#### 3.1 Introduction

In the previous chapter, rates of change in foods under constant processing conditions were introduced, but many food processes have changing conditions. What matters to the technologist controlling processing is the overall consequence of the change in the materials during processing – the outcome, the final product. The questions to answer are: what can be obtained from the raw materials, and what processing conditions produce this product? From a technical viewpoint, this means summing all of the step changes that occur over the total process time to give the final product attributes. Then the process conditions in each step can be manipulated to best advantage by the operators to give the optimum final product attributes. The extent of each reaction is controlled and thus the specified levels of the critical and important product attributes can be achieved. In this chapter, the processing conditions of time and temperature are studied. There are other conditions, such as relative humidity, pressure, packaging, and surrounding atmosphere, that also affect the reaction rates, and these are discussed later.

## 3.2 Steady Conditions of Time and Temperature

Early in the exploration of systematic food technology, questions were asked about the extents to which necessary processing times could be altered by varying processing conditions. One important practical application was heating under varied pressure, in which the working temperatures were dropped by processing in a closed container under a vacuum, or lifted by processing under increased pressure (1). Another practical application explored very extensively (2) because of its great consumer significance was killing microorganisms in heat sterilisation or reducing microorganism numbers in foods by heat pasteurisation. It was found, not surprisingly, that, as temperatures were increased, times required for a given process were decreased, and vice-versa. But perhaps more surprising were the early findings that these changes were systematic and consistent, and then later on that the changes could be fitted into the patterns of reaction technology and were therefore predictable.

It is first necessary to build the general patterns of processing reactions. This will enable the logic to be demonstrated, but it is more important to build up a logical platform on which future extensions and applications can be erected. The

immediate need is to determine how the necessary times relate to the working temperatures for a defined change in the food achieved through processing. Careful inspection of the equations developed in Chapter 2 show that this question has already been answered.

For a first order reaction, such as acid hydrolysis of sucrose, it was shown that:

$$t = (-1/k_{T}) \ln (C/C_{0})$$
or 
$$-k_{T} t = \ln (C/C_{0})$$

This tells us that the product of k and t is constant, for a defined extent of processing in which the targeted concentration goes from initial value  $C_0$  to a final value C. Now k changes by changing the temperature T; therefore, the required time t for the same extent of processing will also have to change with temperature change, and more significantly, change so as to keep the product kt constant.

There is nothing that is specific to first order except the form of ln ( $C/C_0$ ) arising from the integration. Therefore, the constancy of (kt) is equally true for a reaction of any order moving at a constant temperature between a particular initial value  $C_0$  and a particular final value C. This is very useful. It means that a graph of rate of change against temperature can be re-figured to produce a graph of reaction time against temperature. This can be called an outcome/time-temperature (OTT) chart. The theory for the OTT chart is shown in Theory 3.1.

# Theory 3.1: Basis for the OTT chart – integration of general rate equations

For the typical process looked at generally:

rate (r) = 
$$dC/dt$$
 = -  $k$  (T)  $f(C)$ 

where f(C) is a function of concentration (for a first order reaction f(C) is kC) and writing k(T) draws attention to k being a function of temperature (T), whereas  $k_T$  denotes k at a particular temperature level T.

## Theory 3.1 (contd)

Following the Arrhenius equation,  $k = k(T) = A \exp(-E/RT)$ 

and so 
$$dC/f(C) = -k$$
 (T)  $dt = -A \exp(-E/RT) dt$ 

in which the left-hand side (LHS) is some function of *C*, which can be integrated algebraically or numerically,

and the right-hand side (RHS) contains time and on integration gives the time needed for the change in the relevant food ingredient from  $C_O$  to C.

$$\int_{C_0}^{c} dC / C = - \int_{0}^{t} k dt = -kt \text{ if k is constant}$$

=  $\ln C/C_0$  for a first order reaction

=  $(1/C - 1/C_0)$  for a second order reaction, and so on.

If temperature varies with time, along some experimental temperature/ time curve, T = T(t) then k is not constant over the time and so.

$$\int_{C_0}^C dC / C = - \int_{0}^t k \{T(t)\} dt$$

The LHS is unchanged but the RHS has to be integrated, either analytically if T(t), expressing T as a function of time (t) can be suitably expressed (27), or numerically/graphically if it cannot.

For a defined change between the concentrations  $C_0$  and C, and irrespective of the form that the relationship takes (zero, first, ...order), the LHS is constant between any particular limits  $C_0$ , C, and therefore the RHS must total to that same constant sum.

If measurements are made of k at different temperatures and the data are found to fit the Arrhenius equation, on plotting  $\ln k$  against 1/T where T is measured in degrees K, a straight line with slope -E/R results. This is the traditional Arrhenius plot.

For a particular concentration extent of a first order reaction, the product kt is constant and this can be put = K. Then:

$$\ln k$$
 is equal to  $\ln (K/t) = \ln (K) - \ln (t)$ 

and so a plot of  $\ln(t)$  against 1/T will also produce a straight line with slope E/R but displaced vertically by  $\ln(K)$ . This result is equally true for orders other than one. This is the basis of the OTT chart.

The Arrhenius graph can thus be converted to the outcome/time-temperature (OTT) chart, remembering that each line on this chart connects conditions for one specific extent only. For the hydrolysis of sucrose, the Arrhenius plot of reaction rate constant against the reciprocal of T (1/T) (Fig. 2.3) can be converted to a similar plot of time against the reciprocal of temperature in degrees K (Fig. 3.1(a)) or into an OTT plot of time against degrees C (Fig. 3.1(b)). The X-axis in the OTT chart is a linear scale in degrees C.

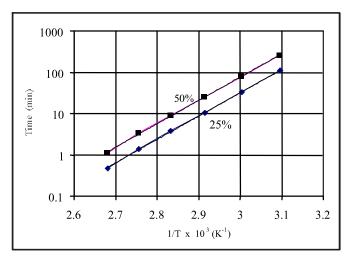
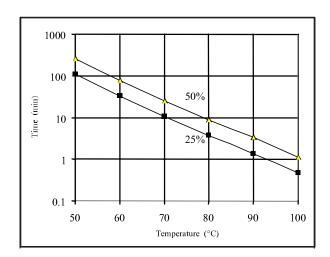


Fig. 3.1(a). Sucrose hydrolysis – "Arrhenius" plot for time



Data from International Critical Tables (3)

Fig. 3.1(b). Sucrose hydrolysis – OTT chart

Note that the slopes of the lines are opposite because of temperature and reciprocal temperature. Looking carefully at these graphs will show that, whereas the lines in Fig. 3.1(a) with reciprocal temperature in degrees K are straight, those in Fig. 3.1(b) with linear temperature in degrees C are slightly curved. The reciprocal temperature correlation fits the data slightly better than the straight temperature, although the discrepancy is small and can be ignored within the

tolerances of most processing specifications. Although these are not equivalent mathematically, they are approximately so, and more nearly so as the total temperature interval gets smaller (say 10 or 20 °C). For intervals of 10-20 °C, either can be used for calculations with accuracy as good as that of the available data. Experimental data for most reactions for small temperature intervals show that a plot of both 1/T and also degrees C against the logarithm of the reaction time to reach a particular outcome follow a straight line. For larger intervals, the 1/T plot generally fits better, so should be preferred unless comprehensive data show otherwise.

The OTT presentation is a very powerful and useful tool, and one that has a number of applications in food process technology including on the factory floor. The OTT chart can be drawn for various outcomes such as 25% reacted, 50% reacted, and so on, with a separate line for each outcome as shown in Fig. 3.1(b). These clearly show the effect of time and temperature on the outcome. They can readily be extended to give data for any desired degree of hydrolysis that may be appropriate to a particular processing need. From such Arrhenius/time, and OTT charts, time and temperature combinations can be chosen for specified product attributes.

## Think break

- \* Consider and reflect on the outcome/time-temperature (OTT) chart and the possible uses in food processes with which you are familiar.
- \* If in a particular sugar boiling, the aim is to reach 50% hydrolysis, how long would this take at 50, 80 and 100 °C?
- \* Explain how the sucrose hydrolysis OTT chart could be directly applied by an operator boiling jam in vacuum pans where the process steam supply variation can cause a temperature variation of 10 °C.

When the conditions of processing are constant, and in our case this implies at constant temperature, the extent of the reaction is obtained from the rate per unit time multiplied by the time interval over which the process continues. For this use, the symbol  $\nabla$  is sometimes used for convenience; therefore  $\nabla = kt$ .

For a first order process,  $\nabla = -\ln C/C_0$ Note  $\nabla$  is dimensionless

It is sometimes expressed in terms of decimal (D) reductions. For example:

• when  $C = 0.01C_0 = C_0 / 10^2$ , this is called a  $10^2$  or a 2D reduction (and  $\nabla = -\ln 10^{-2} = -2.303 \log 10^{-2} = 4.61$ );

• when  $C = C_0/10^3$  this is called a  $10^3$  or a 3D reduction (and  $\nabla = -\ln 10^{-3} = 6.91$ ), and so on.

This nomenclature is particularly convenient for processing changes in bacterial numbers, or counts, and these may reach 10D or more.

# 3.3 Variable Conditions of Time and Temperature

In a process, conditions may vary as the process goes along; for example, on heating a starch solution in a jacketed pan, the temperature will rise gradually from ambient to boiling, i.e. 100 °C. There can also be variations in temperature with space – for example, in a can, where parts heat faster depending on the consistency of the food material and the type of steriliser (static or continuous).

# 3.3.1 Sequential changes in temperature with time

Where temperatures are changing during the process, the times can be converted to the time at a reference temperature. Then the times can be added to give the total time of processing at the reference temperature.

Temperatures can vary over quite a wide range, but for food processing there are some *reference temperatures* on which attention can readily be focused.

- Boiling point of water at atmospheric pressure, 100 °C. Water is a universal constituent of food; often it is the major component, and at altitudes not too far from sea level water boils at close to 100 °C over the normal ranges of atmospheric pressure variation.
- Two atmospheres absolute pressure, under which pressure water boils at 121 °C (250 °F). This is based on pressure processing, and canning in particular, where an early and convenient 'pressure cooking' level was at around two atmospheres absolute pressure (or one atmosphere above atmospheric pressure). Under this pressure, water boils at a temperature of close to 250 °F, so this, and nowadays its Celsius equivalent of 121.1 °C, which can be rounded to 121 °C, forms a good reference temperature.
- Frozen storage, -18 °C (0 °F). Below-freezing temperatures for frozen storage have never really needed a reference temperature. A quite widely encountered reference temperature has emerged of 0 °F or -18 °C, possibly for no better reason than that it is a conveniently low level for much of frozen food storage and is such a nice round number on the Fahrenheit scale.
- Chilled storage. There is no fixed reference temperature, but many chillers operate around 4 °C. With superior control, they can be operated down to just above food freezing temperatures of around -1 °C. Reference temperatures of 0 °C and 5 °C have been used.

#### Think break

For two food processes – concentrating milk in an evaporator, and chilling of fruit after harvest:

- \* What are the important temperatures in the two processes?
- \* What is the temperature history in each process how does temperature change with time?
- \* What reference temperatures could be useful in standardising the temperature criteria?

So for a constant temperature process,  $kt = \nabla$  and is constant for a given level of processing. If  $k_{ref}$  is the value of k at the reference temperature, then a value of  $t_{ref}$  can be calculated:

$$t_{ref} = \nabla / k_{ref} = k_{T} \cdot t_{T} / k_{ref} = (k_{T} / k_{ref}) t_{T}$$

where  $k_T$  is the reaction rate constant and  $t_T$  is the processing time during a certain step of the process at a constant temperature, T.

*F values* are encountered in canning and sterilisation, where the reference temperature is 121 °C, and  $t_{121}$  has been given a special symbol of its own, F. More strictly speaking, any relativities involve not only a reference temperature but also the sensitivity of the rate of reaction to temperature. Then either activation energy (E) or z or  $Q_{10}$  values should be designated for the reference data.

For example, in sterilisation,  $F_x^y$ , where x and y are the appropriate z and temperature reference values, traditionally  $F_{10}^{121}$  is given the symbol  $F_0$ . So a whole range of equivalent processes arises, such that the extent of sterilisation at any temperature can be expressed in terms of an equivalent time of processing at the reference temperature by working out its  $F_0$  value, remembering that this refers only to the standard 'canning' system with z value of 10 °C.

C values have been defined, particularly for cooking where the reference temperature is the temperature of water boiling under atmospheric pressure. So the time of heat processing at  $100 \,^{\circ}\text{C}$ ,  $t_{100}$ , can be called the 'cook time' and given its own symbol "C". Equivalent cook times for processing can be worked out at  $100 \,^{\circ}\text{C}$ . Examples are cooking at much elevated locations, where the atmospheric pressure, and therefore the boiling temperature of water, are substantially lower than at sea level, cooking at some non-boiling temperature, and comparisons between cooking at different temperatures are sought. Strictly, a cook time should define the reference temperature ( $100 \,^{\circ}\text{C}$ ) and the z value. In Example 3.1, values of  $F_0$  and C for sucrose hydrolysis are calculated.

## Example 3.1: Determination of $F_0$ and C values

# (1) Find the $F_0$ value for a process taking 1 min at 128 °C.

From the basic relationship, kt = constant

Therefore  $k_{T1}$ .t  $_{T1} = k_{T2}$ .  $t_{T2}$  and so  $t_{T1} = t_{T2} (k_{T2} / k_{T1})$ 

But "z theory" holds that  $k_{\text{T2}}$  / $k_{\text{T1}}$  =  $10^{(\text{T2-T1})/z}$ 

And for standard  $F_0$  calculations, z = 10 °C and for  $T_1 = 121$  °C,  $t_{T1} = F_0$ 

So t 
$$_{\text{T1}} = F_0 = t_{\text{T2}} \, x \, 10^{_{(\text{T2}-\text{T1})/10}} = t_{\text{T2}} \, x \, 10^{_{(\text{T2}-121)/10}}$$

Now for the example  $T_2 = 128$  °C and  $t_{T2} = 1$  min

So 
$$t_{121} = F_0 = 1 \times 10^{(128-121)/10} = 1 \times 10^{0..3} = 1 \times 5.0 = 5.0 \text{min*}$$

(\* This calculation has been chosen to illustrate the asterisked term in Example 3.3)

Compare by "Arrhenius theory" for z = 10 at 121 °C, then E = 297 kJ/mol and  $T_1 = 394$ K,  $T_2 = 401$ K

$$(k_{T2}/k_{T1}) = \exp\{ E/R (T_2 - T_1) / T_1 T_2 \}$$
  
=  $\exp\{ 297,000/8.314 (401-394)/394.401 \}$   
=  $\exp 1.58 = 4.9$ 

and so 
$$t_{121} = F_0 = t_{T2} (k_{T2}/k_{T1}) = 1 \times 4.9 = 4.9 \text{ min}$$

# (2) Find the C value for a cooking process of 10 min at 95 °C.

To show how equivalent times other than  $F_0$  can be calculated, find the C value of a cooking process of 10 min at a temperature of 95 °C. For this, the reference temperature is 100 °C and the z value 24.7.

So C = 
$$t_{100}$$
 = 10 x 10 (95-100)/24.7  
= 10 x 10<sup>-0.2</sup> = 10 x 0.63 = 6.3 min

and writing this formally  $C^{100}_{24.7} = 6.3$  min.

This could also be worked out by Arrhenius relationships.

Notice that C here should have been designated  $C^{100}_{24.7}$  (100 being the reference temperature in degrees C and 24.7 the chosen z value for which  $C_0$  is sometimes used.).

#### Think break

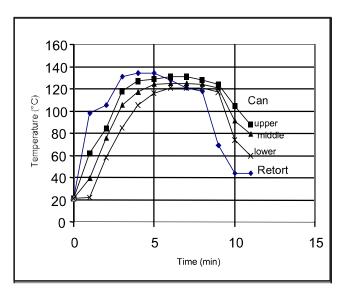
Reflect on the following time/temperature relationship as the measures of temperature sensitivity for reactions in foods:

- \* contrast OTT charts using degrees C and Arrhenius time plots using 1/T as the x-axis.
- \* contrast activation energies with z values
- \* suggest processes in which it would be useful to use each method.

# 3.3.2 Space and time/temperature

The relationship of temperature variations to reaction rate constant variations merits further attention because it introduces important areas that complicate not only calculations of reactions in food processing but also the outcomes in the final food product.

In a steam-heated experimental static retort, temperature measurements were taken during a complete process cycle at three different positions along the centreline of a can, held vertically and stationary and filled with water (4). The temperatures were carefully measured, using fine thermocouples mounted in a sealed commercial-sized can (7.8 cm x 11.6 cm) with a liquid fill and air headspace, and were recorded at intervals during the process cycle. A group of these temperatures is shown graphically in Fig. 3.2.



Data from Packer (4)

Fig. 3.2. Temperature profiles in a can of water during static retorting

The time/temperature graphs are plotted from experimental data for three different points: one at the geometric centre (middle), and two on the long centre line at the upper and lower third-points. This shows the considerable variation of the temperatures at different times during the processing, and therefore of the reaction rates. Note, in this case, the temperatures of the lowest point in the can rose more slowly than those of the middle point; in the case of more solid packs, the centre could be expected to rise the slowest.

 $F_{\rm O}$  values were calculated at these three points in the can for spore destruction (see Example 3.3). Such data can be incorporated in calculations working towards a volume-based average, in other words adding the various component concentrations weighted in proportions to their relative volumes. Then the final number of organisms present in the total volume of the food can be obtained by multiplying that volume by the average concentration of the organisms.

Complications that can arise include the following:

- Inadequate mixing for example in semi-solid foods in static retorts can cause variation in composition and counts.
- In many foods meat for example the initial muscle tissue is sterile and the only contamination may be on the surface, so that a volume average is not meaningful. Mincing or cutting the meat will alter this situation, but may still produce great variations in counts per unit weight throughout a volume.
- In processing liquid foods say, by pumping them through a pipe heat exchanger, the liquid velocity distribution is not uniform, often with an average velocity only about half that at the centreline. This means that an element on the centreline spends only half as long in the process as an average element, let alone one in the slowest moving regions towards the wall of the pipe.
- In food that is non-homogeneous, with aggregates of one component in a continuous mass of another, there is variation in process extent between the liquid and the solid. Peach halves in syrup are a simple example; casein micelles in milk are a more complex one.

These problems can be tackled by considering residence times at particular positions in the food being processed, looking at both the temperatures and the process time of all of the parts of the food where these are different. Averages, extremes, and particular elements can all be critical. The analysis is complex and sometimes can be safely ignored, but the processor has to be alert and aware that it may be important and that it can, if necessary, be explored in detail.

#### Think break

Consider the variations in temperature at different levels in a 2 kg beef roast of 10 cm minimum dimension, heated in an oven at 170 °C to an internal temperature of 65 °C in the centre.

- \* Estimate the initial and final temperatures at the different parts of the food structure.
- \* Sketch the possible final temperatures from the outside to the inside of the roast.
- \* What are the required product attributes at the different levels of the meat?
- \* Identify the important reactions occurring in the meat that affect the final product attributes.
- \* Identify the reaction rate constants for these reactions or predict comparative rates for the reactions, e.g. from Table 2.IV.
- \* Reflect on the consequent relative extents of processing that might occur at different points in the foods.
- \* Reflect on how some foods, such as roast meat, depend on these temperature differentials to provide structures such as the crust and the crackling.
- \* What would be the impact of different cooking times and oven temperatures on the product outcomes?

## 3.4 Microbiological Outcomes from Process Reactions

Microbial constituents of foods can be treated in many respects as concentrations, that is by considering the number of viable organisms, normally measured as colony-forming units (cfu) in unit volume, although sometimes the number per unit surface area is more pertinent. These numbers change, by growth, by decay, or by processing to deliberately reduce or increase them.

# 3.4.1 Microbial growth

Microorganisms increase by division, and it has been found experimentally that, after initiation, called the lag phase, with no or little growth in cell numbers, the divisions occur at a fairly constant rate and give rise to logarithmic growth in cell numbers. The number of cells dividing is proportional to the number of cells present; the logarithmic phase produces a first order growth in numbers. So the

changes in cell numbers correspond to a first order reaction. The numbers cannot increase indefinitely in this way, and they reach a limit (5), which seems to represent more or less a universal 'house full', of somewhere around  $10^9$  to  $10^{10}$  per ml. Since it is the numbers that most affect quality, it is the logarithmic phase that is critical. Treated as a first order increase, this can be calculated by the reaction rate procedures. For historical reasons, the symbol for the reaction rate constant used for microbiology is  $\mu$  (the Greek letter mu), but for present purposes it is convenient to use k to emphasise the consistency of processing. The value of k will vary with the species and the environment, and has to be found by experimentation.

The growth has been found to behave generally as shown in Fig. 3.3, displaying at first virtually static numbers for a period known as the lag phase, then a logarithmic growth phase during which cell division occurs at constant time intervals, and finally the growth tails off and numbers decline.

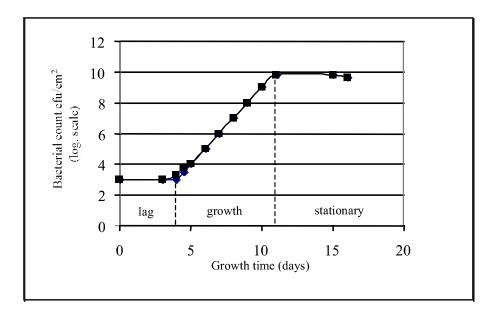


Fig. 3.3. Representative bacterial growth curve

For the logarithmic phase,  $\mathbf{kt} = \mathbf{ln} \ \mathbf{N/N_0}$  (Note the positive sign, with growth) For the total growth, time = (t + the time for the lag phase). An example of this calculation is shown in Example 3.2.

# Example 3.2: Microbial growth in meat wrapped in polythene (from Zamora & Zaritzky (6))

Freshly killed meat is sterile but can be contaminated during the initial processing and storage.

**Minimum levels:** Some degree of contamination is inevitable but, of course, procedures are rigorously mandated to reduce this to a minimum, which is normally about 10<sup>3</sup> of general colony-forming units (cfu) per square centimetre. At times, it may be slightly lower and the actual incidence depends on both dressing methods and the particular region of the carcass considered.

**Maximum levels:** The increase in viable organisms depends upon local circumstances, principally temperature, moisture levels, and the gaseous environment, especially if this is deliberately modified, for example by packaging. Spoilage becomes evident with manifestations such as odour, slime, and sometimes discoloration. These start to be apparent at surface microbial counts of about 10<sup>7</sup> - 10<sup>8</sup> cfu cm<sup>-2</sup>.

In studies of bacterial growth on meat in a polyethylene wrap (giving essentially aerobic conditions because of the high oxygen permeability of thin polyethylene) it was found by Zamora and Zaritzky (6) that *Pseudomonas* species had a constant growth rate of 0.795 day<sup>-1</sup> and had a lag time of 5 days at 0 °C. Assuming an initial count of 10<sup>3.5</sup> cfu cm<sup>-2</sup>, calculate the time available before the count will reach 10<sup>8</sup> cfu/cm<sup>-2</sup> at 0 °C.

Total time to reach  $10^8$  cfu/cm<sup>-2</sup> = lag time + logarithmic growth time = t That is the logarithmic growth "time" = {(total time) - (lag time)}

$$= (t-5) \text{ days at } 0 \text{ °C.}$$

$$\ln \text{ N/N}_0 = k(t-5)$$
and so 
$$\ln(10^8/10^{3.5}) = \ln(10^{4.5}) = 2.303 \text{ x } 4.5 = 10.4$$

$$= 0.795(t-5)$$

$$t = (10.4 + 0.795 \text{ x } 5) / 0.795 = 14.4/0.795$$

$$= 18 \text{ days}$$

Total available time is 18 days.

There is some evidence that lag times vary with temperature and that the variation can be correlated by an "Arrhenius" type dependency.

*Outcomes* can be specified at a maximum, shown by deteriorations in the food, such as production of slimes, discoloration or bad odours related to the numbers of microorganisms. This is not usually an exact relationship, and often there is difficulty in setting the upper limit as a microbiological standard. So far as pathogenic organisms are concerned, their incidence is much more arbitrary, as also is any question of an upper end level that can be tolerated. Of course, ideally no level of pathogen is tolerable. But pathogens exist, and they may arise in practical situations. However, there are levels below which they cannot be detected in the food by any present microbiological method. This is about 1 cfu in 25 g of food, corresponding to  $4 \times 10^{-2} \, \text{g}^{-1}$ . In infection and epidemiology studies, there has been work on inoculum levels below which it seems particular organisms cannot establish themselves in hosts (infective levels), but these are only partly definitive, and vary with individuals as well as with their state of health. So working from these is at best difficult, although it is sensible to take them into account when dealing with any defined organism.

A practical way of handling the permitted numbers is to determine experimentally the detection level for the organism, say the 4 x10<sup>-2</sup> g<sup>-1</sup>, and to set this as a maximum. This gives a starting prescription for handling a difficult and important situation. The question of shelf life can then become one of determining pathogen growth rates, and calculating how long the product would take to reach the minimum measurable contamination level at that rate. This raises the difficult issues of the pathogen source, and the initial numbers involved. Some of these points are discussed in a review paper by Simoni & Labuza (7).

The influence of temperature on microbial growth rates has been studied extensively (8). Growing patterns of different organisms fall into temperature bands, and have been classified according to their temperature ranges for growth: psychrophilic (0-30 °C), mesophilic (10-40 °C) and thermophilic (30-60 °C). The rates of growth increase as temperatures rise within their growth ranges, then decrease and finally cease. A reasonable logarithmic fit, growth rate with temperature, has been found for many organisms over useful ranges of growth, so allowing an Arrhenius type equation; also sensitivities and z values can be used for prediction.

As an alternative for temperature coefficients, a parabolic equation has been suggested labelled the square-root relationship, which corresponds better to some data (8,9) and which has been further elaborated (10). Additional constants in empirical equations can always be introduced to improve fits, but both the precision of the available data and the appropriateness of the applications have also to be taken into account.

For many practical purposes it does not seem critical which is used (11,12). A straightforward constant sensitivity approach provides some feel for the quantities, relates them to other temperature coefficients, and has proved helpful in many practical situations in food processing such as that illustrated in Fig. 3.9. More elaborate treatments can be added as circumstances justify.

### 3.4.2 Microbial death

When heated and held above the temperature ranges for growth, microorganisms die. Experimentation has shown that the death rates (the number of cells dying per unit time) at any particular temperature are related to, and in fact substantially proportional to, the number of organisms that are viable. Therefore, death rates conform to first order kinetics; at least this is a good approximation over what might be called normal numbers. When numbers become much reduced, then experimental results and any possible rationale become more tenuous and harder both to reach and to justify (13).

Temperature coefficients of death rates have also been found to fit reasonably to logarithmic relationships, so the z and the Arrhenius relationships can be applied. In fact, it was in the context of bacterial death that the z concept was first developed as it seemed a natural measure for the temperature coefficient.

The question of survival is complicated by the need to extend probability ranges right down to considering very small numbers, estimating the chance of retaining one viable organism in large numbers of food entities – for example, cans. This need was shown from the early experimental work. Essentially, the workers started with maximum numbers of viable spores, of the order of  $10^{10}$  to  $10^{11}$  in each of ten tubes. They heated these tubes as quickly as possible, then they measured the minimum time of holding, at a particular constant elevated temperature, after which there was no viable spore found in any of the tubes. This time was termed the 'thermal death time'. Repeating this for the same organism at different temperatures led to a thermal death time curve, relating thermal death time to temperature. The effective reduction in total viable spore numbers was from about  $10^{12}$  to below 1 in the ten tubes, and so the reduction ratio N/N<sub>O</sub> was  $10^{-12}$ , and  $\log N/N_O = -12$  (or to base e,  $\ln N/N_O = -12$  x 2.303 = -27.6).

The concept is analogous to the logarithmic change ratios already seen for other components in a food on processing *following first order reactions*. But there is a decided difference with the magnitudes of bacterial death ratios. For many chemical ingredient components covering a logarithmic (base 10) change ratio of 1 or 2 is sufficient (corresponding to a 90% or a 99% decrease, say, in a component), and 4-5 is larger than most changes encountered in food processing, including microbial growth. In bacterial death, however, the logarithms of such reduction ratios, at least in theory, are 12-15 or even larger. Justification for such wide ranges, and extrapolations, is that, when applied to canning, this early theory not only survived much experimentation, but also seemed to explain observations in canning and provided a useful theory for commercial practice and experience. It has also proved demonstrably safe for most foods.

Current research is active in the areas of continuous processing, in tubular or plate heat exchangers, and where the food contains discrete particles, lumps such as meat balls or mushrooms (14). It is well known that velocity distributions of fluids flowing within a pipe, or between plates, are not uniform. But, even when the fluid is non-Newtonian, a fair guess can be made at the actual velocities and the fastest, where process time is least, quantified (15). The fluid part of the pack

can also be temperature/time monitored reasonably easily. What happens inside particles is not so accessible. Even though contamination is generally only on surfaces, it can be inside and there it is difficult for heat to penetrate and even more difficult to be sure that it does so everywhere adequately. Some research investigations have explored this situation, using inoculated food particles (16). Based in part on this work, the US regulatory authorities (USFDA) have quite recently agreed to consider licensing continuous processing under such circumstances, although it is not certain that manufacturers have taken this up. In Europe, limited continuous commercial processing of foods containing particulates (for example mushrooms in a liquid) is in use, and processing specifications seem to be adequate judging from their results.

#### Think break

A habit has grown in the food science literature of assessing temperature sensitivities for bacterial deaths in z values and for chemical reactions in activation energies. Discuss the logic and the practicalities of this approach.

# 3.5 Process Integration

So far we have been considering constant temperature processes, and we have also shown how to put times for real processes, operating at different temperatures, in terms of time for an equivalent extent of processing at a reference temperature. Therefore, we now have the knowledge to deal with normal food processing in which temperatures vary during the course of the process.

## 3.5.1 General principles

Integration is done by dividing the total process time into sufficiently small pieces during which the temperature is effectively constant, and converting the times for each of these into their equivalent times at the reference temperature. The total time of the whole process is the sum of the individual times. Mathematically, this is equivalent to integration. In fact, integration can be used formally to do exactly the same thing if an analytical expression can be found for the time/temperature relationship (17), but mostly it cannot without rather sweeping approximations being invoked. Although formal integration may seem more elegant, it is no more accurate in practice because of inevitable assumptions that have to be made to enable the mathematical equations to be handled, and it is often no quicker as both can be programmed quite readily using computers.

The basis for the "step" process of integration is shown in Theory 3.2.

# Theory 3.2: Basis of the 'step' process for integration

For a 'step' process at a constant temperature:

$$\begin{array}{ccc}
c & t & \\
- \bullet & C / C & \bullet & k dt & = k_{T1} t_{T1} & = k_{T2} t_{T2} & = \text{constant} \\
c_{O} & & & & & & & & & & \\
\end{array}$$

and so 
$$t_{Tl} = (k_{T2}/k_{Tl}) t_{T2}$$

This allows calculation of the time at  $T_1$ , the reference temperature, equivalent in processing outcome to the actual time at  $T_2$ .

Now  $k_{T2}/k_{T1} = 10^{(T_2-T_1)/z}$  by the z method

So for this one step  $t_{TI} = t_{T2} 10^{(T_2 - T_1)/z}$ 

If, for example, for a first order process, f(C) = 1/C

And choosing  $T_1 = 121$  and z = 10 (for standard  $F_0$ )

we have 
$$t_{121} = t_{T2} 10^{-(T_2 - 121)/10} = \Delta F_0$$
 by definition of  $F_0$ 

where  $\Delta$  F<sub>0</sub> is the step contribution to F<sub>0</sub>

And so 
$$(\Delta F_0) = -(1/k_{Tl})$$
.  ${}^{c}_{O} C = -(1/k_{Tl})$ .  $\ln C_1/C_0$ 

$$\Sigma(\Delta F_0) = F_0 = -(1/k_{121}). \left[ \ln C_1/C_0 + \ln C_2/C_1 + \ln C_3/C_2 + \dots \right]$$

$$= -(1/k_{121}). \left[ \ln C_n/C_0 \right]$$

$$= t_{T1} 10^{(T_1 - 121)/10} + t_{T2} 10^{(T_2 - 121)/10} + t_{T3} 10^{(T_3 - 121)/10} + \dots \right]$$

taking the process over n steps at temperatures  $T_1$ ,  $T_2$ , ..... $T_n$ , which can be chosen to suit particular circumstances.

In words (total  $F_0$ ) = (sum of "step" $F_0$ 's), each calculated for its individual temperature by the above formula.

#### 3.5.2 Sterilisation/canning

The actual method used for the integration can take many forms. One is to assemble the total  $F_0$  value from piecemeal step contributions, working from calculated times for the reference temperature derived through z value (or Arrhenius) conversions applied to an experimental heat penetration curve. In the canning literature, this has a special name and it is called the General Method. To

do it, you need the time/temperature curve, and the kinetic data for the significant reaction(s) in the process – in canning, usually critical spore death.

An example of a simple calculation is shown in Example 3.3.

# Example 3.3: An experimental investigation on sterilisation in a can

In the canning experiment shown in Fig. 3.2, the temperatures during the retorting cycle were:

	]	Heating cycle ] [				]				
Time (1	nin)	3	4	5	6	7	8	9	10	11
Temperature (°C)										
	Retort	131	134	134	128	121	118	69	44	44
In can	- upper	118	127	129	131	130	128*	124	104	88
	- middle	105	117	124	125	125	124	121	91	79
	- lower	85	105	116	121	121	121	117	74	60

Calculations were made on the numerical data for each set, working out the equivalent processing time at the standard temperature of 121  $^{\circ}$ C from the observed time at temperature T with z = 10 by using the relationship

$$k_{121} = k_T 10^{(T-121)/10}$$

where  $k_{121}$  is the reaction rate constant at 121, which was set at 1, and the T was temperature in degrees C. So for time interval of 1 min at temperature T  $\Delta$  F<sub>0</sub> =  $k_T/k_{121}$ 

A sample calculation for the  $\Delta$   $F_0$  term, at time 8 min, 128 °C, is shown in Example 3.1.

The relative values of the reaction rate constant at the various temperatures were:

Elapsed time (min) Δ F <sub>0</sub> (min)		3	4	5	6	7	8	9	10	11
	Retort	10.0	19.9	19.9	5.0	1.0	0.5			
In can	- upper	0.5	4.0	6.3	10.0	10.0	5.0*	2.0	0.01	
	- middle		0.4	2.0	2.5	2.5	2.0	1.0		
	- lower			0.3	1.0	1.0	1.0	0.4		

(...indicates regions where data have no appreciable effect on the total integrals)

# Example 3.3 (contd)

```
Integration F_0 = \sum (k_T / k_{121} \Delta t) = \sum k_T / k_{121}
Because \Delta t = 1 min, being all 1-min intervals
Therefore \Delta F_0 = k_T / k_{121} for each temperature
```

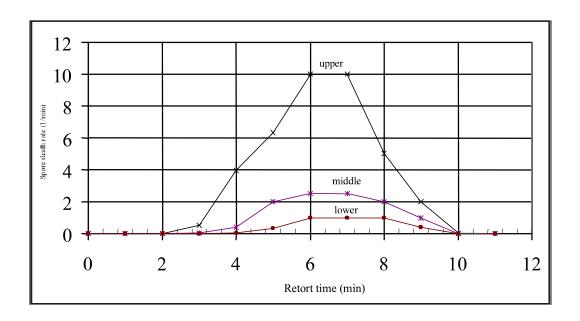
Adding these component  $\Delta F_O$  values for each minute of the processing together, over the temperature history, gives the total  $F_0$  of the process for each element of the can.

Therefore  $F_0$  values can: top = 37.8, middle = 10.4, lower = 3.7, and for retort = 56.3

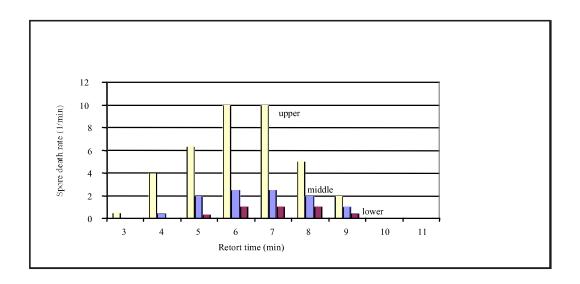
The numbers have been rounded and the integration is simplified to make the calculation transparent. Both the experimentation and the integration can be improved if more precise figures are required.

The  $\Delta F_0$  are graphed in Fig. 3.4(a) with line graphs and Fig. 3.4(b) with bar graphs, which also illustrate the integral that is the area below the respective lines.

It is interesting to consider the three measurements of the  $F_0$  criterion, which were taken at the different locations on the centre line in the one representative can during one process cycle: 37.8, 10.4, and 3.7 min. These figures demonstrate clearly the point that, if the process adequacy is determined by the fate of potential spores at the least processed region (in this case with an accomplished measured  $F_0$  of 3.7 min.), then other regions, and they could be large proportions of the food volume, can receive a good deal more processing. From the point of view of health hazards they are all safe if the minimum  $F_0$  is safe. But other parallel reactions induced by heat at the same time in the can will have continued on average well beyond any optimum. Since these are all almost certainly detrimental to quality, and some may be substantially so, this means that quality suffers.



(a) Linear plot



(b) Bar chart

Temperature data from Packer (4)

Fig. 3.4. Rates of spore destruction in an experimental can during processing

One evident problem arises if not all parts of the food being processed have the same time/temperature relationship. Quick reflection will show that, unfortunately, this is true of virtually every practical process, although its impact will vary. Traditionally, this problem has been met by selecting that part of the food that has the lowest F<sub>0</sub> value, the least processed part, and taking the F<sub>0</sub> value for this as also being applicable to the whole food. This assumes that, if all other parts have more processing, they will at least be subject to adequate treatment, and that the critical aspects of the processing are safety and prevention of spoilage, which is true of canning. But it also includes other assumptions that are more equivocal. For example, the theory of canning and sterilisation depends on probabilities, and therefore must include over-probabilities and under-probabilities cancelling each other out. This means that over-processing should be taken into account and offset against under-processing, but the method singles out only the least processed, which may be just a small proportion of the whole. It would not matter if overprocessing were positive, or at least neutral to the other product attributes, but almost always it is detrimental to nutrition and to sensory attributes, sometimes seriously so. These problems have been illustrated for canning, but they also apply to other processing.

There are other numerical methods of integration, all essentially equivalent to the so-called General Method. Today, there is computer software to determine  $F_0$  values from a temperature record of the processing. The software includes programming the working on a computer spreadsheet, and is a simple, easy and accurate way to reduce the work of numerical calculations.

In the past, the area under the rate/time graph was measured (counting squares, or using a planimeter, or using the trapezoidal rule or Simpson's method, or cutting out the area and weighing it) to carry out the integration. Unit area on this graph was determined by measuring the area for a known number of units. The appropriate unit area, the value of  $\nabla$ , which is the integral of  $k\{T(t)\}dt$  over that process can then be determined.

A drawback of all of the numerical methods is that they do not incorporate 'feeling' for the sensitivities of the calculated single answer to aspects of the process, which can be controlled by an operator or an instrument controller, and so can be manipulated during the course of the process to give a better product. Sensitivities can be explored through 'what ifs', especially accessible on a computer spreadsheet, but it can be rather a hit and miss procedure. Several time/temperature charts or process rate constant/temperature chart can be plotted on the same graph and the extents of processing compared visually.

Another alternative, covered in detail by Ball & Olsen (2), but also in many other publications (e.g. 18) is to fit heating and cooling curves by equations that can be integrated. This operates essentially by converting the temperature data for heating and cooling to a logarithmic form to fit a straight line and then measuring values for the slope (f) and intercepts (J) to define these lines. Situations can be then integrated and particular cases solved by using published tables.

Example 3.3. concerns sterilisation in an experimental static can. Much current large-scale processing involves agitating the cans, for example in hydrostatic

cookers, but even in these there will be temperature gradients and therefore variability of processing. This variability leads to overprocessing, which may be substantial, in all regions other than the least processed. To reduce overpressing, the safety criterion might be altered to work to a defined maximum probability of there being a viable spore in a can, as was discussed many years ago (19). This could also take the level of initial contamination into account rather than just spore reduction ratios, as in the current theory.

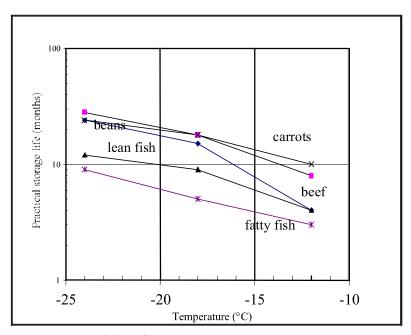
Such an approach has never found adequate acceptance. The reason may be, at least in part, that there remain substantial uncertainties in the theory and, therefore, the current factor of safety/ignorance is still considered necessary. Where up to hundreds of millions of cans are produced in each one of many factories annually and sold to large fractions of the population for them to eat, a cautious approach to safety is the only one possible. The canning industry has had an excellent record, using the theory outlined or close variants of it, and working from heat penetration curves applied to the least processed region in the can, however large or small this may be. Such an approach has been demonstrated through massive experience to be safe and robust wherever it has been properly applied, and this is a powerful argument.

# 3.5.3 Shelf-lives of frozen foods

There is a great deal of data available on the shelf lives of frozen foods, as described in Chapter 1. Results are summarised in many books and conference reports (e.g. 20-22). Comprehensive publications continue to come from the International Institute of Refrigeration (IIR), which include wide-ranging and specialised conference reports with many technical papers, and booklets on 'Recommendations for the Processing and Handling of Frozen Foods' (23), which are updated at intervals.

The straightforward experimental findings for frozen foods suggested an Arrhenius (and also corresponding z type) response, and this is illustrated in Fig. 3.5 (23).

One unique storage problem with frozen foods is their anomalous behaviour at temperatures near to the freezing point. In this region, 0 ° to -5 °C or so, only some of the water present is actually frozen as pure ice, with the remainder being still liquid. Inevitably, with water subtracted in pure ice, the solutes dissolved in the rest become more concentrated. Reactions in this liquid accelerate because reaction rates are higher at the higher concentrations. Lower temperatures systematically decrease the rate constants. The net effect, the resultant of the relative magnitudes of these two opposing influences of temperature and concentration in this critical region can be an increase as the temperature falls. So it is generally most undesirable to dwell in this temperature range any longer than needed for freezing. There may also be special problems with some foods – for example, complex reactions of protein constituents such as enzymes with changing salt concentration and pH, and changes in the size and location of ice crystals, which create mechanical stresses.



Data recommendations from IIR (21)

Fig. 3.5. Storage lives of representative frozen foods

Otherwise, the general behaviour is sufficiently consistent for the standard reaction technology procedures to be used with reasonable confidence. One that is convenient to use is a variant of the equivalent time concept used for  $F_0$ , in the form of fractional changes occurring in times during which temperatures are constant. This assumes *zero order reactions*, a reasonable assumption as the total extent of the reactions is normally relatively small.

For a particular frozen food held at a temperature of T  $^{\circ}$ C, the storage life has been found to be t months; then the average rate of quality loss per month at that temperature is 1/t per month. After x months, the loss is then x/t; after t months the loss is t/t = 1. The fractions of life lost, (x/t), thus determined can be added arithmetically to other corresponding fractions at other temperatures assuming that the storage lives at these temperatures are known, and the resulting sum compared with 1. Less than 1, some storage life still remains; greater than 1 means that the food has deteriorated further than permissible in terms of the acceptable quality measures. This is illustrated in Example 3.4 for the storage life of fatty fish.

## **Example 3.4: Storage life of fatty fish**

A consignment of a fatty fish has been held in storage for 3 months at -20 °C. It is then received into a different store held at -15 °C, and the store operator wishes to have some idea how long it can be held there while still leaving 20% of the storage life for subsequent handlers.

Suggested times for fatty fish to deteriorate to an unacceptable quality are shown in Fig. 3.5.

Reading from Fig. 3.5, and assuming steady deterioration rates, i.e. zero order:

Storage life at -20 °C = 7.5 months. Fraction of life already expired = 3/7.5 = 40% Fraction that must be retained = 20% and so 100 - (40+20) = 40% is still available for the -15 °C store, Storage life at -15 °C = 6 months

That is (40/100) x 6 = 2.4 months is available for holding in store at -15 °C.

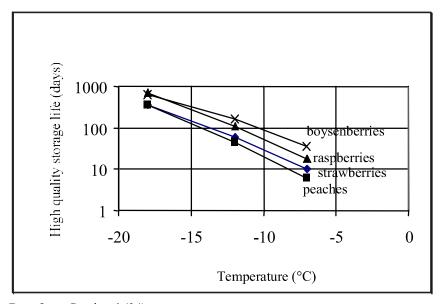
The numbers in the example have been kept simple, but the method has quite extensive application. It is kinetically justified, whatever the order of the deterioration reaction, so long as initial and end 'concentrations', or their corresponding sensory panel assessments, are maintained the same. Only for zero order reactions will intermediate concentrations behave *pro rata* to the percentages, but this seldom matters because there is little interest in intermediate stages and, in any event, discrepancies are normally small. Often it is only the beginning (fresh frozen) and end (total assessed life) points that are important. If the temperature/time line on the OTT chart is straight, the slope of the line (or the corresponding E or z values) can be used for interpolations.

Complex and multi-temperature storage histories can be accommodated so that they can include storage, transportation, and handling. Although the precision of the results is not high, it is as good as that of the actual storage-life data and is adequate for many purposes, such as cold-store stock management, and setting of store temperatures to give enhanced or designed product life where this is practicable.

Storage life experiments are never easy, and, if conducted at storage temperatures, from definition the experimentation takes 'storage' time and in freezer stores this can be years. If the temperature coefficients of the storage deterioration rates can be shown to conform to some defined pattern, Arrhenius for example, then accelerated testing becomes practicable, which can clearly speed things up substantially. Towards the end of the storage life, the measurements become more significant, and Fu & Labuza (11) give an account of

a hazard analysis procedure in which sampling is intensified over critical regions by a systematic procedure.

Another plot is shown in Fig. 3.6 taken also from a table in IIR (23), and giving data on high-quality storage lives of frozen fruit in syrup originally from Guadagni (24). All of these show the same general patterns and how shelf lives can be obtained from the literature; the IIR tables cover a great many common products. They also have the advantage of international acceptability, which can be critical at times, especially for export products, and entry into new markets. When data are not available for products of concern, then the same methodology can be used experimentally, but it can be a long task.



Data from Guadagni (24)

Fig. 3.6. Storage life of frozen fruit in syrup

Most storage reactions are zero order, for ambient, chilled and frozen foods.

## Case study 3: Shelf-life of fish

This case study shows how reaction technology can be used to predict shelf lives of foods in a product area, fish. It is worthwhile to explore how seemingly theoretical reaction technology patterns can be applied to predictions that can then be industrially helpful.

Maintaining fish at the highest quality, closest to fresh out of the water after catching, has always been a challenge for food technologists. It has long been recognised that low temperatures at all stages are advantageous, but, because of the expense and practical problems of rapid cooling, the response has continually been 'yes' but how much chilling, and when, and what difference does it make?

Neat tidy categorisation could hardly be expected, because of:

- diversity of species, difference in shape, size and composition,
- fishing all over the world under very varied conditions,
- fish with major variations such as different fat contents, microbial flora and different physiological states such as at spawning,
- different judgement factors that come together to constitute the quality called 'freshness'.

The first problem is how to measure quality? An early measure was the increasing concentrations of trimethylamine, which has a noticeable off-odour and results from bacterial growth and activity in the fish flesh. It was found to rise regularly with time and also to correlate with sensory panel assessments of the condition and deterioration of the fish. Figure 3.7 shows that, over time, the concentration of trimethylamine in the fish increases, but not linearly (data drawn from Lovern, in (25)).

The author commented that for cod and haddock, 'fresh' seemed to imply trimethylamine levels:

- 'Fresh' not more than 1.5 mg/100 g,
- 'Good' not more than 6 mg/100 g,
- 'Poor' not more than 12 mg/100 g; thereafter 'inedible'.

This is not a zero order reaction (or the graph would be a straight line), or a first order reaction. But it smooths to a monotonic increase, which can be fitted reasonably by a second order polynomial, which runs well up into the inedibility range, as shown by the trend line on Fig. 3.7.

## Case study 3 (contd)

Another measure was consumer acceptability testing, as ultimately it is consumers who determine whether fish for them is fresh or not and have opinions on how fresh (20). Two different studies were compared, about 30 years apart (26 and 27). The later data were composites from a large number (70 sets) of results reported in the literature for protein foods in the range 0 °C to 15 °C, and so seem to have wide applicability. In both studies, freshly caught fish were stored at selected fixed temperatures and for measured times, and then sampled by the sensory panel. Kuprianoff's panel compared stored fish against three quality standards: excellent to very good A, good quality B, and satisfactory C; Bremner's panel judged them for acceptability. The time to reach either the end of the Grade for Kuprianoff or the end of acceptability for Bremner were determined for each storage temperature.

The relative rates of the two sets of data are shown in Table 3.I. The rate at 0 °C was taken as 1 and the other rates were relative to this.

TABLE 3.1
Relative rates of fish deterioration at different temperatures

Temperature (°C)	0	2	4	6	8	10	12	14
Rate – Kuprianoff (26)	1	1.3	1.6	2.1	2.7	3.4	4.3	5.5
Rate – Bremner et al. (27)	1	1.2	1.9	2.5	3.2	4.0	5.0	6.0

Note: rate is the rate relative to the rate at 0  $^{\circ}$ C, which is taken as 1.

The relationships between the rates at different temperatures are remarkably similar for the two sets of data. These relative rates were plotted against temperature (Fig. 3.8), on both a natural (a) and a logarithmic scale (b) to show how they might be extrapolated.

Consider the implications of the storage life data for fish. Fish on ice (at around 0  $^{\circ}$ C) have a high-quality life of only about 10 days. It is quite possible on board a catching vessel for fish to be subjected to temperatures between 10 and 20  $^{\circ}$ C for a substantial number of hours. For example, the relative rate for 10  $^{\circ}$ C is given as 3.4, that is the fish deteriorates 3.4 times as fast as it would do at 0  $^{\circ}$ C. Therefore:

- 10 hours at 10 °C deteriorating at 3.4 times the rate at zero (ice temperature) is equivalent to  $3.4 \times 10 = 34$  h on ice.
- If 10 days (240 h) at zero is the high-quality life on ice, then this fish has already lost 34/(240) = 14% of its available high-quality life before it is even stowed in the chiller on board.

## Case study 3 (contd)

This is a substantial additional quality burden for the distribution system if it is to provide customers with the freshest fish. Alternatively, it places a premium, and a measurable one, on getting that fish temperature down more quickly and holding it down.

The activation energy for fish deterioration was found to be about 78 kJ/mol, and this relates to a sensitivity of about 13% per degree C at around 0 °C. For practical prediction purposes, a reasonably quick estimate of relative deterioration rates at chiller temperatures can therefore be obtained using a constant sensitivity of about 13%/°C over the range.

In fact, the total fish deterioration story is much more complicated and more is known about it now. Deterioration is rapid, it is strongly dependent on temperature and there is only a short high-quality life available. See Fig. 3.9 for an OTT chart for fresh chilled fish, based on experimental results from sensory panels.

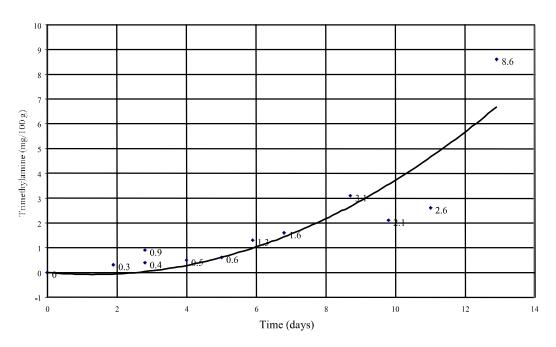
The straightforward practical remedy is to maximise life by reducing the temperature. This reaction technology information can be used to assess the value of temperature regimes that might be practicable set against the probable market values of fish either for direct sale or as raw material for subsequent processing. In effect, this analysis reveals two significant quality sensitivities, one chemical and one sensory, and both of these can be used by the fish process technologist to make useful predictions. Other parameters have also been measured: changes in other chemical constituents of the fish, physical changes such as the tensile strength of the fish fibres, biochemical changes in fish proteins, and rates of growth of microorganisms. These may not fit the same reaction orders or temperature sensitivities as noted above. It is not their individual but their overall net impacts that come together to register the consumer panel assessments. From the point of view of industry, individual components may or may not be significant, but the consumers' overall view certainly is.

If the fish is a raw material to be continued into further processing, then it may be one of the constituent properties that becomes critical and so has to be looked at in greater depth. An example is tensile strength, particularly in some species that are inherently particularly sensitive in this regard. Tensile strength is relatively easy to measure and is highly correlated with fish fillet cohesion. In one species, hoki, this tensile strength was found to

# Case study 3 (contd)

have a somewhat different activation energy, of around 70 kJ/mol, or temperature sensitivity of 12%/°C, making it marginally less sensitive to temperature than the general fish acceptability (28). It indicates greater temperature tolerance. Had it gone the other way with a higher activation energy, however, it could have been critical because the hoki goes mostly to processing, and flesh gaping, a manifestation of tensile weakness, is an important quality issue.

This illustrates that such shifts of quality emphasis arising from different customer needs could indicate different handling requirements. Competitive advantage could hang on appreciating or not appreciating these finely poised situations. So specific measures, as well as the more general acceptability, may justify quite detailed investigations of the processing technology.



Data from Lovern, quoted in Bate-Smith & Morris (25)

*Fig. 3.7. Storage of fish on ice – generation of trimethylamine* 

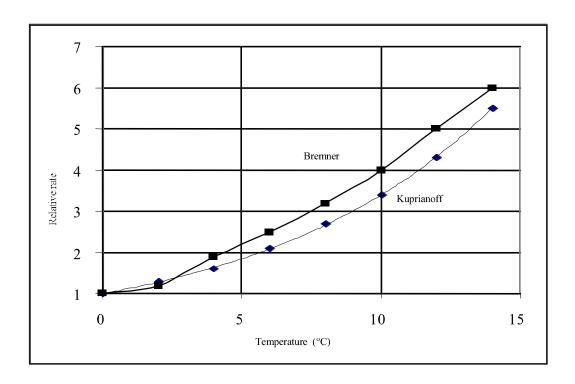


Fig. 3.8(a). Fish deterioration with temperature - natural scale

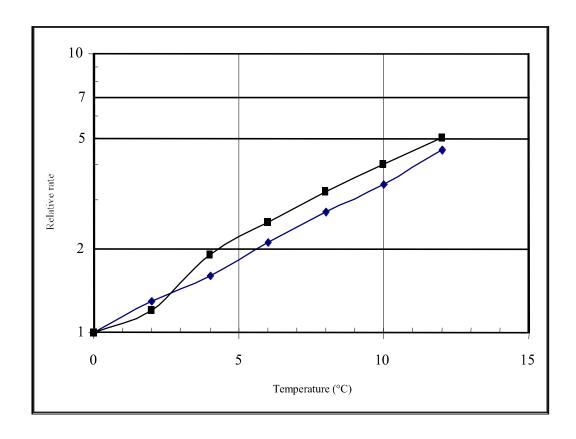
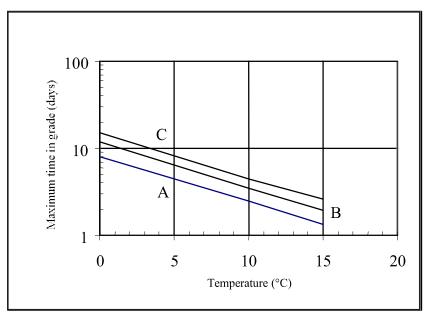


Fig. 3.8(b). Fish deterioration with temperature - logarithmic scale



Grades: A = Excellent to very good, B = Good, C = Satisfactory Data from Kuprianoff (26)

Fig. 3.9. Storage of chilled fish: OTT plot of time and temperature

### Think break

Select appropriate values for the deterioration rates and temperature coefficients for fish after catching:

- \* Examine the deterioration occurring in the various steps in a typical temperature chain for fish reaching your table.
- \* Identify the weakest links and suggest practical steps that might be taken to improve quality.

## 3.6 Practicalities

Applications of the outcome/temperature/time (OTT) charts are numerous, but, in particular, they give quantitative data that can be used to answer directly many important and practical questions with sufficient accuracy for many of the food processors' purposes. They also have wide application, including all manner of ingredients, microbiological aspects, and consumer acceptances. They extend beyond processing conditions studies, to impacts of raw material suitability, and storage lives. Once the data and the charts have been plotted, then application is quite direct and immediate.

## 3.6.1 Designing the process

In designing a process, there are limits to the processing conditions from food regulations, product specifications and plant factors. Within these limits, the process designer can develop an optimum process by using reaction technology. For example, if a set of outcomes such as bacterial reduction ratios of 10<sup>3</sup>, 10<sup>5</sup>, 10<sup>7</sup>,10<sup>9</sup> (conveniently abbreviated to 3D, 5D, 7D, 9D reductions) and intermediate ones, if needed, is plotted on an OTT chart for a particular situation, this can be used to judge processing conditions for particular outcomes. Should an outcome be stipulated, the process conditions can be selected to achieve this.

In heat sterilisation, judgement and experience may suggest that an expected maximum of 1 viable spoilage organism in  $10^4$  items (packs), after heat processing, provides an adequate shelf life. Average levels are  $10^3$  per pack in the raw contents on filling. Therefore, any combination of time and temperature on the 7D line  $(10^4 + 10^3 = 10^7)$ , taken down to 1 by 7 decimal reductions) should be adequate. If contamination of the raw ingredients is found to increase to  $10^4$  per container, the process outcome should move to half way between the 7D and the 9D lines, and the time/temperature combination needs to be altered to achieve this.

Such straightforward calculations do not remove the need for judgement, but they provide a powerful reinforcement tool and an added feeling of confidence when making decisions. The charts can facilitate calculation of  $F_0$  values, and also evaluation of the impact of different temperature coefficients of reaction rates (different activation energies and z values) with all the implications these can have for product quality, and consumer safety and nutrition.

## 3.6.2 Controlling the process

Some questions that can be answered are:

- How precise does the temperature control need to be?
- How precise does the time control need to be?
- How can the process meet the regulatory standards for heating processes?
- How can changing the time and temperature improve the overall standard of the product?

Historically, one important example of this was in the field of pasteurisation of milk. The impetus for heat treatment of milk for drinking came with the knowledge that tuberculosis organisms could be present and that they could be reduced to harmless proportions by heating for a determined time, originally in large batch vats. Then it was found that the same effect on the pathogens could be obtained by heating for shorter times but at higher temperatures and some of the basic quantitative work involved one of the earliest uses of OTT charts in this context to find the correct temperature/time combinations. This led to so-called

high-temperature/short-time (HTST) continuous processes. The stipulated requirements were unattainable in large batch vats, so novel equipment had to be invented. What emerged was the plate heat exchanger based originally on the filter press, combining a large heating surface and the possibility of rapid response and good control, with ready access to exposed surfaces for cleaning (1). There were many ramifications, but basically other parallel processes in the milk proceeded less under the higher temperatures and shorter times while still retaining the pathogen reductions required.

Similarly, if the actual working temperature in the plant is a degree or so above normal design, the chart can quickly indicate the impact of this on the colour or the vitamin content or the bacterial reductions, and action taken if it is judged necessary. 'Piecemealing' is also relatively easy, in that part-processing effects can be estimated, and therefore processing additions made that have the impact to produce the necessary quality outcome. So interruptions can be handled with greater assurance. A widely extending use is when, as is almost always the case, the many reactions that are proceeding simultaneously have important consequences for the quality of the product and so the best obtainable trade-offs have to be sought and secured.

## 3.6.3 Benefits of outcome/time-temperature charts

Combined effects of time and temperature can be explored systematically on the relevant OTT charts.

Experience, over many years, exemplified by milk pasteurisation investigations, has shown that OTT charts have provided:

- New and deeper insights into an important and very widely used process.
- Better quality product with easier and more certain bacterial reduction.
- Methodology that increased understanding of process systems with wide application.
- Possibility of extension from fixed temperature to variable temperature and continuous operations, and therefore much wider process design scope.
- Simplicity of understanding, and ready manipulation, of data and conditions.
- Insights and drive for new equipment leading to process hardware innovation.
- Gradual recognition in regulations that overall process outcome, as opposed to step details, could be equally effective and less restrictive, yet leave much more scope for process development.

# 3.6.4 Relating outcomes to process conditions

Another important insight given by the charts is the effect on the outcome (the product) of different degrees of treatment because of differentiated time/temperature conditions arising inevitably within different parts of the product. This has been briefly examined with respect to contents located in different parts of a can, but its impact is very widespread indeed in foods being processed. It can sometimes be possible to alter the conditions, or the packing, or the flow patterns to improve uniformity. Of course, sometimes non-uniformity is desirable. But, in any event, the OTT charts provide a useful tool to explore, quantitatively if the relevant different temperature histories are known, just what are the consequences of non-uniformity in the processing in the various regions of the food materials.

Overall, the great advantage of the OTT charts is the amount of process information they can contain compactly, combined with accessibility and adaptability. So that it could be very worthwhile to investigate their availability in particular situations and to undertake the modest amount of effort involved in preparing such charts and gaining familiarity with them.

## Think break

Using appropriate values give your answers to the questions posed in 3.6.2 for a canning process and a milk pasteurisation process.

To what extent are these questions covered or accommodated in regulatory regimes?

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