1.130$

= (1+ sensitivity)

Therefore sensitivity = 0.13 = 13% per degree C

Sensitivity at 100 °C

E = 100,000 J/mol at 120 °C = 393

$E/RT^2 = 0.078$

$\exp\{E/RT^2\} = 1.08$

= (1+ sensitivity)

Therefore sensitivity = 0.08 = 8% per degree C

So both 13%/ °C and 8%/ °C sensitivities are seen to work out to the values shown in Table 2.IV. Notice that, according to the Arrhenius equation, sensitivities decrease with rising temperatures and conversely increase at lower ones for a fixed activation energy.

Looking generally, it is possible to view the whole realistic reaction spectrum available to the food processor. From this overview can come some understanding so far as temperature manipulation is concerned of:

- processing possibilities,
- degree of precision within which control has to be exercised if end results are to be defined and reproducible,
- degree of process control that is practicable, and
- accuracy that needs to be obtained from the instrumentation and the analysis of particular processes.

The results discussed in Example 2.4 are not from well-defined situations, but they are not untypical of exploratory work in processing.

Example 2.4: Temperature sensitivities in process development

You are faced with two processing problems in which working temperatures have shifted owing to circumstances beyond your control, so you have to accept them and make what time modifications you can to reach the same product results. One process is spore destruction and the other a hydrolysis.

For the spore destruction, the process is supposed to operate at 120 °C, but the temperature has fallen to 117 °C. By how much should you increase the standard processing time as a trial?

Contd..

Example 2.4 (contd)

From Table 2.IV, (1+ sensitivity) is 1.31 at 120 °C

The rate of spore destruction from 120 to 117 °C is predicted to decrease to $1/1.31^3 = 0.44$ times, i.e. 44% of its original value.

Therefore, processing times should be multiplied by 100/44 = 2.3.

For the low-temperature hydrolysis, the working temperature at 40 °C has risen by 2 °C. By how much should you decrease the former processing time to expect the same extent of hydrolysis?

From Table 2.IV, (1+ sensitivity) is 1.16 at 40 °C

The rate of hydrolysis, from 40 to 42 °C, is predicted to increase to $1/1.16^2 = 1.38$ times, i.e. 38% of its original value.

Therefore, processing times should be multiplied by 1/1.38 = 0.72.

If the standard time was 10 min, the run should be completed at the higher temperature in 10/1.38 = 7.2 min.

Sensitivities of process reaction rates to temperature can be used to design and control processes. They also give the product developer a feel for the experimental temperature ranges that should be tried in early experimentation, and also for control difficulties that might arise in the product line.

In a specific case, with more knowledge and tighter definition of the parameters, more precise process control could be exercised, and this is illustrated in Example 2.5. It should be noted that, even though the justification for the very large extrapolations implicit in the example may be questioned, relative changes calculated are rational and can be very helpful in guiding the process operator.

Example 2.5: Sensitivity of sterilisation processing

In a continuous fluid sterilising operation, you have included in your standard process calculations for sterilisation that your holding tube holds the product at 118 °C with a residence time of 7 min.

One morning, you discover from the product output that your fluid pump has unaccountably increased the flow rate by 30% and the only available way to correct in the short term and get usable product is by lifting the holding temperature. To what new temperature should you lift it?

You check out the sensitivity of the spore destruction, and find that it is 26%/°C at these temperatures. The activation energy for this spore death is 298kJ/ mol; the gas constant, is 8.314 joules/mol K; the temperature is 118 °C = 391K.

Contd..

Example 2.5 (contd)

$$\exp\{E/[R.T^2]\} = \exp\{298{,}000/[8.314.391.391]\} = 1.26$$

The flow rate has been increased by 30%, i.e 1/(1-0.3) = 1.43.
So you have to increase the rate of spore destruction by this factor.

Therefore, $1.26^{x} = 1.43$, which you find with your calculator = $1.26^{1.55}$.

So you need to increase the temperature by 1.55 °C, say 2 °C.

After this change, the process should then, assuming that heating and cooling contributions are substantially unaltered, slightly exceed the specification.

You do not need any tables, or a computer, although if you check them out you should find that they give the same answer. The added advantage of this 'first principles' approach is that the alarm bells of (technologically informed) common sense should ring because of the 'feel' that the 26%/°C gives for the sensitivity of the critical reaction, if results of calculations at any stage do not seem to be about right.

2.7 Reaction Rate/Temperature Relationship: Other Temperature Coefficients

There are several temperature coefficients used to characterise the effect of temperature on reaction rates. So far, only activation energies have been considered, together with a derived unit, sensitivity to temperature, that is convenient for quick calculations. There are more traditional measures that relate to these, two of them defined by the arbitrary symbols (**z**) and $\mathbf{Q_{10}}$, which are commonly used and will probably be familiar to many.

*The small-case letter, **z** , is conventionally used to denote the experimentally found temperature increase necessary to multiply the rate of a reaction ten-fold.* In our nomenclature,

$$\mathbf{z \text{ is defined by } 10 = k_{T+Z} / k_T}$$

The two *k*s are rates z degrees apart and z therefore is a temperature difference, and has the dimension of a temperature.

The symbol, $\boldsymbol{Q_{10}}$, is defined as the ratio of the reaction rate constants at temperatures 10 °C apart. In our nomenclature,

$$\mathbf{Q_{10} = k_{T+10} / k_T}$$

The two *k*s are rates 10 degrees C apart and Q_{10}, being a ratio, has no dimensions.

The higher rate is in the numerator, so Q_{10} is always greater than 1. Q_{10} tends to not get much use these days although it was formerly common, especially in biochemistry.

Since z, Q_{10}, E, the activation energy and the sensitivity are all different ways of quantifying temperature coefficients of reaction rates, and they must all accurately fit to the same experimental findings, they must all lead to the same predictions. It follows that they must all be related to each other. Their full relationship is not straightforward, but, for practical purposes, useful approximate equations can be written to connect them:

$$\mathbf{E/RT^2 = 2.303 / z = \{ln\ (Q_{10})\} / 10 = ln\ (Q_1)}$$

where T is taken as the absolute temperature appropriate to the range of interest, often the mean in the range, and $\mathbf{Q_1}$ is a ratio of reaction rates, just as is Q_{10}, but with temperatures only 1 °C, rather than 10 °C, apart. So $Q_1 = (k_{T+1})/(k_T)$. As already discussed, Q_1 is closely related to the reaction sensitivity per degree, the numerical relationship being:

$$\mathbf{sensitivity = (Q_1 - 1) = exp(E/RT^2) - 1}$$

so that, for a sensitivity of 13% = 13/100, $Q_1 = (1 + 13/100) = 1.13$.

An example of conversions of these measures is shown in Example 2.6, and some mathematical detail of the calculations is set out in Theory 2.3.

Example 2.6: Sucrose hydrolysis: conversions of temperature coefficients

The extent of hydrolysis with time was followed experimentally at several temperatures around 100 °C, and the reaction rate constants determined for each of the temperatures. These rate constants were plotted against the corresponding °C temperatures, and the slope of the plot showed the Sensitivity to be 10%/°C.

Now sensitivity = $(Q_1 - 1) = 10\% = 0.1$, and so $Q_1 = 1.10$
Using the relationships, $E/RT^2 = 2.303 / z = \{ln\ (Q_{10})\} / 10 = ln\ (Q_1)$, determine the value of Q_{10}, Z, and E.

Now	$ln\ Q_1$	$= ln\ 1.10 = 0.0953$
But	$ln\ Q_{10}$	$= 10\ ln\ Q_1 = 0.953$, and so $Q_{10} = 2.6$
And	z	$= 2.303 / ln\ Q_1 = 2.303 / 0.0953 = 24.2$ °C
And also	E	$= ln\ Q_1\ R\ T^2 = 0.0953 \times 8.314 \times 373 \times 373$
		$= 110{,}000$ J/mol

Of these measures, the most familiar to the food technologist will be z but the others relate quite straightforwardly.

Think break

Two reactions have z values of, respectively, 7 °C and 30 °C. At a working temperature of 70 °C (343 K), determine:

* the corresponding activation energies and
* the corresponding sensitivities.

For example, with a z value of 10 °C (= 18 °F) and at 70 °C, 343K

$2.303/z = E/RT^2 = \ln Q_1$,

$2.303/10 = 0.2303 = E/ 8.314\ (343)(343) = \ln Q_1$

so E = $0.2303 \times 8.314 \times 343 \times 343 = 225$ kJ/mol ,

and $Q_1 = \exp(0.2303) = 1.26$

$= (1 + \text{sensitivity})$,

so the sensitivity = 26%/°C

The detail of the relationships of these various temperature coefficients tends to be confusing and complicated. They have arisen from historical circumstances. For example, z arose about 80 years ago in the context of thermal death rates for spores in canning; it was convenient, it related to what was a useful temperature interval, and it became familiar. However, to work with it, particularly in the days before hand calculators, extensive tables were necessary. These were prepared and made available, but tables are always cumbersome and in factories they are messy. These days they have been incorporated into computer software that can work well, but software does not invoke much intuition in the technologist, or give a mental intimation when something has gone wrong.

Greater exploration of food processing in the wider field of reactions introduced activation energies more extensively, but they are also not very friendly to deal with either for calculations, or intuitively. This is why the temperature sensitivity, straightforward in concept and very easy to manipulate using a y^x key on a calculator, is used so freely in these present discussions. Some may find it interesting to work out the mathematics, and so these are briefly explored in Theory 2.3.

Theory 2.3: Temperature coefficients of reaction rate constants and their relationships

Writing the Arrhenius equation:

For temperature T_1

$$k_{T1} = A \exp\{-E/RT_1\}$$

and for temperature T_2

$$k_{T2} = A \exp\{-E/RT_2\}$$

Taking their ratios

$$k_{T1}/k_{T2} = \exp\{-E/R[1/T_1 - 1/T_2]\} = \exp\{-[E/R][(T_2 - T_1)/(T_1T_2)]\} \quad *$$

and putting $\varepsilon = T_2 - T_1$ then $T_1 = T_2 - \varepsilon$ and expanding

so $$k_{T1}/k_{T2} = \exp\{-E\varepsilon/RT_2\}\{1 - \varepsilon/T_2 + (\varepsilon/T_2)^2 - (\varepsilon/T_2)^3 + \ldots\ldots..(**)$$

Because ε/T is small (if ε is say < 20, and negative for $T_1 > T_2$) and remembering that E is large, say 100,000 + , and T is normally 300 +

Then by definition Q_{10} • •$\exp\{10E/RT^2\}$ for $\varepsilon = 10$

or $\ln Q_{10}$ • •$10\ E/RT^2$

and Q_1 • •$\exp\{E/RT^2\}$ so $\ln Q_1$ • • E/RT^2 for $\varepsilon = 1$

also by definition 10 • •$\exp\{z\ E/RT^2\}$ for $\varepsilon = z$

or $\ln 10 = 2.303$ • •$z\ E/RT^2$

or z • •$2.303\ RT^2/E$

and so $E/RT^2 = (\ln Q_{10})/10 = 2.303/z = \ln Q_1$ approximately

The series expansion (**) reveals the connection, and the reason for the fundamental differences and complications arising, between the Arrhenius approach, which includes the power terms, and the other (z, Qs), which can be seen to include only the first term in the bracket, 1. This follows from writing E/RT^2 as $\ln(Q_{10})/10$ or as 2.303/z. where T is a reference temperature.

For example, using the latter then from * above:

$$k_{T1}/k_{T2} = \exp\{-2.303\ \varepsilon/z\} = 10^{-(T_2-T_1)/z}$$

because $\exp(2.303) = 10$ and $\varepsilon = (T_2 - T_1)$.

This expression is found extensively in the standard food canning and thermobacteriology literature e.g. Stumbo (4).

For further exploration, there are complete books about these topics, such as Johnson *et al*. (3) for the Arrhenius equation in biological systems, and they are also discussed in general food processing technology books such as Singh & Heldman (5).

One remaining aspect of temperature sensitivity arises, and it is implicit in the approximations that are alluded to in Theory 2.3. When plotting temperatures against ln (reaction rate constants), the z plots give straight lines against the temperature, T, which can be either in °C or K. In contrast, the Arrhenius plots give straight line plots against the reciprocal of the absolute temperature, 1/T, in $(K)^{-1}$. This detail may seem confusing, but it is significant within the precision limits of most food processing work only when quite substantial temperature shifts (say 50 °C and up) are involved.

2.8 Reaction Rate/Concentration Relationships

The dependence of rate of reaction on concentration can generally be expressed by proportionality to some power of the concentration,

$$r = dC/dt = - kC^n$$

The value of *n* denotes the order of the reaction, n=0 being zero order, n=1 being first order. Whilst formally the exponent n in the general rate equation can have any value, the range is only of practical interest when needed for a fit or to help in understanding experimental observations in food processing. Two conditions, those of rates directly proportional to the concentration (n=1) and of rates that are constant (n=0), cover very many of the observed food processing situations.

Where they do not fit as closely as might be needed, then careful choice of averaged data can often improve fit. For example, rates calculated from slopes of concentration/time curves taken at a mid-point rather than an extreme, will often bring predictions into line with observations sufficiently closely to zero or first order for industrial purposes. Also, for the first 50% or so of any reaction, the orders are virtually indistinguishable.

2.8.1 First order reactions

Up to this point, first order reactions have been described, where the logarithmic increase or decrease in concentration is related linearly to time (see Fig. 2.2(b)). First order describes many useful reactions, and, even where it does not fit over the whole range, or exactly, it can still be a very useful approximation for part of the range.

Example 2.7: Sucrose hydrolysis: calculations of concentration changes with time

To see how concentration change is calculated, consider again the sucrose hydrolysis. It is known that its half-life at a particular temperature is 20 min. This means that starting at a concentration of 0.5 kg sucrose/litre,

- after 20 min it will have fallen to (0.50/2) = 0.25 kg/l, and
- after a further 40 min to $(0.25/2^{2)} = (0.25/4) = 0.063$ kg/l.

This can be extended to take into account any desired time by returning to the fundamental first-order equation:

$$\ln \{C_o/C\} = k\,t$$

and finding k from the fundamental first order constant/half-life relationship of

$$k = 0.693/t_{0.5}\ .$$

In this case, for a half-life of 20 min, $k = 0.693/20 = 0.035$ min^{-1}.
If the time to reach 0.20 kg/l is required, then:

$$\ln (0.5/\ 0.20) = \ln (2.50) = 0.92$$
$$= k\,t$$
$$= 0.035\ t$$

$t = 0.92/0.035$, so that the required time is 26.3 min.

Or, if the sucrose concentration is wanted after 20 min,

$$\ln (0.5/C) = (0.035)\ (20) = 0.70 \text{ and so}$$
$$C = 0.5/\exp(0.70) = (0.5)/2 = 0.25 \text{ kg/l}.$$

Fairly obviously, temperature and concentration changes can be combined, but the detail of this is best handled in a later section on process integration.

2.8.2 Zero order reactions

Another important class of food processing reactions is found experimentally to move at apparently steady rates, a constant amount decreasing or increasing rather than a constant fractional amount with time. These reaction rates can be seen in the overall scheme as proportional to concentration raised to the power of zero,

and thus they are independent of concentration because $C^0 = 1$. They therefore move steadily at one constant rate and for them the calculations are rather straightforward, levels of reactants decreasing from their initial levels steadily with time. Unlike reactions of other orders, they continue to zero concentration within a finite time. The concentration increases or decreases with time linearly, as shown in the loss of ascorbic acid on storage of a multivitamin mix in Example 2.8.

Example 2.8: Ascorbic acid loss on multivitamin storage

In a classical investigation of loss of ascorbic acid in a multivitamin mix on storage at different temperatures, the concentrations of ascorbic acid at different times when stored at 50 °C were:

Time	(days)	10	20	30	40	50	60	70
Ascorbic acid	(mg/ml)	21	19	16	14	12	10	8

These data are shown in Fig. 2.4.

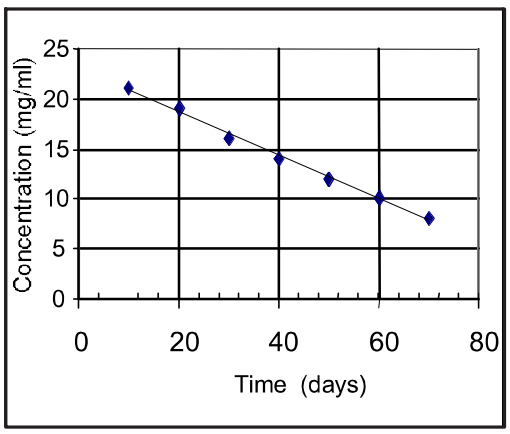
The actual figures in this case scarcely need analysis; the graph in Fig. 2.4 clearly shows the linear relationship with time, independent of concentration.

So this is a zero order reaction.

The rate k can be determined by taking:

(change in concentration)/(time taken) from the tabulated data or the graph trend line = (21 - 8)/(70 - 10) = 13/60 = 0.22 mg/ml/day.

Adapted from Garrett (6)



Data from Garrett (6)

Fig. 2.4. Ascorbic acid loss in a multivitamin mix on storage at 50 °C

Because it is the simplest form, it is always worthwhile to try zero order for any food processing situation to see whether it can be made to fit adequately for the purposes in hand.

Zero order reactions also conform to the Arrhenius equation in the relationship between temperature and reaction rate constant. In Example 2.9, data from Garrett (6) measuring rates of deterioration of vitamin C (ascorbic acid) in a multivitamin mix in storage experiments at different temperatures are given. They are plotted in Fig. 2.5 relating the logarithm of the reaction rate constant to the reciprocal of the absolute temperature. This is an Arrhenius plot showing that the data conform to the Arrhenius equation, and the graph is a straight line of slope (- *E/R*). Note that, in a zero order Arrhenius plot in Example 2.9, the reaction rate constant is in mg $ml^{-1}day^{-1}$, as compared with first order plot in Example 2.2, which is in min^{-1}. Reaction rate constant units are always for zero order concentration and time and for first-order time only.

Example 2.9: Loss of ascorbic acid on storage: Arrhenius plot

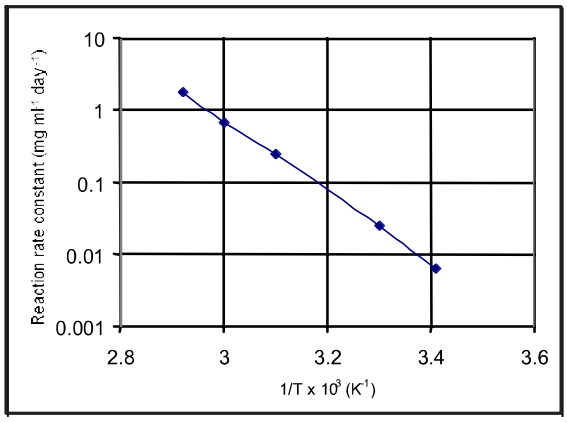
The reaction rate constants for an investigation of ascorbic acid deterioration in a multivitamin mix during storage at different temperatures were:

Temperature (°C)		20	30	50	60	70
	(K)	293	303	323	333	343
1/T	(1/K)	3.41×10^{-3}	3.30×10^{-3}	3.10×10^{-3}	3.00×10^{-3}	2.92×10^{-3}
Reaction rate constant (k)						
	mg $ml^{-1}day^{-1}$	6.2×10^{-3}	2.4×10^{-2}	2.4×10^{-1}	6.6×10^{-1}	1.8×10^{-1}

k is plotted against 1/T in Fig. 2.5.

This conforms to an Arrhenius plot.

Adapted from Garrett (6)



Data from Garrett (6)

Fig. 2.5. Ascorbic acid loss on storage: Arrhenius plot for reaction rate and temperature

2.8.3 Other rate/concentration relationships

There are some situations where other orders of the reaction are needed to secure sufficiently close fits, or where there may be some additional understanding of the reactions themselves resulting from more elaborate treatment of the data. A more practical reason for persisting with other orders is the examination of the general behaviour of reactions with order, and this is shown in Fig. 2.6, which shows the change of concentration with time. This displays the way in which ($1-C/C_o$) changes with relative time($t/t_{0.9}$); that is fractions of C_0 remaining as the concentration decreases from its initial value down to 10% of it (which can be called the 90% life) plotted against fractions of $t_{0.9}$. There are separate lines plotted for a number of different orders of reaction between 0 and 2. To cover the range more extensively, the time for a 90% change ($t_{0.9}$), rather than the 50% change in a half-life ($t_{0.5}$) has been chosen. The background to these curves is explained in Theory 2.4.

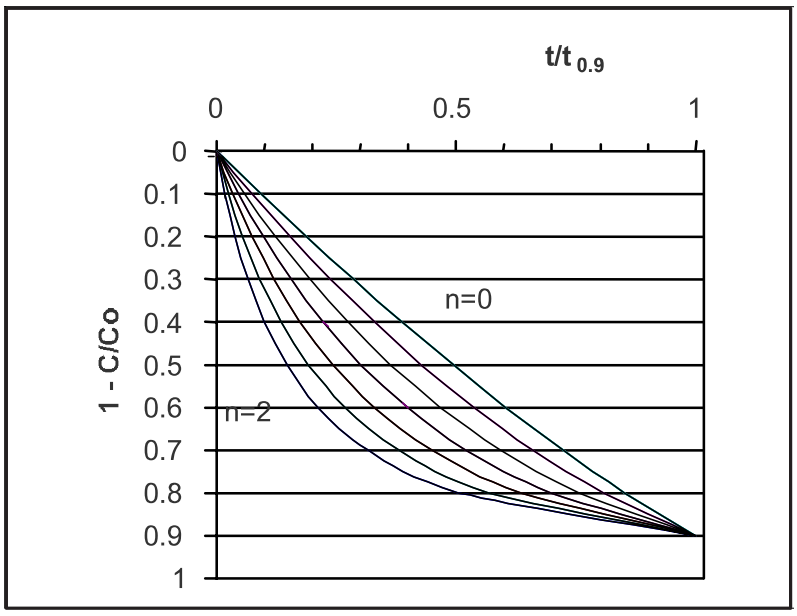


Fig. 2.6. Relative changes in concentrations with relative times for different values of reaction orders (n): 0, 0.25, 0.5, 0.75, 1, 1.5, 2.0, reference curves

Figure 2.6 shows quite clearly that higher order reactions progress more quickly, relatively, than do lower order ones in the initial stages. Then, to compensate, they move more slowly later as they get towards the common 90% point. Higher order reactions are relatively more sensitive to time in their early

stages, compared with lower order reactions. And, of course, zero order reactions have constant progression with time, as would be expected. The graph also demonstrates that, with a suitable choice of a mean rate, taking a tangent rather than following the actual curve, any of the orders can be fitted closely by a straight line over the first 50% or so of the reaction. Thus, for many situations of practical relevance, zero order behaviour is a very reasonable approximation.

As an aside, but quite useful and sensitive in practical determination of order, it can be observed that the position of a given reaction on this graph is characteristic of its order. So, if an unknown reaction is plotted on such a graph, against a background of the characteristic lines for a number of selected orders, as in Fig. 2.6, the position of the line of the unknown reaction reveals its order (it fits over the curve appropriate to its own order).

These curves in Fig. 2.6 reveal clearly the considerable differences in the controllability of reactions of different orders as they move to completion, in terms of the extent (perhaps 50% or 90%) of the total change in their constituent components. Zero order moves steadily, at a constant rate, whereas, as the order increases, reactions move more quickly at first, then more slowly later and so the controllability of the reaction changes accordingly. As the order increases, their early rate of change with time is relatively much steeper for higher order reactions than for lower order reactions, so in their early stages higher order reactions are more difficult to control. If a critical reaction is of high order, and only proceeding to a few per cent, time sensitivity of concentration will be at its highest and control most difficult. Looking at the shapes of the curves also shows how the reactions of higher order depart much further from the simple approximation of uniform rate (graphically extrapolating by using a simple tangent at one point on the graph), and so order justifies being taken into account.

In foods that contain several simultaneously changing constituents, sensitivities may thus differ considerably between components, so some constituents have to be watched much more closely than others. When automatic controllers are substituted for human operators, this may have important implications for achieving consistency of quality. This discussion brings into consideration extents of reaction and their relative significance in different aspects of food processing.

The basis for the calculation of values of C/C_0 for different values of n against relative time $t/t_{0.9}$ is described in Theory 2.4.

Theory 2.4: Comparative progression of different orders: reference curves

The progression of reactions of different orders is shown by consideration of the reference curves.

From the general order integration equation

$$\{C^{1-n}-C_0^{1-n}\} = (n-1)\,k\,t$$

and if $t = t_{0.9}$ when the reaction is 90% complete, i.e. $C_{0.9}/C_0 = 0.1$

$$\{C^{1-n}-C_{0.9}^{1-n}\} = (n-1)\,k\,t_{0.9}$$

dividing one equation by the other to put $t/t_{0.9}$ in terms of the C's

$$\{C^{1-n}-C_0^{1-n}\}/\{C^{1-n}-C_{0.9}^{1-n}\} = t/t_{0.9}$$

then dividing through by C_0

$$\{(C/C_0)^{1-n} - 1\}/\{(C/C_0)^{1-n} - 0.1^{1-n}\} = t/t_{0.9}$$ (remembering that $C_{0.9}/C_0 = 0.1$)

From this equation, values of $1 - C/C_0$ can be calculated for different values of n against relative time $t/t_{0.9}$.

If $(1 - C/C_0)$ is plotted against $t/t_{0.9}$ with order values n as a parameter at say 0, 0.25, 0.5, 0.75, 1.0, 1.5, 2.0, then the curves of Fig. 2.6 (called reference curves) result.

2.9 Relative Extents of Food Processing Reactions

The extent to which a critical food processing reaction proceeds is obviously of central significance to the processor. In our continuing example of processing, that of sucrose hydrolysis, reaction is desired to the extent of, say, 30% to 55% hydrolysed, that is in fractional terms C/C_o running over a range from 0.7 to 0.45. This sort of figure covers a good number of food processing situations, and might be termed a medium range in the chemical sense. In other cases, substantially more complete reaction is required, for example in blanching, where 95-99% enzyme destruction might be necessary in order to sufficiently inhibit any undesired reactions that the enzymes might catalyse. Similar requirements might arise with nutritionally undesirable components, an example being protease inhibitors in soya beans. Chemical undesirables might also be in this same

category, or they might be required to diminish even further. Rather loose nomenclature often speaks of removal when what is actually implied is removal down to below some hazardous, or sometimes analytically just detectable, level. This could be down to 0.1 or 0.01%, or lower, of initial levels depending on the particular hazard, or the extent of the 'undesirability'.

In other cases, the focus is on the products of a reaction, where in some instances even quite small concentrations may be significant. Examples are the off-flavours caused by some free fatty acids from fat hydrolysis, and the oxidation of fats creating rancid odours. In such cases, only a very small fractional change, say dropping the C/C_0 only to 0.99, that is 1% of some fats hydrolysed to fatty acids, may create detectable and unacceptable flavours and so be the 'processing' limit.

Looking at Fig. 2.6 it can be seen that, in the initial stages of a reaction, and up to 50% of the reaction completed, there is little practical difference between the different orders of reaction. For example, a straight line can be a reasonable approximation to them all. So the simplest constant rate calculations are adequate and these can cover all that matters in such applications. This may apply to storage reactions, which often appear to be zero order up to and beyond the point where sensory panels find the product unacceptable or below a necessary standard.

However, in another very important area, that of microbiology, the changes in concentrations can be quite dramatic. For microorganisms, the concentrations per unit volume or unit surface area can be interpreted as:

- most probable number (MPN) counts, or
- numbers of colony-forming units (cfu), or
- numbers of viable organisms.

For present purposes, these measures are all equally applicable and they are selected to suit particular circumstances. Increases in numbers of microorganisms, i.e. growth, can often be by multiples such as 10^4. In microbial death, measured experimental changes can be of the same order, whilst extrapolated changes (as in the conventional canning calculations to incorporate adequate safety) invoke multiples such as 10^{-12}. Putting aside for the moment any questions of justification for such large extrapolations, these differences in 'reaction extents' do not themselves provide problems in rate determinations. But they affect the apparent calculations when, as often happens in food processing, several simultaneous important reactions with differing extents occur at the same time in the same food product.

In summary:

- Reactant chemical composition in terms of C/C_o changes from 1 at the beginning through to as little as 0.99 or 0.95 at a limit of acceptance in some critical flavour changes (and more often undesirable rather than desirable), through 0.5 to say 0.1 to 0.01 in component changes such as gelatinisation or protein denaturation in general processing.

- In bacterial or spore death, bacterial 'concentrations', taken in terms of, say, viable spores per can could move from, say, a measured 10^4 in one can down to an assumed 1 present in 10^8 cans, giving a total swing ratio of $10^{4+8} = 10^{12}$.
- In surface bacterial growth, bacterial 'concentrations' may move from a measured 10^3 per cm^2, to a measured and becoming obvious (smell, slime, colour) 10^7 per cm^2, which is a concentration ratio change from 1 at the beginning to 10^4 ($10^7/10^3$).

Case study 1: Retention of vitamin A in liver processing

This case study shows how some laboratory research can be used as a basis for designing a heating process.

For foods that are significant sources of essential nutrients in the diet, it is obviously important that as much as possible of the nutrient content, for example of vitamins, is retained for the consumer if the food is processed. This was the subject of a study on the vitamin A content in a processed liver product intended for an infant food by Wilkinson *et al*. (7). Liver is a rich source of this vitamin, so that, if the liver is heat processed to make a baby food, it is desirable to retain as much as possible commensurate with meeting whatever other processing stipulations may be dictated, such as, for example, ensuring microbiological safety.

The experimental laboratory study of the retention of vitamin A in liver during heat processing showed systematic behaviour. The loss of vitamin A on heat processing conformed closely to the first order pattern (Fig. 2.7a).

At 126.7 °C (399.7 K) the vitamin A concentration as a function of heating times, was:

Time (min)	0	10	16	22	28	34
Concentration (μg/g)	271	109	58	30.5	18	10

The plot of log (concentration) against time in Fig. 2.7a gave a good straight line, so fitting first order.

Contd..

Case study 1 (contd)

The first order rate-constants and corresponding temperatures were:

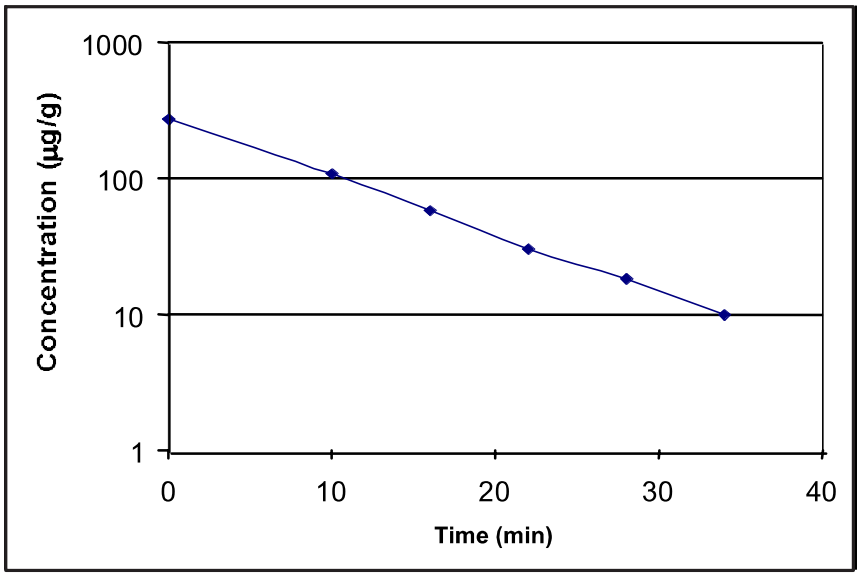
Temperature	(°C)	102.9	111	118.3	122.1	126.7
	(K)	375.9	384	391.3	395.1	399.7
$1/T \times 10^{-3}$	(K)	2.66	2.60	2.56	2.53	2.50
Reaction rate constant k (s^{-1}) $\times 10^5$		17.9	38.6	68.0	96.1	162.3

The relationship between 1/T and the reaction rate constant is shown in Fig. 2.7b. and the effect of temperature is seen to follow the Arrhenius relationship.

From the slope of the line in Fig. 2.7b, the activation energy was calculated as 112kJ/mol. This activation energy translates into a sensitivity of the reaction at 118 °C of around 9%/°C.

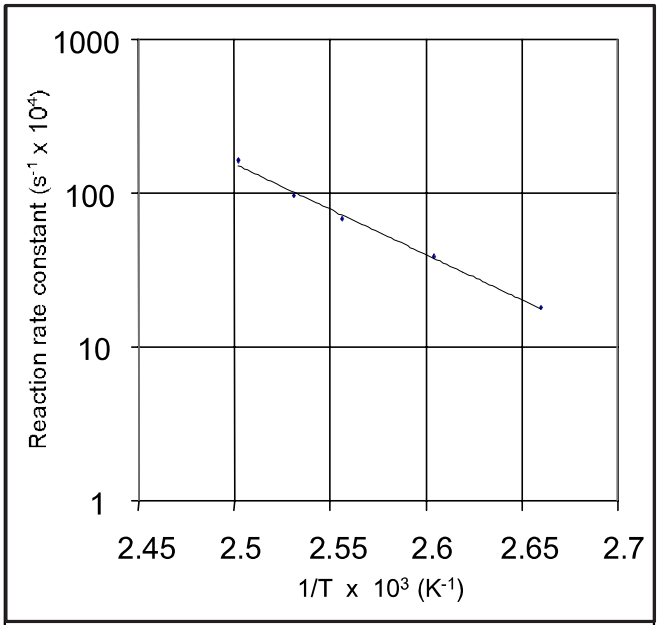
As an example, work out the residual concentration of vitamin A initially 300 μg/g, after processing for 20 min at 120 °C. We know that $k_{118..3} = 68 \times 10^{-5}$, and with the sensitivity as 1.09, then $k_{120} = 68 \times 10^{-5} (1.09)^{(120 - 118.3)} = 78.2 \times 10^{-5}\ s^{-1}$. And so, for 20 min at 120 °C, $kt = 20 \times 60 \times 78.2 \times 10^{-5} = 0.938 = -\ln C/C_0$, and therefore $C/C_0 = 0.39$ and so the initial concentration of vitamin A would be reduced from 300 to 300 x 0.39 = 117 μg/g.

This is about a 60% reduction and would obviously be of importance if the purée were effectively the only source in the diet of an infant and if the quantity provided daily had been prescribed on the basis of unprocessed liver. Reducing the processing time to 10 min, if this were permissible, would reduce the loss to 37%, and further reducing the processing temperature to 115 °C, the loss would be only around 26%. So it can be seen that the technique provides the processor and the formulator with useful information, in which various processing strategies can be compared. This illustrates the application of reaction technology in producing data applicable to industrial production, in this case of baby food, providing necessary information for the specification of the processing conditions so that an infant diet ingredient could contain sufficient of an important constituent.



Data from Wilkinson *et al*. (7)

Fig. 2.7a. Vitamin A loss on processing: change of concentration with time at 126.7 °C



Data from Wilkinson *et al*. (7)

Fig. 2.7b. Vitamin A loss on processing: change with temperature: Arrhenius plot

Case study 2: Yellowing of whey protein coating on storage

This case study illustrates the use of reaction technology in storage tests. It is an example of the use of a physical method, reflectance measurement of colour, as the measure of change.

Panned confectionery products can be coated to give them gloss and to protect their exterior, and whey protein concentrates can be used in these coatings. However, on storage, the coatings gradually change from almost colourless to deeper shades of yellow, and this has been studied as a function of time, as reported by Trezza and Krochta (8). The yellowing was measured by an arbitrary but standard (ASTM) reflectance method. The increase in yellowing with time at 23 °C was:

Storage time (months)	0.09	0.27	0.69	1.92	3.1	4.33	5.0	6.48	7.96	9.76
Yellowness Index	9.7	9.8	10.0	9.8	11.1	11.8	12.7	13.3	14.8	17.0

These results have been plotted on Fig. 2.8 and show a reasonable straight line over a considerable period of storage (10 months).

Thus the time before some critical degree of discolouration is reached, say 15 units, could be read from the graph.

The rate of increase of the yellow colour can be determined either crudely from the extreme values:

$$(17.0 - 9.7) / (9.76 - 0.09) = 0.75 \text{ units per month}$$

or more accurately from the trend line of the graph, established most readily by computer program, which is shown as the trend line equation on the graph. In the case of the 23 °C results, where C_0=9, this is (rounding off):

$$\text{Yellowing} = 0.7 \text{ (months)} + 9$$

Also plotted on the graph are storage results for temperatures of 40 °C and 55 °C, which plot to give straight lines.

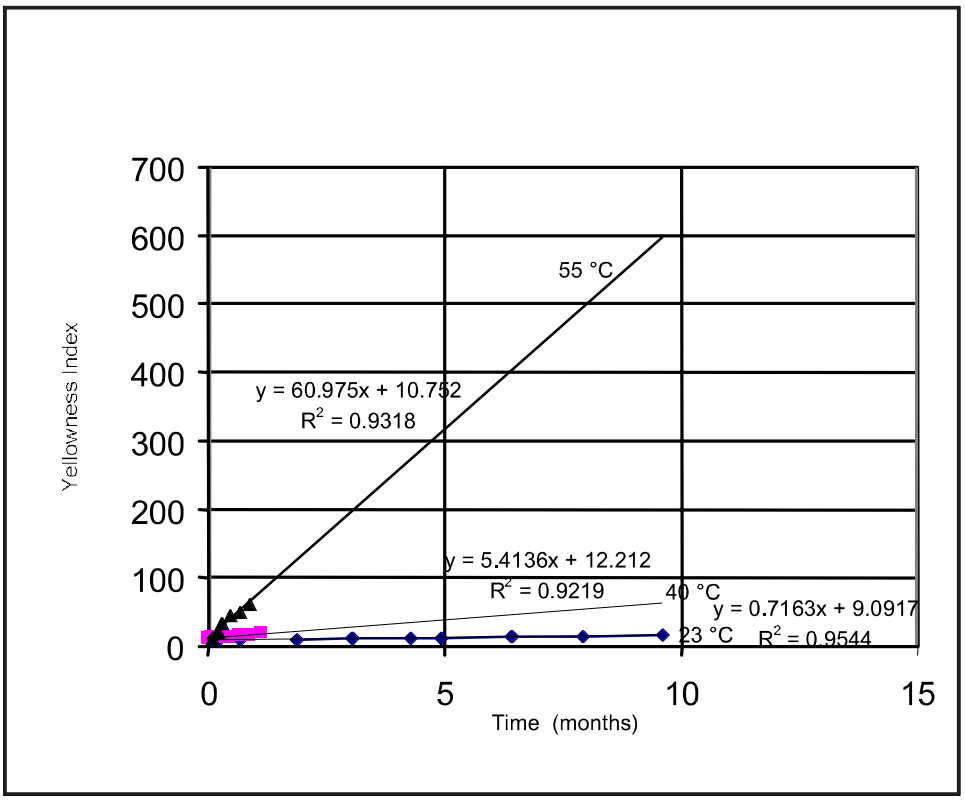
When the slopes of these lines were plotted against the reciprocals of the absolute temperatures in an Arrhenius plot, an activation energy of 95 kJ/mol was obtained and this can be used, for example to determine storage lives under warehousing temperatures.

Contd..

Case study 2 (contd)

The authors commented that, with the higher temperatures, there was deviation from straight line behaviour after 4.5 weeks, which is why results for longer periods are not shown. However, if, say, 15 units were the maximum tolerable, then the zero order behaviour could be used for the predictions over the whole temperature range reported. The equation indicates that the 'storage life' at 23 °C to a maximum yellowness of 15 should then be about 8.5 months. The other lines with their equations would indicate lives at their respective temperatures, and the activation energy with the Arrhenius equation would fill in for other storage conditions as needed.

The study demonstrates that arbitrary units can be used if convenient, and particularly when there are no fundamental units available. Units chosen do need to be consistent and reproducible, and there are obvious advantages if they fit standard specifications, as do these, and can therefore be reconciled with measurements in other situations.



Data from Trezza & Krochta (8)

Fig. 2.8. Yellowing of whey protein on storage

2.10 Practicalities

In practical terms, how can this approach, rate equations and temperature coefficients, be incorporated usefully into industrial food processing? The first step is to obtain adequate data. It may be that suitable results can be obtained from the food research literature and data tables; there is often a surprising amount available. In larger companies, there may be laboratory and factory trial results in the files. Even in small companies there will usually be experience, and this can at least give ideas as to rates and even to temperature sensitivities. Otherwise, experimental evidence is needed and this means measuring the rates at which the desired processes actually progress. The steps in building a reaction technology approach to process control and development are shown in Fig. 2.9.

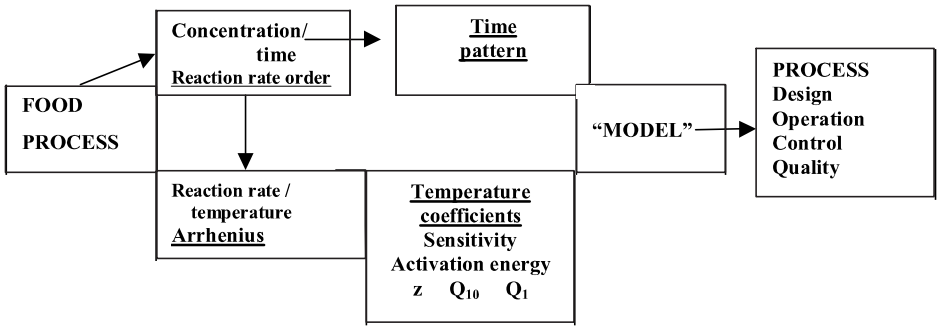


Fig. 2.9. Overview of reaction technology approach

2.10.1 Studying change in concentration with time

'Suitable' readings of the relevant measures at 'suitable times' are made as the reactions progress. 'Suitable' is something that has to be found by trial and error, but common sense and experience produce it quite quickly. The measures have to be related to the necessary controls during processing and the specified product attributes. Refinement thereafter is just natural progression. Experimentation can be done by following one concentration variable at a time, keeping other ingredient concentrations and the temperature constant. The alternative is to use systematic experimental designs and to study several variables together over the practical range, taking limit values and sorting out the effects of the different variables statistically. The traditional approach is simpler but sometimes it is less efficient, not practicable, or unduly cumbersome.

What emerges is a set of times and corresponding concentrations. Initially, these can be plotted linearly, and if a straight line fits then the reaction is zero order. For the other orders, it is easiest to set up the corresponding version of the general equations in linear form, so that straight lines plots result when you have got it right. For example, this means plotting the logarithm {ln C} against time for

first order, and the reciprocal of the concentration {1/C} against time for second order, as illustrated in Table 2.V.

TABLE 2.V
Straight line plots for reaction orders

Plot experimental data using X axis and Y axis to produce a straight line for different orders:

Order	X axis	Y axis	Slope Y/X
0 order	time	C	- k
1 order	time	ln C/C_0	k
2 order	time	$(1/C - 1/C_0)$	k

where 'C' is typically concentration, but may be some other convenient, consistent measure, and k is the reaction rate constant.

The reaction rate constants (k) can be determined from the slopes of the graphs.

2.10.2 Studying rate of reaction/temperature relationships

So we end up with an order and a rate constant. This has then to be repeated over a range of temperatures. From the resulting set of rate constants and corresponding temperatures via an Arrhenius or similar plot, an activation energy, a z value, or a temperature sensitivity can be calculated, according to preference. Remember that the natural logarithm of the reaction rate constants is plotted against 1/T (in degrees K) for activation energies, and for all the others against just T (which can be in °C or K as this just moves the zero), as summarised in Table 2.VI.

TABLE 2.VI
Straight line plots for temperature coefficients

Plot experimental data to obtain temperature coefficients of reaction rates:

	X axis	Y axis	Slope Y/X
Arrhenius(1/T in exponent)	1/T (K)	ln (rate)	-E/R
z (linear T in exponent)	T (°C or K)	ln (rate)	-2.303/z
Q (linear T in exponent)	T (°C or K)	ln(rate)	$-(\ln Q_{10})/10$

If you cannot distinguish the orders within the precision of the results, and yet this precision is adequate for demands of assuring the final product, then order is probably not critical. For very many practical purposes zero or first order, if carefully fitted and maybe with a little extra care in selection of average rather than extreme values, sufficiently good predictive systems for industrial use can be produced. The worked examples and figures illustrate some of the important points. When predictions involve major extrapolation, always keep in mind that even quite minor poorness of fit of the equations can build up into substantial discrepancies between predicted and observed outcomes.

2.10.3 Studying temperature coefficients

What is often much more reliable than trying to predict an output from scratch is where the output under one set of conditions is already known and you have only to predict how it changes after a known change in conditions. Then the resulting movement in the outcome can be predicted through the sensitivities to the change. In other words, when process variabilities, as they always do, push the process away from the correct settings, then these methods will help predict how to move quickly and accurately back to where it should be.

You may have found sensitivities easy and convenient, but, if not, of course all the other measures work as they must if they are reliably based on real data. If the change in more than one constituent is important, then you have to go through the procedures for each. Take comfort from the fact that, if such constituents are in fact important, then they justify attention.

The resulting data and the framework into which they have now been fitted can be used in predictive calculations. They can also be used in 'what if' scenarios, in examining and specifying artefacts like instrumentation and control valves and heat transfer surfaces so that they are responsive to process disturbances with the speed and the precision needed to ensure the product quality required, in determining suitable 'ambient' reaction conditions such as water activity, pH and gas pressures, and in preparing charts and other aids for operating personnel.

As a very simple example, if operating a process with a critical reaction having a sensitivity of around 25%/°C, then a thermometer that is unable to discriminate reliably to better than 1 °C can present problems for control.

2.10.4 Time patterns

The changes with time, and the changes of times with temperature are very important, and are discussed in detail in Chapter 3.

From all this information, a 'model' can be built for the process. Very often the model is in reality a set of quantitative relationships with which reliable predictions of component behaviour can be made. It may be simple or complex! Remember that, with all of these methods, if the analysis is reliable then interpolations will be just as reliable, but extrapolations should always be treated with caution and the greater the extrapolation the greater the caution needed. However, much of the point of the analysis is to be able to extrapolate, and so familiarity with the data and with the analytical framework and its basis, and experimental checks, using critical cases, will build both confidence and skills.

2.11 References

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