# 4. ACHIEVING BETTER FOOD PRODUCTS

## 4.1    Introduction

To apply reaction technology in practical processing and storage, a broad range of factors may need to be considered. So far, only one basic model of rate prediction has been considered, and it has been shown that this fits many commonly encountered and practical food processes. But, for some important food processing systems, the simple power law relationship that was introduced in Chapter 2 does not fit experimental results and practical situations sufficiently. Some further elaboration of the model is required to cope with the needs of processing and process control. Fortunately, fairly straightforward extensions can be used to explore many of these situations, to either adapt or confirm the model. Two important aspects are firstly the changes in reaction rates during a process, and secondly the presence of multiple reactions in many food processes.

Some reaction patterns and apparent orders of reactions change as the reactions proceed. Changing process conditions, particularly temperature, can cause these. There can be complex changes in the nature of enzyme-catalysed reactions, because of denaturation of the proteins. These changes can be built into the whole kinetic analysis. It may prove adequate to consider only part of the whole reaction spectrum because that part is enough to cover the situations in practice.

Multiple reactions are often important in food processing – both chains in which a series of reactions follow one on the other, and also parallel reactions in which a number of reactions occurs at the same time. Reactions can be alternative paths from the same initial reactants, leading to different products that may have very different levels of desirability in the food. Or they may be reactions that are independent, but linked by identical process conditions that accelerate all the reactions. Because of the multiple constituents of the food, processing conditions, such as a temperature rise, will simultaneously be applied to all the components present. Therefore, these components will change and some of their changes may not be desirable. So conditions have to be sought that accomplish the required process change on one critical component or attribute because it is the primary or dominant reason for the processing but minimise or modify the simultaneous changes in important components or attributes. For example, safety may be a critical product attribute, but the texture may be important. The process conditions need to satisfy the critical attribute, but also optimise the important attributes.

Such possibilities can be found from consideration of the changes and the kinetics. Optimum ways of controlling reactions and obtaining the best overall product can then be explored through analysis by the reaction technology.

## 4.2    Changing Reaction Rates

Changes in reaction rate constants can be caused by changes in the processing conditions – for example temperature. Changes in reaction rate constants can also occur in enzyme-catalysed reactions. Shelf storage changes often follow apparently zero order, which changes to first order with time. Concentration levels thus seem to influence not only the reaction rate constant but also the observed order of some processing reactions.

### 4.2.1    Changes in temperature

In the rate equations considered so far, it is implied that they cover the whole concentration range quite irrespective of whether all, or only part, of that range is encountered by the food processor. However, the food processor is interested only in the range needed for the processing; what goes on outside that may be interesting theoretically but is not of importance to practice. This can give scope for considerable simplification; for example over limited concentration ranges it may be possible to use zero order, although overall the reaction may be of a higher order. In shelf-life calculations and the product-life dating that stems from them, only zero order, that is constant reaction rate, needs generally to be taken into account and this still retains accuracy adequate for day-to-day store and warehouse practice.

Storage often involves changing temperatures, which means changing reaction rate constants. An example of changing storage conditions at common ambient conditions in temperate countries (15-25 °C) is shown in Example 4.1, which is using the reaction technology data in Case Study 2 to predict the storage life of the whey-coated confectionery products. The yellowing was found to follow zero order by Trezza & Krotcha (1).

**Example 4.1: Whey protein coated confectionery: calculation of shelf-life over different holding temperatures**

In Case Study 2, the yellowing of whey protein concentrate coated confectionery was zero order, and it is illustrated in Fig. 2.8.

If, after storage for 6 months at 15 °C, the confectionery were transferred to a retail store at working temperature of 25 °C, for what maximum time should it remain on the shelf if yellowing is not to exceed 15 Yellowness index units?

This can be calculated by determining the monthly rate of yellowing at the two temperatures of 15 °C and 25 °C, and then the fractional loss of total storage life in each.

The monthly reaction rate constant (k) for the yellowing of the coating can be taken at 23 °C as 0.29 index units/month, with corresponding activation energy as 95 kJ/mol.

Rate of deterioration at 23 °C, $k_{23}$, is 0.29 index units/month,
(15 °C=288 K, 23 °C=296 K, 25 °C=298 K)
$k_2 = k_1 \exp\{-95000 \times (T_1 - T_2)/(RT_1 T_2)\}$ where $T_1 = 23$ °C, $T_2 = 15$ °C

so at 15 °C, $k_{15}$ = 0.29 exp{-(95000 x 8)/(8.314 x 296 x 288)}
= 0.29 x 0.342 = 0.1 index units/month

So, after 6 months, 0.1 x 6 = 60% of its available life would have been lost, 40% left.

at 25 °C, $k_{25}$ = 0.29 exp{-(95000 x -2)/(8.314 x 296 x 298)}
= 0.29 x 1.3 = 0.38 index units/month

And so in 1 more month the remaining storage life fraction of 40% would essentially be gone at a loss rate of 0.38/month, i.e. 38%/month.

If there were to be other further calculations on the same material, it would be routinely easier and adequate for most purposes if the sensitivity were calculated at the mean temperature of about 20 °C and used as below:

Sensitivity = exp{95000/(8.314 x 293 x 293)}-1 = 0.14
for example, reaction rate constant at 15 °C = 0.29 (1.14)$^{-8}$ = 0.1 index units/month.

In Example 4.2, the decrease in concentration of the sweetener aspartame, during storage was studied in the ambient range of temperature under tropical conditions from 20 °C to 55 °C. This was found to be a first order reaction. The example shows that reactions determining shelf life are not always zero order, and there is a need to check in order to study them for order.

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**Example 4.2: Shelf-life of a sweetener, aspartame**

One of the sweeteners used in soft drink manufacture is aspartame, which is built up from phenylalanine and aspartic acid. Aspartame has a relatively short shelf life in solution, and obviously this is of importance to the extensive industrial use of this sweetener.

The rates of this degradation in a solution with caramel colouring were investigated by Wang & Schroeder (2). They reported a first order degradation reaction over the range of their experiments, 20 °C to 55 °C. The reaction rate constants were:

| | | | |
|---|---|---|---|
| 55 °C | 0.0786 $d^{-1}$ | 45 °C | 0.0277 $d^{-1}$ |
| 35 °C | 0.0119 $d^{-1}$ | 20 °C | 0.00267 $d^{-1}$ |

If a quantity of this solution is stored for 3 weeks at 40 °C and then for a further 5 weeks at 25 °C, what fraction of the aspartame originally made up into the solution would be expected still to be present?

An Arrhenius plot of the rate data, plotting ln (reaction rate constant) against 1/T is shown in Fig. 4.1.

The slope from this gives an activation energy of 77 kJ/mol, so that working from the 35 °C (308 K) rate of 0.0119 $d^{-1}$ gives:

At 40 °C (313 K) $k_{40}$ = 0.0119 exp{(-77000 x -5)/(8.314 x 308 x 313)} = 0.0192 $d^{-1}$

At 25 °C (298 K) $k_{25}$ = 0.0119 exp {(-77000 x 10)/(8.314 x 308 x 298)}= 0.00433 $d^{-1}$

$t = (-1/k) \ln(C/C_0)$

And so on storage for 3 weeks at 40 °C:

    3 x 7 = (-1/0.0192) x $\ln(C/C_0)$

    $C/C_0$ = 0.67 so about one third (33%) has been lost.

And on further storage for 5 weeks at 25 °C:

    5 x 7 = (-1/0.00433) x $\ln(C/C_0)$

    $C/C_0$ = 0.86 so 14% has been lost.

**In total, after the two periods: the residual content would be 0.67 x 0.86 = 0.58 or about 42% lost in all.**

The experiment was repeated with different levels of caramel up to 700 ppm, and it was found that reaction rate constants were approximately the same, but above this level of caramel the rate of reaction increased.
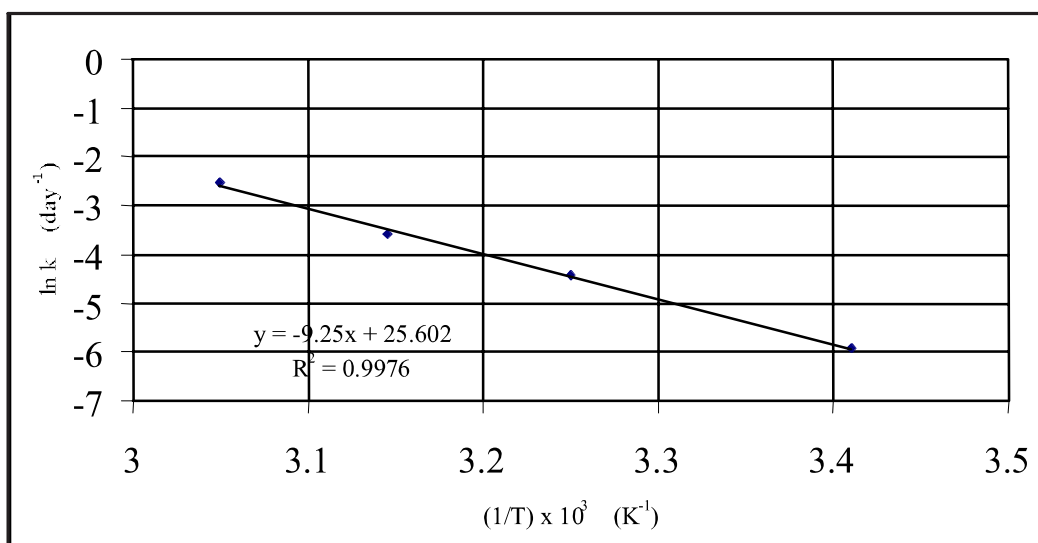
Data from Wang & Schroeder (2)

*Fig. 4.1. Loss of aspartame on storage: Arrhenius plot*

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*Think break*

Consider two reactions that can be important in storage tests on a tomato salad dressing: fat oxidation and loss of red pigments (e.g. lycopene):

* How does altering the temperature of storage affect these reactions?

* How might these reaction changes significantly alter the resulting product composition and product attributes?

* What other storage conditions could be altered to affect the rates of the reactions?

*Note: in the Think breaks in this chapter, you may have to find the information from textbooks and data bases.*

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### 4.2.2 *Enzymic-catalysed reactions*

Some very important reactions occurring in food processing are initiated by the presence, and modified by the concentration of non-reacting catalysts. These cause the reaction to occur but do not themselves undergo change as the reaction proceeds. The catalysts include chemical constituents, one being hydrogen ions whose concentration is measured by pH. They include enzymes that are biological catalyst proteins, which can affect the rate of reaction, but may themselves be denatured by the processing conditions. Sometimes the enzymes can be used for promoting desired changes, for example in coagulation of milk or tenderising of

meat or softening the centres of chocolates. But other times they may promote undesired deterioration, in which case processing may be employed to substantially eliminate this. So inactivation of the enzymes by heat denaturation may be the important reaction, for example in the blanching of vegetables. The blanching of carrots is shown in Example 4.3.

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**Example 4.3: Enzymic action in carrots**

Blanching to inactivate enzymes is common in vegetable processing. In a study of blanching of carrots, Roy *et al*. (3) reported that the removal of the enzyme, lipoxygenase, was a first order reaction. Blanching treatments in water for 71 min at 70 °C, 11.64 min at 80 °C, 2.12 min at 90 °C and 0.58 min at 100 °C resulted in the reduction of enzyme activity by 80%.

These results have been plotted in Fig. 4.2.

From this Arrhenius time plot, the activation energy for the enzyme destruction was estimated, as 167.5 kJ/mol.

The reduction in the activity of the enzyme, lipoxygenase, was specified as 80%, from which the reaction rate constant could be worked out. The resulting calculation of the activation energy, 167.5 kJ/mol, was true for the range of concentration from 100% to 20%.

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$$y = 20.143x - 54.571$$
$$R^2 = 0.9994$$
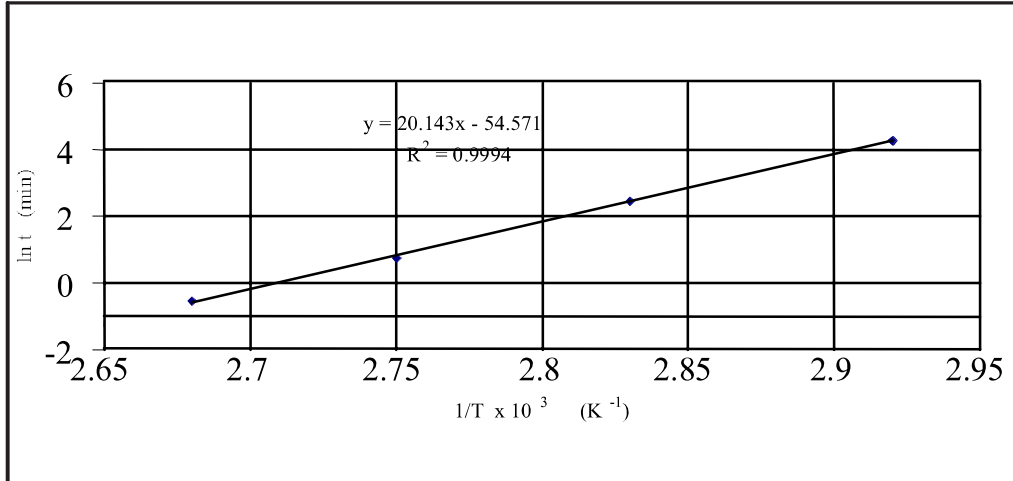
Data from Roy *et al*. (3)

*Fig. 4.2. Enzymic reduction in hot-water blanching of carrots*

It has been found that many enzyme-catalysed reactions proceed at rates that can be characterised by an equation of the form

$$- r_A = k_1 C_A / (1 + k_2 C_A)$$

where $k_1$ is the reaction rate constant for the enzyme-substrate reaction (the substrate being the food constituent that is reacting), $k_2$ *is* the reaction rate constant

of (heat) denaturation of the enzyme and $C_A$ is the concentration of the substrate. The equation arises from the net reaction rate constant being related directly to the enzyme/substrate reaction rate constant, and inversely to the enzyme activity-loss reaction rate constant.

On examination of this equation, its apparent order is determined by the relative magnitudes of the two terms in the denominator. When 1 is large compared with $k_2C_A$, then the denominator is effectively 1 and the overall rate is approximately first order, whereas when $k_2C_A$ is large compared with 1, then the apparent order is zero as the 1 becomes negligible and the $C_A$ cancels out from above and below the line. This implies that, at large concentrations $C_A$ of the substrate, the effective rate is zero order. But when the substrate gets down towards disappearing and the products dominate, then the net order becomes first order. Rather than the substrate concentration becoming zero, it instead diminishes exponentially.

Another important outcome of such kinetics, more directly related to enzymes, arises from the relative magnitudes of the activation energies found for enzyme/substrate reactions and enzyme denaturation reactions; usually the activation energy for the enzyme denaturation reaction is much greater than that for the enzyme/substrate reactions. For example, the enzyme/substrate reaction can be as low as 20, but it is usually around 100 kJ/mol; and enzyme denaturation reactions are usually upwards of 150 kJ/mol. This focuses on the $k_2$ rather than $C_A$, but again the effect is to shift the product $k_2 C_A$ relative to 1. Because of the high activation energy incorporated in $k_2$, this shifts the overall rate quite dramatically with changing temperatures.

This explanation accounts for the well-known effects of temperature on an enzymic food processing operation, a common example being encountered in the formation of curds from milk when clotted with the enzyme rennin. Here, as the temperature rises through 30 and 40 °C, the clotting (milk protein denaturation) proceeds ever more rapidly, which is the reason why the vats are heated in cheese making. However, if the temperature continues to rise above 50 °C, the clotting rate decreases, slowly at first and then much more rapidly as temperatures continue to increase because of the denaturation of the enzyme.

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*Think break*

Two food processes in which enzymes are significant are the manufacture of soft-centred chocolates and the production of maltodextrins and glucose syrups from starch.

* What are the enzymes and the related reactions for each of these processes?

* In what ways would the process reactions be altered if the processing conditions, particularly temperature, were modified?

* How would these changes affect the final food products?

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One enzymic reaction that has been explored in detail is the decomposition of hydrogen peroxide by peroxidase enzymes, such as catalase that can be obtained from liver. To gauge the rate of the reaction, it is convenient to measure the evolution of the oxygen, which can be done by simple collection in a volumetric cylinder. Early results from such an experiment are plotted in Fig. 4.3, where the logarithm of the reaction rate is plotted against the reciprocal of the absolute temperature in the usual way.
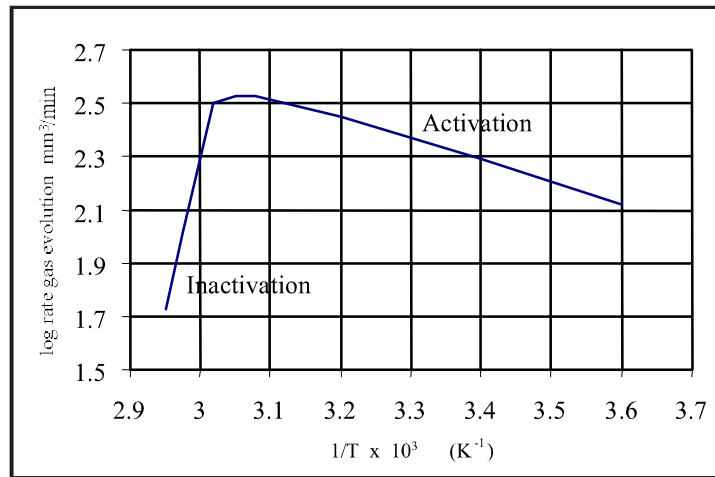


Data from Aiba *et al.* (4)

*Fig. 4.3. Decomposition of hydrogen peroxide by catalase: Arrhenius plot*

Looking at Fig. 4.3, and recalling that, because reciprocals are being plotted, temperature is highest on the left and falls to the right, it can be clearly seen to fit into two sections. The one that is on the left has a very steep slope and therefore very high value of E, which in this case can be called "inactivation" energy. On the right is a more gentle slope corresponding to a much lower activation energy, which corresponds to the decomposition reaction of the hydrogen peroxide speeding up in the usual way as the temperature increases.

This is the typical pattern, and can be used in processing by heating to initiate the enzymic action, continuing heating to speed it up, but then terminating the action by a still further rise in the temperature and so inactivating the enzyme and ending activity. Between the two defined regions lies a "turnover" temperature range, which is not very well defined but in which the reaction rate is at a maximum. Within the range of possibilities, temperatures can be manipulated to suit processing requirements. An equation of the enzymic form can be fitted, both in practice and in theory. For hydrogen peroxide decomposition, in this equation, $k_1$ in the numerator corresponds to the activation energy of the enzyme/substrate reaction (17.6 kJ/mol), and $k_2$ in the denominator corresponds to the inactivation energy of the enzyme denaturation (230 kJ/mol) (4).

Kinetic understanding of this behaviour can also be used to prescribe heating rates that need to be applied in processes such as blanching. This is primarily to

destroy enzymes that react deleteriously with the foodstuff, but, if the heating is too slow, there will be time for the enzyme to cause substantial deterioration before being sufficiently denatured.

## 4.3 Sequential (Chain) Reactions

In some reactions encountered in food processing, the first products of the reaction are themselves unstable, and, as the reaction-promoting conditions of the processing continue, they, initially products, become themselves reactants and form further products. This process can continue, and so in the final food product a whole string of components from the original reactant can arise. Some of these may be desirable, some less desirable, and some undesirable, and both their presence and their relative concentrations can be of considerable significance in the final food product. The craftsman recognises these changes and adjusts processing to optimise the product that is wanted. The technologist seeks understanding both to obtain the specific levels of the desired attributes in the final product, and also to use instrumental signals to control process conditions to adapt to changing inputs so that the specific product attributes are achieved and maintained.

As might be anticipated from the diversity of reactions, each with its own reaction rate constants and activation energies, and each dependent on upstream and downstream situations, the analysis of chains of reactions becomes complicated. However, consideration of the simplest situation with one initial reactant, A, moving with rate constant $k_1$ to one intermediate product, B, moving at rate constant $k_2$ to one final product, C, demonstrates the patterns to be expected and provides a useful guide as to what process manipulation might be possible. Assuming that, at the outset of the reaction, at time 0, neither of the products has been formed, and assuming all reactions are first order, after time $t$ the concentrations of the three components are given by:

$$C_A = C_{AO} \, exp(-k_1 \, t)$$
$$C_B = C_{AO} \, k_1 \{ \, exp(-k_1 \, t) - exp(-k_2 \, t) \} / \, (k_2 - k_1)$$
$$C_C = C_{AO} - C_A - C_B$$

These equations for sequential reactions give rise to graphs of the form shown in Fig. 4.4.
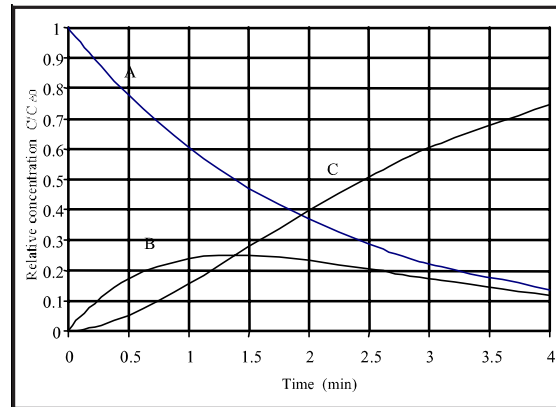
*Fig. 4.4. Behaviour of components in a chain reaction*

This shows that, as time progresses, the concentration of the initial reactant, A, decays exponentially, whilst the concentration of the intermediate, B, starts from 0 and then rises to a maximum before declining finally to 0. The final product, C, starts at 0 and thereafter rises smoothly, ultimately reaching asymptotically a value equal to $C_{AO}$, by which time both A and B have disappeared. An outline of the derivation of the equations is given in Theory 4.1.

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**Theory 4.1: Consecutive (chain) reactions**

The equations for the simplest set of consecutive reactions A→B→C, with first order rate constants $k_1$ and $k_2$ respectively, can be written:

$$r_A = d\,C_A\,/\,dt = -\,k_1\,C_A$$

$$r_B = dC_B\,/\,dt = k_1\,C_A - k_2\,C_B \text{ and}$$

$$r_C = k_2\,C_B$$

The first equation is familiar and leads to

$$C_A = C_{A0}\,exp(\,-\,k_1\,t)\ \text{where } C_{A0} \text{ is the initial value of } C_A$$

This value can then be substituted into the second equation, which leads to:

$$dC_B\,/\,dt + k_2\,C_B = k_1\,C_A = k_1\,C_{A0}\,exp(\,-k_1\,t)$$

This equation can be solved for $C_B$ by the mathematical technique of multiplying by an integrating factor to make the left-hand side into the differential of a product, which can then be integrated. Without going into the detail, which can be found in textbooks on differential equations, this leads to the solution, assuming that at time 0 there is neither *B* nor *C*:

$$C_B = k_1\,C_{A0}\,[\,exp(-k_1\,t) - exp(-k_2\,t)\,]\,/\,(k_2 - k_1)$$

and $C_C = C_{A0} - C_A - C_B$ where we now know $C_{A0}$, $C_A$, and $C_B$

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The equations indicate how the balances of the components change with time and with the particular rate constants. Consideration of the effect of the activation energies of the $k$'s in the sequential reactions shows that the intermediate component concentrations, maxima and relative, can be changed by altering temperatures. This gives the processor a powerful tool, manipulation of times and temperatures to reach optimum products.

The effect of changing the ratio $k_1 / k_2$ can be demonstrated by inserting typical values into the various $k$'s and activation energies. The shape of the curves change as the ratio of the reaction rate constants change. If $k_1 / k_2$ is very large, then effectively A becomes B almost instantaneously, the processing time is occupied by the change of B into C, and the process shape and rate are dominated by the value of $k_2$. Conversely, if $k_1 / k_2$ is very small, the processing is dominated by the transformation of A, and there is little or no B to be found at any time in the mixture, as immediately B is formed it reacts to become C. Essentially, A reacts at a rate determined by $k_1$ to form C. In between these extreme ratios, especially if B is a wanted product, process times and ratios of the $k$'s can be selected to suit to a limited but still significant extent.

A number of examples of sequential reactions are found in food processing and storage. In the Maillard browning reaction (non-enzymic), the intermediate products are many and diverse and they can polymerise, changing from colourless to yellow and finally to a sticky brown mixture. Important to the processor in the case of the browning reaction are the flavours, colours and nutritional significance, of the intermediate compounds, and the relative extents to which these are formed. An intermediate product that can be used to monitor browning is hydroxymethyl furfural (HMF), but often colour measurement is used to follow browning development. That the reaction equations can be built up into broad but quite detailed kinetic schemes that can handle and simplify even the very complex systems such as the Maillard reaction system is described by Jousse *et al.* (5). They classified the volatile compounds, which are the basis of browning flavour. In a kinetic scheme with 11 reaction steps, they were able to correlate pseudo-first order rates of generation of these compounds, which predicted the actual build-up of flavour through processing with the temperature and concentration of the reactants. The equations were then integrated to follow the build-up of flavour. Although the mathematics involved 11 differential equations that had to be solved simultaneously, once the equations had been written and parameters such as rate constants, concentrations and temperatures inserted, the numerical solutions were produced through standard computer programs.

*Think break*

Select a chain reaction system occurring in food processing – for example, a browning sequence in the manufacture of toffee or of caramel:

* Consider how important consumer characteristics of the food could be altered by modifying the timing sequence and, or, the temperatures of the operating sequences.

* To what extent might knowledge of the kinetic sequences improve operation or control of the processing?

Unsaturated fats found naturally are generally softer than corresponding fats with the same carbon chain length but higher degree of saturation. If such fats are to be used in spreads that require firmness, it is desirable to increase the degree of saturation. This can be accomplished by catalytic hydrogenation. In the hydrogenation (catalytic) of unsaturated fats, the intermediate components are fats of progressively lower unsaturation, and the final fats would be completely saturated if the reaction continued to this extent. In the case of fat hydrogenation, important measures of the reaction are:

- degree of residual unsaturation

- hardness of the fat, which rises as saturation rises and which is the reason for conducting the reaction industrially

- nutritional value, where higher unsaturation is generally preferable.

An example of multiple double bonds being progressively saturated is found in the sequence of 18-carbon fatty acids, with linolenic acid (3 double bonds), to linoleic acid (2 double bonds) to oleic acid (1 double bond), to stearic acid, completely saturated. In fats this is related to progressive hardening. Because of their commercial importance, these reactions have been extensively studied. One study is described in Example 4.4.

**Example 4.4: Hydrogenation of soya bean oil**

In one report, Chen *et al.* (6) reported values for the first stages in hydrogenation, that is linolenic to linoleic, and linoleic to oleic. These were both first order reactions.

The reaction rate constants at 200 °C under one particular set of experimental conditions were:

Linolenic to linoleic    $k_1$ = 0.25 min$^{-1}$ and an activation energy of 44kJ/mol

Linoleic to oleic        $k_2$ = 0.42 min$^{-1}$ and an activation energy of 48.5 kJ/mol

Consider the first three acids in the sequence, linolenic A, linoleic B, and oleic C. These lead through the equations for sequential reactions to progressive concentration ratios ($C/C_0$) for linolenic and linoleic acids as time (t) proceeds, as illustrated in Fig. 4.5.

Figure 4.5 shows that, as hydrogenation time progresses, the compositions change. Although the curve for linoleic acid is rather flat, there is a predictable time for its maximum value.

The shape of the curve can be altered, because of the different activation energies, by shifting the temperature of operation.
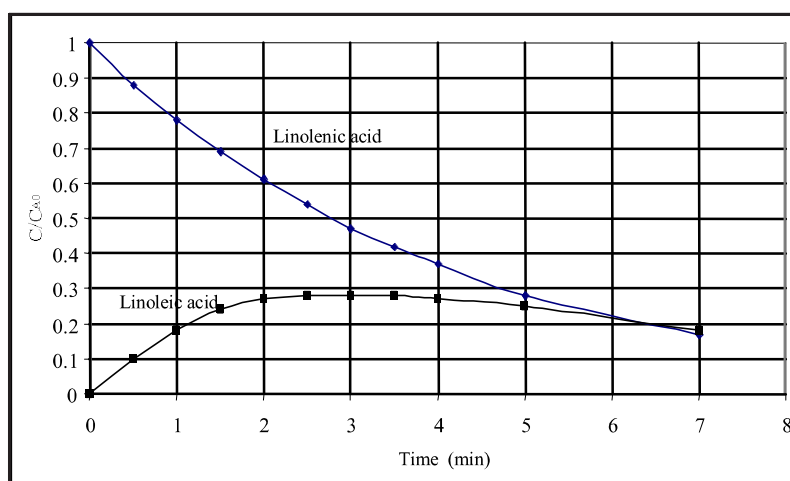


Data from Chen *et al.* (15)

*Fig. 4.5. Progress of a hydrogenation reaction*

The investigations necessary to set up and use such analysis are extensive, and may be worthwhile only in a large-scale higher-technology context such as fat hydrogenation. But the general pattern and nature of the chain reaction, and the implications, can be helpfully considered in quite a number of chain reaction systems that are encountered widely in food processing.

## 4.4 Parallel Sets of Reactions

Most foods are complex mixtures of constituents. The processing conditions, such as temperature, are necessarily applied to all the components. Sometimes, components can be easily isolated and processed separately, but, under other circumstances, this is not practicable and the food, or appreciable portions of it containing a number of constituents, has to be processed as a whole. So there are a number of reactions occurring in parallel; e.g., in bread baking, there are sugars going to carbon dioxide and alcohol, starch gelatinisation, protein denaturation, and caramelisation of sugars. On heating the bread, all reactions are speeded up, and these increased changes will affect the final product attributes.

A further complication is that, in many heating situations, for example those involving conduction such as baking, regions of the food remote from the heat source rise in temperature much more slowly than those close, so impacts of processing differ through the food.

So the situation commonly arises of sets of potential reactions implicit in the nature and composition of the food, starting up and proceeding, each at different rates and with often quite different degrees of desirability so far as the ultimate product is concerned. Therefore, the processor should consider all the possibilities and then optimise the processing conditions over these sets of parallel and linked reactions to arrive at the best food product outcome.

One example of this has already been encountered when considering the F values throughout a can containing a convection-heated product in an experimental retort, shown in Fig. 3.4. Here the differences in the extent of processing for the critical reaction, food poisoning spore destruction, in selected regions of the can are at once apparent. By inserting the kinetic parameters for other reactions within the product, for example enzyme destruction and starch gelatinisation, the relativities for these can be explored; and so on for any other reactions that are of importance and for which the necessary kinetic data are known.

Now each set of different processing conditions will in general give a different pattern of product composition and attributes – a different final product profile. So the problem for the processor is to assess the relative value of each product profile. Then potential processes can be explored with a view to optimising desired product attributes.

In some cases, it may be adequate to consider averaging – probably best done on a volumetric basis and effectively equivalent to finding the hypothetical concentration that there would be in the completely mixed product. In other cases, there may be absolute limits, upper or lower, such as, for example, with critical

spore-forming bacteria, where a prescribed maximum spore concentration may be laid down in regulations.

One way in which to visualise these reaction patterns is to make use of the OTT chart. For example, if a critical requirement is overriding, then this will specify a line on the diagram "below" which processing cannot be considered complete. All regions in which the extent of processing for the critical constituent is equal to or greater than the level defined by a line on the diagram will lie on or above this line. Processes corresponding to all points on the line will have the same critical processing, so they will meet this requirement. But these processes may, and generally will, have differing extents of other parallel reactions, and therefore result in different product profiles. So the OTT chart can be used as the basis for exploring the possibilities and judging between them. In Example 4.5, the use of OTT charts in selecting times and temperatures for the pasteurisation of milk is described. These approaches are discussed further in a number of accounts, including Kessler (7) and Lewis & Heppell (8).

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**Example 4.5: Pasteurisation of milk**

An important industrial process is the pasteurisation of milk, whereby the milk is heated for a period principally to destroy possible pathogenic microorganisms.

Taking one processing specification of 15 s at 72 °C and assuming a z value of 8 °C, then an OTT chart can readily be constructed for this, and if desired extended to include under- and over-pasteurisation expressed for example as percentages.

Alternatively, if it is assumed that at 72 °C the 1D time of *Mycobacterium tuberculosis,* the original organism for which the treatment was designed, is about 1 s, then lines of equal effect can be plotted. To indicate levels of destruction, three lines are shown 12D and 18D, as well as the 15D line for "pasteurisation" in Fig. 4.6.

Tests have evolved for adequacy of pasteurisation using chemical assays, and one of these is to test for alkaline phosphatase. If it is assumed that the test registers a level of 95% destruction of alkaline phosphatase, reached in about 20 s at 72 °C, and the z value for the phosphatase is about 7 °C, then a line for the destruction of this enzyme can also be added to the OTT chart.

All of these lines are shown in Fig. 4.6.

This OTT chart shows that, if 95% destruction of phosphatase is measured and therefore has occurred, then the processing required for 15D destruction of the critical bacteria has also occurred (and also that, of course, for 12D destruction, but not necessarily that for 18D).

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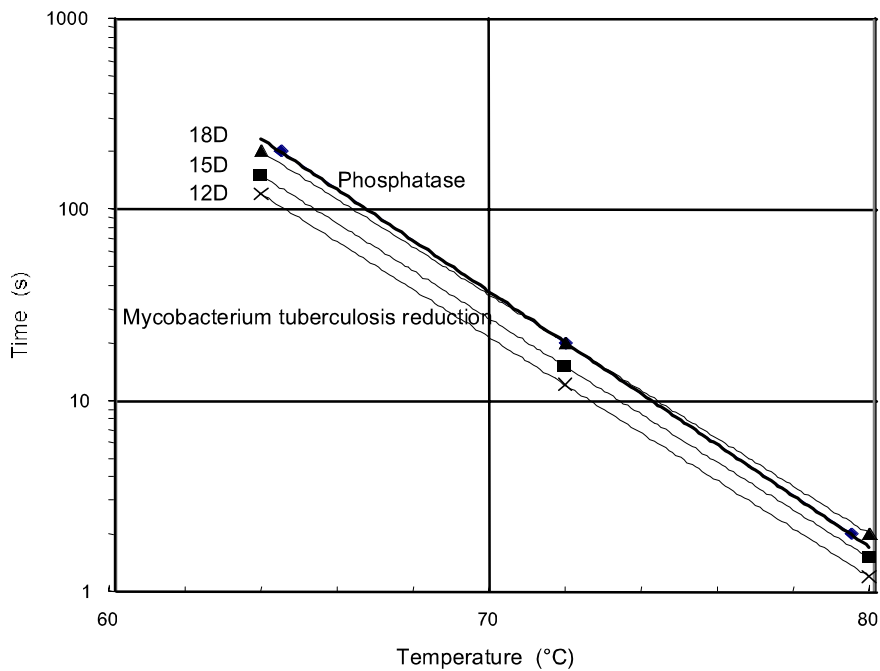
Data from Kessler (7)

*Fig. 4.6. Pasteurisation of milk – OTT chart*

If sufficient information is available, then the important reactions encountered in the processing of a single food can be explored kinetically, and the results of these experiments entered onto a single diagram. This then allows the overall processing situation to be assessed by the technologist. Obviously, critical requirements must be met. If there is more than one of these, then that with the most stringent demands overrides, and the OTT chart provides a minimum process line, on or above which any selected process must lie. However, this still allows a complete region for allowable processes, and just where in this region the actual process conditions will be selected becomes a matter of priorities and judgement.

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*Think break*

\* Can you think of other food processing examples in which the kinetics are well enough understood to set up an OTT chart for the significant reactions?

\* If you have difficulty in finding such examples, why do you think this might be so?

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Data have been published that provide sufficient detail on the high-temperature processing of milk, to be used for illustration of optimising a set of reactions, and are studied in Example 4.6.

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**Example 4.6: High-temperature processing of milk**

A number of reactions have been explored in the high-temperature processing of milk, and from these an OTT chart can be constructed, which is shown in Fig. 4.7. These reactions are extensively discussed in Kessler (7).

This OTT chart includes:

- bacterial reduction, looking at both thermophilic and mesophilic sporeformers. It can be seen that the activation energies (z values) are equal but, as would be expected, the thermophilic spore-formers can tolerate higher temperatures. These lines can be regarded as typical rather than specific; with further specific data, lines that are important in any particular situation can be substituted.

- destruction lines for constituents that have nutritional significance, such as lysine and thiamin, at two destruction levels, and destruction of 90% of a protease enzyme. Assuming kinetics for these, other lines can also easily be inserted to demonstrate the nutrients reaching other levels of destruction.

- a line indicating a panel judgement of the level at which a significant detectable change occurs in acceptability criteria, in this case colour and a cooked flavour, which emerge essentially simultaneously.

To indicate how such a chart might be used in practice, assume a critical requirement is that the mesophilic spores must be reduced by $10^9$. Also, the protease destruction is important to the 90% level. Therefore, the allowable processes must lie in the regions on or "above" lines H and D. Taking flavour also into account limits selection to the region bounded by lines H, D and E.

This then restricts the possibilities to quite a small region on this particular diagram, and for example it can be seen that a process of about 5 min at 120 °C meets the requirements. Any further exploration of feasible conditions can then roam over the allowable region to see whether other criteria, such as, for example, minimising the residual lipase, line C, also needs to be considered. The effects of such a process on the thiamin and lysine can also be interpolated by inspection.

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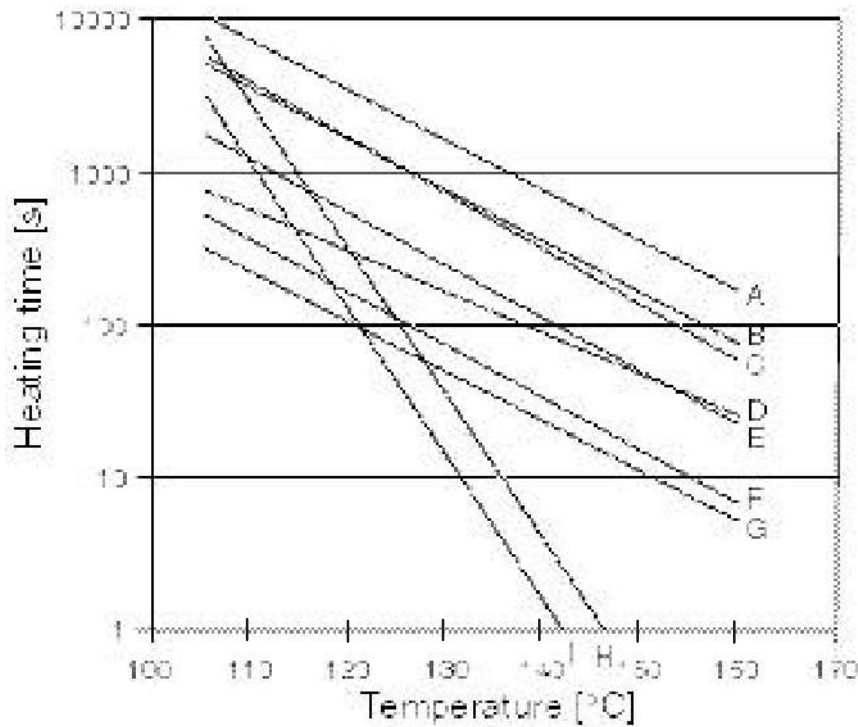
Destruction of **A** 50% thiamin; **B** 10% lysine; **C** 90% lipase; **D** 90% protease.
Just noticeable appearance of colour and cooked flavour, **E**.
Destruction of **F** 1% lysine; **G** 3% thiamine.
Reduction by $10^9$ of **H** thermophilic spores; **I** mesophilic spores

Data from Kessler (7)

*Fig. 4.7. High-temperature processing of liquid milk OTT chart*

The OTT charts are constructed for a constant temperature process, and, of course, this is seldom if ever totally true in practice. However, quite a number of real situations are reasonable approximations, such as those encountered in many continuous heat exchanger situations. In some other real processes, sufficient of the bulk of the reaction occurs at the "working temperature" for constant temperature to be a reasonable approximation overall. Where this is not the case, then the OTT chart can still be used, reading off the reaction rate constants corresponding to actual temperatures and inserting these into the kinetic integrations. In other cases, processes can be divided into different segments, and each segment treated as a separate process. This is straightforward in the case of zero order reactions using simple proportioning. This can also be used as an approximation for reactions of other orders that is often compatible with what may be only quite moderate accuracy of the available data, and sufficiently close for the needs of practice.

## 4.5    More Complex Situations

Normally, the OTT chart giving lines of equal extents of processing shows a family of parallel lines, because, for a single reaction, the activation energies, which determine the line slopes, are constant irrespective of the stage of the reaction. This is illustrated for example in Figs 4.6 and 4.7. The families of lines can easily be extended if the reaction orders are known.

However, for some systems, the experimental lines when measured are not parallel, and an illustrative set of these for the precipitation of whey proteins from milk, derived from data given by Agrawala & Reuter (9) is given in Fig. 4.8.
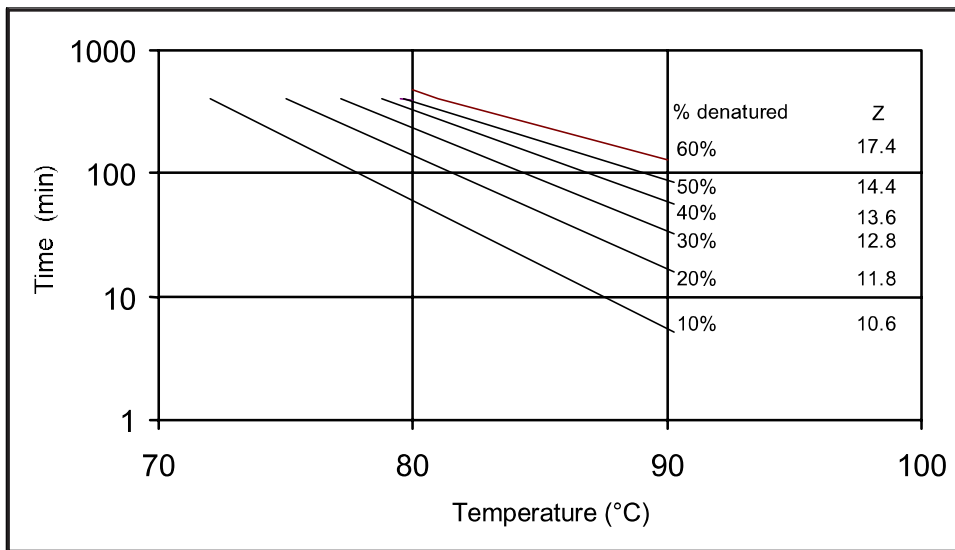


Data from Agrawala & Reuter (9)

*Fig. 4.8. Precipitation of whey proteins: OTT chart*

In Fig. 4.8, process lines of equal percentage of proteins precipitated are shown in the usual way, and it can be seen visually and from the tabulated equivalent z values that they are not parallel but systematically decrease in steepness as the fraction precipitated increases. This suggests that the residual proteins, as parts are removed by precipitation, change composition significantly. The residual proteins have progressively lower activation energy, thus contributing to a lesser slope of the curve.

Thus it can be seen that the OTT charts can provide much useful information. This can be both of direct and of inferential use to the processor. The major problem is often obtaining the data necessary for them to be constructed. It will have been noticed that many of the cited examples are of milk products, and the major reason for this is that milk systems have been both subjected to extensive scrutiny and widely published by the dairy industry. With milk so widely consumed and the dairy industry so extensively organised, it is not surprising that so much detail is available publicly about its kinetic properties.

Another feature emerging from experimental plots of d(lnk) against 1/T is the existence of broken Arrhenius curves for milk protein heat denaturation. This probably indicates a change in the reaction mechanism with temperature. When there are two pathways available, with different activation energies, then their relative significance changes with temperature. The pathway with higher activation energy "takes over" from that with the lower activation energy at the appropriate temperatures. This is illustrated in Fig. 4.9, from the work of Dannenberg (10). From 70-80 °C, the denaturation of α-lactalbumin has an activation energy of 268.6 kJ/mol; and from 85-150 °C, an activation energy of 69.01 kJ/mol.
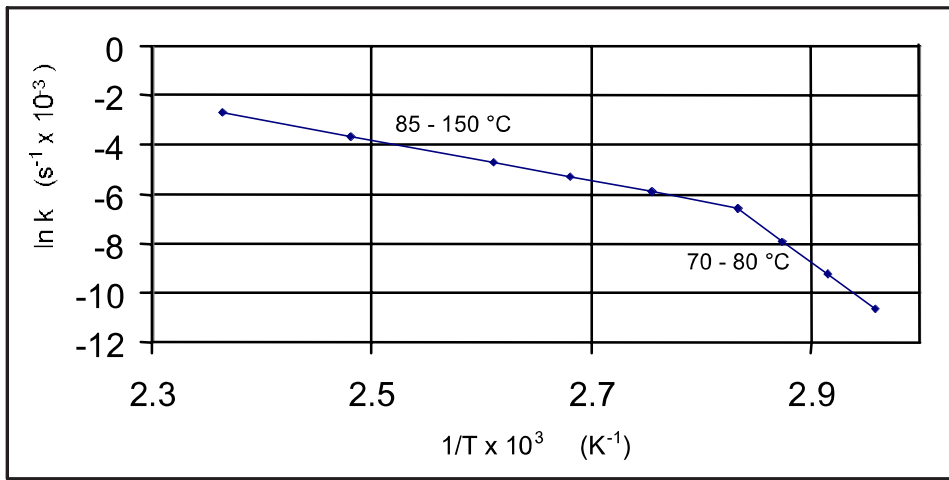


Data from Dannenberg (10)

*Fig. 4.9. Denaturation of α-lactalbumin: broken Arrhenius plot*

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**Example 4.7: Denaturation of α-lactalbumin**

If the denaturation of α-lactalbumin in milk is a first order reaction, as suggested by Dannenberg (10) and the rate constant is given by:

$k = 10^{36.87} exp( - 268,600 /RT)$ for temperatures between 70 and 80 °C
and
$\quad$ $k = 10^{6.93} exp( - 69,010 / RT)$ for temperatures between 85 and 150 °C
$\qquad$ where k is measured in $(s^{-1})$

What is the expected time needed for the 90% denaturation of this protein constituent of milk at temperatures of 75 °C and 100 °C

$\quad$ **At 75 °C** $k = 10^{36.87} \exp( - 268,600/RT) = \exp( - 268,600 / \{8.314 \times 348)$
$\qquad$ $= \exp(-7.924)$
$\qquad$ $= 3.62 \times 10^{-4} s^{-1}$
$\qquad$ $- \ln C/C_0 = -\ln 0.1 = 2.303 = kt$
**and so time for 90% denaturation = $t_{0.9}$ = 2.303/k = 2.303/3.62x10$^{-4}$ = 6,363 s = 106 min**

$\quad$ **At 100 °C** $k = 10^{6.93}.\exp ( -69,010/R \times 373) = 1.85 \times 10^{-3} s^{-1}$
and again
$\qquad$ $- \ln C/C_0 = -\ln 0.1 = 2.303 = kt$
**and so time for 90% denaturation = $t_{0.9}$ = 2.303/k = 2.303/1.85 x10$^{-3}$ = 1,245 s = 21 min**

The broken curves can be handled by treating the straight line portions separately but using the standard methods.

---

The behaviour of the denaturation/temperature curves in Example 4.7 could be explained by postulating two consecutive reactions. The first reaction, dominant at high temperatures and having low activation energy, and the second dominant at the lower temperatures and having high activation energy, but more evidence would be needed to establish this.

## 4.6 Process Optimisation

In practical process situations, the temperature histories throughout the mass of the food are physically linked. This is obviously and inevitably true, for example, in a conduction heating system. In this, it takes time for changes in temperatures to penetrate through from the heat transfer interface, which could be fat in a frying system, into the more remote regions of the food, perhaps into an emulsified

sausage that is being fried. It can be assumed that the various constituents of the food are evenly mixed at any one point, that is the food is homogeneous. Then the temperature histories of all the different constituents will be the same. But, because of the different reaction rate constants, the reaction patterns will not be the same in all, or perhaps indeed any, of these constituents.

The set of time/temperature conditions throughout the food can be thought of as a "process envelope", of identical temperature histories, but leading to different outcomes for the different ingredients. The processors usually have direct control over the temperature and time conditions; for example, the heating medium temperature can be altered. They have some indirect control – for example by modifying flow patterns to change the heat transfer coefficients at the surfaces. They have some possible control by changing the size or the composition of the food pieces (but this also changes the product). But, over thermal conductivity and activation energy, they have no control, as they are determined by the ingredients used and their constituents. Of course, the ingredients can be replaced with substitute ingredients, which may have constituents with different physical properties, for example replacing native starch with treated starch, or milk protein with soya protein.

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*Think break*

In a typical food process based on heating:

* List the actual process controls available to the processor.

* How might the extent, the precision, and the repeatability of these controls be modified? Improved?

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Unfortunately, because of the non-linear nature of most of the reaction processes and of the temperature coefficients of the reaction rate constants, the process outcomes from multiple reactions, even when the whole set is subject to the same overall temperature, are complex and analysis is not straightforward. However, by using the methods set out, so long as the kinetic behaviour of the critical and important reactions are known, outcomes can be predicted for any given process envelope. Then these can be re-evaluated for any other process envelope. So, with the aid of computers and spreadsheets, outcomes can be explored without too much labour. In particular, it should be possible to reveal overall trends in the significant constituents. These are generally sufficient to show the areas where actual processes will be both operationally practicable and straightforward, and also yield something close to optimum product outcomes.

Much time and energy have been expended over the years, and at an accelerating rate with the increasing exploration of new techniques, on seeking optimum processes. A wide-ranging but brief summary of many of these techniques was given by van Loey *et al.* (11). Another account, also with references and some detail, is in Holdsworth (12). Because most of the processes

are complex, the procedures tend towards searches of possible alternative heating strategies, which are then explored for their relative effects on critical and important variables. Amongst the published material are accounts of both fixed temperature and variable temperature strategies. If process variables other than temperature were driving the reaction, the same general methods could be used.

For example, an early paper by Teixeira $et$ $al.$ (13) illustrated the complexity of optimising the product profile from conduction-heated systems in can sterilisation. Safety is, of course, critical and there has to be a fixed least-processed-point lethality ($F_0$). In considering the other product attributes, the normal inference is that higher temperatures and shorter times favour overall quality but the Teixeira paper (13) showed that this was true only up to a point so indicating an optimum process. In these heat-conduction packs, it was the relative importance of the heating and cooling rates in the different regions going down to the can centre that affected the average levels of the other product attributes. This led towards what amounted to an optimum process condition for such solid packs.

Another examination of conduction systems by Silva $et$ $al.$ (14) looked systematically at both average pack quality and also surface quality, and at the relative effects of sterilisation temperatures on these. Durance $et$ $al.$ (15) examined variable retort temperatures for the canning of salmon to see whether quality could be improved or process times decreased, within constraints practical in cannery operation. They treated it as a conduction-heated pack, and looked at surface "cook" effects and nutrient retention while maintaining constant centre point lethality ($F_0$). They used relatively straightforward mathematical techniques. They concluded that programming variable retort temperatures offered advantages over fixed ones, although the differences were not major.

Optimal heating strategies for a convection oven, considering the problems of re-heating pre-prepared meals but also more generally applicable, were discussed by Stigter $et$ $al.$ (16) using quite elaborate mathematical procedures. They were looking particularly at control and regulator design for the ovens, and achieved their objective of achieving uniform temperatures within the food at the end of the heating time. The examples briefly outlined seem to offer possibilities and ideas for controlling processing reactions.

These few case studies indicate something of the extent and scope of optimisation investigations in food processing. They demonstrate how reaction technology, together with the necessary accompanying experimental data, can be used to seek improved conditions for working processes across a very wide range of industrial situations. There are several research groups, internationally, that are working hard and effectively in this field. The academic groups, especially, are generally publishing their results. Examination of the current literature, both the published papers and the extensive bibliographies cited in many of them, quite rapidly focuses on the information that has a bearing on any particular processing problem, and provides important indicators towards investigation, selection and operation of better processes.

*Think break*

To find recent information on kinetics of reactions, search the last 2 years of the Food Science and Technology Abstracts for:

* shelf-life of whole milk powder
* blanching of vegetables
* bread baking

Case study 4: Heat treatment of milk

*This case study shows how, when there are several critical and important reactions, an optimum process can be designed.*

The various reactions in milk processing have been assembled in a study by Arteaga *et al*. (17), as shown in Table 4.I.

**TABLE 4.I**
**Kinetic data for reactions in the heat treatment of milk**

| Reaction (order) | $k_{120}$ | E<br>kJ mol$^{-1}$ | ln A<br>s$^{-1}$ |
|---|---|---|---|
| Lipase inactivation (1) | 0.0115 s$^{-1}$ | 53.037 | 11.767 |
| Protease inactivation (1) | 0.0125 s$^{-1}$ | 63.963 | 15.194 |
| Furosine formation (0) | 0.497 $\mu$mol l$^{-1}$s$^{-1}$ | 81.637 | 24.286 |
| Lysinoalanine formation (0) | $3.87 \times 10^{-2}$ $\mu$mol l$^{-1}$s$^{-1}$ | 101.377 | 27.775 |
| Lactulose formation (0) | 5.38 $\mu$mol l$^{-1}$s$^{-1}$ | 120.224 | 38.478 |
| Thiamin loss (2) | $7.53 \times 10^{-4}$ l mg$^{-1}$s$^{-1}$ | 100.800 | 22.742 |
| Lysine loss (2) | $2.12 \times 10^{-8}$ l mg$^{-1}$s$^{-1}$ | 100.900 | 15.691 |
| Colour formation (1) | $1.66 \times 10^{-3}$ s$^{-1}$ | 116.000 | 29.101 |
| HMF formation (0) | 0.22 $\mu$mol l$^{-1}$s$^{-1}$ | 135.098 | 39.833 |
| *Micrococcacea* destruction (1) | $1.29 \times 10^{-5}$ s$^{-1}$ | 329.985 | 112.759 |
| *B. stearothermophilus* spore destruction (1) | $1.10 \times 10^{-2}$ s$^{-1}$ | 345.357 | 101.188 |

k: reaction rate constant, E: activation energy, A: frequency factor
Data cited by Arteaga *et al*. (17)

*Contd..*

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Case study 4 (contd)

From Table 4.1, OTT charts can be drawn. However Arteaga *et al*. (17) took a somewhat different, a numerical, approach.

They postulated what they called a *four-step process*, where the UHT heating process was divided into four time/temperature steps. Each step was assumed to be at a constant temperature, which were rising and then falling, for example sequential temperature steps at 80, 120, 140 and 100 °C.

They then assumed some critical process outcome requirements, that is levels of product attributes, which they termed constraints. For example, in one of their illustrative systems, they required that at least 40% of the protease and lipase activity be destroyed, while minimising the increase in the colour and hydroxymethyl furfural (HMF) formation, which is an indicator of the browning reaction.

They then used an interactive procedure using a constrained simplex ("Complex") method, starting from an initially arbitrarily assumed four-step process with specific time/temperature limits for each step. The computer program included a kinetic subroutine, which was based on the kinetics constants according to the Arrhenius equations. For each of the reactions, the total heat effect at the end of the time/temperature profile was taken as the sum of the effects at each step.

The Complex method, from the original process meeting the constraints, by reiteration developed new temperature profiles, maintaining the constraints on lipase and protease, but at the same time minimising the effects on colour and the HMF. This then generated systematically improved minimal colour and HMF, until an optimum was reached, whilst still meeting the constraints.

The optimum result they obtained is summarised in Table 4.II.

**TABLE 4.II**
**Seeking optimum time/temperature profiles in four-step heat process**

**Initial time/temperature profile**

| | |
|---|---|
| **Step 1** 8.4 s @ 80 °C | **Step 2** 25 s @ 120 °C |
| **Step 3** 20 s @ 140 °C | **Step 4** 19.5 s @ 100 °C |

Process result: HMF 20.66, colour 0.16, residual lipase 40.2%, residual protease 35.5%.

**Optimum time/temperature profile**

| | |
|---|---|
| **Step 1** 20 s @ 79.3 °C | **Step 2** 21.1 s @ 115.7 °C |
| **Step 3** 6.9 s @ 139.8 °C | **Step 4** 19.6 s @ 99.8 °C |

Process result: HMF 8.05, colour 0.07, residual lipase 59.97%, residual protease 58.33%.

Units: HMF mg ml$^{-1}$, colour in arbitrary units. Lipase and protease are residual activity as % of original activity. These were constraints that had to be less than 60% residual activity.

*Contd..*

133

Case study 4 (contd)

This result minimises the heat damage effects, HMF down from 20 to 8, and colour change about halved, while at the same time meeting the required level of enzyme destruction (at least 40% destroyed).

Constraints on other product attributes can be set either as stipulated constraints or minima. The final values for all the product attributes with the optimum time/temperature process are also calculated so that effects on the other attributes as well as the constrained and minimised attributes are known.

While the four-step process may seem rather arbitrary, it is a reasonable compromise in terms of complexity and it indicates the manner in which such procedures can be employed. Higher levels of complexity could be taken into account although they may not yield substantial improvement in the total process. While the method itself does not necessarily picture the field of possibilities all together, its use would also serve to generate familiarity and understanding of the reaction system and build a basis for process design.

Once again, the method depends upon sufficient knowledge of the kinetics of the important reactions, and the effectiveness of such an approach obviously stands or falls by the adequacy of this knowledge.

Because the OTT chart is helpful and instructive, it is tempting to invest it with wider strict application than it actually has. Recall, from its derivation, the OTT chart applies only to what can be called isothermal processes. These are processes where the temperature is lifted from a lower level, at which effectively no reaction occurs, suddenly up to one at which there is substantial reaction. The temperature remains at this elevated constant value for some time, during which the reaction progresses to the controlled extent, and thereafter is instantaneously lowered again to a temperature at which reaction effectively ceases. Strictly, such a process cannot occur in practice, but close approximations can, such as in continuous heat exchangers, steam jet heating and vacuum cooling. Other practical processes sometimes come close enough for the analysis to have application. Thus the OTT chart provides the technologist with valuable and perhaps otherwise unobtainable insights, such as appear to have been important in developing a liquid egg pasteurisation process.

Case study 5: Pasteurisation of liquid whole eggs

*This case study shows how knowledge of reaction technology can be used to design a process that can be protected by a patent.*

Adding storage life to food ingredients adds important flexibility, and therefore processes that can increase high quality holding times are important and valuable.

Eggs are a widely used food ingredient, and qualities that have to be retained during holding include functionalities – for example the ability of the egg proteins to remain soluble and to whip up into typical egg products such as batters and cakes. Also, eggs may become contaminated by pathogens so that some degree of heat pasteurisation may be highly desirable. If the heating is sufficient to remove health risks, then it can easily coagulate the protein and destroy functionalities (Hou *et al*. (18)). So this is an area in which it might be possible to organise the heat processing to reduce possible pathogens to safe levels and at the same time preserve protein structures, by knowledge of the kinetics of the important reactions and then application of reaction technology.

A practical method of doing this in continuous flow, high temperature, short time pasteurisation equipment, is claimed in a US patent (19). The patent includes kinetic data, and an OTT chart, which is used to explain some of the basis for the claims. Figure 4.10 is a redrawn OTT chart, taken from equations included in the patent descriptions.

Figure 4.10 includes a destruction line for *Salmonella* spp, which are well known to be problem pathogens in eggs, and for which the 9D reduction conditions as shown may be regarded as a target reduction ratio. It includes a 7D reduction line for another common pathogen found in eggs, *Streptococcus faecalis*.

It also includes a line indicating the heat treatment that results in 5% loss of the soluble egg proteins and which may be seen as an acceptable price, in terms of degree of loss, to pay for much enhanced product safety. The 5% loss of soluble protein line shown is a broken one, indicating something of the complexity of the proteins, and was determined by detailed experimental studies (18).

In the upper right-hand corner of Fig. 4.10 is a region of much increased protein coagulation within which the eggs become functionally inadequate for many ingredient applications. Thus an OTT diagram was used as background to the design of novel processing, described in the patent, and claimed to make liquid whole egg products with pre-selected, extended, refrigerated shelf-lives.

*Contd..*

Case study 5 (contd)

This patent is instructive, entirely apart from any intrinsic merit it may have, because it displays a considerable kinetic background to the product claims, and apparently regards this as important to the invention. This seems to imply that the process might not have been discovered without the kinetic analysis. It also shows how the kinetic information relates to the advantages claimed to derive from use of the patented process, and which are exemplified by product applications such as sponge cakes and custards.
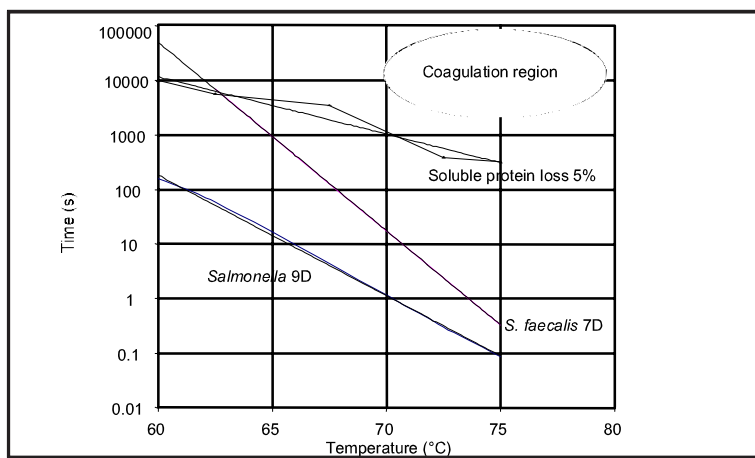


Data from Swartzel *et al.* (19)

*Fig. 4.10. Pasteurisation of whole egg – OTT chart*

## 4.7    Processing in Continuous Systems

Some foods are processed continuously. The continuous flow processing of foods that can be pumped introduces a new constraint imposed by the physical situation, residence time distributions. For example in pipe flow, elements on the centreline move faster and therefore spend less time in the processing than elements on the periphery, and this is inevitable from the flow patterns. Therefore, they will be much less processed and so will affect the overall quality assumed to be an average over the whole flow. A distribution of residence times is needed to cover all the elements. Analysis of flow systems is complicated but some of the features encountered are illustrated in a Case Study of an industrial food process that uses a continuously stirred tank reactor. In this, the reactor is a large tank maintained at the process temperature. The food is pumped in continuously, immediately heated and uniformly mixed, and an average sample from the whole tank flows out at the same rate as the inflow to keep the tank contents volume constant. This system achieves very rapid, effectively instantaneous, heating of the food, but it

also inevitably incorporates an exponential spread of food residence times in the tank.

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Case study 6: Continuous heat processing of tomato paste

*An example of the use of reaction technology analysis in continuous processing has been investigated in an industrial application, the processing of tomato paste.*

To provide adequate keeping properties for concentrate for sauces, it is important to heat-process the pulped tomato, but this heating has, as far as possible, to avoid breakdown of the pectins that give the resulting paste its structure. Hydrolysis causing breakdown of the pectins is enzymically catalysed by pectinase (polygalacturonase) and is quite strongly heat-dependent. So to minimise hydrolysis the processes can destroy the enzymes by moving quickly to higher temperatures above 50-60 °C, at which temperatures the enzyme activity effectively ceases. A further complication arises from differential reaction rates in tomatoes of different ripenesses, input tomatoes to a plant being not always equally ripe.

In a recent account of experimental and theoretical work by Srichantra (20), activation energies of the various potential reactions have been related to the rates and temperatures of the reactions in the processing. The work shows that reduction in pectin concentration, as measured by galacturonic acid, which is a breakdown product of the pectin indicating structural loss, can be predicted and quantified for various possible conditions of processing.

To obtain rapid heating, a large heated "break" tank was employed, with pulp continuously pumped in and removed. To analyse the situation, Srichantra inserted appropriate and measured values for tank volumes, flow, reaction rates including those for tomatoes at different ripenesses, and activation energies, into differential equations. These equations were then solved for selected tank temperatures by using computer algorithms. The results demonstrated the effects of both various tank temperatures and nominal paste residence times, and were extended to tomatoes of differing ripeness. The method could be further adapted to other processing circumstances.

Particular effects of tank temperature, paste residence time, and tomato ripeness are illustrated in Figs 4.11(a) and 4.11(b), clearly demonstrating the peaking pectin loss at temperatures around 60 °C. This effect, leading to the cold break (temperatures <60 °C) and hot break (temperatures >60 °C) processes for tomato paste, is well known, but the analysis

*Contd..*

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Case study 6 (contd)

explains how it results from the interaction of the rates of concurrent reactions – enzymic breakdown of pectin and enzyme denaturation. The advantage of the analytical approach is to quantify the behaviour and so provide data for more precise operation of existing processes as well as indicate possibilities for the design of new ones.

This general behaviour involving enzyme activation/inactivation by heating is encountered often in fruit and vegetable processing so the analysis has wider applicability. It demonstrates that quite sharp process changes can occur and so the labour of experiment and analysis to identify these quite precisely may well be worthwhile. The model also shows quantitatively how both changes in factors such as fruit ripeness leading to differing rate constants, and also rapid heating that can be obtained by pumping directly into hot material, can be used in process design to explore quality outcomes.
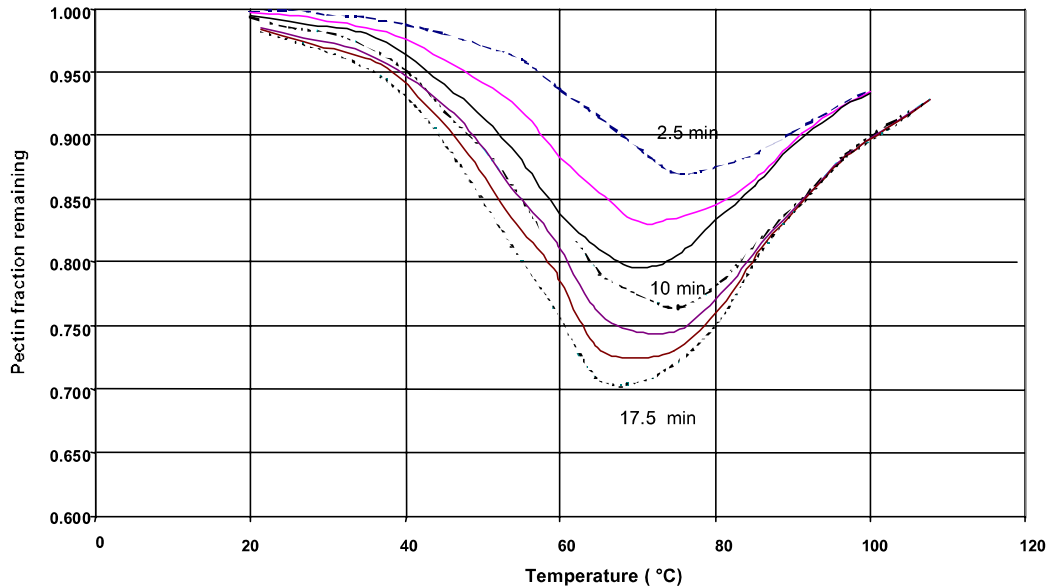


*Fig. 4.11(a). Pectin remaining as a function of residence time and break temperature*
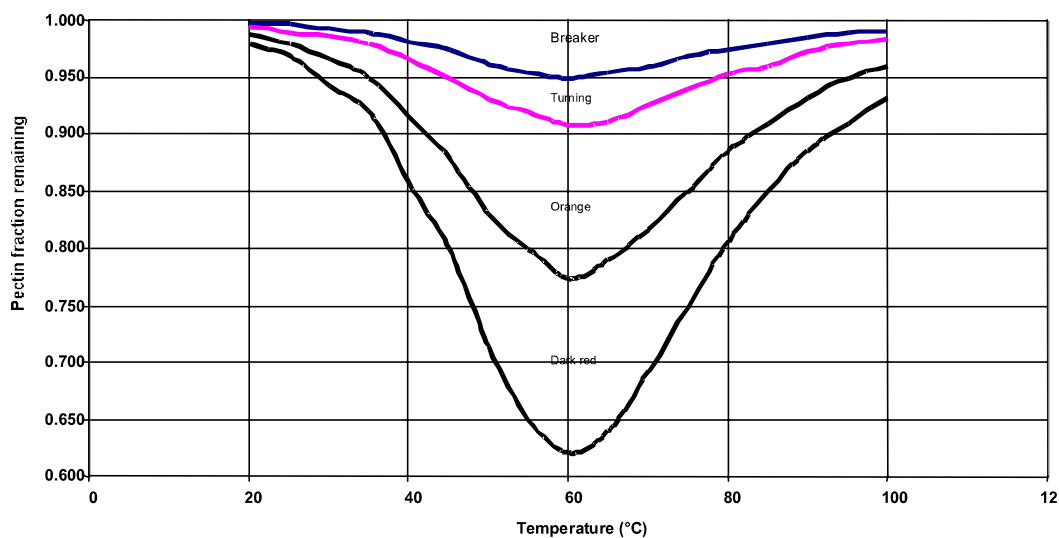
*Fig. 4.11(b). Pectin remaining as a function of ripeness and break temperature*

## 4.8    Practicalities

The methods of reaction technology can be applied in all food processing situations in which the food constituents undergo the reactions that change them and therefore alter quality attributes in the food. So they are very practical, and it is worthwhile to briefly summarise some of the important practical approaches that have emerged. These may also indicate the scope that undoubtedly exists for further analyses along the same lines, but extending beyond what has been accomplished already.

### 4.8.1    Examining constituents and attributes

The last four chapters have emphasised that in every process there are raw materials that change in the process to give the final product. This final product can be characterised by critical and important attributes, and the aim of the processing is to achieve the specified levels of these attributes. These attributes can be identified with specific reactions occurring in the process. The reactions are controlled by the processing conditions, and in particular temperature, time and concentration have been studied in detail in the previous chapters. The OTT charts and the related reaction rate constant calculations can be used to determine the effect of time, temperature and concentration on the extent of individual reactions. For example, the OTT plots can be compared under different conditions, and the critical conditions can be identified, as can also the processing "area" for optimum levels of the important product attributes.

This gives the basis for either improving a present process or designing a new one. More generally, for the future it leads food processing into an expanding area of knowledge, developing it as a more advanced processing technology. In the past, the complexity of food processing has seemed a barrier to applying the reaction technology widely used in the chemical and pharmaceutical industries. With the modern techniques of product development, product attributes and compositions are well recognised in the food industry, and the reactions leading to them are now being increasingly identified.

### 4.8.2   Improving existing processes

Processes are usually specified by the critical product attribute, very often safety. In the past, there was optimisation of food processing, but it was done as a craft by craftspeople. When the craftspeople were highly competent, the results were very good; but they were not able to take advantage of the systematic methods of modern technology. Therefore, their results were limited by the knowledge and instrumentation available; they were not always reproducible, and not easily transferred to new operators and operations, or to automatic control equipment. Much advanced optimisation is now practicable.

Various processing regimes can be compared for their effects on the reaction rates and therefore the levels of the product attributes. The dairy industry has recognised this over many years and has developed new processes such as high temperature/short time (HTST) heating. They have built, from large-scale research in the laboratory and in the plants, knowledge of reactions and the effects of the processing conditions on the reactions. Information technology has given them the tools to relate the levels of product attributes (from quality assurance records) to the processing conditions (from the plant records). From this and the laboratory research, they have built models of the process. These models can then be used for process control to improve the effectiveness and the efficiency of the process. Another food industry developing these approaches to processing is the Australian and New Zealand wine industry, which has moved from a craft to large-scale technological industries.

Some food industries may think that, for them, it is too difficult; they have multiple raw materials, and are producing a wide variety of the products on the same plant. But they can also analyse what are the fundamental product attributes in all the products and the reactions causing them. This may simplify what they think is a confused situation, and so lead to more systematic processing. They can examine the possible variations of the process conditions, and their effects on the reactions related to the fundamental product attributes.

Perhaps the greatest use has been in the prediction and control of the shelf-lives of foods during distribution and marketing. Because the times are comparatively long and the reaction rates are usually slow, predictions can be well within the accuracy of the distribution control. As has been seen in the examples in Chapters 3 and 4, shelf-lives can be predicted for storage at all temperatures, from frozen storage to tropical conditions. Therefore, reaction technology has proved a

useful tool in design and control of distribution systems. Computer software programs based on such predictions have been developed and are available (21).

Processing possibilities, such as speed of heating, accuracy and uniformity of process control, can be studied using OTT charts, and Arrhenius plots. Reaction rate constants and sensitivities can develop a "feel" of the process as regards time and temperature.

### 4.8.3    *Application to new product design and process development*

The recognition of the inter-relationships between product design and process development in some companies has led to some fruitful innovations. Food product design came from the craft base of the chef and the small food processor, of empirical (although knowledgeable) try and taste. But, in recent years, the technological knowledge has grown. There is an ever-increasing knowledge of product attributes and the methods of measuring them – chemical, physical, biological and sensory. Perhaps the greatest advances have been in sensory science, with the increasing identification of attributes, quantitative methods of measuring them and correlation with physical methods.

This has led to the use of experimental designs to study the effects of different levels of ingredients/raw materials and processing conditions on the individual product attributes, and the optimising of the important product attributes. By use of the OTT charts for different product attributes, the "ball park" areas for time and temperature can be identified, as described in the section on multiple reactions, and these can be used as the basis for the experimental designs. Knowledge grows on the effects of different raw materials and other process conditions, such as pH, humidity, pressure and controlled modified atmospheres. This can be used as the knowledge base for product development. Examples of new products, which have already come from knowledge of reaction technology, are the various milk protein fractions that are manufactured for a wide variety of food products. These ideas will be examined further in the final chapter.

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*Think break*

In Think breaks in Chapters 1 and 2, you studied four food processes, identifying the critical and the important product attributes and the related reactions. Choose one of these food processes, identify the "envelope" of the process and study how you could optimise the process.

*    Identify and consider the present and possible processing conditions.

*    If available, study the OTT charts for the critical and important reactions. If not, use the data from the last three chapters as "general" reaction kinetics for comparison of the temperature and times for the different reactions.

*Contd..*

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*Think break (contd)*

\*    Identify the process envelope for the times and temperatures.

\*    Discuss how optimisation procedures might be applied to the possible processing conditions to secure the specified product.

\*    Design experimental procedures to study your suggested process(es).

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