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The Development of a Chemical Analogue
of Thermal Destruction of Bacterial Spores

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SUMMARY

A study has been made of methods in which chemical reactions are used to evaluate the total lethal effect of heat on the bacterial population in a sealed container of food material. The chemical reaction technique has also enabled a study to be made of the effect that the movement of the material within the container has on the lethality of the applied heat.

The relationship between the extent of a chemical reaction and the degree of destruction of bacterial spores is shown to depend both on the activation energies and decimal reduction times of the chemical and bacterial systems, and on the "heat penetration" characteristics of the material being processed.

Acid hydrolysis of sucrose, in buffered solution, was chosen as the model chemical reaction systems. It was used in the experimental study of two types of process, one with cans stationary, as in ordinary commercial batch retorts, and the other with the cans rotated "~~and over and~~" as in some commercial agitating batch retorts and continuous cooker-coolers.

The effect of convection on the extent of sucrose hydrolysis has been investigated. By combining records of can temperature with data on the rate of sucrose hydrolysis, the final concentration of sucrose has been calculated for a range of processes. These calculated values have been compared with those actually obtained in the can.

Theoretical considerations show that the effect of heat on bacterial and chemical systems as calculated from temperatures measured at points fixed with respect to the container, is not necessarily the same as that actually obtained in the container if convection takes place during the process. Simple convection models have been used to relate the extent of sucrose hydrolysis calculated from the temperature data, to that actually obtained in the can. These convection models show that the temperature at the geometrical centre of the can could be considered typical of the whole can for both static and agitated can processes.

The degrees of destruction of two micro-organisms with different "heat-resistances" have also been calculated from the can temperature data. These have enabled relationships between the sucrose hydrolysis and the spore destruction to be established. The effects of the various processing factors on these relationships, and on the rate of heat transfer to the can have been studied. The factors investigated were processing pressure and length of process, for static can and agitated can runs, and type and speed of rotation for agitated can runs only. The processing pressure in the agitated can runs, and the length of the process in both agitated and static can runs do not appear to have significant effects, but the effects of all other factors studied are significant.

The concept of equivalent time difference, which arises from the relationship between the extent of a chemical reaction and the degree of spore destruction has been defined and examined. Model temperature vs time curves for a greater range of processes and can sizes than that used in the experiments have been calculated using heat transfer rate data based on the agitated can runs, and the dependence of the equivalent time difference on the type of process and on the size of can is discussed.

Multiple reaction systems in which measurements of the extents of several chemical reactions, each with different activation energies, are used to estimate the degree of destruction of spores have been investigated. The model temperature vs time curves, derived for the analysis of the equivalent time difference concept, were used with data on the rates of the sucrose hydrolysis reaction, which has an activation energy of 22.35 kcal/mole, and on the rates of two hypothetical reactions with activation energies of 30 and 45 kcal/mole. Estimation of the degree of spore destruction using reactions in pairs or in groups of three is discussed.

If a pair of reactions is used, a knowledge of rates of heat transfer to the can is required for satisfactory estimation of the lethal effect of heat. If three reactions are used, the lethality of the process can be estimated without heat transfer rate data.

Errors arising in the estimation of the lethal effect of heat on bacterial spores using chemical reactions singly, in pairs, or in groups of three are discussed. The maximum errors in the lethality of the process as estimated using the various chemical reaction techniques were found to be less than one quarter of those arising from the same sources in traditional process calculation methods, in quite a number of instances much less. It is also shown that uncertainties arising from the necessary experimental measurements can be evaluated much more readily with a chemical reaction technique, especially the three reaction system, than they can in other methods of process evaluation.

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INTRODUCTION

INTRODUCTION

THE DEVELOPMENT OF CANNING EQUIPMENT AND PROCESSING METHODS

Canning as a method of food preservation has its origin in the work of Nicolas Appert (1750-1841) who was the first to use heat as a means of preserving food in hermetically sealed containers. Although he did not understand the principles of his method, his systematic experimentation (and generous sharing of his discoveries) laid the foundations of thermal food preservation methods.

Appert initially processed his food in cork sealed glass jars and bottles in boiling water baths for periods varying from 15 minutes to two and a half hours. Storage trials were the basis of his processing methods, some foods being kept up to ten years. His products ranged from meats, soups and vegetables to fruit and even cream and evaporated milk. He recognized the value of quick clean handling of good quality raw materials. Blanching was used with some products, and he was also aware of the distinction between acid and low-acid foods in regard to their length of processing.

Appert's understanding of the process was that heating eliminated the "air" which was believed to be the cause of spoilage. This belief was to persist for nearly 100 years.

Appert's work in glass containers led to the development in England about 1815-20 of tin containers for preserved foods. Appert himself used oans in some of his later work.

Some time before 1830 the autoclave was introduced (apparently by Appert) as a means of cooking canned foods under pressure. By 1870, autoclaves were being used quite widely in industrial canning.

Because pressure vessels tended to be dangerous, and tended to over processing (Prestcott and Underwood, 1897) the desirability of obtaining high temperatures without the use of pressure resulted in the use of salt baths from about 1850. Common salt and calcium chloride were

both used (Bitting, 1916; Oren, 1914).

Macphail (1897) credited Tyndall with enunciating the principles of the intermittent method of sterilization, which involved three or more relatively mild heat treatments on successive days. The success of the method relied on viable spores germinating after heating, and the vegetative forms being destroyed during the next processing period. Dormancy of spores made the method unreliable, and the method was abandoned for processing of non-acid foods.

A significant advance in the use of autoclaves was made by Raymond Chevallier-Appert (successor to Nicolas Appert) who was granted a patent in 1852 for a retort with manometer which made possible much closer control of temperature - to within 5° instead of about 20° .

Further development in processing equipment came with the introduction of agitating cookers, and continuous sterilizers. The first spiral continuous cooker was patented in 1899. Spiral cookers were limited to atmospheric pressure until the introduction of the pressure sealing can transfer valve system about 1915. Revolving crate batch sterilizers were already in wide use. The hydrostatic pressure sterilizer was first installed in Europe in 1936. Other continuous agitating processes have been described, e.g., Thermo-Roto Cooker, Ball and Olson (1957), a high speed spinning cooler using two long rollers and inclined guide rails (Van Blaricom, 1952), a spin cooker-cooler using belts (Casimir, 1962). A very unusual experimental batch sterilizer has been described by Borges and Desrosier (1954) in which a crate of cans is spun on two axes simultaneously.

Another significant advance in canning technology is the introduction of aseptic filling of some products after sterilization in plate or scraped surface heat exchangers. Ball and Olson describe several of these processes; Beauvais et al (1961) describe an agitating sterilizer using gas flame heating. Sporle (1955) describes a continuous milk sterilization plant in which cans are conveyed on belts through a hot air sterilizer, using air at 293°F .

MICROBIOLOGICAL DEVELOPMENT IN CANNING PRACTICE

Most of the development in canning methods before 1900 took place with no knowledge at all of the causes of food spoilage, and process times were based mainly on trial and error. Spoilage rates were used as criteria for successful processing and all cans were inspected for vacuum, i.e., absence of "swells", both during processing and before finally leaving the plant. Prestcott and Underwood (1897) report that losses were large.

Pasteur in 1864 was the first to recognise the microbial nature of food spoilage, and his solution to the spoilage of wines and beers was, in fact, a mild heat treatment (Frobisher, 1957).

The significance of his observations was not noted in the canning industry where it was believed for another 40 years that the "vacuum" was the essential element in food preservation. The work of Prestcott and Underwood (1898) confirmed conclusively the assertion of earlier workers that vacuum was not necessary for sterilisation.

The first recorded bacteriological examination of spoiled canned foods is that of Russell (1895) who isolated two species of bacteria from spoiled peas, one of which reproduced the swelling when inoculated into sound cans. In this case the solution to the spoilage problem was an increase in temperature rather than in time. Similar findings were made by Prestcott and Underwood on spoiling of canned clams and lobsters (1896)* and souring of sweet corn (1897)*. They recognised the need for the accurate determination of minimal retort times, and used small registering thermometers to measure the maximum temperatures. It is evident that they also made crude estimates of the "heat resistance" of the isolated thermophiles. Inoculated cans were used to show that retorting was superior to water bath processing.

Harding and Nicholson (1904) investigated spoilage in canned peas, and isolated two organisms which were shown by inoculation to be responsible for the spoilage. The limits of successful processing were determined, presumably by inoculated pack experiments.

Early workers (Vaillard, 1900; Pfuhl, 1904; Bushnell, 1918; Weinzirl,

* These were reported in 1897 and 1898 respectively.

1918) recognized that viable organisms may be present in a food after processing without spoiling the material. The concept of 'commercial sterility' was established within the canning industry well before 1924. The term denoted "the absence of organisms capable of spoiling canned food under conditions of commercial manipulation" (Esty and Stevenson, 1925).

Experimental inoculated pack experiments have been used extensively in establishing processes, especially for low acid foods as recommended by the National Canners Association (1955). The use of this type of experiment is described by Meyer (1931), Lang (1935), Cameron (1936) and Ball (1943). Ball and Olson (1957) have discussed the difficulties and uncertainties in establishing reliable process times by this method, and conclude that much larger numbers of containers than are commonly used are necessary to get statistically significant results. A very strong case is made for alternative methods of evaluating processes.

DEVELOPMENT OF CALCULATION METHODS OF PROCESS EVALUATION

Process evaluation may be defined as the estimation of the process that will obtain a state of 'commercial sterility' in a canned food. In terms of more recent understanding of bacterial destruction, it is the calculation of the probability that a given process will obtain such a state in a container of food.

To date, all methods of process evaluation (with the possible exception of Hersom, 1964) have involved measurement of the 'heat resistance' of spores (either thermal death times or 'decimal reduction times') and measurement or calculation of the temperature time function within the container of food. These are then combined to estimate the total lethal effect of the heat.

(a) Basic Bacteriological Data

(1) Heat Resistance Determination Methods

Methods of process calculation and the basic assumptions involved are dependent on the type of 'heat resistance' data available.

As the experimental methods for obtaining 'heat resistance' data have a considerable bearing on the understanding of thermal destruction of bacterial spores, it is necessary to trace the development of these methods and their interpretation, and discuss some of the salient experiments on heat resistant organisms.

All work to date has used the failure of the organism to reproduce as the criteria of death. Bahn (1945) has discussed this concept, and has suggested that cells that do not reproduce be termed 'sterile' rather than dead. For practical purposes the distinction is unnecessary (Stumbo, 1965).

Prestcott and Underwood (1897) and Russell (1895) were among the first to isolate thermophilic heat resistant spoilage organisms from canned foods, and these early workers realised the need for some quantitative measure of 'heat resistance'.

Very little accurate work on the effect of temperatures greater than 100°C on resistant spores had been reported before 1920. The work of Lawrence and Ford (1916) and Laubach, Rice and Ford (1916) ignored the effect of the heating and cooling periods.

Bigelow and Esty (1920) introduce a thermal death time tube method in which sealed tubes containing 1 ml of spore suspension were subjected to temperatures in the range $100-140^{\circ}\text{C}$. Their results (shortest time to destroy and longest time of survival) were plotted time against temperature on linear co-ordinates. The effects of pH, initial spore concentration, age and condition of spores were studied.

Bigelow (1921) reports that replotting his thermal death time data on semi-logarithmic paper (temperature vs log time) gave a substantially linear relationship for quite a number of organisms. The lines for the various organisms are parallel, although the mean slope for four non-spore bearing organisms in the range $40-65^{\circ}\text{C}$ is about half of that of the spore destruction curves in the range $100-140^{\circ}\text{C}$.

The term 'z' is introduced by Bigelow for the "slope" of the thermal death time curve, and is defined as the temperature increase for a tenfold decrease in thermal death time. For spore destruction the mean value of z was 18°F and for the vegetative cells was found to be 8.4°F .

Deviations from linearity of the thermal death time curves were explained in terms of technique (heating and cooling times at high temperatures and short times) and spore characteristics (deviations at low temperatures near the maximum for growth).

Bigelow and Esty do not comment on the mechanism of 'death' of spores or on the reasons for the observed effect of concentration. They report the work of Schmidt (1906) who concluded that the resistance of spores increased with concentration. Gage and Stoughton (1906) are reported as assuming different heat resistances of individual spores, particularly the few that survive significantly longer times or higher temperatures than the majority. Eijkman (1908) had also noted the effect of initial concentration of spores on rates of destruction and concluded that differences in thermal death rates were due to substances given off into the media by the killed bacteria. The concepts of Schmidt, and of Gage and Stoughton persisted for quite some time. Ball and Olson (1957) use these concepts somewhat unconvincingly in a discussion of Stumbo's basis of process calculation.

Esty and Meyer (1922) used a method substantially that of Bigelow and Esty (1920) in a study of the heat resistance of C. botulinum and related anaerobes. Problems encountered in this study included the effect of different spore preparation media, pH changes, and retarded germination of spores. Some death rate data is plotted (log spore numbers against time) showing a substantially linear relationship from 10^{10} spores/cc down to spore concentrations of about 1 spore/cc in neutral phosphate buffer. Their thermal death time data is presented as maximum survival time and minimum destruction time, and the slope, or z value, of the thermal destruction curve for the most resistant strain of C. botulinum studied is very nearly the same as the mean slope of the thermal destruction curve for the range of organisms studied by Bigelow and Esty (1920).

Levine, Buchanan and Lease (1927) developed a 'flask' method for studying rates of destruction of spores at temperatures less than 212°F. Inoculum is introduced into preheated media in a well stirred flask, and samples withdrawn at intervals.

Williams, Merrill and Cameron (1937) used a small (900 ml) stirred stainless steel jacketed tank with four sampling valves at the bottom. The inoculated substrate was heated from cold in 2-3 minutes. Temperatures up to about 250°F can be studied in this apparatus.

Townsend, Esty, and Baselt (1938) used a method in which inoculated food is processed in very thin, quickly heated 208 x 006* cans ($2\frac{1}{2}$ in diam. x $\frac{5}{8}$ in. high). Their method involves corrections for heating and cooling times. The heating and cooling lags are about the same as for glass tubes. Results are expressed either as number of spoiled containers, or as number of surviving spores if the cans are opened and subcultured.

A number of early studies on rates of destruction had indicated that the order of death was logarithmic both for spores and vegetative cells (e.g. Chick, 1910; Esty and Meyer, 1922; Watkins and Winslow, 1932), but this observation was not used in characterization of the 'heat resistance' of micro-organisms until 1942 when the term 'decimal reduction time' was introduced by Katzin and Sandholzer in a study of milk pasteurization. Ball (1943) in a study of the application of his process calculation methods to milk pasteurization introduces the same concept - apparently independent of Katzin and Sandholzer - as the quantity of z (zeta), which Stumbo uses in 1948. Ball discusses the meaning of thermal death time measurements and their use in terms of z but continues to base his calculations on the existence of a finite thermal death time. It was left to Stumbo (1948a) to formally redefine some of Ball's process calculation parameters to include the concept of logarithmic spore destruction rates.

With the introduction of the decimal reduction time concept into process calculations, bacteriological destruction studies tended to concentrate on the measurement of thermal reduction times. It should be pointed out that the earlier methods (prior to 1942) can be used to calculate decimal reduction times if the data are presented in a suitable form.

* For nomenclature of can sizes see Appendix XI.

For thermal resistance measurement above 240°F, Stumbo (1948b) developed the 'thermoresistometer' which has been used up to 300°F. The device consists of three steam chambers in series, and a sample transfer mechanism which carries six small samples (0.01 - 0.02 ml) in small open cups from the loading chamber into the heating chamber, and later to the final chamber where they are dropped into tubes of culture medium or diluent. Cooling in the centre chamber is by sudden release of steam pressure.

Pflug and Esselen (1953) developed an instrument similar to Stumbo's thermoresistometer. The samples were cooled by dropping them into tubes of culture medium. This instrument has been used to study thermal resistances of various spores in the range 235-300°F. Measurements of the rate of destruction of thiamine in pH 7.5 phosphate buffer at 295°F are also reported.

Small sealed capillary tubes were used by Stern and Procter (1954) to obtain decimal reduction times. Some results are given for B. stearothermophilus.

Wang, Humphrey and Eagleton (1964) developed a method for measuring the rate of spore destruction using flow techniques. Flow time distributions were considered, and found to have a very significant effect - the actual destruction being less than that calculated assuming plug flow. Data in the range 127-143°C (261-290°F) were identical at the 95% confidence level with unpublished data of Soharer (1963) on the same spores of B. stearothermophilus. Soharer used a capillary tube method at lower temperatures.

(11) Heat Resistance Data Interpretation

In studies of the destruction rate of micro-organisms the logarithmic order of death has been confirmed or assumed. Of the many explanations offered for this phenomena, that of Rahn (1929,1945) is probably the most plausible. He suggests that loss of reproductive power of a bacterial cell when subjected to moist heat is due to denaturation of a single gene essential to reproduction. While the actual mechanism of bacterial death is unimportant in process calculations, the concepts - in

particular those as advanced by Rahn - have made their impact in the development of process calculations methods. These concepts have resulted in a rational basis for the statistical methods for calculating decimal reduction times ("skips" are no longer a problem in the interpretation of heat resistance data), and have given rise to the concept of probability of spore survival as an end point in process calculations (Gillespy, 1951). The application of Arrhenius' equation to thermal destruction data can also be traced to these concepts.

A number of methods of treating data obtained from thermal destruction rate experiments have been described. A graphical method for decimal reduction time (D) has been found quite satisfactory, particularly where reasonably straight lines are obtained. Where straight lines are not obtained, and it is difficult to decide which portion of the curve is describing thermal death alone, the logarithmic order of death is assumed, and methods of statistical analysis are used to get the values of D. Stumbo (1965) discusses the methods of Halvorson and Ziegler (1932), Schmidt (1954) and Lewis (1956). These different methods give results which are generally in good agreement.

The effect of temperature on thermal resistance can be expressed in a number of ways. Thermal death times were not of great precision and semi-logarithmic plots were found to be more or less linear (Bigelow, 1921). Bigelow, who was the first to plot heat resistance data in this manner does not discuss the significance of this type of plot in terms of any other similar or related phenomena. As pointed out by Ball and Olson (1957) the use of z (the number of Fahrenheit degrees for a ten-fold decrease in thermal death time (TDT) or decimal reduction time (D)) is equivalent to the use of the Q_{10} concept, which is the rate quotient for a temperature interval of 10°C . This Q_{10} concept arises from the common observation that the rate of a chemical reaction doubles or trebles for a 10°C rise in temperature. This is known as the R.G.T. (Reaktionsgeschwindigkeit Temperatur) rule, or the Van't Hoff rule.

Because the early methods of process calculation using thermal death times were adapted to the decimal reduction time concept by the

redefinition of some of the terms (Stumbo, 1948a) the log D against linear temperature has remained as a basis for process calculation.

Better methods have enabled more precise thermal resistance measurements to be made over wider temperature ranges than was possible in earlier TDT studies. Gillespy (1948) reports that plots of log D against the reciprocal of absolute temperature were more nearly linear than the same data plotted as log D against linear temperature. This is the form of relation predicted by the Arrhenius equation for chemical reactions.

$$\text{i.e., } k_T = A \exp\left(\frac{-E_A}{RT}\right)$$

$$\text{or } \ln k_T = \frac{-E_A}{R} \cdot \frac{1}{T} + \log_e A$$

$$= \mu \frac{1}{T} + b$$

k_T is the rate of reaction at absolute temperature T.

A, b, μ are constants for a particular reaction

R is the universal gas constant, and

E_A is the activation energy of the reaction.

Gillespy points out that over small ranges of temperature, the linear plot gives a good approximation to the Arrhenius plot. His process calculations are based on the linear plot. He also gives the relationship between E_A and z;

at a given temperature, T_1 to T_2 -

$$z = \frac{T^2 R}{E_A} \cdot \log_{10} e$$

over a range of temperature,

$$z = \frac{T_1 T_2 R}{E_A} \cdot \log_{10} e$$

Webb (1964) has discussed these alternative relationships between thermal destruction rates and temperature. A table is presented showing the variation of E_A with temperature if a constant Q_{10} is assumed. Differences of up to 45% between activation energies at 37°C and 100°C are shown.

Aiba, Humphrey and Millis (1965) also discuss the types of relationship between reaction rate and temperature, and include Eyring's theory of absolute reaction rate with the Q_{10} (or z) approach and the Arrhenius equation. According to Eyring -

$$k_T = gT e^{-\Delta H^*/RT} \cdot e^{\Delta S^*/R}$$

ΔH^* and ΔS^* are heat of reaction of activation, and entropy change of activation respectively and g is a factor including Planck's and Boltzmann's constants.

To compare these three methods of correlating rate and temperature, Aiba et al have fitted each theory to typical spore destruction data at two points, and used each theory to interpolate and extrapolate the decimal reduction time data. The Arrhenius and Eyring theories are not significantly different from each other. The Q_{10} (or z) basis of calculation gives values of D significantly less than the other theories when used to extrapolate data.

Pflug and Esselen (1956) gives decimal reduction time data on PA 3679 in various food substrates. The curve in the log D vs T plots is attributed to changes in the chemical composition of the substrate with the different processes at the different temperatures used. However, the data are such that a log D vs $\frac{1}{T}$ plot would be more linear than the log D vs T plots as presented.

Although no calculations have been done, it is probable that there are significant differences in the lethal effect of processes as calculated using the different forms of rate vs temperature data, particularly where the material does not spend an appreciable time at retort temperature or where data at one retort temperature is converted to some other temperature.

There are a number of other variations of the rate of reaction vs temperature equations. Some of these are discussed by Moore (1957) in terms of their derivation from the fundamental kinetic theory. He states that it is worthwhile making a correction $E_A = E + \frac{1}{2}RT$ in performing calculations with the theory, but it hardly affects the linear plot of $\log_e k$ vs $1/T$.

Ball and Olson (1957) use the Q_{10} (or z) approach in the prediction of the effect of heat on organoleptic quality of foods, which are essentially chemical reactions (Greenwood, Kraybill, Feaster, and Jackson (1944); Jackson, Feaster, and Pilcher (1945)). Because activation energies are generally much lower than those for spore destruction, wider temperature ranges become significant, and it is probable that larger relative errors in organoleptic quality change calculations will occur if the Q_{10} theory is used, than occur when spore survival probabilities are calculated on the same basis.

(b) Basic Heat Penetration Data

In the evaluation of thermal sterilization processes, bacteriological data (decimal reduction times or thermal death times) is combined with time and temperature ('heat penetration') data.

This heat penetration data is generally obtained by experiment as the complexity of heat transfer within the container of food usually precludes the use of purely mathematical methods for calculating the temperature-time functions. A knowledge of the mechanisms of heat transfer to, and within, the container of food has been useful in extending the usefulness and applicability of experimental temperature-time data to different can sizes and processing temperatures.

The temperature data required from a heat penetration test are influenced by the method of process evaluation to be used (coldest point only, whole can) and the type of food being processed. For example, some products require temperatures on surfaces of the solid portions only, other require temperature data inside the solid pieces. Jackson (1940) has reviewed the different types of heat transfer and

has classified foods into six main groups on the basis of their heat penetration characteristics. The type of container (glass, tin) also has an important effect on the rate of heat transfer (e.g., Merrill, 1948).

The literature is replete with reports of heat penetration studies on different types of foods using various processing methods. Methods of obtaining heat penetration data, with examples of their use, and the mathematical expressions used to represent time-temperature data in the formulae methods of process calculation are reviewed here. The application of heat transfer theory to the main types of food product is also discussed.

(1) Experimental Temperature Measurement Methods

The first recorded heat penetration experiments were those of Prestcott and Underwood (1898) who used maximum recording thermometers mounted inside the cans with the bulb near the geometric centre. Temperature-time curves were obtained by varying the length of the process. Other workers including Belser (1905), Duokwall (1905), Koohs and Weinhausen (1907) used maximum recording thermometers in heat penetration tests. More recently (1964) Hersom tried this method and abandoned it in favour of fine melting point tubes in a study of rotary cooker-coolers.

Apart from the disadvantage of only obtaining one temperature per run, this method has been objected to by later workers (e.g., Bigelow et al (1920)) because the metal mounting tube of the thermometer, or the stem of the thermometer itself if no mounting tube was used, could conduct heat to the bulb, and thus distort the temperature record. No data on cooling curves could be obtained, and the time at which the maximum temperature was recorded could not be determined. Much useful information was obtained however.

The use of chemical thermometers was first described by Bitting (1912). The thermometer was sealed into the can through a stuffing box soldered onto the can top. Modified stuffing boxes enabled the chemical thermometer to be used in retorts. Bigelow et al also object

to the stem heat conduction effect, although Magoon and Culpepper (1922)⁴ point out that the thermal conductivities of glass and water are approximately the same, and the error in foods which heat by conduction will be small as most solid foods have thermal conductivities approximately that of water. Stem conduction errors in convection heating foods are not discussed by Magoon and Culpepper.

Bigelow and his co-workers also describe the use of a mercury in a steel recording thermometer which could be used by ordinary operatives in commercial canning plants. The bulb of this thermometer is much larger than that of a glass thermometer, and is subject to the same heat conduction errors.

Bitting and Bitting (1914) described the use of thermocouples in cans as early as 1907. References to and abstracts of this work do not give details of the construction of this thermocouple probes. The effect of agitation on the shortening of the cooking period is also reported.

Thompson (1919) used a thermocouple probe of glass which was sealed through the can and retort top in a similar way to the chemical thermometer described by Bigelow et al (1920).

Bigelow, Bohart, Richardson and Ball (1920) used a thermocouple probe in an extensive study of heating and cooling rates in a wide variety of products. A thin wall copper tube was used as part of the probe, and is probably subject to greater conduction errors in conduction heating foods than the glass thermometers used by others (Ford and Osborne, 1927).

A 'bakelite' thermocouple probe is described by Ford and Osborne in a study of heat conduction errors in thermocouple probes as used by various investigators. Significant differences were demonstrated. Thermometers were not included.

Various improvements of a mechanical nature have been made to heat penetration thermocouple probes, some of which are now produced commercially for heat penetration studies. Ecklund (1949) describes plastic thermocouples with plug in fittings as developed by Benjamin (1938)

that can be used in high speed closing machines. Conduction errors were shown to be negligible except for small cans of conduction heating products. Ball (1923) and Eklund (1949,1956) have proposed correction factors.

A method of mounting thermocouples in cans without the use of a support is described by Board (1965). The two thermocouple wires pass through diametrically opposed holes in the can wall, or through holes in the can ends, and are sealed with a heat resistant epoxy resin adhesive.

This method is probably the least susceptible to conduction errors so far described, and has the added advantage of minimum disturbance to the convection currents especially in still cooks of liquid products. This factor does not appear to have been discussed, even though it may be as important a source of error in convection heating as stem conduction errors are in conduction heating.

Sensitive galvanometers have been used to indicate the potential produced by the thermocouple junctions (Thompson 1919). Potentiometric devices (zero current at balance) are to be preferred, however, as the voltage indicated is independent of the resistance of the lead wires (Eklund, 1949). Automatic or manual cold junction compensation have both been used as well as ice flask reference junctions. Various types of recording potentiometers have been used (Cliffoern et al, 1950; Hoare and Warrington, 1963).

Errors in thermocouple temperature measurement in food products may also arise from electrolytic e.m.f.'s produced by the different metals of the thermocouples due to breakdown of insulation at points distant from the junction. The potential drop produced by the current flowing between the points of contact of the wire and electrolyte (i.e., food product, cooling water, etc.) is superimposed on the thermoelectric emf. Breakdown of insulation or earthing of thermocouple leads outside the can also can lead to spurious emfs. These effects have been discussed by Middlehurst, Board and Elbourne (1964) who demonstrate that very high emfs (up to 4 mv) can be generated in unfavourable (but not unlikely) conditions.

A number of studies have been made using thermocouples in agitating cookers. Bigelow et al (1920) describe experiments both in a small experimental cooker and in a commercial agitating sterilizer specially modified for the temperature measurement work. A flexible coupling (heavy rubber tubing) and a rotating mercury junction were used to connect the rotating can to the stationary potentiometer. Hoare and Warrington (1963) used mercury troughs in some of their early work, but found that the high impedance of the connections made the method unreliable. This problem was solved by connecting the thermocouples directly to the recording potentiometer which was mounted on a synchronously rotating turntable. Slip rings were used for the mains supply to the potentiometer.

Cliffoorn, Peterson, Boyd and O'Neill (1950) used slip rings to connect the couples in the agitated cans to an automatic strip chart recorder in a study of the effects of agitation (rotation and reciprocation) on the rate of heat penetration. Conley, Kaap and Schuman (1951) also used slip rings in an investigation of a number of process variables on rates of heating and cooling in an end-over-end rotating cooker.

Blaisdell and Zahradnik (1958) used silver plated copper slip rings and silver graphite brushes to connect rotating thermocouples in a scraped-wall heat exchanger to stationary recorders. Errors arising, in part at least, from the slip ring system are recorded. Corrections to temperature based on isothermal tests were made to all readings.

The earliest references to temperature studies in agitated cans are those of Bitting (1912), and Bitting and Bitting (1917). References to this work do not indicate the method of temperature measurement. Alstrand and Boklund (1952) report that Bitting first used thermocouples in cans in 1907.

Direct temperature measurement in some sterilizers (e.g., continuous reel type cooker-coolers) is impossible, and some experiments have been done in special experimental retorts, reproducing the type of agitation as nearly as possible (Wilson 1953, Wilbur 1949). High speed motion picture studies of can motion in a commercial unit have

been the basis of these process simulators. Bacteriological and physical studies indicate that the experimental cooker gives heat penetration measurements corresponding closely to those in commercial units.

(ii) Experimental Heating Curves and Heating Curve Parameters

Most early heat penetration curves were plotted on linear co-ordinates (e.g., Thompson (1919), Bigelow et al (1920), Magoon and Culpepper (1921,1922)). Bigelow et al (1920) observe that the upper part of the heating curve is usually a straight line on a semilog plot, but this observation is only used to check consistency of experimental data. Geometric similarity of the heating curves (linear co-ordinates) was used to calculate curves for different can sizes and processing temperatures. Cooling curves were found to be more variable than the heating curves, particularly for air cooling, and for glass containers where boiling of the contents with rapid cooling could take place when the pressure of steam was removed and the internal pressure in the container is released through imperfect closures. The position in the stack also has an important effect on the cooling of a can in air.

For water cooling the use of the reversed heating curve has been suggested by Thompson (1919) and Bigelow et al (1920). Magoon and Culpepper (1922) object to this suggestion because changes in physical properties of the material on cooking and the reversed effect of heating and cooling temperatures on viscosity alter the curves considerably.

With the introduction of the formula method of calculation (Ball, 1923), the heating and cooling curve parameters f and j were defined. The quantity f or "slope" of the semilog heating or cooling curve is the time for the straight portion of the temperature curve to traverse one logarithmic cycle. When the parameters f and j are related to the fundamental heating equations f is defined as the reciprocal of the slope (on a semilog plot) of the asymptote to the heating curve. (Ball and Olson (1957) and Cowell and Evans (1961) have discussed the effects on f_h of using the tangent to the heating curve instead

of the asymptote, the difference being of particular importance in converting data from one can size to another by calculation.) The quantity j , which is also known as the lag factor is used to define the position of the linear part of the heating curve. It is calculated from one point of intercept of the straight portion of the heating curve and the zero time ordinate. Zero time is usually the time at which the retort is considered to have reached the processing temperature. The effect of non-zero come up times is taken into account by considering 42% of the total come up time to be equivalent to processing at retort temperature and adding this time to the beginning of the process (Ball, 1923).

Some products have been found to show a break in the heating curve when the mechanism of heat transfer changes from convection to conduction as the product forms a gel. The reverse phenomena - a change from conduction to convection - has been reported (Jackson, 1940). It is a rare occurrence probably due to breakdown of a gel structure. The second part of the broken heating curve is described in a manner similar to a simple heating curve.

Because the initial non-linear phase of the cooling curve is very important in sterilization calculations, empirical expressions have been proposed by Ball to describe it. A hyperbolic curve corresponding to typical water cooling curves of conduction heating products is used. The lower portion of the cooling curve is logarithmic, a lag factor or j value of 1.42 being assumed for basic calculation purposes (Corrections to lethal effect of cooling can, however, be made for $j \neq 1.42$). The fact that the successful execution of process calculations depends heavily on the empirical expression chosen to represent the log portion of the cooling curve, and that the assumption has many inherent weaknesses, both theoretical and practical is admitted by Ball (1957). He states, however, that no better useful approximation has been devised or even suggested. No expressions for air cooling have been proposed apart from the complex basic heat conduction equations, e.g. Thompson (1919). Ball's approximation to the log portion of the cooling curve will be seriously in error for air cooling in cases where the temperature at the can centre is not

close to retort temperature at the beginning of the cooling period, as the temperature continues to rise at the centre for some time. Figure 79 in Bigelow et al (1920), and Figures 43 and 44 in Magoon and Culpepper (1921) are graphic examples of this. Temperature increases during the cooling period of nearly 20°F are shown.

(iii) Application of Heat Transfer Theory to Heating Curves

A number of attempts to use basic heat transfer theory in the calculation of heat penetration curves have been made. The complexity of unsteady state heat transfer in finite solid and liquid packs with time and temperature dependent physical properties has limited the application of purely theoretical heat penetration curve calculations. The main value of the theoretical approach has been to extend the application of experimental data to different conditions such as alteration of can size, and changes in processing times and temperatures (e.g. Schultz and Olson, 1938). The theoretical approach has also explained, in part, the types of heat penetration curves obtained in practice (e.g. Olson and Jackson, 1942).

Evans (1958) has, however, solved numerically the fundamental equations using thermal properties of water (considered immobile to simulate a conduction heating pack) and has shown the effect of temperature variation of thermal properties on the heating and cooling curve parameters. Hurwicz and Tischer (1956) also report that the effect of temperature on the heating and cooling curve parameters is significant (processing of beef).

A number of workers (Olson and Schultz (1942); Ball and Olson (1957); Charm (1961); Stumbo (1964), have considered mass average temperatures in conduction heating products during heating and cooling, with particular reference to stack burn and corrosion of cans at the end of the cooling phase. These are based on the theoretical distribution of temperature in the cans as calculated from various forms of the heat conduction equation (Thompson (1919) and Carslaw and Jaeger (1959)).

Conduction heating packs have proved somewhat more amenable to theoretical analysis than convection and mixed mechanism products. Thompson (1919) gives fundamental equations describing heat penetration in uniform

conduction heating finite cylinders, and uses these formulae to calculate values of thermal diffusivity from various experimental heating curves. For practical purposes simplifications are made in the equations by neglecting terms which are important at the beginning of heating only. It is shown that many products behave as pure water in which convection currents are prevented. Prediction of cooling curves was not as satisfactory as prediction of the heating curves. The logarithmic form of the heating curve (after the initial lag) is also demonstrated. The same basis as used by Thompson has been used by later workers who have extended Thompson's work to more general cases. Olson and Schultz (1942) review some of the more important contributions to conduction theory in finite solids. Work on other diffusion processes (e.g. diffusion drying) has also had its impact on the mathematical treatment of the conduction equations, as the form of the fundamental differential equations is identical for quite a number of otherwise unrelated phenomena. Tables for the numerical solution of the heating equations are presented by Olson and Schultz. Ball and Olson (1957) also discuss the relationship of the heating equations to the traditional heating curve parameters f and j as used in the formulae methods of process evaluation.

Gillespy (1953) has outlined a method of calculation of centre temperature in conduction heating cans, based on the fundamental heat conduction equations of Carslaw and Jaeger (1947) and Duhamel's theorem. Complex heating and cooling cycles can be calculated.

Conduction based theory has also been applied to convection heating products (e.g. Thompson (1919); Merrill (1948)). Merrill loosely regards the diffusivity as found from experimental curves for convection heating products as an "eddy diffusivity". Merrill's work extends conduction theory with infinite surface heat transfer coefficients (a good approximation for can heating) to the case of finite heat transfer coefficients at the surface as in glass container heating.

Basic heat transfer theory has had less application to convection heating than it has had to conduction heating. A number of workers have observed convection currents in transparent cylindrical containers and standard commercial glass jars of various shapes. Tani (1939) describes

temperature measurements and convection currents in an aqueous suspension of aluminium powder in a cylindrical glass container. When the temperature difference between initial temperature and heating bath temperature was small, several "cell currents" were observed near the bottom of the vessel. With higher temperatures differences between heating and heated mediums these small cell currents merged with the main current in the vessel. An ascending current was seen in a thin layer near the wall and a slower movement down the centre was observed. This slow current downwards in the centre of the cylinder has been described aptly by Webb (1964) as piston flow.

Fagerson and Esselen (1950) studied temperature distribution in two sizes of glass jars. Results similar to Tani's were obtained, including the 'cell currents' near the bottom. (These are not commented on, but can be observed in photographs of jars being heated.)

Jackson and Olson (1939) did not observe convection currents visually in a study of temperature distribution in No.2 (307 x 409) and No.10 (603 x 700) cans in which suspensions of 1%, 3.25% and 5% bentonite were used to represent typical convection heating, broken heating curve heating, and conduction heating respectively. They deduced from the temperature patterns in the convection heating cans that the rising hot liquid forms a thin-walled tube adjacent to the can wall, which spreads over the upper liquid surface, as it reaches the top of the can. Nearly uniform temperatures on any horizontal plane indicated that the cylinder of liquid moving downward was relatively quiescent. They state that the temperature rise in most of the can was due to the slow downward movement of hot liquid from the top of the can. They considered that this simplified picture would be complicated by some eddy currents and some conduction.

The curves presented by Jackson and Olson are somewhat anomalous. The temperature position plots across the can show a slight dip with sharp point at the axis, (only one side of the can is shown in their figures). This may be explained by an insufficient number of points being taken across the can to define the line adequately, or it may be a result of disturbance of the weak convection currents by the solid thermocouple probes used.

Application of the heat transfer theory in terms of the physical properties of the material and the convection currents set up in the can has been studied by Okada (1939) who considered the fundamental differential equations of convective flow and related these to the dimensionless numbers commonly used in describing other forms of convective heat transfer, viz: Nusselt, Reynolds, Prandtl, Peclet and Grashof numbers. The forms of correlation in terms of temperatures at fixed points within the can for both natural and forced convection are given. It does not appear that correlations of this type have been used to describe convection heating in cans.

Blaisdell (1963) in an extensive study of convection in liquids in unagitated food containers, observed laminar core flow, and relatively fast eddies as well as non-stationary cold points. Quasi-steady-state film coefficients for vertical and horizontal flat plates were incorporated into a Newtonian heating model, and values of f predicted with reasonable agreement. The effects of external film and container wall conductances on the parameters f and j were studied. Also discussed are the design and use of multi-point thermocouple rods, calorimetry, flow visualization, model systems, and dimensionless analysis techniques as tools to assist interpretation of experimental heating curves for real systems.

Schultz and Olson (1938) in a paper on the variation of heating rate with can size for convection heating products assume that the heat transfer rate at the surface is the limiting factor, and that the overall heat transfer coefficient based on the complete surface area of the can is temperature independent and independent of can size. A state of ideal convection in which the temperature within the can is uniform at any instant is considered, although it is only an approximation in practice in unagitated cans. Factors for conversion of the slope of the heating curve ' f ' to different can sizes are derived. They state that their method agrees well with experimental data, although only one example (for an unspecified convection heating product) is given. The derivation of this same factor by Ball and Olson (1957) uses a slightly different argument to arrive at the same result.

As an extension of Schultz and Olson's work (1938), Ball and Olson (1957) propose a convection index based on the conversion factors for the slope of the heating curve to different can sizes as based on pure convection and on pure conduction. They emphasize that the index, which would indicate the relative importance of convection in a product depends on many undefined and unknown factors, and much experimental work will be required if the index is to be of much practical use.

Although Merrill (1948) only considered the mechanism of heat transfer inside a glass jar as conduction (even for convection heating products) he calculated inside and outside heat transfer coefficients. This approach could probably be applied to convection heating products in glass jars with greater reliability than to cans, as the overall heat transfer coefficient would not be as dependent on the properties of the product with the greater contribution from the glass wall.

Clifcorn, Peterson, Boyd and O'Neil (1950) were the first to study the mechanism of heating rates in agitated containers extensively, although there are a number of reports of temperature measurements in agitated containers in experimental and industrial cookers (e.g., Bitting (1912), Bitting and Bitting (1917), Bigelow et al (1920), Ford and Osborne (1928)). Clifcorn et al studied the effect of different can positions for agitation by reciprocation and rotation, and the effect of agitation rate and viscosity on rates of heating. A mechanism of convection was proposed to explain the results obtained, and this was then observed in transparent rotating containers with the use of a synchronously rotating movie camera. Maximum agitation (with the headspace passing through the can centre at the top of each revolution) was obtained when the centrifugal acceleration at the can centre was equal to gravitational acceleration. This maximum observed agitation corresponded with the maximum heating rates (expressed as time for the can contents to reach one degree (F) less than retort temperature) and applied over a range of can sizes. Heat transfer rates were considered but results expressed in this form are not included. Their results as presented do not indicate whether semilogarithmic heating curves were obtained. The experimental results obtained by Clifcorn et al were confirmed and extended by Conley, Kaap and Schuhman (1951) using the same equipment.

It should be pointed out that much of the work relating heat transfer theory to actual heating curves is based on ideal systems, i.e., pure conduction and pure convection heating packs. Most food products do not conform to these models exactly, and accurate prediction of heating curves from other processing conditions is not always possible, because of the large number of factors that can affect the heat transfer in some way or other. Among these factors are non-constant thermal properties of products with time and temperature, non-homogeneous systems, and non-isotropic conduction heating materials, as well as inherent variations between individual cans.

(c) Process Calculation

Although there was some earlier recognition of the factors involved (e.g., Prestcott and Underwood, 1898), Bigelow, Bohart, Richardson and Ball (1920) were the first to define adequately the basis for "process calculation". They state that "...the temperature at the centre of the can is only one of the factors involved in sterilization. It is equally necessary to know the time required at different temperatures to destroy resistant organisms under varying conditions. These two factors, when co-ordinated, can be expressed in terms of process time".

For purposes of the present study process calculation is confined to the methods of applying heat penetration data to the bacteriological data, and expressing the total lethal effect of the heat in some meaningful form, such as F , which is the length of an equivalent process at 250°F . It is assumed that the characteristics of the most likely spoilage or pathogenic organisms in the particular food system are known, as well as the initial spore numbers, and the degree of destruction or probability of survival that can be tolerated. The basic assumptions of the various methods, and the mathematical techniques of process calculation are reviewed, and the type of data required and the information obtained is discussed.

(1) Bases of Process Calculation

Although initial spore numbers in thermal death time studies

were known to have some effect, the earliest methods of process calculation (Bigelow et al (1920), Ball (1923,1928)) were based on the assumption that a finite time of destruction at any temperature existed. It must follow from this assumption that the point of greatest lag, or cold point, in the container is to be considered as the critical point. If the effect of the heat at the point receiving the mildest heat treatment is sufficient to achieve destruction of all micro-organisms at that point, then every other point has received greater amounts of lethal heat and must therefore be sterile. The use of finite thermal death time data is basic to several important variations in process calculation technique.

When the concepts of logarithmic death rates of micro-organisms were introduced into process calculations by redefinition of various terms used in the finite thermal death time methods, the adequacy of considering only the coldest point in a can was questioned (Stumbo, 1948a). The thermal death time (TDT) was reinterpreted as a thermal reduction time, and represented the time to reduce the viable spore population to some very small fraction (say, 10^{-9} , (Ball, 1949)) of its original value. Because the mathematical treatment of the redefined terms was identical to the critical point, finite TDT method, some workers (notably Ball and Olson, 1957) continued to consider the coldest point (or point of greatest lag) in the container as the critical point to be considered in process evaluation calculations. However, the introduction of thermal reduction times into process calculations procedures, and the consequent concept of probability of survival of spores at the critical point brought with it the possibility of spores at other points in the can surviving greater amounts of lethal heat. Hence, various methods (Stumbo (1948a, 1949a), Hicks (1951), Gillespy (1951)) have been proposed for estimating the total probability of survival of micro-organisms in the can, when points other than the traditional cold point are considered.

Ball (1949) has discussed the approach of Stumbo (1948a), who defines a region of greatest probability of spore survival in such a way that this region or layer may be other than the centre point, and bases his calculation of spore survival in the whole can on this point. Stumbo's method is in-

inadequate in that the integration throughout the can is not carried out. The total spore survival probabilities in all other noncritical regions in the can may constitute a greater hazard of spoilage than the layer considered, when either the coldest or some other point or region is considered. Ball objects to Stumbo's application of the term 'probability' to regions of different volumes.

Much of the argument can be resolved if the basis of the integration throughout the can that would follow on from the two apparently contradictory definitions of point of greatest spore survival probability is considered. Ball's approach is based on spore numbers per unit volume, and the integration must be with respect to volume, while Stumbo's method is based on spore numbers in elements of material having unequal volumes and the integration of surviving spore numbers must be with respect to the number of elements.

i.e.,

$$N_{\text{Ball}} = \int_0^V C \, dv$$

$$\text{and } N_{\text{Stumbo}} = \sum_{\text{all } i} n_i$$

where:

N = number of surviving spores,

C = concentration of surviving organisms
(number per unit volume),

n_i = number of surviving spores per layer.

Both integrations, if carried out over the whole container should give identical numbers of survivors.

The discussion of Ball and Olson (1957) is much less cogent than Ball's note on Stumbo's first paper. Some of the considerations introduced into the argument seem not only unnecessary, but also of extremely doubtful validity, e.g., "Differences in intrinsic individual heat resistance of micro-organisms exist, and constitute a critical factor." This adherence

to the concept of "heat resistance" of ^{an} individual spore, and the certainty (not probability) that a certain amount of lethal heat will destroy it seems to be the source of their difficulty.

One factor that has received surprisingly little quantitative attention in food process calculation investigation is the effect of the movement of product by convection within the container. All process calculation procedures are based on temperatures measured at points fixed with respect to the container, while the food product and the spores that the process is designed to eliminate, move around in the container. The temperature time functions to which the spores are subjected may bear little resemblance to the time temperature functions measured at the fixed points. Stumbo (1965) considers product movement in convection heating, and "because temperatures are reasonably uniform during heating and cooling" states that the "temperature at the geometrical centre is thought to approximate closely the effective mean for the container." This is similar to a statement of Hicks (1951) who says that "each spore is subjected to some sort of average of the temperature history of the different points in the can. In a purely liquid pack a good approximation to the actual chances of survival of a spore would probably be given by substituting $\bar{T}$, the average temperature in the can at a particular time for T the temperature at a particular point" in the relevant equations for integration of spore survival probability.

Other workers who have studied convection heating products have ignored the effect. For example, Fagerson and Esselen (1950) and Fagerson, Esselen and Liociardello (1951) calculated F values for liquid (1%) bentonite suspensions, and a number of liquid and liquid-solid food systems. These F values, while adequate for the liquid-solid systems if the assumption is made that spores remaining stationary on the food pieces, have little relationship to the F values that the spores moving about with the fluid are subjected to. Some of Stumbo's calculations (1948a, 1949a) of F requirements at various positions in cans of fluid are also suspect for the same reason.

An equivalent effect in ultra-high-temperature continuous pasteurizers and sterilizers is the effect of residence time distribution. Process evaluation calculations have been made on continuous plant, e.g., Williams et al (1957, 1958), Kiratsous, Francis and Zahradnik (1962). Wang et al in

a study of the use of flow systems for measurement of biological kinetics (spore destruction) found that the lethal effect in practice is less than that calculated assuming plug flow. Where the lethal effect of the heating and cooling periods is significant, a residence time-temperature distribution function rather than a simple residence time distribution for all elements of food will be required.

(ii) Techniques of Process Calculation

Because the newer concepts of bacterial death rates and criteria of process calculation have utilized the older mathematical techniques by redefinition of some of the original terms and use these older techniques to evaluate the lethal effect of heat at various points throughout the container, it is important to review the early methods of process calculation.

Bigelow, Bohart, Richardson and Ball (1920) presented a method involving a graphical integration of lethal rates at the centre point with respect to time using experimental temperature data and lethal rates defined by the equation -

$$L = \frac{1}{TDT}$$

The process was considered sufficient for sterilization if the integral was greater than, or equal to unity. In terms of thermal reduction times, this represents whether or not the same reduction in spore numbers as in the TDT tests is attained.

The 'General Method' of Bigelow et al (1920) may also be used to find the F value of a process (equivalent time at 250°F with respect to destruction of spores) if a straight log TDT vs T curve passing through the point TDT = 1 min., T = 250°F, is assumed. This is equivalent to defining the lethal rate, L, by the equation -

$$\begin{aligned} L &= \log^{-1} (T - 250) / z \\ &= 10^{-(T - 250) / z} \quad \dots \dots \dots (1) \end{aligned}$$

$$\text{or } T = 250 + z \log L \quad \dots \dots \dots (2)$$

Schultz and Olson (1940) introduce the 'Improved General Method' which uses a specially ruled lethal rate paper, on which the temperature-time data are plotted directly. The ordinate scale (marked in units of temperature) is defined by equation (2) above. The F value of the process which has been plotted is determined by planimetry.

Other methods of integrating lethal rate with respect to time without assuming standard forms of the heating and cooling curves have been proposed. Patashnik (1953) used a simple arithmetical summation of lethal rate values at equal time intervals, while Levine (1956) approximates time-temperature by a number of short straight lines, and sums the lethal effect of each interval using tables of his 'Thermal Sterilizing Function'. This function has been calculated on the basis of an Arrhenius expression for the rate of destruction of spores.

The 'General Method' with its variations, is still the most reliable method of calculating the lethal effect of heat for any given set of data (Gross et al (1946), Morris (1967)). Stumbo (1965) has commented that many of the formula methods (introduced to reduce the tedium of graphical integration, and to increase the versatility of the General Method) are complex and time consuming. Data for one set of conditions usually cannot reliably be converted to apply to another set of conditions (Stumbo, 1965).

Ball's 'Formula Method', introduced in 1923 uses heating and cooling curves of a standard form. The reciprocal slopes, f_h and f_c , of the heating and cooling curves are assumed equal, and the cooling curve has a lag factor or j value equal to 1.41. The lag portion of the cooling curve is approximated to by a hyperbolic expression.

The integration is carried out using the expression -

$$F = f L_g C,$$

$$\text{where } L_g = 10^{(250 - T_g) / z}$$

and C is a tabulated function of g , z and $m + g$.

' g ' is the difference between retort temperature and maximum centre temperature T_g at the end of the heating period, and $1/z$ is the slope of the

log TDT vs T plot. 'm + g' is the difference between retort and cooling water temperatures.

Ball's technique was further improved in 1928 with the retabulating of the C:g tables as f_h/U : g tables, where -

$$\frac{f_h}{U} = \frac{e^{2.303 g/z}}{C}$$

'U' is the 'number of minutes required to destroy organism at retort temperature'. In terms of the later thermal reduction time concept it represents the time, at retort temperature, to accomplish some given reduction in spore numbers. Further parameters are introduced to account for broken heating curves, cooling curves of different slope to the heating curve, and a crude correction where the cooling curve lag factor j_c is significantly different from 1.41.

A nomogram method based on Ball's formula method was introduced by Olson and Stevens (1939) for the rapid solution of a limited range of processing problems. Broken heating curves or divided process problems cannot be solved.

Ball and Olson (1957) introduce a great number of new parameters and a number of new tabulated functions. This new method is based on the methods of 1923 and 1928, and arose from the extension of these early methods to calculation of the destruction of nutritive and other factors in thermal processing. The use of the new functions of P or "per cent sterility" is claimed to "increase the scope and flexibility of the formula method."

Although Ball and Olson (1957) claim that the processes thus calculated have "been almost monotonously successful" since the method was introduced in 1923, Powers et al (1952) observed very highly significant differences between Ball's 1928 method and the General Method of Bigelow et al (1920) for some sizes of jar. The differences, while significant, were not very large. Stumbo and Longley (1966) observed that processes calculated by Ball (1923, 1928) seldom agreed with processes calculated by the General Method. They found differences between the methods of up to 15% even with identical processes, and proceeded to show that Ball's tables of f_h/U : g were incorrect. The recalculated tables of Stumbo and Longley

(1966) and Stumbo (1965) cover values of j_0 (the cooling curve lag factor) other than the value of 1.41 as assumed in all of Ball's tables.

Hicks (1958) points out that the tables of the F_h functions of Ball and Olson (1957) (i.e., per cent sterility for heating phase of process) contain a number of discrepancies. He presents a revised table of the F_h functions in a slightly different form. The F_0 functions (for cooling) which are considerably more complex in their derivation have not been checked, and the use of the earlier $f_h/U : g$ functions is recommended as an alternative.

All the methods discussed above treat only a single point, and, depending on whether thermal death time or thermal reduction time data is used, indicate whether a process will achieve 'sterility' or reduce the population of spores by a given ratio. They do not indicate the probability of spore survival at any point other than that considered in the analysis. While the probability of spore survival on the basis of the whole can cannot be inferred from this data, F values obtained by the use of the so-called 'phantom' TDT curve (equation 1), which can be interpreted in terms of probability of spore survival at the can centre, have been of great value in comparison of various processes.

Ball, Olson and Boyd (1948), in an unpublished paper described a method of calculating the effect of heat on nutritional and other factors in processed foods, which involved an integration throughout the container. The details of the method did not appear until much later (Ball and Olson, 1957) when the calculation of the necessary tables of parameters had been completed. The method can also be applied to destruction of spores.

Stumbo (1948a) introduced to process calculation the concepts of logarithmic death rate of bacterial spores and thermal reduction times, although Ball (1943) had indicated the applicability of decimal reduction times to process calculation. Stumbo redefines several terms of the thermal death time calculation method, and using these redefined parameters demonstrated the effect of distribution of spores at points distant from the centre point on the probability of spore survival in a container. An integration for total numbers of surviving spores in the can is not attempted,

and his basis for process evaluation is the reduction of spore survival probability to at least a certain value (10^{-9}) in all of the regions considered in the container.

In a further paper (1949a) Stumbo demonstrated by a graphical integration for numbers of spores surviving processes (conduction and convection) that no one location can be considered typical of the whole container. The convection integration, however, is suspect because the effect of spore movement is not taken into account.

Gillespy (1951), considering conduction heating packs only, interprets the F value for the whole can as being the time at 250°F that, applied throughout the can, would result in the same 'degree of sterility' as calculated by an integration of the effect of heat on all elements of volume in the container, followed by an integration with respect to volume to obtain an estimate of the total number of spores in the container surviving a process. The first integration at the centre (using his own approximations for the cooling curve) is followed by an integration which assumes a linear increase in F with increase in volume as measured from the centre point towards the outside of the can. Unfortunately Gillespy does not appear to have extended his treatment to convection heating products as he had indicated in 1951.

When dealing with conduction heating products Hicks (1951) uses the fundamental heat conduction equations, exponential integral functions, and graphical integrations to evaluate spore survival probabilities for the whole container. He introduces the very useful concept of an equivalent volume, which, when multiplied by the residual number of spores per unit volume at the centre point would give the total number of viable spores to be expected in the container. The factors that affect the equivalent volume are discussed in the light of the uncertainties always associated with the other quantities, especially initial number of spores. It is seen that, if the equivalent volume is known, then centre point calculations can be used very readily for process calculations.

For conduction heating products the equivalent volume is shown to be of the order of 1 - 2% of the can volume, while it is of the order of the can volume for convection heating products.

Stumbo (1953) presented a method for conduction heating foods which uses only tables of parameters as presented by Ball (1928). It uses better approximations than Stumbo's methods of 1948 and 1949, and is relatively simple to operate. The integration throughout the can is based on a linear $(F_\lambda - F_0)$ vs v curve similar to that used by Gillespy (1951). The F_λ value is the F value of the process on an iso- j -surface enclosing a volume v . An equation developed by Olson and Jackson (1942) was used to describe the iso- j -surfaces. This method is also described in Stumbo's useful (and very readable) treatment of the application of thermobacteriology to food processing of 1965, which includes the extended tables of parameters of Stumbo and Longley (1966).

Hicks (1952) has reviewed the similarities and implications of the methods of Stumbo (1948a, 1949a), Gillespy (1951), and Hicks (1951). Stumbo (1949b) in a review of food processing applications of thermobacteriology has discussed the classical methods of calculation and his own work (i.e. Stumbo 1948a, 1949a).

The methods using the whole can as a basis for calculation require information on initial numbers of spores and their rate of destruction characteristics, and give information on the numbers of spores per can that are likely to remain viable after processing. These data can then be related to the probability of spoilage. It should be pointed out that the values of these parameters are not well defined. Much more data will be required from bacteriologists and biometricians in the canning industry on the initial numbers of spores, and the value of the final tolerable spore level will need careful consideration by canning industry executives (Hicks, 1952).

A factor that does not enter directly into process calculation, but is very relevant to the application of process calculation to process specification arises from the non-uniformity of individual cans of product, and the consequent variation in heating and cooling curves and F values. Powers et al (1962) have used statistical methods in a study of the means and variances of F values of a number of products. They review the various statistical methods that have been used to estimate minimal lethality due to variations in heating and cooling rates.

Levine (1956) has used the mean and variance of initial spore populations to estimate the certainty that a given spore survival level will not be exceeded if a uniform lethal value of process for all containers is assumed.

As the overall spore survival probability will depend on both the distribution of initial spore numbers, and the distribution of F values, it may sometimes be necessary to take both factors into account, e.g., in the evaluation of processes for very heat sensitive products.

(iii) Non-mathematical Methods of Process Evaluation

All methods of process calculation so far described (with the exception of the direct method using inoculated packs) involve integrations of the effect of lethal heat after the process, based on data obtained during the process. A method that, in effect, does the integration (for a single point) during the process is described by Hersom in a paper read to the International Food Industries Congress, June 1964. He used a sealed glass tube with an indicator based on a time-temperature sensitive reaction (inversion of sucrose). Details of the construction of calibration curves from which the equivalent process is determined are not described. The technique was used mainly for the rapid checking of a continuous cooker-cooler.

Ball, in oral discussion of this paper commented on the relative slopes (with respect to temperature) of chemical reaction, enzyme inactivation and spore destruction rate curves, and suggested the possibility of using overall colour change in a light coloured product (essentially a system of chemical reactions) as an indicator of the lethal effect of heat on the whole bulk of the canned material. This would in effect be carrying out both integrations (with respect to time and with respect to volume) in the can during the process, and would if found feasible, take account of all convection movement of product within the can.

Hersom's method, which was not published until the present work was under way is similar to this study in some respects, particularly in choice of reaction system. It is limited however in that product movement cannot be taken into account directly, and the lethal effect of heat is only integrated at a single point.

THE PRESENT WORK

All methods of process calculation to date require measurement or calculation of temperatures in the container during processing, followed by graphical or mathematical integrations of lethal rate. Although these methods have been very useful in process evaluation and process comparison, they have introduced a certain arbitrariness into process calculation, either in the integration at a single point (standard forms of the heat penetration curve), or in the integration throughout the container (standard distribution of F throughout the container based on model conduction and convection systems), or in both.

In view of this somewhat empirical nature of process calculation methods, and the trend to continuous processing methods where temperature measurements are difficult (or impossible), it has been considered worthwhile to investigate the possibility of using a chemical reaction in the container as an analogue of spore destruction in the estimation of the total lethal effect of heat.

The present work is therefore a study of the prediction of spore destruction from chemical reaction data, covering both the basic theoretical aspects, and the application of theory to two convection heating systems in which the previously unstudied effect of product movement is important.

ADDENDUM

In a very recent paper (which appeared after this section of the thesis had been completed) Timbers and Hayakawa (1967) describe the use of a digital computer in the calculation of mass average sterilizing values for cans heating by conduction.

In the first section Timbers outlines the measurement of temperature at nine points in the can, and the use of this data in the calculation of the overall spore survival ratios by the General Method, and the methods of Ball and Olson (1957) and Stumbo (1953). Satisfactory agreement between the three methods is reported for normal values of z and D , although the agreement was poorer when Stumbo's method was applied for high values of D .

It should be pointed out that the tables of Ball and Olson (1957) were not used. Instead, a computer sub-program was prepared to generate the required functions, and the discrepancies pointed out by Hicks (1958) and Stumbo and Longley (1965) will not affect the comparison of the three methods.

In the second section of the paper, Hayakawa outlines a new procedure for the calculation of mass average sterilizing values using a digital computer. Solutions of the Fourier equation for both the heating and cooling periods are used, and all numerically significant terms are included (of existing procedures in which only the first term is used). An analytical formula was derived from the Fourier equation solutions which contained a double integration with respect to volume, and a single integration with respect to time. In the computer program these integrations are replaced by a 12 point formula (Tyler, 1953) and Simpson's rule respectively.

Again satisfactory agreement between the calculated and experimental values of the mass average survival ratio was observed.

In this work the $\log D$ vs T curve has been assumed linear rather than the $\log D$ vs $\frac{1}{T}$ curve as derived from the Arrhenius equation. Examination of the schematic computer program indicates that an Arrhenius type of expression for spore destruction rate could be used to replace the $\log D$ vs T function, if it was desired to calculate overall chemical changes (i.e. vitamin losses etc.).

DEVELOPMENT OF THE CHEMICAL

ANALOGUE OF SPORE DESTRUCTION

DEVELOPMENT OF THE CHEMICAL ANALOGUE OF SPORE DESTRUCTION

INTRODUCTION

Development of the Investigation

This project developed from an interest in methods of sterilization of reconstituted milk in cans, with a view to distribution and storage without refrigeration, especially in Asian markets.

It was not known whether a sterile product that would be acceptable to the consumer could be obtained. Hence a study of methods of sterilization in the can would be aimed at an evaluation of the effects of processing variables such as retort temperature, time of processing, type of agitation, etc., on both the bacteriological quality and on the quality of the product.

Development of the Chemical Analogue Concept

In a study of the bases of process evaluation methods, the adequacy of applying temperature data measured at fixed points to spores and elements of food moving about in the container was questioned, particularly in unagitated containers where it was found in early experimental work that large temperature differences existed between the various locations in the can.

A consideration of a general process (see Appendix I) in which the positions and temperatures of all elements of the material in the container were known showed that the 'sterility' as calculated on a basis of temperatures measured at fixed points was not in general identical to the actual sterility (i.e. the sterility calculated for each moving element of food and then integrated over all the elements).

The comparison by Gillespy (1948) of the $\log D$ vs T and $\log D$ vs $\frac{1}{T}$ curves (see p 11) for spore destruction rates (and hence the relationship of spore destruction equations to the Arrhenius equation for rates of chemical reactions (see p 9) along with the absence of any experimental study of the effect of convection movement of product on the total

calculated lethal effect of heat, suggested that measurement of the extent of some suitable chemical reaction in a can could be profitable in a study of convection heating products. As well as making possible a study of the effects of product movement within the container, a chemical reaction technique could also lead to a method for direct evaluation of the lethal effect of a process from relatively simple measurements of the extent of a chemical reaction. This would avoid the complex double integration of lethal rate with respect to time and with respect to volume. The same chemical measurements could also prove useful in evaluating the effect of processing on various chemical factors such as vitamin destruction, colour and flavour changes, etc., which are of great importance in canning operations.

Experimental Plan

The experimental work of this project was planned with both possibilities in mind. The chemical reaction technique was to be used to check the effect of product movement by comparing actual overall chemical measurements and the calculated extent of chemical reaction using traditional process evaluation methods. When an adequate basis for calculation of chemical reaction from fixed point temperature data had been established, spore destruction was to be calculated and the effect of the various kinetic and heat penetration parameters on the relation between chemical reaction and spore destruction was to be investigated for a number of agitated and unagitated processes.

DEVELOPMENT OF BASIC CHEMICAL ANALOGUE THEORY

Nomenclature

The symbols U and F have been used widely in process calculation methods to denote the 'lethality' of a process in terms of equivalent time at some given temperature. To avoid a further redefinition of these functions, which have always been associated with the z concept, it has been considered advisable to use other symbols to represent the lethal

effect of heat, and define these in such a way that they apply to both spore destruction and chemical reaction.

An upper case theta (Θ) is used to denote 'equivalent retort time', while the lower case theta (θ) is used as the variable time. Equivalent retort time for spore destruction can be readily related to U and F in terms of reduction of spore numbers.

Definition of Terms and Integrals

The equivalent retort time of a process, Θ , is defined as the length of a process at retort temperature (with instantaneous heating and cooling) that accomplishes the same relative change in spore numbers or chemical reactant concentration as the process under consideration.

For any first order process -

$$\left(\frac{\partial N}{\partial \theta}\right)_T = -k_T N$$

where N is either the concentration of spores (number per unit volume) or concentration of reactant in the reaction



This gives :

$$\log_e N/N_0 = -k_T \theta$$

From the definition of Θ

$$\Theta = -\frac{1}{k_R} \log_e \frac{N_1}{N_0} \dots\dots\dots (1)$$

where N_1 and N_0 are the final and initial values of N, and k_R is the reaction rate constant at retort temperature, T_R .

For any process $T = F(\theta)$ -

$$d\left(\log_e \frac{N}{N_0}\right) = -k d\theta ,$$

and

$$-\log_e \frac{N_1}{N_0} = \int_{\theta_0}^{\theta_1} k \, d\theta.$$

Therefore

$$\theta = \int_{\theta_0}^{\theta_1} \frac{k}{k_R} \, d\theta \dots\dots\dots (2)$$

The Arrhenius equation gives :

$$\frac{k}{k_R} = e^{-\frac{E_A}{RT} \left(\frac{1}{T} - \frac{1}{T_R} \right)}$$

Putting $\frac{E_A}{RT_R} = B$ and $\frac{T}{T_R} = u$ we get

$$\begin{aligned} \theta &= \int_{\theta_0}^{\theta_1} e^{B \left(1 - \frac{1}{u} \right)} \, d\theta \dots\dots\dots (3) \\ &= -D_N \log_{10} \frac{N_1}{N_0} \end{aligned}$$

D_N is the decimal reduction time at retort temperature of component N.

If a non-first order reaction is used the definition of the equivalent retort time (equation 3) is unchanged, but the equation

$$\theta = -D_N \log_{10} \frac{N_1}{N_0}$$

no longer applies.

Spore destruction estimation from chemical reaction (I)

Consider the simple case where a chemical reaction can be found such that

$$E_A (\text{chem}) = E_A (\text{baot})$$

(a) Integration of lethal rate with respect to time at a single point.

Consider an element of food, dv . It can be seen from the definition of θ (equation 3) that $\theta_{\text{bact}} = \theta_{\text{chem}}$ for all values of B , and all time-temperature functions $u = G(\theta) = \frac{1}{T_R} \cdot F(\theta)$

$$\text{Hence, } D_N \log_{10} \left(\frac{N_{1v}}{N_0} \right) = D_A \log_{10} \left(\frac{A_{1v}}{A_0} \right)$$

$$\text{and } \frac{N_{1v}}{N_0} = \left(\frac{A_{1v}}{A_0} \right)^{D_A/D_N}$$

where A is the concentration of reactant A in the reaction



N refers to spore numbers only, and subscript v refers to an element dv .

(b) Integration with respect to volume.

$$\begin{aligned} \frac{\bar{N}_1}{N_0} &= \frac{1}{V} \int_0^V \frac{N_{1v}}{N_0} dv \\ &= \frac{1}{V} \int_0^V \left(\frac{A_{1v}}{A_0} \right)^{D_A/D_N} dv \end{aligned}$$

$$\text{Hence } \frac{\bar{N}_1}{N_0} = \frac{\bar{A}_1}{A_0} \quad \text{if} \quad D_A = D_N$$

$$\text{and } \frac{\bar{N}_1}{N_0} = \left(\frac{\bar{A}_1}{A_0} \right)^{D_N/D_A} \quad \text{if } D_A \neq D_N, \text{ and } \frac{N_{1v}}{N_0} \text{ and } \frac{A_{1v}}{A_0}$$

are not functions of volume.

The final values of A and N averaged over the whole container are denoted here by $\bar{A}_1$ and $\bar{N}_1$ respectively. The average concentration change of a chemical reactant can thus be used as a direct measure of reduction in spore numbers if the reaction is such

that the bacterial and chemical decimal reduction times are equal at retort temperature. If the decimal reduction times of the two systems are not equal, then the $\Theta_{\text{chem}} : v$ and $\Theta_{\text{bact}} : v$ distribution functions become important. This dependance of the integration with respect to volume on equality of the decimal reduction times can also be deduced from the work of Gillespy (1951) and Stumbo (1953). Both these workers point out the dependance of F_g (the lethal value of a process obtained by integrating with respect to volume) on the decimal reduction time or 'heat resistance' at retort temperature.

Spore destruction estimation from chemical reaction (II)

It is not very likely that chemical reactions can be found such that the bacterial and chemical activation energies are identical. Activation energies for spore destruction reactions are generally in the range 60-110 k cal/g-mole (corresponding to a range of z 's (see page 6) of approximately 22 to 12), while chemical reaction activation energies range from about 10 to 45 k cal/g-mole, with most in the range 20-30 k cal/g-mole. Hence the case when $E_A (\text{chem}) \neq E_A (\text{bact})$ must be considered.

(a) Integration of lethal rate with respect to time at a single point.

$$\Theta_{\text{chem}} = \int_{\theta_0}^{\theta_1} B_{\text{chem}} \left(1 - \frac{1}{u}\right) d\theta, \text{ and}$$

$$\Theta_{\text{bact}} = \int_{\theta_0}^{\theta_1} B_{\text{bact}} \left(1 - \frac{1}{u}\right) d\theta$$

It can be seen that the $\Theta_{\text{chem}} : \Theta_{\text{bact}}$ function is not in general independent of the time-temperature function $u = G(\theta)$ at the given point. Because B_{chem} and B_{bact} are known for a given set of chemical and bacterial systems, a knowledge of the time-temperature function $u = G(\theta)$, and its influence on the $\Theta_{\text{chem}} : \Theta_{\text{bact}}$ function becomes of paramount importance.

It should be pointed out that processes may appear to be quite different in form, although they are equivalent with respect to spore destruction prediction from chemical reaction. A change of variable in the integration -

$$\Theta = \int_{\theta}^{\theta} \frac{k}{k_R} d\theta$$

leads to -

$$\Theta = \int_{\left(\frac{k}{k_R}\right)_0}^{\left(\frac{k}{k_R}\right)_{\max}} (\theta_o - \theta_h)_T d\left(\frac{k}{k_R}\right)$$

$$= \frac{1}{k_R} \int_{k_o}^{k_{\max}} (\theta_o - \theta_h)_T dk$$

where θ_o and θ_h are the times on the cooling and heating curves respectively at which the temperature of the food is T . $(\theta_o - \theta_h)_T$ is therefore the length of time that the food has a temperature greater than T . Any processes that give identical $(\theta_o - \theta_h)_T$ vs T functions are therefore equivalent with respect to the calculation of Θ_{bact} from Θ_{chem} . This becomes important in a discussion of curves of best fit (see Further Development of the Chemical Analogue, p 194) where the process of best fit may not appear to resemble closely the time-temperature function from which it is derived.

A number of approaches have been used in an initial study of the $\Theta_{\text{chem}} : \Theta_{\text{bact}}$ function.

(1) The Θ vs E_A function for a general process.

An expression was sought that would enable Θ to be calculated directly from the activation energy E_A , or from $B = E_A/RT_R$

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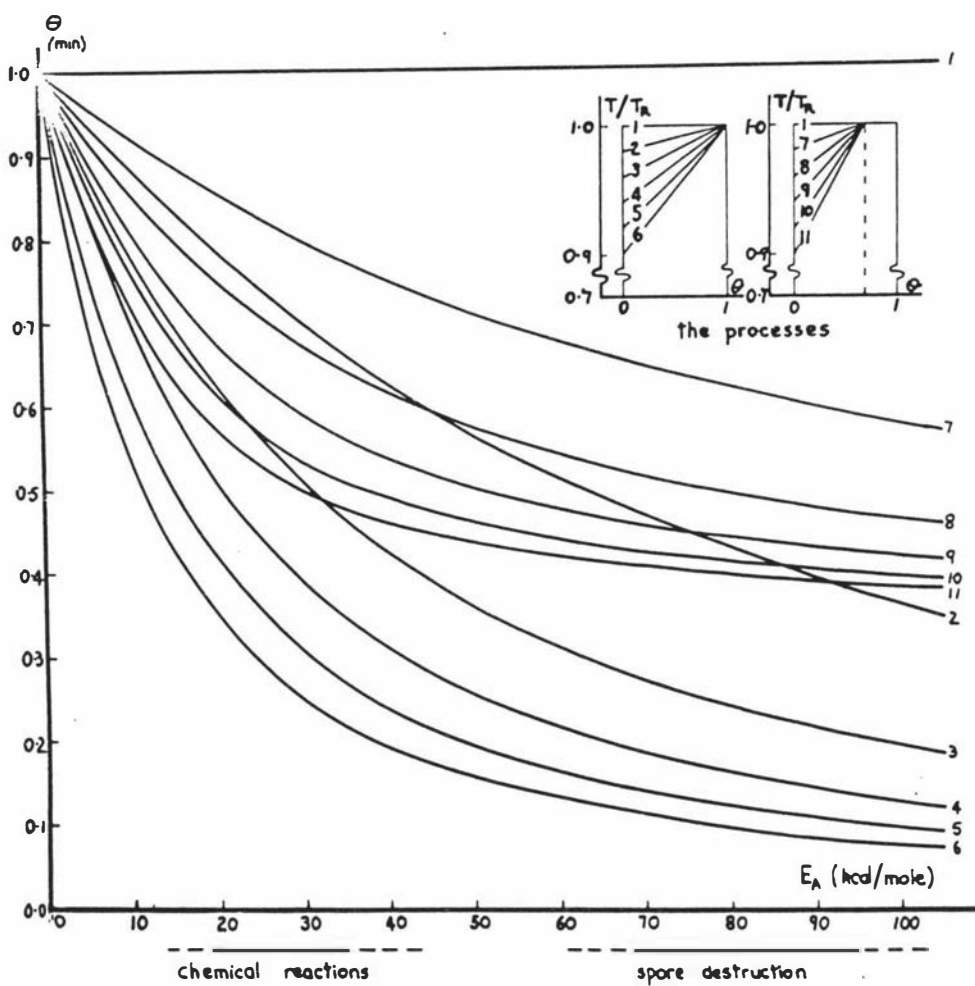


Fig. 1 Θ vs E_A for simple linear processes

Expansion of $e^{-B(1 - \frac{1}{u})}$ in the integral -

$$\Theta = \int_{\theta_0}^{\theta_1} e^{-B(1 - \frac{1}{u})} d\theta$$

leads to an infinite series in B,

$$\text{viz. } \Theta = \sum_{n=0}^{\infty} \frac{C_n}{n!} B^n,$$

where the C_n are defined by -

$$C_n = \int_{\theta_0}^{\theta_1} \left(\frac{u-1}{u}\right)^n d\theta$$

$C_n \rightarrow 0$ as $n \rightarrow \infty$, because $\frac{1}{2} < u < 1$ for all real processes, and hence $0 < \left|\frac{u-1}{u}\right| < 1$ and the series in B^n for Θ is convergent.

Values of B are such that many terms of the series are required to evaluate Θ , and hence the expression will be of little use in predicting spore destruction from chemical reaction data.

(11) The Θ vs E_A function for processes of known or assumed form.

1. The Θ vs E_A function.

It has been shown that Θ as a function of E_A is dependent on the function $u = G(\theta)$. A number of integrations were done for simple processes with linear heating and cooling curves (see Appendix II), to find the order of magnitude of the differences between the E_A vs Θ functions for a range of process shapes similar to that obtained in practice.

These Θ vs E_A functions (see Figure 1) are similar in form, but the differences are significant enough to prevent calculation of Θ_{best} from one measurement of Θ_{chem} . Although the heat penetration curves used here are somewhat artificial, the log Θ vs E_A curves probably

illustrate quite well the influence that the $u = G(\theta)$ (or $T = F(\theta)$) functions might be expected to exert in practice.

2. Number of parameters for standard heat penetration curves.

If a real process can be completely described by equations involving n independent parameters, then the values of $n-1$ parameters must be measured or assumed to define the Θ vs E_A function, and hence enable the estimation of Θ_{bact} to be made from a single measurement of Θ_{chem} .

The processes used in the above calculations of Θ vs E_A curves can all be defined in terms of four parameters. The three parameters initial temperature, temperature of the holding period, and ratio of heating to holding period lengths, define the shape or form of the process, and hence the $\Theta : E_A$ function. The fourth parameter, the length of the process is determined by a measurement of Θ_{chem} , and hence Θ_{bact} can be determined.

The standard heat penetration curve of Ball (1923, 1928) (simple process, unbroken heating curve) can also be defined in terms of four parameters, viz: T_R , T_0 , f_h and g , with all other parameters being defined in terms of these. T_R and T_0 , the retort temperature and cooling water temperatures respectively, are known from the process specification, and g , the difference between T_R and maximum product temperature, can be determined with a maximum recording thermometer. Using tables of $f_h/\Theta_{\text{chem}}:g$ (of $f_h/U : g$ tables of Ball), f_h (the reciprocal slope of the semilogarithmic heating curve) can be determined from a single measurement of Θ_{chem} , and Θ_{bact} (or U) can then be determined in the usual way from $f_h/\Theta_{\text{chem}}:g$ tables. Alternatively tables of $(\Theta_{\text{bact}}/\Theta_{\text{chem}}):g$ could be used. The term U can be regarded as the equivalent in Ball's system of the term Θ_{bact} used here to denote equivalent retort time.

If g is very small, another point on the linear portion of the semilog heating curve (such as $(0, \log j(T_R - T_0))$) or an experimentally determined point $(\theta, \log T_R - T_0)$ can be used, and the simultaneous equations for g and f_h are solved graphically, or by successive approximations.

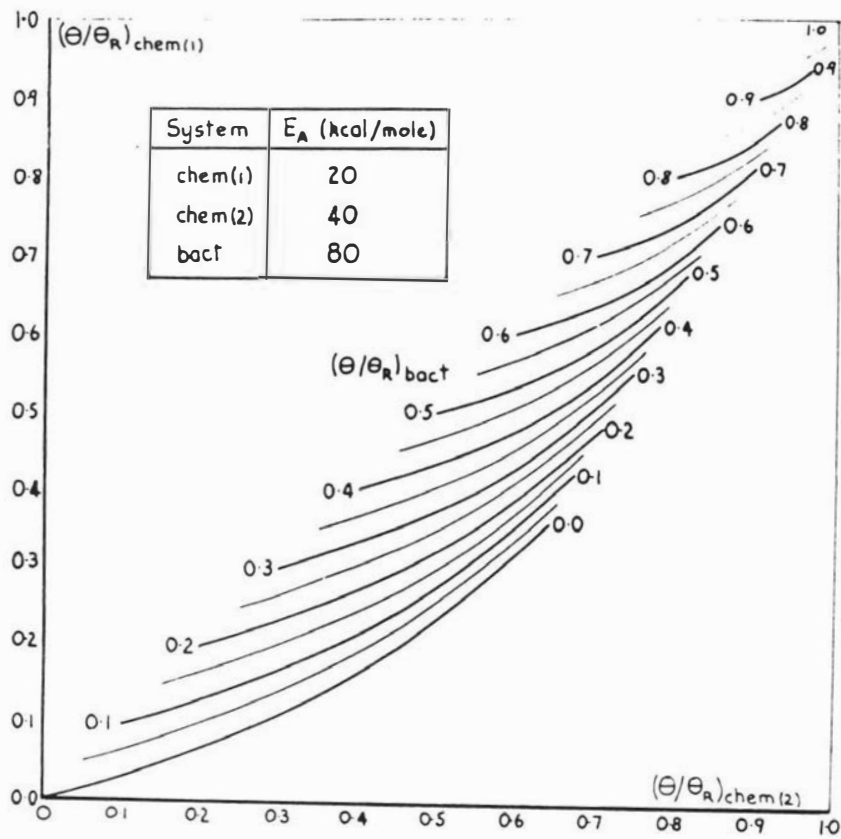


Fig.2a The Θ_{bact} vs $(\Theta_{chem(1)}, \Theta_{chem(2)})$ function for simple linear processes

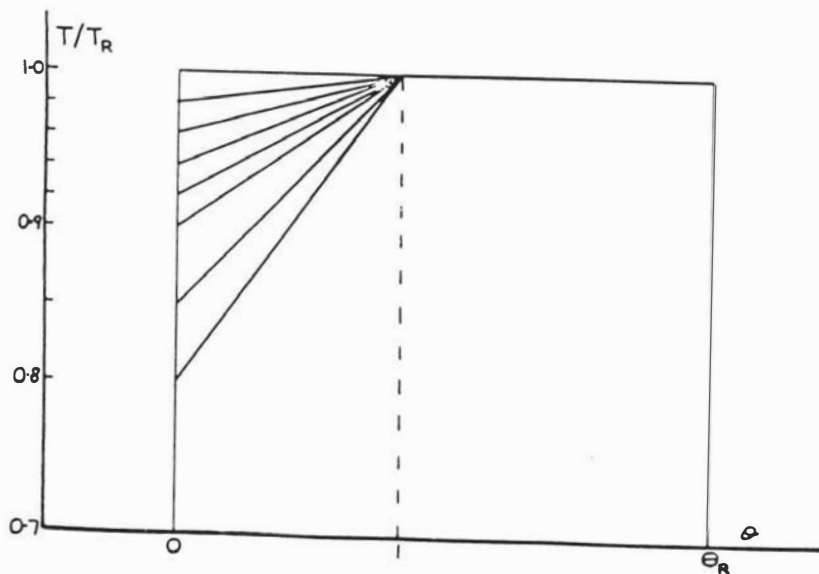


Fig.2b Processes used in calculation of the Θ_{bact} vs $(\Theta_{chem(1)}, \Theta_{chem(2)})$ function.

Even if the real process does not correspond exactly to the assumed form, the estimation of Θ_{bact} from Θ_{chem} is probably better than that based on the heating curve parameters alone, as deviations from ideality especially in the cooling period will tend to be compensated for in the estimation of f_h . Comparison of processes of form similar to that assumed will also be facilitated.

(iii) The Θ_{bact} vs ($\Theta_{\text{chem}(1)}, \Theta_{\text{chem}(2)}$) function.

This is a special case of (ii) above in which values of E_A are calculated for three values of E_A , viz: $E_{A \text{ bact}}$ and two values of $E_{A \text{ (chem)}}$. If a heat penetration curve is assumed which is described by n parameters of which only $n-2$ can be determined by measurements external to the can, values of Θ_{chem} for two reactions of different activation energies are required for the determination of the form of the Θ vs E_A function and hence Θ_{bact} .

To demonstrate the application of this method $\Theta_{\text{bact}}, \Theta_{\text{chem}(1)}$ and $\Theta_{\text{chem}(2)}$ were calculated for a number of four parameter processes (again with linear heating curves). Contours of $(\Theta/\Theta_R)_{\text{bact}}$ were plotted against $(\Theta/\Theta_R)_{\text{chem}(1)}$ and $(\Theta/\Theta_R)_{\text{chem}(2)}$, (Fig. 2a), from which Θ_{bact} for any linear process (with initial temperature and rate of heating unknown) may be found from two measurements of Θ_{chem} . It is assumed that the retort-temperature (T_R) and the overall length of the process (Θ_R) (see Fig. 2b) are known.

Similar curves could be constructed for other cases in which $n-2$ parameters can be measured outside the can. If Ball's curve for a simple process is assumed Θ_{bact} vs ($\Theta_{\text{chem}(1)}, \Theta_{\text{chem}(2)}$) curves or tables may be prepared, and any process with both f_h and g unknown may then be determined very simply.

An advantage of the direct Θ_{bact} vs ($\Theta_{\text{chem}(1)}, \Theta_{\text{chem}(2)}$) curve method is the ease with which errors in Θ_{bact} can be estimated from the known uncertainties in $\Theta_{\text{chem}(1)}$ and $\Theta_{\text{chem}(2)}$. Error analyses in the formula methods are difficult as there are many variables with non-independent errors to be taken into account. The General and

Improved General Methods in which lethal rates are plotted and integrated graphically enable errors to be estimated somewhat more readily than the Formula Methods.

(b) Integration of Θ with respect to volume.

(i) General unknown $\Theta_{\text{baot}} : v$ and $\Theta_{\text{chem}} : v$ distributions.

The overall equivalent retort time, $\bar{\Theta}$, is the time at retort temperature that would give the same chemical reactant concentration reduction or spore number reduction as that obtained by averaging over all elements of food -

$$\text{i.e. } \bar{\Theta}_{\text{chem}} = -D_{\text{chem}} \log_{10} \frac{\bar{A}_1}{A_0} \dots\dots\dots (4)$$

$$\text{and } \bar{\Theta}_{\text{baot}} = -D_{\text{baot}} \log_{10} \frac{\bar{N}_1}{N_0} \dots\dots\dots (5)$$

The average concentration reduction of reactant A in the container $\frac{\bar{A}_1}{A_0}$ has been defined by -

$$\frac{\bar{A}_1}{A_0} = \frac{1}{V} \int_0^V \frac{A_1 v}{A_0} dv, \dots\dots\dots (6)$$

where V is the volume of the container.

Similarly for spores -

$$\frac{\bar{N}_1}{N_0} = \frac{1}{V} \int_0^V \frac{N_1 v}{N_0} dv \dots\dots\dots (7)$$

Substitution of $10^{-\Theta_{\text{chem}}/D_{\text{chem}}}$ for $\frac{A_1 v}{A_0}$ in equation (4)

and $10^{-\bar{\Theta}_{\text{chem}}/D_{\text{chem}}}$ for $\frac{\bar{A}_1}{A_0}$ in equation (6) gives -

$$10^{-\bar{\Theta}_{\text{chem}}/D_{\text{chem}}} = \frac{1}{V} \int_0^V 10^{-\Theta_{\text{chem}}/D_{\text{chem}}} dv$$

which gives -

$$\bar{\Theta}_{\text{chem}} = -D_{\text{chem}} \log_{10} \left(\frac{1}{V} \int_0^V 10^{-\Theta_{\text{chem}}/D_{\text{chem}}} dv \right) \dots\dots\dots (8)$$

Similar substitutions in equations (5) and (7) lead to -

$$\bar{\Theta}_{\text{bact}} = -D_{\text{bact}} \log_{10} \left(\frac{1}{V} \int_0^V 10^{-\Theta_{\text{bact}}/D_{\text{bact}}} dv \right) \dots\dots\dots (9)$$

where Θ_{chem} and Θ_{bact} are both functions of volume v .

The $\bar{\Theta}_{\text{chem}} : \bar{\Theta}_{\text{bact}}$ function is only ⁱⁿ dependent of the $\Theta_{\text{chem}} : v$ and $\Theta_{\text{bact}} : v$ functions if these functions are such that -

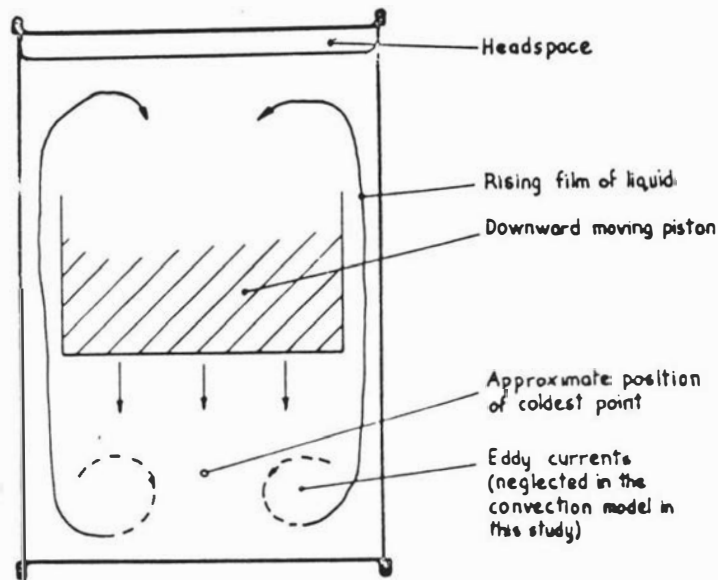
$$\frac{\Theta_{\text{chem}}}{D_{\text{chem}}} - \frac{\Theta_{\text{bact}}}{D_{\text{bact}}} = C \text{ for all } v,$$

where C is a constant. If this condition obtains -

$$\frac{\bar{\Theta}_{\text{chem}}}{D_{\text{chem}}} - \frac{\bar{\Theta}_{\text{bact}}}{D_{\text{bact}}} = C.$$

As in case I where $E_A(\text{chem}) = E_A(\text{bact})$, it is seen that the values of D_{chem} and D_{bact} at retort temperature are involved in the condition that the $\bar{\Theta}_{\text{chem}} : \bar{\Theta}_{\text{bact}}$ function is independent of the $\Theta_{\text{chem}} : v$ and $\Theta_{\text{bact}} : v$ distributions.

This integration is discussed further under Further Development of the Chemical Analogue p 201, where a three parameter process of best fit is used for spore destruction estimation for each element of food.



Note: In the cooling phase the direction of flow is reversed.

Fig.3a Convection pattern in a static can.

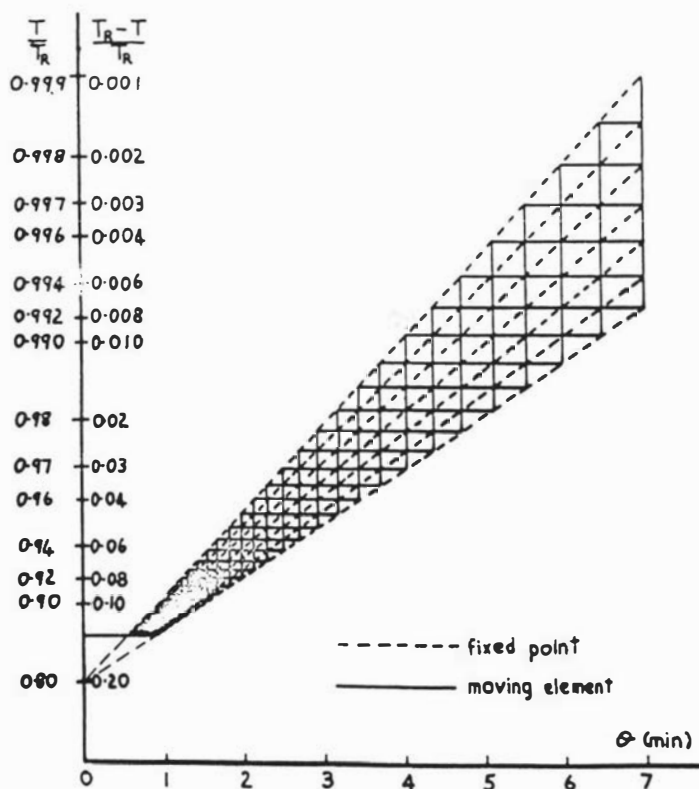


Fig.3b Fixed point and moving element temperature curves for static can convection model.

(11) Known $\bar{\Theta}_{baot} : v$ and $\bar{\Theta}_{chem} : v$ distributions - development of convection models.

Two cases of known $\bar{\Theta} : v$ distribution are considered for convection heating products on the basis of simplified convection models. These models give a basis for calculation of spore destruction from fixed point temperature data, and also make possible an examination of the validity of the prediction of $\bar{\Theta}_{baot}$ from $\bar{\Theta}_{chem}$.

(1) Stationary can.

The model is based on the piston flow concept (see Fig. 3a) in which any small eddies near the bottom of the can are neglected. The liquid is considered to consist of a number of elements which move slowly down the can at constant temperature (i.e. piston flow). The heating of each element as it moves up the can wall in a very thin layer is considered to take place instantaneously. It is seen that the temperature history of each element of fluid is a series of steps (Fig. 3b).

In the example calculated the fixed point temperatures (see Fig. 3b) are assumed to approach retort temperature (274°F) logarithmically. Because the cooling curves will be similar in general pattern to the heating curves, the cooling phase has not been considered here.

The specific chemical reaction rate curve is based on sucrose hydrolysis ($E_A = 25.9$ kcal/g-mole) and the specific spore destruction rate curves are based on a z value of 14°F at 240°F , which gives $E_A = 89.1$ kcal/g-mole. Because the value of z chosen represents a steeper than average log D vs T curve, the effect of E_A on the calculation of $\bar{\Theta}$ from fixed point data will be emphasized.

The equivalent retort times based on the fixed and moving point data are shown in Tables 1 and 2 respectively. These values of $\bar{\Theta}$ are obtained by graphical integration of the specific rate curves (Figures 3c and 3d).

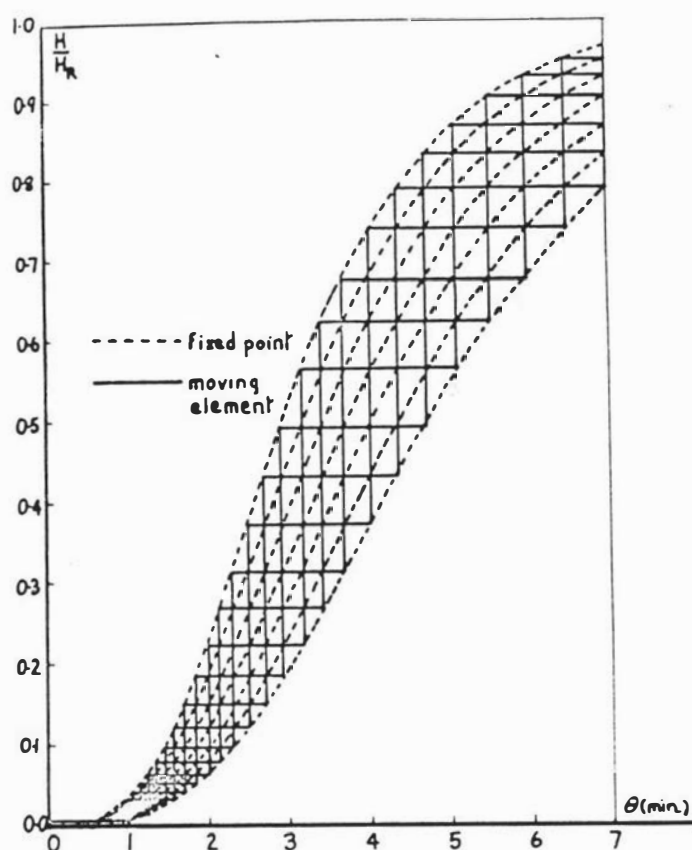


Fig. 3c Specific chemical reaction rate vs time curves for the static can convection model.

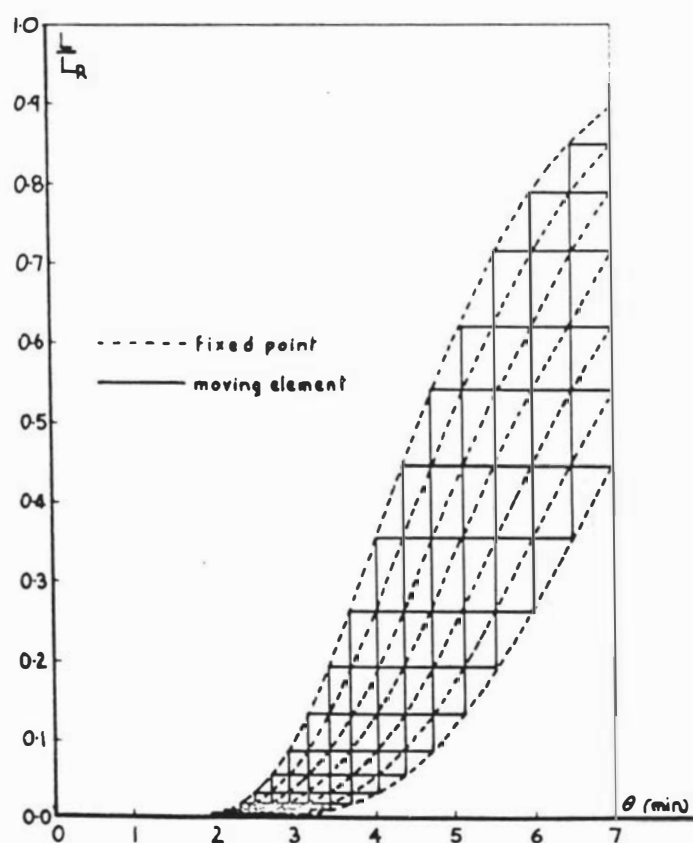


Fig. 3d Specific spore destruction rate vs time curves for the static can convection model.

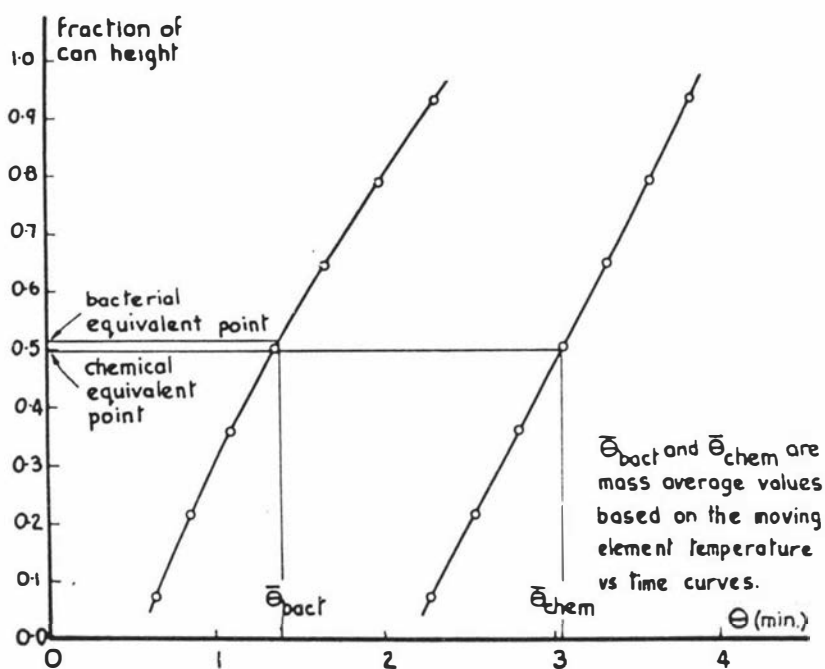


Fig. 3e Graphical calculation of equivalent points for the static can convection model.

Table 1 : Equivalent retort times; fixed point temperature data.

Fixed point number	1	2	3	4	5	6	7
θ_{chem} (min.)	3.811	3.565	3.311	3.049	2.789	2.524	2.262
θ_{bact} (min.)	2.288	1.973	1.653	1.363	1.089	0.843	0.632

Table 2 : Equivalent retort times; moving element temperature data.

Moving element number	1	2	3	4	5	6
θ_{chem} (min.)	3.025	3.056	3.069	3.055	3.040	2.988
θ_{bact} (min.)	1.355	1.419	1.468	1.435	1.397	1.269

Putting $D_{chem} = D_{bact} = 1.0$ min. gives -

$$\theta_{chem} = -D_{chem} \log_{10} \left(\frac{1}{n} \sum_{r=1}^n \log^{-1} \left(\frac{-\theta_{chem}(r)}{D_{chem}} \right) \right) = 3.038$$

$$\text{and } \theta_{bact} = -D_{bact} \log_{10} \left(\frac{1}{n} \sum_{r=1}^n \log^{-1} \left(\frac{-\theta_{bact}(r)}{D_{bact}} \right) \right) = 1.385$$

The overall equivalent retort times θ_{chem} and θ_{bact} are very nearly equal to the equivalent retort times for the can centre (point 4, in Table 1). Hence it is proposed to use the centre point temperature data in the calculation θ_{bact} (of Stumbo 1949, 1953). If comparison of θ_{chem} and θ_{chem} (centre point) indicates that the approximations used in the above analysis are not valid for actual stationary processes, then some point other than the geometrical centre point of the container can be defined as an equivalent point such that the temperature-time function at that point can be considered to apply to the whole can.

This analysis also confirms the validity of the use of the $\bar{\theta}_{chem} : \bar{\theta}_{baot}$ function. θ_{chem} and θ_{baot} are approximately the same for all elements, and therefore -

$$\frac{\theta_{chem}}{D_{chem}} = \frac{\theta_{baot}}{D_{baot}}$$

will be the same for all elements, and $\bar{\theta}_{chem}$ can, therefore, be validly used as a measure of $\bar{\theta}_{baot}$ for any time-temperature function involving a piston flow type of convection. It is likely that the use of $\bar{\theta}_{chem}$ measurements for $\bar{\theta}_{baot}$ estimation will be valid for any process where circulation of the can contents takes place. The validity of this assumption could be checked by a comparison of equivalent points for two chemical reactions of different activation energies.

(2) Agitated can.

The convection model proposed is one of complete mixing. It is assumed that the agitation of the product is such that all elements of fluid are at the same temperature at any instant. The equivalent retort times are, therefore, the same for all elements of fluid, and hence -

$$\frac{\bar{\theta}_{chem}}{D_{chem}} = \frac{\bar{\theta}_{baot}}{D_{baot}}$$

is constant, and $\bar{\theta}_{chem}$ can, therefore, be used as a valid measure of $\bar{\theta}_{baot}$ for all time-temperature functions. The equivalent retort time calculated using fixed point temperature data is identical to the equivalent retort time for any element, and hence for the whole can.

CHEMICAL ANALOGUE EXPERIMENTS

CHEMICAL ANALOGUE EXPERIMENTS

INTRODUCTION

Aim of the Project

The experimental work was planned with two major aims :

- (a) to study convection heating for two types of process, using the chemical reaction technique to evaluate the effect of product movement within the container; and
- (b) to study the relationship between the extent of a chemical reaction (expressed as ϕ_{chem}) and the total calculated spore survival fraction (expressed as ϕ_{bact}) for the two types of convection heating.

Resume of the Work

A suitable first order chemical reaction (acid hydrolysis, or inversion, of sucrose) was selected and the rate of reaction as a function of temperature was determined. Thermocouple wire was calibrated over the range of processing temperatures, and temperature measuring and recording systems were, in turn, set up for the stationary and rotating can experiments. Cans of sucrose were processed and the degree of inversion determined. The extent of sucrose inversion was calculated from the temperature data and compared with the measured degree of inversion. The temperature data were then used to calculate the spore destruction equivalent retort time, and correlations of ϕ_{chem} vs ϕ_{bact} were obtained.

EXPERIMENTAL WORK

Chemical System Development

- (a) The ideal system.

In particular cases it may be possible to use a reaction taking place in the food product itself - for example, the development of brown-

ing in dairy products. As this would entail the determination of the kinetic characteristics of the reaction for each product, and as variations between batches are likely to be important, this approach is not likely to be of general application. The ideal reaction system would then be one which could be added to any food product without disturbing the product physically and without the reaction itself being disturbed chemically by the food product. It may be possible to find reactions in solution which are suitable. Alternatively reactions taking place in the solid phase (e.g. colour changes or structure degradations), which can be added in finely divided or colloidal form may prove to be satisfactory.

(b) Selection of the chemical system.

In this study the chemical system itself forms the product. The system was chosen to be similar in physical properties to milk, industrial interest in which stimulated this investigation.

The system chosen, acid hydrolysis of sucrose has a number of advantages, both kinetic and analytical.

(i) Kinetic characteristics of sucrose hydrolysis.

The rate of inversion of sucrose :



can be expressed -

$$\frac{d[S]}{d\theta} = -k \cdot [S] [H^+]$$

where $[S]$ is the concentration of sucrose. This gives, for any given hydrogen ion concentration, $[H^+]$

$$\frac{d[S]}{d\theta} = -k' [S]$$

because the hydrogen ion concentration remains constant.

The reaction is, therefore, first order with respect to sucrose, with a rate constant k' that can be adjusted by acid concentration or pH to any desired value.

(ii) Analytical characteristics of sucrose hydrolysis.

1. Analysis :

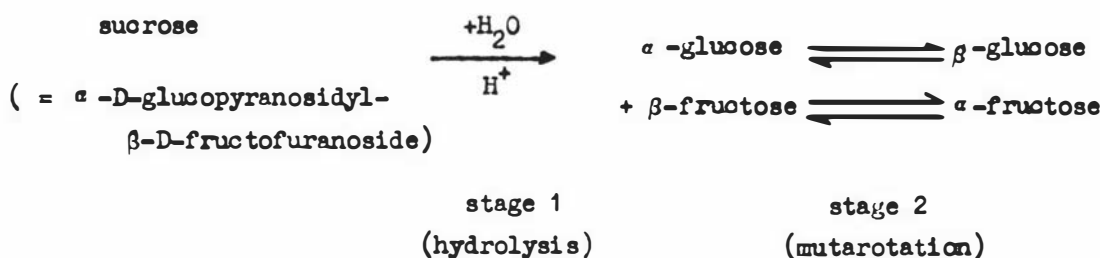
The polarimetric analysis of the reaction is extremely simple. The method relies on the widely different specific rotations of the reactant sucrose and the products glucose and fructose. A table of concentration of unhydrolysed sucrose against angle of rotation (in 200 mm polarimeter tube at 25°C) has been prepared for a solution initially 0.750M in sucrose using data from the literature. (See Appendix III).

2. Effect of temperature :

The specific rotation of the fructose in the invert sugar has a high temperature coefficient. It is, therefore, essential to water jacket the polarimeter tube for analyses of all solutions in which the invert sugar concentration is appreciable.

3. Mutarotation :

In the preliminary work on sucrose inversion, unsteady polarimeter readings of the freshly cooled partially inverted sucrose solutions were observed. This phenomenon was caused by mutarotation as the equilibrium between the α and β forms of glucose and fructose was being established. The reaction, sucrose $\rightarrow$ invert sugar, is more completely described by the scheme



The activation energy of the hydrolysis reaction (stage 1) is about 25 kcal/mol : the activation energy of the mutarotation reaction (stage 2) is about 15 kcal/mol (Moelwyn-Hughes 1961). The relative rate of the second stage is, therefore, much lower than the hydrolysis stage at high temperatures, and the equilibrium of the α - and β - forms of the monosaccharides is not immediately established.

On cooling, the inversion reaction is essentially stopped, but the mutarotation reaction proceeds. Experiments based on a run at 90°C, with samples analysed immediately after cooling and at later intervals showed that the equilibrium was established after three hours. No significant change in rotation of any sample was found between three and twenty-four hours at 25°C. Approximately $4\frac{1}{2}$ hours would be required if a holding temperature of 20°C is used. Processes using temperatures substantially higher than 90°C with fast cooling may require slightly longer holding times. This can be quite easily checked in any particular situation.

(iii) Stability of the system.

Unbuffered sucrose (0.001 N HCl) was found to give suitable reaction velocities and a constant activation energy over the range 70 to 270°F. Serious disagreement between the measured Θ_{chem} and the Θ_{chem} calculated on fixed point data was observed for stationary commercially lacquered cans. Measurements of pH before and after processing showed that even in lacquered cans a significant interaction between the can and chemical system occurred. The change in pH was even greater in unlacquered cans.

An acetic acid-sodium acetate buffer (0.250 M acetic acid, 0.0143 M NaOH, giving pH 3.5) calculated on the basis of the maximum loss of acid (calculated from pH changes) and the minimum tolerable change in the rate of reaction (see Appendix IV). Variation in the composition of stock buffer, arising from experimental errors in the standardization of the buffer components and mixing of the buffer, was found to be significant. Standard rate determination at a reference



Fig.4 Technique of filling polarimeter tube.

temperature (212.0°F) were therefore required, and all rates at other temperatures are expressed in terms of this standard rate. To determine the effect of can type on the extent of hydrolysis of this buffered sucrose solution, a run of nine cans - three lacquered, three unlacquered and three coated with a special high temperature insulating varnish (viz, "Formvar" *) - was processed. Two samples were taken from each can. The angles of rotation from solutions processed in commercially lacquered cans gave the lowest variance, and the differences between the lacquered and "Formvar" coated cans and between the lacquered and unlacquered cans were significant (Student's t) at the two and five per cent levels respectively. These differences were equivalent to errors of 1.4% and 0.8% respectively in the pR value. 'pR' is the negative logarithm of the fractional concentration reduction, i.e. $\text{pR} = -\log_{10} ([S_1]/[S_0])$. The estimated standard deviation of the mean polarimeter readings for each can (two samples per can, five readings per sample) was 0.03° , which in this case represented an error in pR of 0.2%. Commercially lacquered cans have therefore been used for all runs using buffered sucrose solution.

(c) Measurement technique.

Sucrose solution can be measured satisfactorily in any polarimeter that is capable of reading to approximately 0.01° . A Bellingham and Stanley Limited polarimeter (No. 532016) was used in this work.

The measurement technique used in this study is outlined below.

1. Samples of sucrose solution (approximately 10 ml for a 200 mm tube) in stoppered 20 ml test tubes are placed in the water bath at 25°C .

2. Samples for analysis are withdrawn from the bath after at least three hours, and poured into the vertically clamped jacketed polarimeter tube with the aid of a glass rod (see Figure 4).

* "Formvar" made available by J. Middlehurst, CSIRO, Sydney.

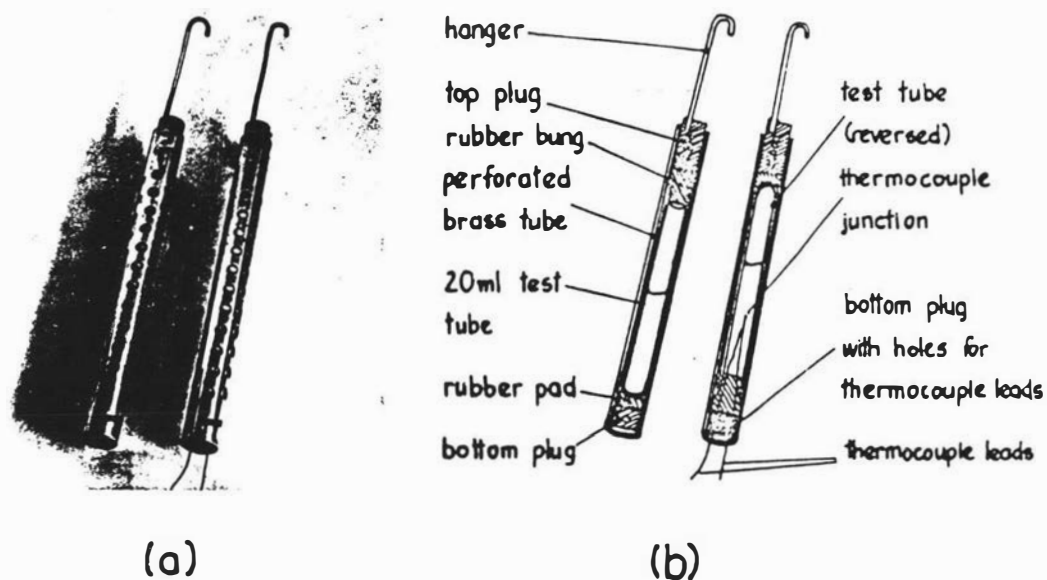


Fig 5. Brass test tube holders.

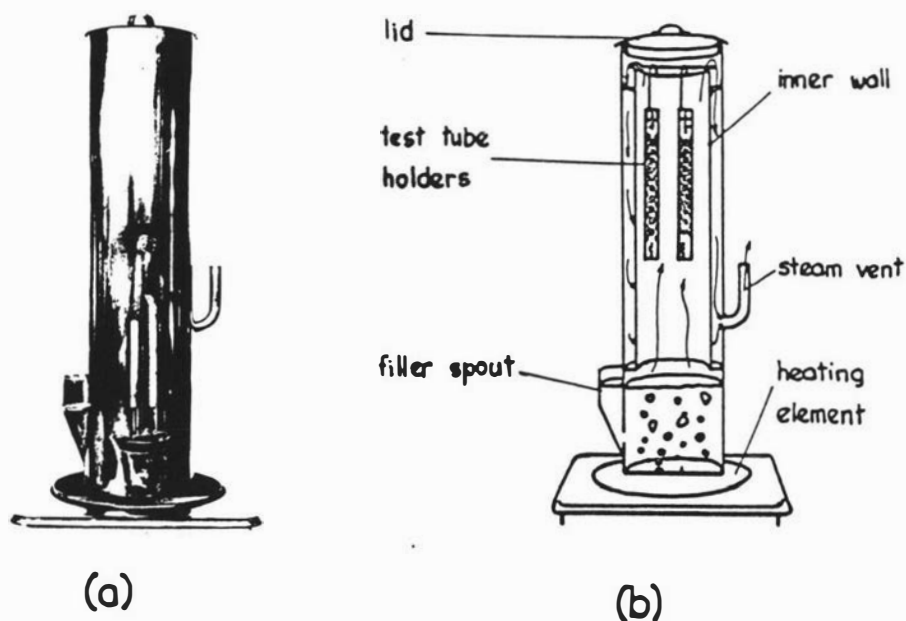


Fig. 6 Hypsometer for hydrolysis rate determinations at 212°F.

3. The top end glass is put in place and any excess solution wiped off before placing the tube in the polarimeter.

4. Five readings are taken for each sample (preferably in a partly darkened room).

5. The tube is removed from the polarimeter and clamped. Removal of the end glasses (lower glass first) allows the solution to drain into a beaker.

6. The interior of the tube is cleaned with a "pull-through" and the end glasses wiped dry.

7. The bottom end glass is replaced in readiness for the next sample.

With practice this routine can be reduced to about $2\frac{1}{2}$ minutes per sample without loss of accuracy.

(d) Rate of hydrolysis determination.

(i) Low temperatures.

At temperatures less than 90°C (194°F) a flask method was used. Samples of approximately 10 ml were withdrawn at intervals using a pipette with a slightly widened tip. The samples were cooled in test tubes in the 25°C water bath. The time taken to transfer the sample to the cooling bath was insignificant in terms of the total heating time. The rate of hydrolysis, $H (= \partial pR / \partial \theta)$ was determined from a plot of pR vs θ .

(ii) High temperatures.

At temperatures greater than 90°C , the 10 ml samples were heated in stoppered 20 ml test tubes in brass holders (see Figures 5a, 5b).

1. For hydrolysis rate determinations at 212°F a hypsometer was constructed (see Figures 6a, 6b). Two pairs of tubes were heated for not less than ten minutes, and two pairs for about two hours, before cooling in cold water. The rate was determined from the differences in pR and θ ;

$$H = \Delta pR / \Delta \theta$$

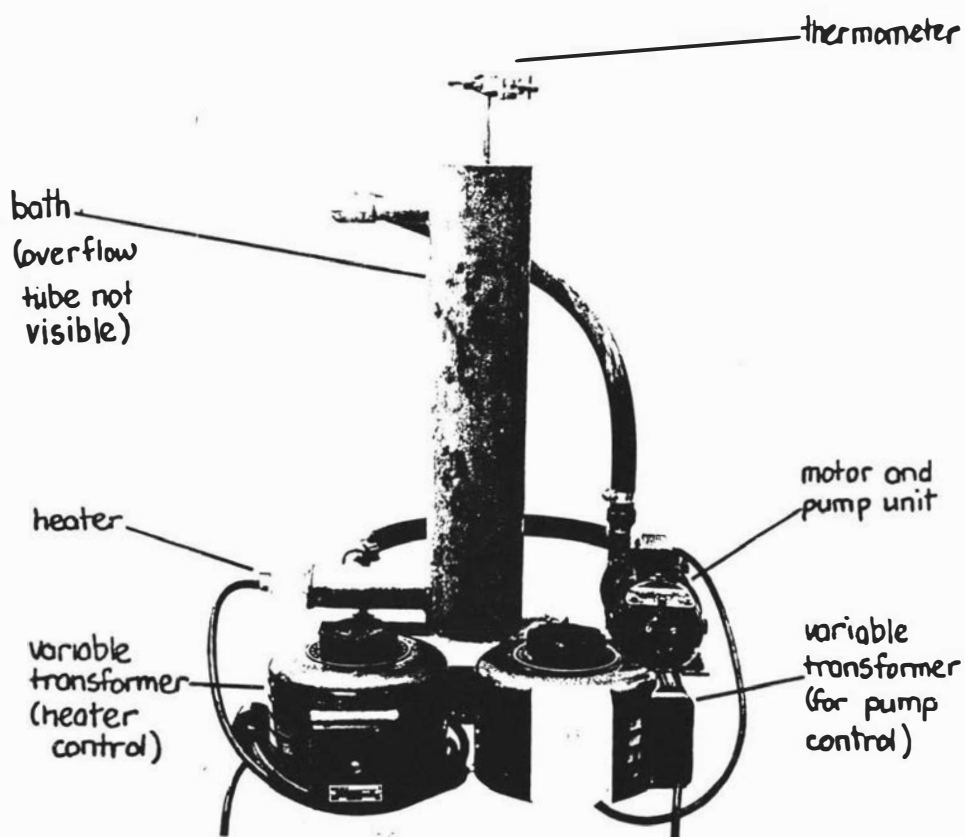


Fig 7. Recirculating glycerol bath for hydrolysis rate determinations and thermocouple calibrations at high temperatures ($212 - 280^{\circ}\text{F}$)

The temperature was calculated from the barometric reading;

$$T (^{\circ}\text{F}) = 212.00 + 0.0675 (B - 760)$$

where B is the barometric height in mm. Hg.

The hypsometer gave the most precise rate determinations. The maximum and minimum rates calculated from any set of data (four points at each time) seldom differed by more than $1\frac{1}{2}\%$.

2. Rate determinations at temperatures greater than 212°F were made in a recirculating glycerol bath (see Figure 7) of sufficient depth to allow complete immersion of the reference thermometer ($50-150 \pm \frac{1}{10}^{\circ}\text{C}$). Tubes were heated in pairs for varying periods and the rate determined from the linear portion of the pR vs t graph. In general these curves were linear for times greater than four minutes, and this was used as a minimum time for all high temperature runs. Temperature control was by manual adjustment of the variable transformer in the heater line, and variations during a run were usually less than $\pm 0.2^{\circ}\text{C}$. The temperature of the bath before a run was set 0.7°C . higher than the desired run temperature to allow for heating of the tubes. All tubes were cooled by plunging into the 25°C bath.

The lower precision of this method was mainly due to variations in heating rates of the tubes. These variations tended to become quite noticeable with the very short high temperature runs.

(e) Calculation of the specific rate vs temperature tables.

(i) Unbuffered sucrose : 0.00101 N HCl, 0.750 M sucrose.

Although ^{un}suitable for use in cans, the more easily prepared unbuffered sucrose solution should be quite satisfactory in glass containers. The kinetic data are summarized in Table 3.

Table 3 : Decimal reduction times : unbuffered sucrose

Temperature ($^{\circ}\text{F}$)	77	194	212	230	248	266
Decimal Reduction Time (min.)	2.97	141	56.7	23.7	12.0	4.54
	$\times 10^5$					

All the data (with the exception of the point at 248°F) are fitted by a straight line ($\log D$ vs $\frac{1}{T}$) well within experimental error. The activation energy is, therefore, taken as constant over the range 70 - 270°F .

The equation -

$$D = 4.54 \log_{10}^{-1} (9925.3/T - 13.6767)$$

which gives $E_A = 25,230$ cal/mole, was used for interpolation.

The data can be extended to other concentrations of acid if required if the specific rate H/H_0 is used. The equation then becomes :

$$\frac{H}{H_0} = \log_{10}^{-1} (13.4635 - 9925.3/T)$$

This can be compared with United States Department of Commerce, National Bureau of Standards data (1942) which give $E_A = 25.58$ kcal/mole and $\frac{H}{H_0} = \log_{10}^{-1} (13.6533 - 10066.7/T)$

This data was obtained with 0.01 N HCl.

(ii) Buffered sucrose solutions pH 5.5

The data from which the specific rate vs temperature curve was plotted are shown in Table 4, with the weights given to each point in the calculations also being shown.

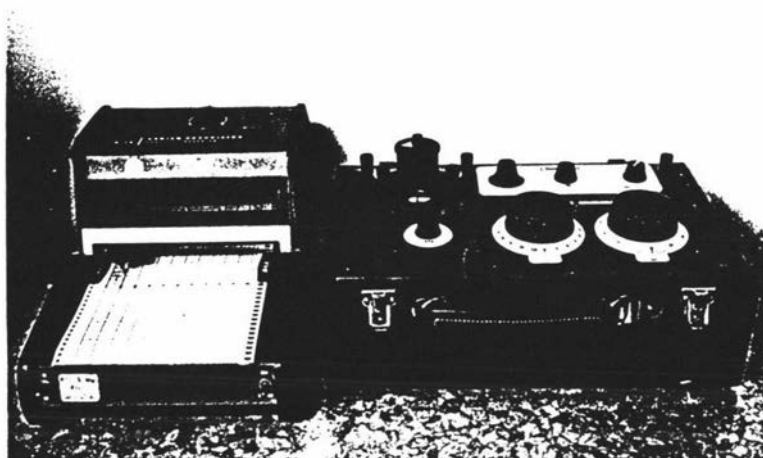


Fig.8 The potentiometers: Varian (left) and Cambridge.

Table 4 : Specific hydrolysis rates : buffered sucrose

Temperature (°F)	140.0	176.0	248.0	274.5	274.8	275.0	284.0
	0.0 ⁴ 725	0.0 ³ 645	0.0198	12.89	13.33	13.60	17.8
$\frac{H}{H_0}$	0.0 ⁴ 758			12.48		12.93	
				13.08		13.42	
	3	4	2	1	2	2	1
weight	1			1		1	
				1		1	

Because the $\log \frac{H}{H_0}$ vs $\frac{1}{T}$ plot was not linear, a parabola of best fit passing through the point ($H/H_0 = 1$, $T = 212^\circ\text{F} = 671.7^\circ\text{R}$) was used for interpolation of the data. The equation of this curve is

$$\log_{10} \frac{H}{H_0} = 9.275 \left(\frac{10^3}{T_0} - \frac{10^3}{T} \right) - 3.922 \left(\frac{10^3}{T_0} - \frac{10^3}{T} \right)^2$$

The table of $\frac{H}{H_0}$ vs T appears in Appendix V.

Temperature Measurement

(a) Instruments.

All temperatures in the retort and in the cans were measured with copper-constantan thermocouples, and recorded as emf on a single pen recording potentiometer.

The potentiometer used (see Figure 8) was a Varian, model G-14 with a five inch chart and ranges of 0-1 mV, 0-10 mV, 0-100 mV and 0-1V. Chart speeds of 6 in./hour and 2 in./min. were used. A Cambridge workshop potentiometer (type 44228, with built in potential source) was used to check the Varian calibration. Thermoelectric measurements were made on the 0-10 mV range during heating and cooling cycles, the maximum emf being approximately 6 mV at 270°F . For maximum sensitivity to small

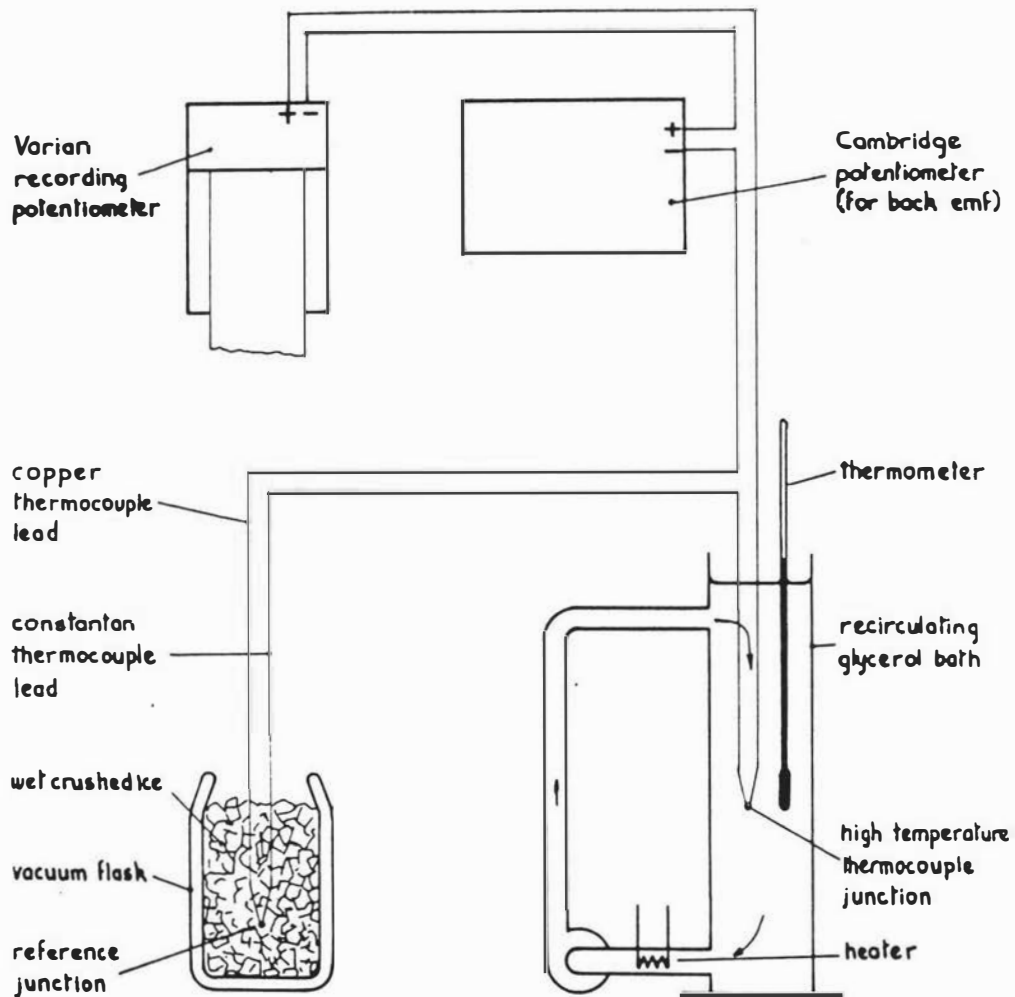


Fig.9 Thermocouple calibration apparatus.

changes of temperature at or near the retort temperature an opposing emf (up to 5 mV, from the potential source on the Cambridge potentiometer) was inserted in the thermocouple line to the Varian, and the resultant signal recorded on the 0-1 mV range.

(b) Calibration of thermocouple wire.

The glycerol bath used for the high temperature sucrose hydrolysis rate measurements was used for calibration of the thermocouple wire (see Figure 9). Wet crushed ice was used as the reference point for all temperature measurements. The thermocouple wire was taped to the stem of the reference thermometer ($50-150 \times \frac{1}{10}^{\circ}\text{C}$) with the junction close to the bulb, and emf's recorded using the Varian (0-1 mV range) and the back emf from the Cambridge potentiometer. The reference thermometer was checked at the steam point (100°C) in a hypsometer before each calibration.

Readings of emf were taken from the chart to the nearest 0.002 mV ($1/5$ of smallest chart division). Differences between the recorded temperature and temperature at the same emf using standard tables (British Standard 1828:1961) were plotted against emf, and the smoothed differences used to calculate the temperature vs emf tables. These tables are not presented here as they are not of general application.

(c) Thermocouple circuits.

The single pen potentiometer was used with special switching circuits to record the emf's from several thermocouples in a single can or the temperatures of several cans during each run. Using the high chart speed (2 in./min.) and switching intervals of $2\frac{1}{2}$ -4 seconds, up to eight temperatures could be recorded at least twice per minute (stationary can runs). With four can thermocouples and one retort thermocouple (agitated can runs) recording frequencies of up to three per minute for can thermocouples and six per minute for the retort thermocouple could be obtained.

(1) Can thermocouple junctions.

Rigid thermocouple probes were not used at any stage of this work. Instead, a tension method of thermocouple mounting was used, in which the

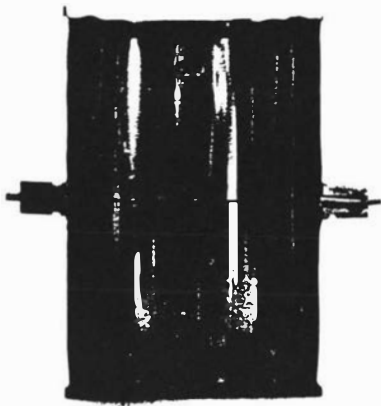


Fig. 10a Can with gland fitting for thermocouple seal.

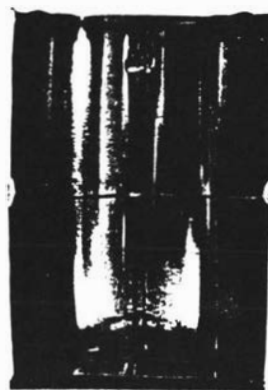
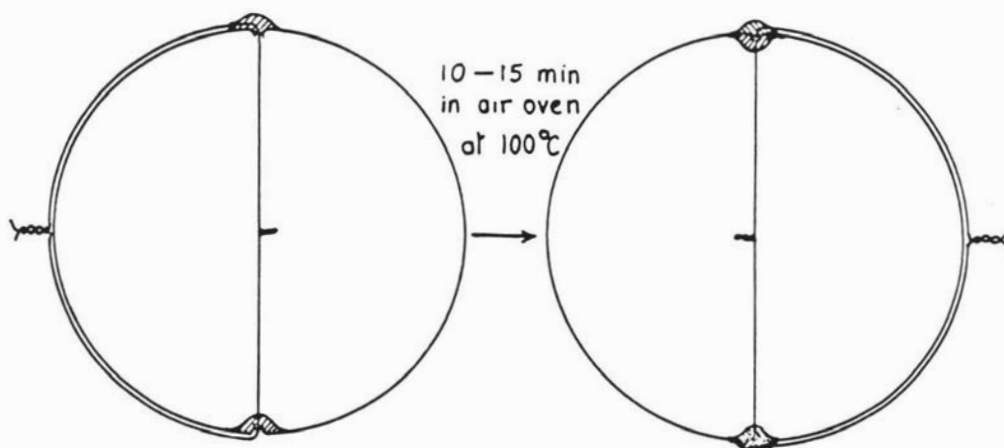


Fig 10b Can with epoxy resin adhesive thermocouple seal.



(i) First application of adhesive

(ii) Second application of adhesive

Fig.10c Method of application of epoxy resin adhesive.

copper and constantan wires from the carefully twisted and soldered junction are sealed through diametrically opposite holes in the can walls.

Two methods of sealing have been used. The first (see Figure 10a), used only on early static can runs, employed 1/16 in. I.D. copper pipe-olive compression fittings, cut in two, with a gland of 1/8 in. insertion rubber making the seal. These proved quite satisfactory, but were rather tedious to prepare. The second method used an epoxy resin adhesive* to seal the thermocouple wires through the can wall (see Figures 10b, 10c). Holes, which are located by a wrap-around strip of paper, are pierced through the can wall with a sharp point. The thermocouple wires are threaded through the holes and held in position with adhesive tape on the outside of the can. The epoxy resin adhesive is applied in two stages as shown in Figures 10c(i) and 10c(ii). Ten to fifteen minutes in a hot air oven at about 100°C are sufficient to set the resin, and enable the second application to be made. The resin is completely hardened after three hours at 100°C although most cans were heated overnight. Fracture of the wires at the seal could be avoided by twisting each pair of wires together (see Figures 10c(i) and 10c(ii)).

(ii) Stationary can circuits (Figure 11a)

Insertion rubber ($\frac{1}{8}$ "), in 1/8 in. olive compression fittings with 1/8 in. male gas threads screwed into a reinforcing plate on the top of the retort, was used to make a pressure-tight seal around the thermocouple leads where these passed through the retort shell. The leads passed from the retort to the ice flask where all reference junctions were electrically isolated in separate kerosene filled glass tubes. An electrically-driven cam-operated set of microswitches (see Figure 11b) operated P. and T. type 3000 relays (double pole on-off) which connected each thermocouple in turn to the recording potentiometer. When required the back emf was applied and the recording potentiometer used on the 0-1 mV range. Because the 'zero' on the Varian recorder shifted slightly with change of range, it was necessary to short the input terminals of the recorder once per cycle.

* "Araldite", Ciba Limited.

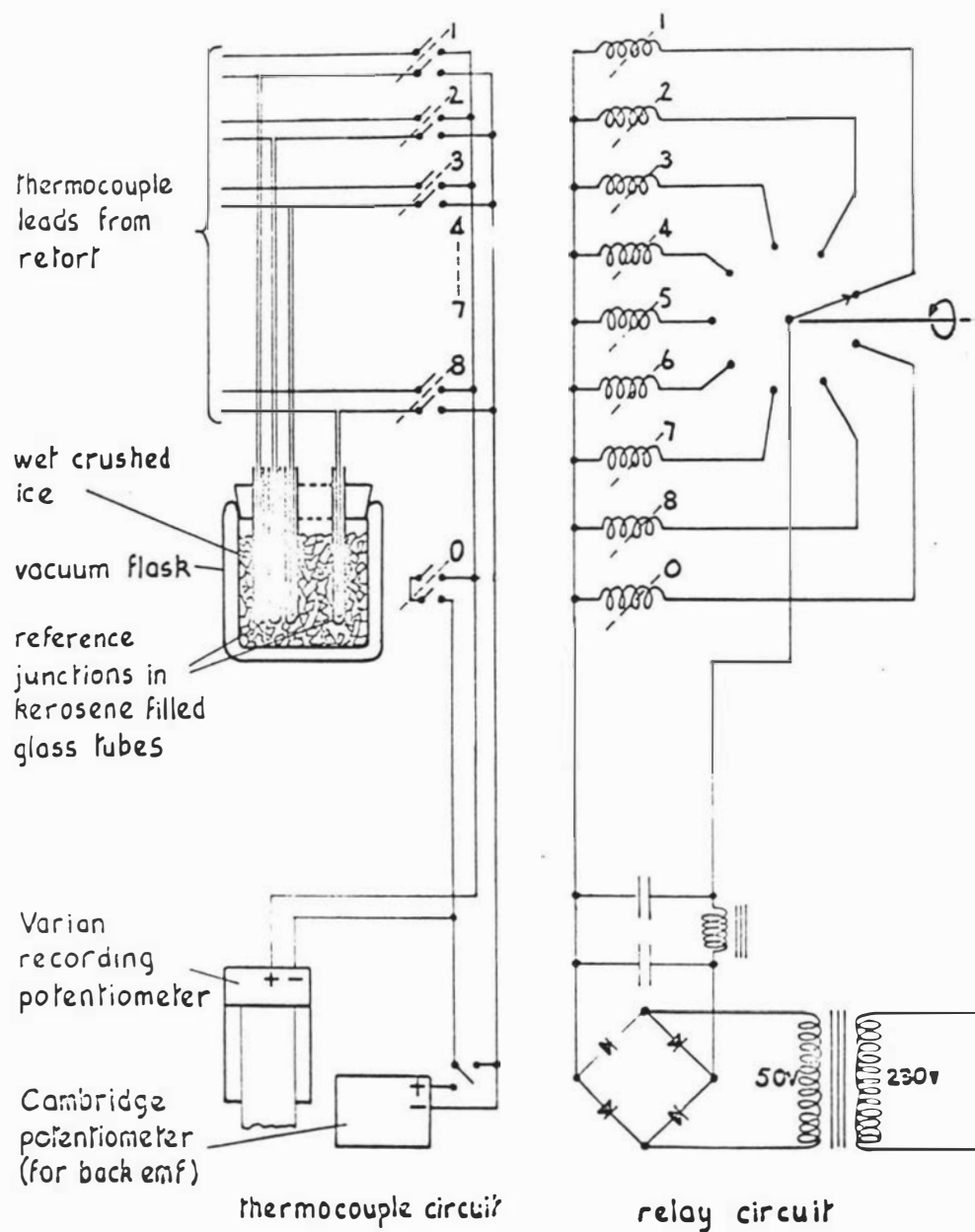


Fig.11a Static can thermocouple circuits.

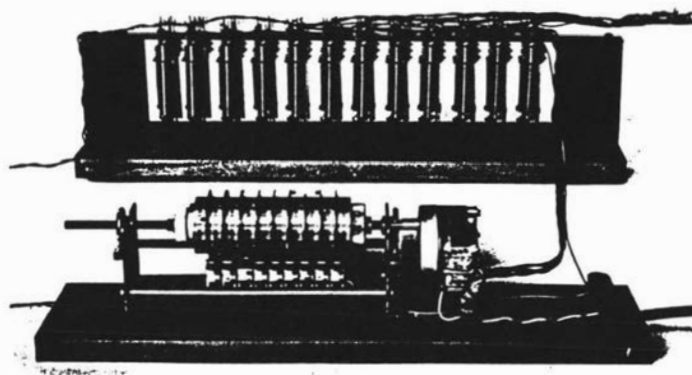


Fig.11b Cam operated thermocouple switching relays.

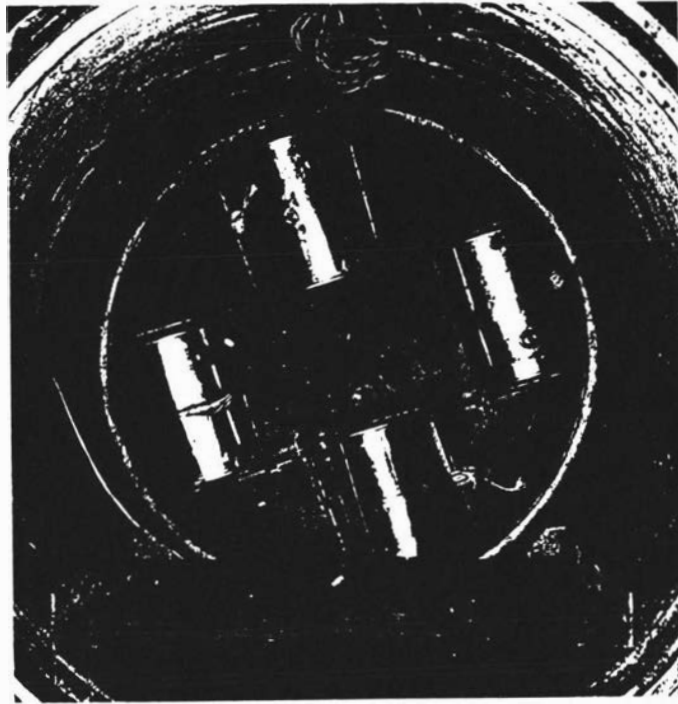


Fig. 12a Rotating basket and thermocouple leads.

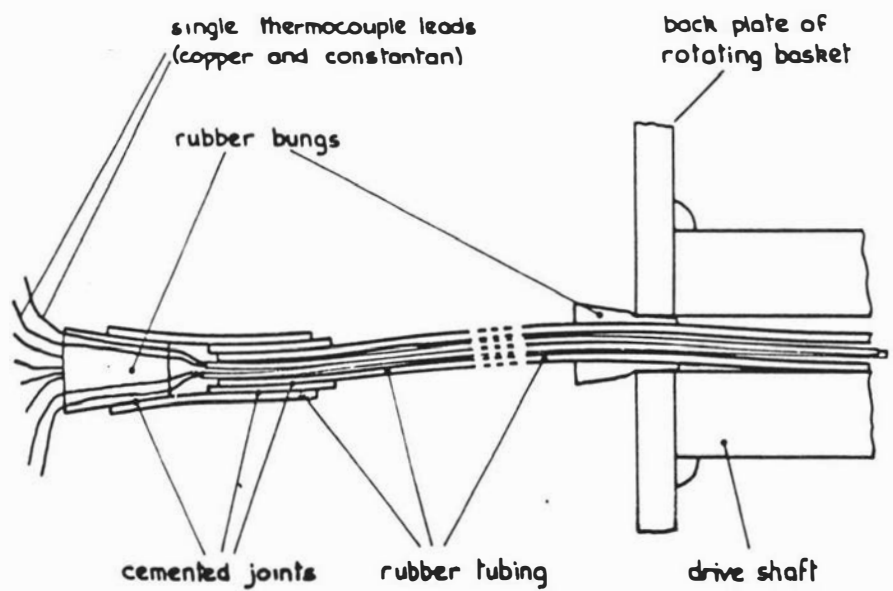


Fig. 12b Detail of thermocouple sealing for rotating can experiments.

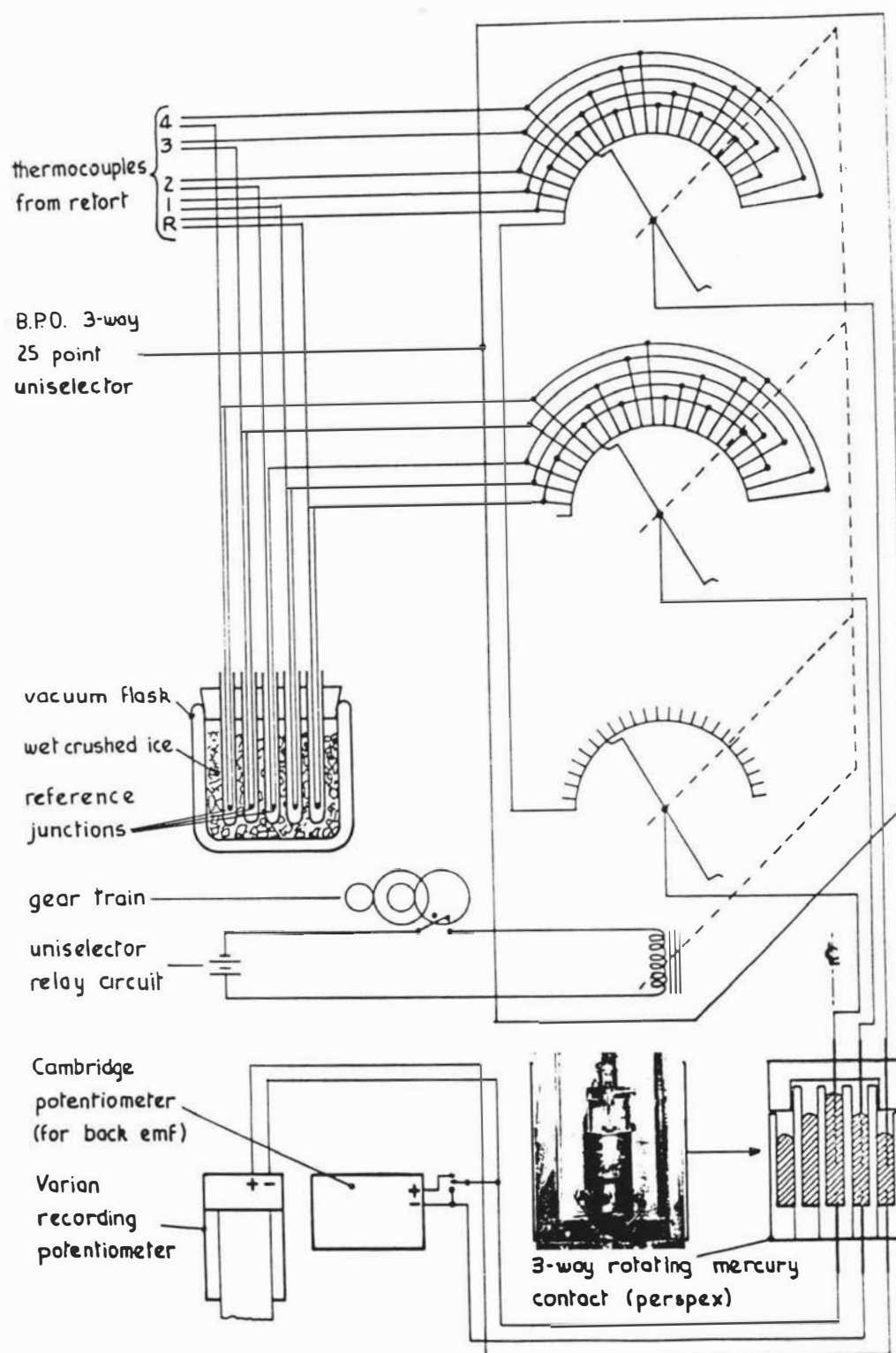


Fig.13a Rotating can thermocouple circuits.

This also served as an identification index for the recorded emfs. The recording potentiometer was used with a floating input - i.e. the negative terminal was not earthed. This reduced interference by stray earth currents.

(iii) Rotating can circuits (Figure 13a).

The thermocouple wires from the revolving cans were sealed through a rubber stopper in the end of a length of rubber tubing. This tubing passed through the centre of the drive shaft to the outside of the retort (see Figures 12a and 13c). A 16 in. diameter, $\frac{1}{2}$ in. thick steel plate was mounted on the end of the drive shaft, and mounted on this were the ice flask for the reference junctions, and a 3-pole 25 position P. and T. unselector. The unselector relay had been rewound for operation from a 12 volt source which was supplied by two No.6, 6 volt lantern batteries mounted opposite the ice flask. A system of gears closed a simple contact in the unselector relay circuit once every four or six revolutions of the plate (see Figure 13b). The thermocouple leads from the ice flask were connected to the unselector in various ways, depending on the number of thermocouples in use. With four cans plus the retort thermocouple the connections were such that the retort thermocouple emf was recorded eight ~~six~~ times per sweep of the unselector contacts, and the emfs from each of the four can thermocouples ~~three~~^{four} times per sweep. The 25th position was used to short the input terminals of the Varian for the zero reading and thermocouple identification index (see Figure 23b, p 104).

The three lines from the unselector were wound around a flexible coupling (plastic covered curtain wire) to a rotating mercury contact which was totally enclosed in a wooden case. The stationary terminals of the rotating contact device were connected to the Varian and Cambridge potentiometers as in the static can set-up.

The third wire through the rotating contact was necessary to enable the recording potentiometer terminals to be shorted by the rotating switch-gear on both the 0-10 mV and 0-1 mV ranges.

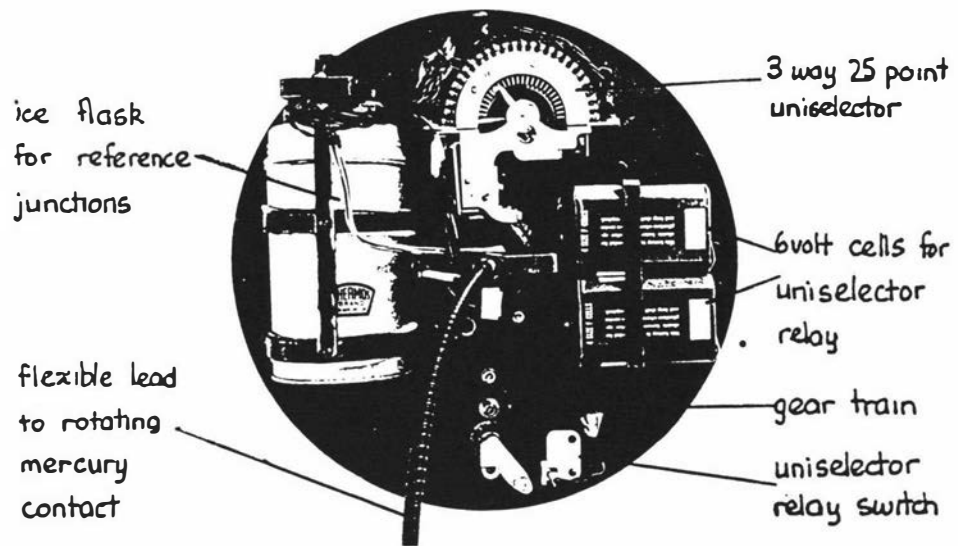


Fig. 13b Rotating plate (elevation)

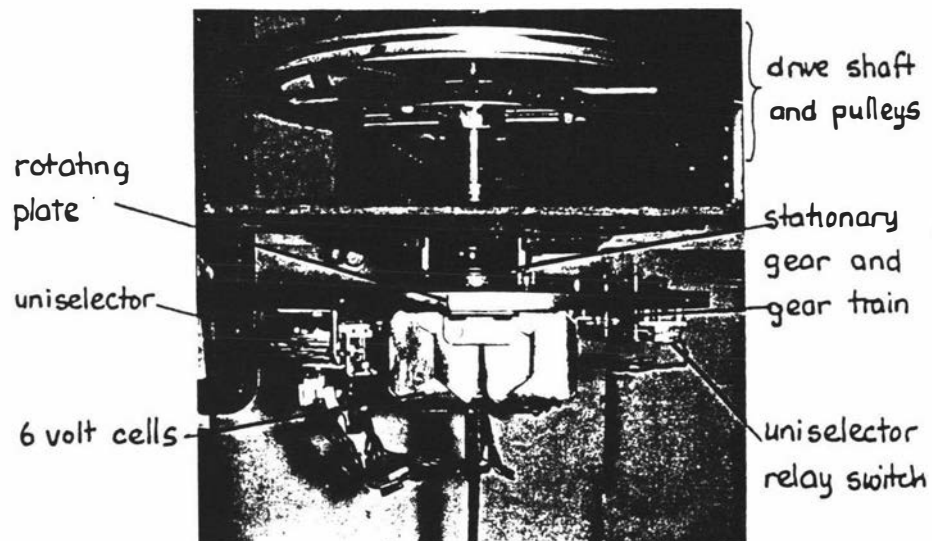
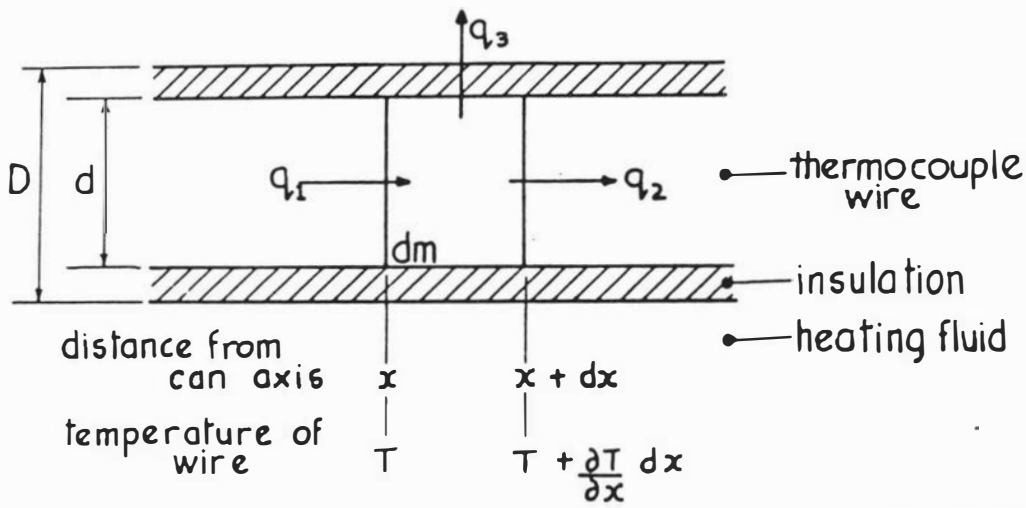


Fig. 13c Rotating plate (plan)



$$q_1 - q_2 - q_3 = dm \cdot c_p \frac{\partial T}{\partial \theta} = \rho c_p \frac{\pi d^2}{4} \frac{\partial T}{\partial \theta} dx$$

$$q_1 = -\frac{k \pi d^2}{4} \frac{\partial T}{\partial x}$$

$$q_2 = -\frac{k \pi d^2}{4} \frac{\partial}{\partial x} \left(T + \frac{\partial T}{\partial x} dx \right)$$

$$q_3 = -U_o dA (T - T_L)$$

whence

$$\frac{\partial^2 T}{\partial x^2} - \frac{4U_o}{kd} (T - T_L) = \frac{\rho c_p}{k} \frac{\partial T}{\partial \theta}$$

$$\text{or } \frac{\partial^2 u}{\partial x^2} - \alpha^2 (u - u_L) = \beta^2 \frac{\partial T}{\partial \theta}$$

Fig. 14 Heat conduction along the thermocouple wire.

(d) Sources of error in temperature measurement.

(1) Conduction errors in thermocouples.

Errors in temperature measurement arising from conduction of heat along the thermocouple wire or probe from the outside of the can to the junction have been shown to be significant in some cases (e.g. Ford and Osborne, 1927). A check on this source of error was made by setting up the heat conduction equations (see Figure 14) with boundary conditions approximately those obtained in stationary pans, i.e. the temperature of the retort is assumed to rise instantaneously to processing temperature (i.e. a "square" process). The wire is assumed to have no discontinuities (i.e. copper or constantan right across the can) and the ends of the wire are assumed to be at retort temperature for all time after zero. The temperature of the fluid surrounding the wire is assumed to approach retort temperature logarithmically, and heat transfer between the wire and liquid is based on the physical properties of water and the rate of liquid movement past the wire as deduced from static can temperature measurements, e.g. see Figure 27, p 111.

The solution of the partial differential heat conduction equation (see Appendix VI A) by a method of eigen-function transforms (due to J. Gamlen) is the slowly converging series :

$$U_{\Delta}(x, \theta) = \frac{4}{\pi} \sum_{\substack{n=1 \\ (\text{odd } n)}}^{\infty} \left[\frac{1}{n} \cdot \frac{n^2 \pi^2 - 4\alpha c \beta^2}{n^2 \pi^2 + 4\alpha^2 \alpha^2 - 4\alpha^2 c \beta^2} \cdot \left(e^{-c\theta} - e^{-\frac{1}{\beta^2} \left(\frac{n^2 \pi^2}{4\alpha^2} + \alpha^2 \right) \theta} \right) \cdot \sin \frac{n\pi}{2\alpha} (x+\alpha) \right]$$

where :

$$U_{\Delta} = \frac{T_L - T_W}{T_R - T_0}$$

T_W = wire temperature

T_L = liquid temperature

T_0 = initial temperature

T_R = retort temperature

$$\alpha^2 = \frac{4 U_0}{k d}$$

U_0 = overall heat transfer coefficient based on wire diameter, d

k = thermal conductivity of wire material

and $\beta^2 = \frac{\rho c_p}{k}$

ρ = density of wire material

c_p = specific heat of wire material

$$\phi = \frac{2.303}{f_h}$$

$1/f_h$ = slope of the logarithmic heating curve

$2a$ is the diameter of the can, x is the distance along the wire measured from the midpoint, and θ is time.

If the transient term :

$$e^{-\frac{1}{\beta^2} \left(\frac{n^2 \pi^2}{4a^2} + \alpha^2 \right) \theta}$$

which is much less than $e^{-\alpha^2 \theta}$ for large values of θ is neglected,

$U(x, \theta)$ can be expressed as a fraction of the unaaccomplished temperature difference which is independent of time.

$$\text{i.e. } \frac{U_\Delta(x, \theta)}{1 - U_L} = \frac{4}{\pi} \sum_{\substack{n=1 \\ \text{odd } n}}^{\infty} \left[\frac{1}{n} \frac{n^2 \pi^2 - 4a^2 c \beta^2}{n^2 \pi^2 + 4a^2 - 4a^2 c \beta^2} \sin \frac{n\pi}{2a}(x+a) \right]$$

$$\text{where } U_L = 1 - e^{-\phi \theta} = \frac{T_L - T_0}{T_R - T_0}$$

This series has been summed to approximately 80 terms for a number of values of x for 24 gauge copper wire with and without the nylon insulation, and for constantan wire with nylon insulation. Even at $n = 201$ the terms of the series are still large (0.1 of the greatest term) and a

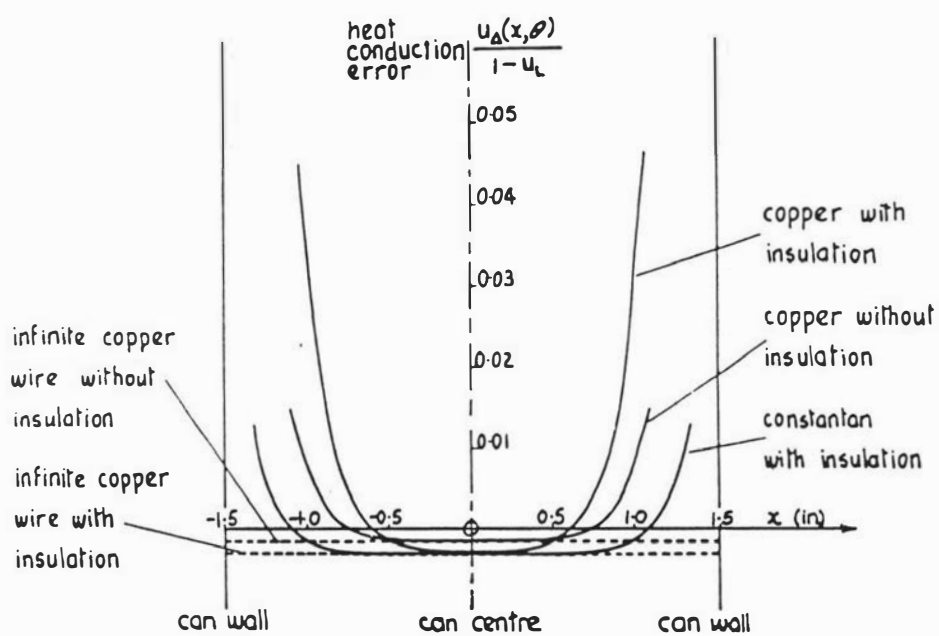


Fig.15 Heat conduction errors in thermocouple wires.
(24 gauge wire in 3 inch diameter can.)

weighted mean of the sum to n_1 , n_2 and n_3 terms has been used to calculate the sum to infinity. The sums to n_1 , n_2 and n_3 terms are successive maximum minimum and maximum values respectively of the summation when the sum to n terms is plotted against n (see Appendix VI B).

The error, as a function of unaccomplished temperature difference is shown in Figure 15. Heat conduction is seen to be significant near the can wall, and the lag at the centre of the can is due to the finite heat transfer rate from the liquid to the wire. The solution of the equations for heating of the wire in the can closely approaches the solution for the lag in heating of an infinitely long wire, which is also shown in Figure 15.

In all experiments in which temperatures are measured near the can wall, the copper wire passes across the can to the opposite wall, and the constantan wire passes through the wall closer to the junction.

The maximum error in unaccomplished temperature difference is therefore less than 0.006 or 0.6%. An error of 0.6% of the unaccomplished temperature difference represents a time lead of 0.3 seconds, while at the centre the temperature of the wire is approximately 0.1 second behind the temperature of the liquid. Hence conduction is not a significant source of error.

(ii) Electrolytic errors.

Considerable trouble was experienced with spurious emf's in the rotating can experiments, in spite of continuous insulation through all wet regions with the exception of the junction in the can, and two soldered junctions in the retort which were well taped to prevent direct contact with the can or retort wall. Even when all temperatures had become steady, apparent differences of several degrees between the steam and can solution temperatures were often observed. Noise, which appeared to be related to the rotation of the retort was superimposed on these offset recordings of emf. Attempts to electrically insulate the junctions in the cans and experiments with the recording potentiometer alternately earthed and unearthed

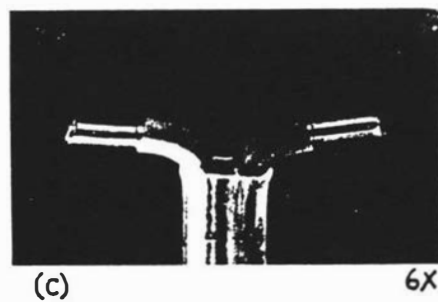
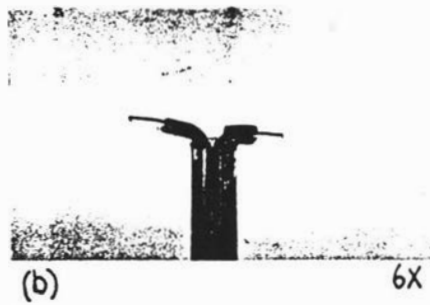


Fig 16. Thermocouple wires : (a) 24 gauge, used in all static can experiments; (b) 36 gauge, used in initial rotating can experiments; (c) 24 gauge, used in later rotating can experiments.

indicated that leakage between leads or leakage to ground was occurring at several places other than the can centre. A "Megger" insulation tester indicated temperature dependent resistances between the wires and ground, down to about 6000 ohms. Electrolytic emf's between the leads or between the leads and ground could, therefore, be set up (Middlehurst, Elbourne and Board, 1964) with the currents in the leads arising from these electrolytic emf's introducing errors in the measured thermoelectric emf's.

Complete rewiring of the copper-constantan part of the circuit in 24 gauge wire of the same calibration reduced the effect of the stray currents as the resistance of the 24 gauge is $1/16$ that of the 36 gauge wire. Rewiring did not, however, eliminate the source of the spurious emf's.

After only two runs the noise level and offset were becoming intolerable. It was then noticed that water was being forced along the wires inside the outer covering (see Figure 16) during pressure cooling. Resealing of the wires at the wet end (see Figure 12) almost completely eliminated the trouble. On the few occasions when offset did occur it was small enough to allow corrections (in the calculation of equivalent retort times) to be made.

Processing experiments

(a) Equipment

(i) Steam supply

Steam was supplied by a 4HP fire tube boiler in the adjacent engineering workshop and laboratory. The pressure controller was set 50-60 psig so that the pressure drop in the line did not limit the come-up rate (to a maximum of 30 psig).

(ii) Experimental retort

The unagitated cans were processed in the front half of the retort, and the agitated cans in the revolving grate in the back section. Figures

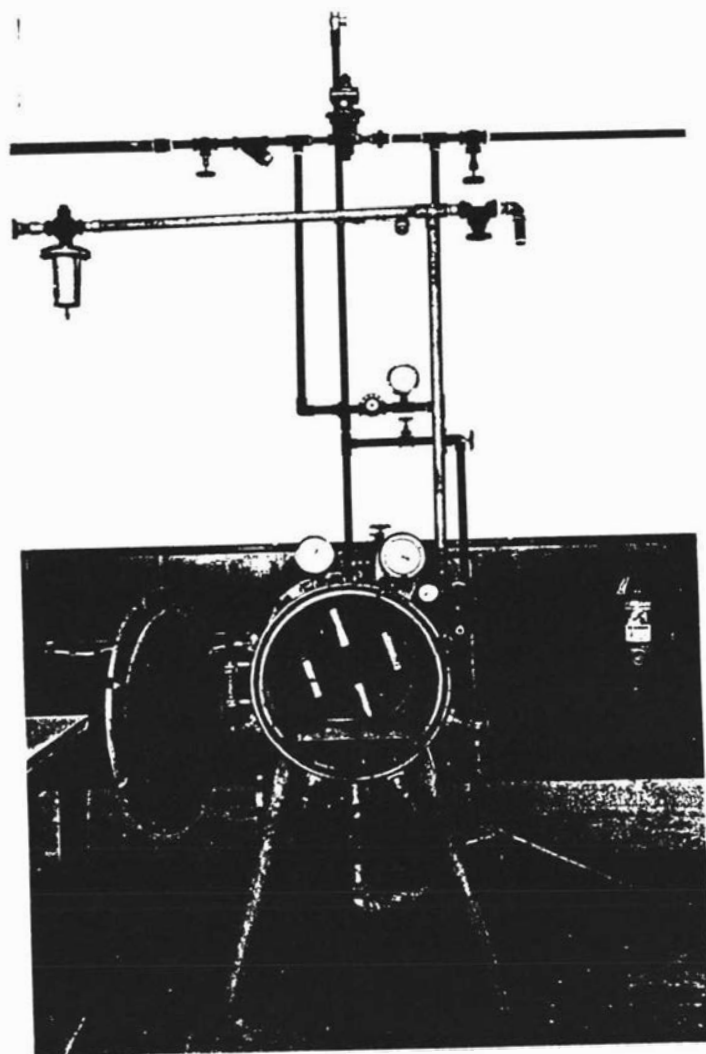


Fig 17. Experimental retort (front view).



Fig.18 Experimental retort (side view)

17 and 18 show the instrumentation, and the steam, air and water connections.

1. Instrumentation

The main retort pressure gauge (a "Budenburg", 4 in. diam. 0-60 psi x 2 psi) was checked on a deadweight gauge tester. The temperature gauge ("British Teltherm" 4 in. diam., 0-300°F x 5°F) was a mercury-in-steel type with the bulb in the back of the retort behind the revolving grate. Other smaller gauges were provided on the steam line and air regulator.

2. Steam supply

Steam from the main steam line was supplied to the retort either through a regulator or through the by-pass line to the spreader in the bottom of the retort. The three vents on the retort were a petcock (always open to bleed non-condensable gases) and two larger vents, one from the safety valve line, and the other from the retort.

3. Compressed air supply

Compressed air for pressure cooling of cans was introduced at the side of the retort through a regulator and valve in the supply line from the compressor.

4. Water supply

Cold water could be introduced into the retort for cooling either at the bottom of the retort through the drain outlet, or through a spray header in the top of the retort.

5. Revolving grate drive

The revolving grate was driven by a 1 HP electric motor with a variable speed drive unit (Charples and Hunting Pty. Ltd., Melb. Aust.) with an output range of 73-440 rpm. This was situated underneath the retort, and the drive to the grate shaft was by V belt. Several pulleys were provided for an even wider range of grate speeds.

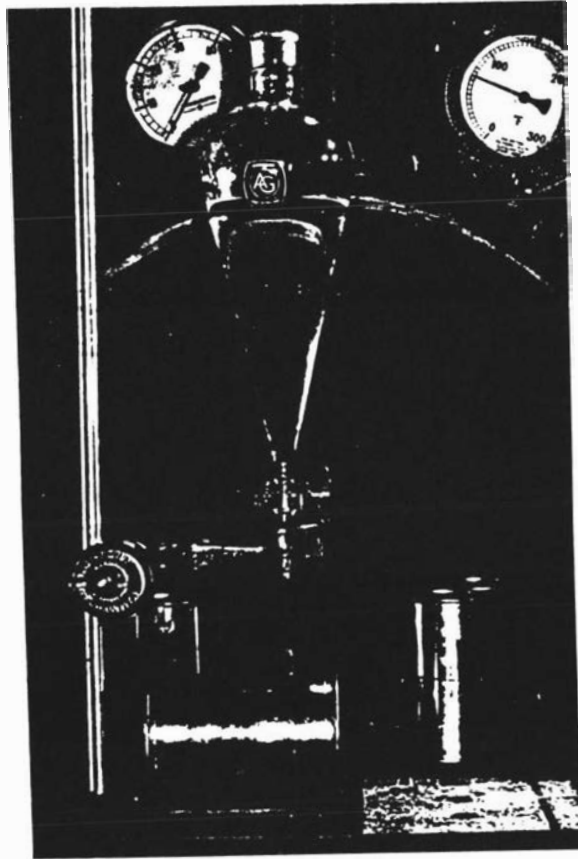


Fig. 19 Can filling apparatus

(b) Preparation of the retort for processing experiments.

(i) Instruments

Before each run the crushed ice in the reference junction flask was topped up. Excess water was removed from the mounted flask in the rotating experiments with a syphon.

The input terminals of the recorder were shorted, and the pen adjusted to read zero on the 0-1 mV range. The back emf of the Cambridge potentiometer was also checked against the internal standard cell. The speed of the revolving crate was adjusted until the correct number of points per minute on the Varian chart was obtained.

The potentiometer chart and the thermocouple switching equipment were arranged so that the chart would record from the zero point at the beginning of the run.

(ii) Wiring and filling of cans.

The thermocouple lines in the retort from the recording potentiometer were connected to the can thermocouple leads and the joints soldered. All joints in the retort were taped to prevent contact with the can or the retort wall, and all circuits tested for continuity.

Cans were filled with the sucrose solution without disconnecting the thermocouples (see Figure 19). Filler nipples made from the olive compression fittings used for early thermocouple sealing were used (see Figure 20a). If a vacuum was required (mainly to prevent blowing of can ends during cooling in the 30 psi runs) this could be applied as shown in Figure 20b, and the seal tightened while still under vacuum. This method of sealing was quite satisfactory if the 3/16 in. steel balls were used no more than 2 or three times with the corrosive acidic sucrose solutions. The balls had been well seated in the brass fittings before these fittings were soldered onto the can.

Head space in the cans was controlled by filling with a constant volume of solution (454 ml for a 301 x 409 can).

The stationary cans were arranged on the tray in the front of the retort, usually with at least one can diameter between adjacent cans. The cans for the rotating experiments were fixed into the crate as shown in

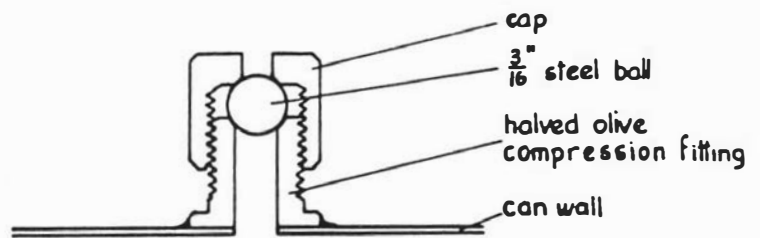


Fig.20a Filler nipple



section AA

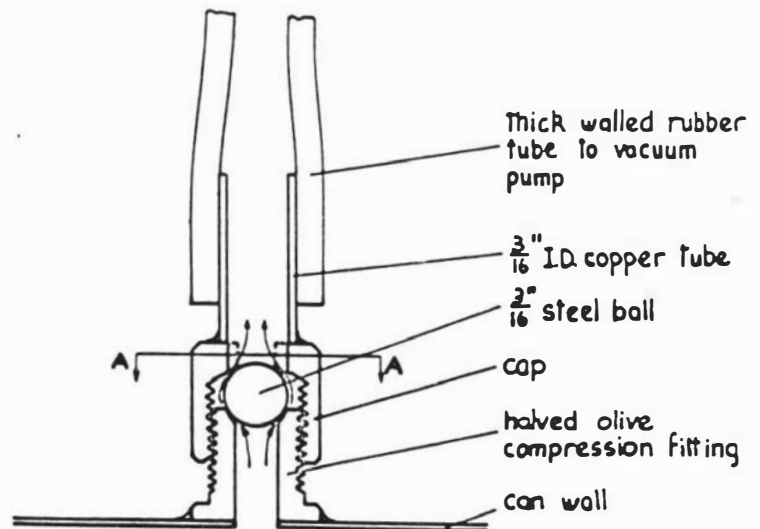


Fig.20b Filler nipple for vacuum sealing.

figure 12a, taking particular care to ensure that the cans on their sides (i.e. with their axes tangential to the direction of movement) were securely fastened. Loose thermocouple wire was wound around each can before it was fixed in the crate.

(iii) Arrangement of retort thermocouples.

Before closing the retort, the retort temperature thermocouples were arranged in their proper positions, i.e. near the centre of the retort above the stationary cans, or near the cans in the revolving crate. Three junctions were used in parallel in the rotating can experiments, and widely fluctuating emf's at the beginning of the air cooling phase were avoided by ensuring that these retort thermocouples were out of the line of the incoming cold air which is admitted at the side of the retort just in front of the revolving crate. The end of the rubber tube covering the thermocouple wires (rotating can runs) was securely tied to one of the can supports.

(iv) Closing

The retort door was closed and a check made to ensure that the bypass, drain and vent valves were open, and all others closed.

(a) Process cycle.

In this investigation only two processing factors, viz: the pressure and the length of the process were varied. Other processing factors were kept as nearly constant as possible.

Measurements of retort temperature and pressure after various lengths of venting showed that two minutes was sufficient time to purge the air from the retort. This was therefore used as the venting time for all static and agitated can runs.

At the end of the venting period, the drain valve and then the two vent valves were closed. Retort pressures of 15 psig (approximately 250°F) and 30 psig (approximately 272°F) were reached 0.4 - 0.5 min., and 0.8 - 1.0 min. after closing the vents.

(i) Holding period.

As soon as the required retort pressure was reached, the by-pass valve was closed, and the pressure controlled manually either by the by-pass valve or the main steam valve. A stopwatch was started as soon as the desired retort temperature was reached, and the corresponding point marked on the recorder chart as soon as the control settled down. Temperature variations were usually less than about $\pm 0.2^{\circ}\text{F}$, although larger variations sometimes occurred just after retort temperature was reached.

(ii) Cooling period.

As the main steam valve was closed at the end of the holding period, the air valve was opened and the retort pressure held at 15 psig or 30 psig for three minutes. After three minutes the cooling water was applied. The spray was used for the static cans, and the bottom inlet (through the drain) for the agitated can runs. The air valve was closed as soon as the pressure in the retort system began to rise after the initial drop, and the pressure held steady at about 20 psig until the retort was approximately $\frac{3}{4}$ full of water. This water was immediately drained and the retort filled a second time. The second fill was drained as soon as all can temperatures were less than about 150°F . This gave a can temperature of about $100\text{--}120^{\circ}\text{F}$ when the retort was opened.

(iii) Sampling.

The sucrose solution was drained into 500 ml measuring cylinders without disconnecting the thermocouples. The volume was checked because occasional leakage of can fittings did occur. Two 10 ml samples from each cylinder were transferred to 20 ml test tubes, stoppered and placed in the 25°C ^{bath} for holding before analysis.

(d) Processing experiments.

(1) Sucrose hydrolysis rate determination

Variations in the preparation of the stock buffer solution and preparation of the sucrose solution from the stock buffer made it necessary

to determine the rate of hydrolysis at some reference temperature for each batch of solution. Two methods, at 212°F and at retort temperature have been used.

(1) Hydrolysis rate determination at 212°F.

This method was used for the static can runs and for some of the rotating can runs.

H'_O , the rate of hydrolysis at the temperature of steam T' is determined in the hypsometer using the method outlined under rate of hydrolysis determination, section (ii), paragraph 1. The rate of hydrolysis at 212.0°F (H_O) is determined from H'_O and the $\frac{H}{H_O}$ vs T curve -

$$\text{i.e.} \quad H_O = H'_O + \left(\frac{H}{H_O} \right)_{T'}$$

(2) Rate of hydrolysis determination at retort temperature.

A disadvantage of the determination of the reference sucrose hydrolysis rate at 212°F is that the rate of hydrolysis at retort temperature (used in calculation of equivalent retort times), is sensitive to small changes in the slope of the $\log H$ vs $\frac{1}{T}$ curve. A method of determination of sucrose hydrolysis rate at or near retort temperature was therefore sought.

Use of the glycerol bath is unsatisfactory as the number of samples to be processed for a reasonably precise determination of hydrolysis rate is too large. Four of the brass test tube holders were, therefore, modified to include a thermocouple with each tube (see Figure 5a) and these four tubes were processed in the retort four minutes at retort temperature, with two minutes pressure cooling. The tube holders were fixed to the can supports in the revolving crate and the crate revolved at a speed (72-108 rpm) that would ensure thorough mixing of the solution.

Heat penetration into the tubes was much faster than cans. Differences in temperature and measured sucrose hydrolysis between tubes were very small. The method of calculation of the hydrolysis rate at retort temperature (H_R) is discussed under calculation methods.

(ii) Static can runs.

1. Temperature distribution runs.

A single water-filled 301 x 409 can with seven thermocouples (see Fig. 21a) was used to study the temperature distribution during the heating and cooling phases. A longer air cooling phase than usual was used (5 min. instead of 3 min.). This allowed a clearer picture of the temperature distribution in this phase to be obtained.

2. Sucrose hydrolysis runs.

Buffered sucrose solution was processed in static cans as shown in Table 5.

Table 5 : Static can processes - sucrose hydrolysis runs.

Run No.	10	11	12	13	15	16	17
Pressure (psig)	30	30	30	30	15	15	15
Time (min.)	1.0	3.0	5.0	7.0	1.5	3.0	7.0

Five 301 x 409 cans were processed in each run, two with three thermocouples (Figure 21b), one with one thermocouple at the centre, and two cans without thermocouples.

3. Sucrose milk and water comparison.

Four runs (2 min. and 5 min. at 15 psig and 30 psig) with cans of milk (town supply), sucrose solution and water were carried out. Each can had two thermocouples on the can axis, $\frac{3}{4}$ in. and $3\frac{1}{4}$ in. from the bottom.

(iii) Rotating can runs.

Speeds of rotation of 72, 80, 96 and 108 rpm were used in the agitated can runs. The various time-temperature combinations are shown in tables 6a and 6b.

Table 6a : Summary of rotating can runs

Process	2 min. 30 psig	5 min. 30 psig	2 min. 15 psig	5 min. 15 psig
Speed (rpm)	Run number			
72	28	50*, 55	57	58
80	44	51	59	61*, 69
96	45	52	62*, 70	63*, 71
108	53	54	64	65

* Irregularities in the sucrose hydrolysis measurements of run 50, leading to disagreement of the measured and calculated equivalent retort times were observed. Two determinations of sucrose hydrolysis rate at retort temperature for the solution used in runs 61, 62 and 63 were unsatisfactory. The sucrose hydrolysis measurements have therefore been discarded for these runs. The time-temperature data are quite satisfactory, however, for calculation of the chemical and bacterial equivalent retort times.

Table 6b : Miscellaneous rotating can runs

Run number	Speed (rpm)	time (min)	pressure (psig)	
38	80	2	30	} Long slow come-up due to failure of boiler pressure con- trol unit.
40	80	2	30	
46	126	2	30	) Only one run at this speed.

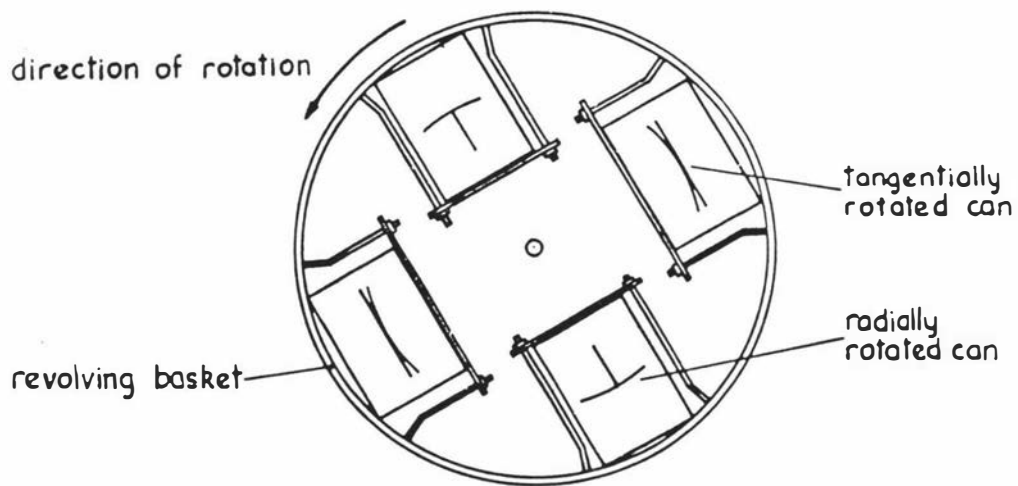


Fig.22a Tangentially and radially rotated cans.

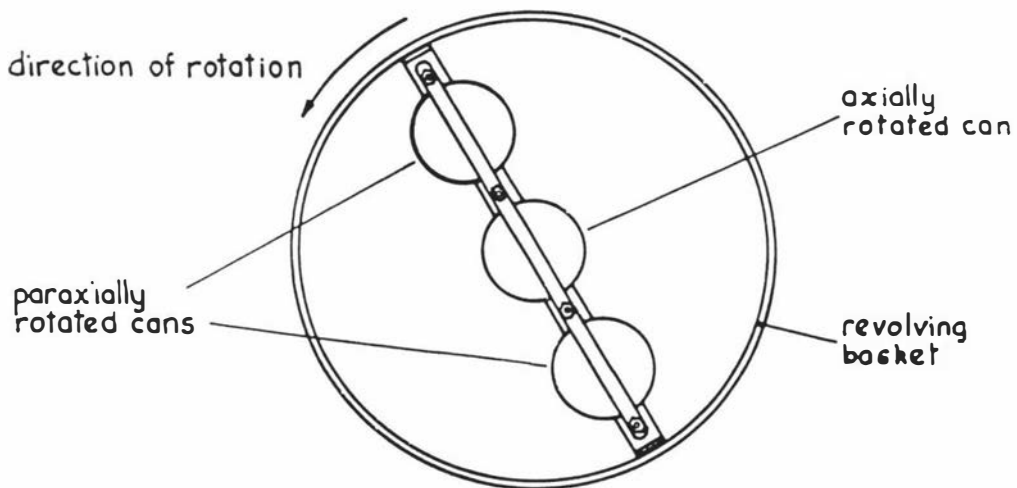


Fig.22b Axially and paraxially rotated cans.

Initial runs with rotating cans indicated that no significant differences in temperature, at different positions within the can, occurred for cans rotated radially or tangentially (Figure 22a). Temperature differences were apparent in axially and paraxially rotated cans (Figure 22b). Temperatures at points not on the can axis (axially and paraxially rotated cans) showed fluctuations of the same frequency as the cage rotation.

The results of Clifcorn et al (1950) indicate that optimum heat transfer to cans rotated radially is in the range of speeds that give centrifugal acceleration at the can centre approximately equal to the acceleration due to gravity. Their results also show that the maximum heating rate of axially rotated cans occurs at much higher rotational speeds than the maximum heating rate of radially rotated cans. This investigation was therefore confined to radial and tangential rotation of cans, with rotational speeds giving centrifugal accelerations at the can centres in the range 0.65 to 1.5 times that due to gravity. The accelerations shown in table 7 are based on the radial cans, the centres of which were 4.5 inches from the axis of rotation.

Table 7 : Centrifugal acceleration at can centres

rotational, speed (rpm)	72	80	96	108
acceleration a_c (ft/sec ²)	21.3	26.3	37.9	48.0
relative acceleration $\frac{a_c}{g}$	0.66	0.82	1.18	1.49

The rotational speeds were chosen, within the required range, to give an integral number of readings of emf per minute. This made for easy adjustment of the variable speed drive, using the synchronously driven chart as the timing base. Four cage revolutions per reading were used on the two slowest speeds, and six revolutions per reading on the

two highest speeds, giving 18, 20, 16 and 18 readings of emf per minute for the speeds of 72, 80, 96 and 108 rpm respectively.

CALCULATION METHODS

Graphical integration (with respect to time) of chemical reaction rate data and bacterial destruction rate data has been used to calculate equivalent retort times for the chemical and bacterial systems respectively.

Calculation data

(a) Chemical reaction rate data.

The determination of sucrose hydrolysis rates at various temperatures and the calculation of the specific rate of hydrolysis vs temperature table has been described in (d) and (e) of the section on Chemical System Development.

(b) Bacterial destruction rate data.

For purposes of calculation of bacterial equivalent retort times, spore destruction rate tables have been calculated for a number of organisms, using data from the literature. Two of these organisms, (Bacillus stearothermophilus (Strain TH24, in milk) and Bacillus subtilis (Strain 786, in milk) from the data of Franklin et al (1958) and (1958) respectively), have been used extensively in calculation of equivalent retort times.

B. stearothermophilus is one of the most heat resistant organisms occurring in processed foods, while B. subtilis is an organism commonly responsible for spoilage of sterilized milk.

From the point of view of process calculation B. stearothermophilus can be considered a typical organism. A value of z of 17.0°F has been calculated from the data of Franklin et al (1958). This is very close to the value of z of 18.0°F often assumed in traditional process calculations. B. subtilis, however, has the very low value of z of 12.0°F (Franklin et al (1958)). Organisms which give lower z 's, i.e. steeper $\log D$ vs T or $\log D$ vs $\frac{1}{T}$, curves are likely to be rare, and hence this strain of B. subtilis can be considered an extreme type. Activation energies for the destruction of both organisms have been calculated, and used for interpolation and extrapolation of the data.

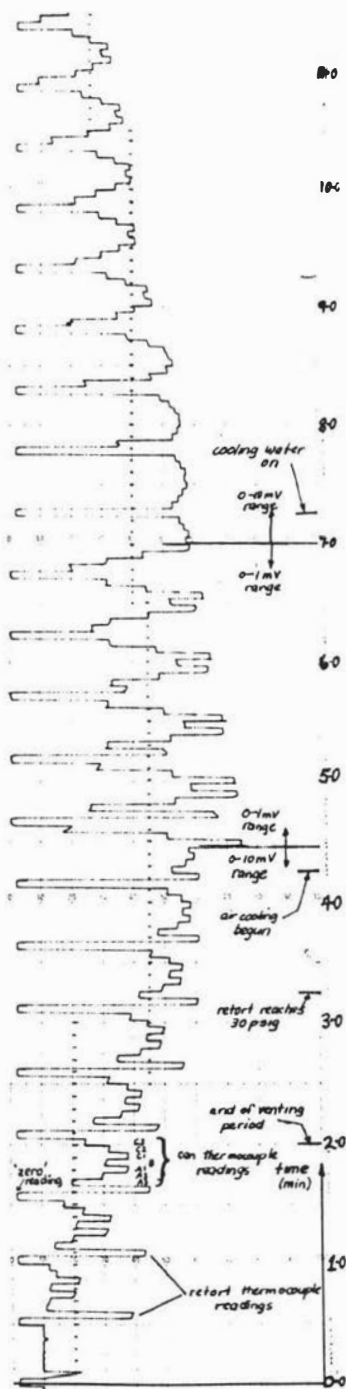


Fig. 23a Potentiometer recording: static can run no. 10 (1 min. at 30 psig).

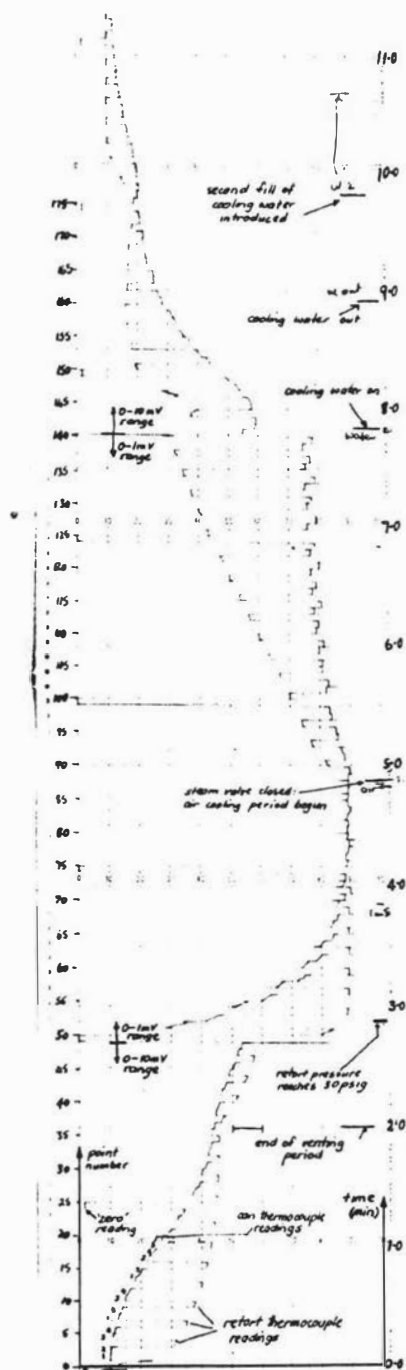


Fig. 23b Potentiometer recording: rotating can run no. 53 (108 r.p.m., 2 min. at 30 psig).

(1) Lethal rate vs temperature : B. stearothermophilus

Franklin et al (1958) give $Q_{10} = 11.5$ in the range 110 to 125°C. Using the interval 112.5 - 122.5°C gives an activation energy for the destruction of B. stearothermophilus of 74.1 kcal/mol. The spore destruction rate at 115°C is 0.0833 decimal reductions per minute. Hence the rate of destruction of B. stearothermophilus TH24 spores in milk is given by -

$$\begin{aligned} \left(\frac{\partial \log_{10} N}{\partial \theta} \right)_T &= \frac{1}{D_T} \\ &= 0.0833 \exp \left[\frac{74100}{1.987} \left(\frac{1}{388.2} - \frac{1.8}{T} \right) \right] \\ &= \log_{10}^{-1} \left[\frac{-29120}{T} + 40.620 \right] \end{aligned}$$

decimal reductions per minute, where D_T is the decimal reduction time at T °R. Rates of destruction for B. stearothermophilus (and for B. subtilis) are shown in Appendix VII.

(11) Lethal rate vs temperature : B. subtilis

Franklin et al (1958) give for B. subtilis (Strain 786 in milk) a value of Q_{10} equal to 31.7 in the range 112.5 - 120°C (from which $E_A = 102.0$ kcal/mol), and rate of destruction at 112.5°C equal to 0.188 decimal reductions per minute.

Hence for B. subtilis spores the rate of destruction is given by -

$$\begin{aligned} \left[\frac{\partial \log_{10} N}{\partial \theta} \right]_T &= \frac{1}{D_T} \\ &= 0.188 \exp \left[\frac{102000}{1.987} \left(\frac{1}{385.7} - \frac{1.8}{T} \right) \right] \\ &= \log_{10}^{-1} \left[\frac{40100}{T} - 57.045 \right] \end{aligned}$$

decimal reductions per minute.

Tabulation

Potentiometer recordings are shown in figures 23a and 23b for typical static and agitated can runs respectively. The thermocouples

are identified and the time from the beginning of the process is shown on the right hand side of each chart. In the rotating can runs readings of emf are numbered consecutively from the beginning of each run. These point numbers are shown in figure 23b and changes of potentiometer range and other relevant process data are marked on each chart.

Time was marked on the static can chart at intervals of 0.05 or 0.10 minutes, and the time and emf entered in the table against the thermocouple number (see figure 24a, columns 1 to 3). The emf for each point on the recorder chart, for the agitated cans, was taken at the end of each interval and entered in the table against the thermocouple number and point number (figure 24b, columns 1 to 3). The emf was read directly from the chart, using a pair of dividers in the 0-10 mV range to take account of the offset at the zero mark (see figures 23a and 23b).

The temperature corresponding to each emf in column 3 is entered in column 4, and the specific sucrose hydrolysis rate and the rate of destruction of B. stearothermophilus spores and B. subtilis spores, in columns 5, 6 and 7 respectively (figures 24a and 24b).

Plotting and integration

The hydrolysis rates and spore destruction rates were plotted against time (static can runs) or against point number (agitated can runs). Typical curves are shown in figures 25a (static can) and 25b (agitated can). The integrations were done with an Allbrit planimeter set to read 15.0 in^2 per revolution of the measuring wheel, and the areas recorded directly in revolutions. A third integration was done if the difference between the first two readings was greater than 0.004 rev (i.e. 0.06 in^2).

Hydrolysis and spore destruction rate curves for a hypothetical sample of material whose temperature followed that of the retort exactly were also plotted on the same graphs. The area under this curve (ABCDEA in figure 25b) and also the area under the curve while the retort is at the required pressure (BCFGB in figure 25b) were also measured. The process time at retort temperature (θ_{GR} in figure 25b) is measured from the Varian chart.

Run 53 - Sucrose Hydrolysis

Temp	Time	Temp	Time	Temp	Time
100	0	100	0	100	0
100	10	100	10	100	10
100	20	100	20	100	20
100	30	100	30	100	30
100	40	100	40	100	40
100	50	100	50	100	50
100	60	100	60	100	60
100	70	100	70	100	70
100	80	100	80	100	80
100	90	100	90	100	90
100	100	100	100	100	100

Fig.26 Typical calculation of equivalent retort time for sucrose hydrolysis; agitated can run no. 53.

Calculation of Equivalent Retort Times

(a) Equivalent retort time from temperature data.

The equivalent retort times are calculated from the area PQESTP and the area BCFGB (see figure 25b).

Area BCFGB is equivalent to θ_{GF} min. at retort temperature.

Therefore :

$$\theta = \frac{\text{area PQESTP}}{\text{area BCFGB}} \cdot \theta_{GF}$$

If "offset" (page 88) was observed after all can temperatures had become steady, a correction was made to the equivalent retort time by multiplying the equivalent retort time by -

$$\frac{\left(\frac{H}{H_0}\right)_R}{\left(\frac{H}{H_0}\right)_I}$$

$\left(\frac{H}{H_0}\right)_R$ is the specific hydrolysis rate at retort temperature and $\left(\frac{H}{H_0}\right)_I$ is the specific hydrolysis rate at the indicated can temperature.

Corrections were not often greater than about 2% for sucrose hydrolysis equivalent retort times (indicated temperature error of 0.4°F) and the error on the corrected equivalent retort time is probably less than 0.5%.

Similar corrections were applied to the spore destruction equivalent retort times.

A typical calculation of equivalent retort time for sucrose hydrolysis is shown in figure 26.

(b) Equivalent retort time from sucrose hydrolysis data.

The mean retort temperature T_R is calculated from the mean height of the retort rate curve between B and C in figure 25b.

The rate of hydrolysis (H_o) at the reference temperature is known (see (d), (i) of the section on Processing Experiments) and hence the hydrolysis rate at retort temperature can be determined,

$$\text{i.e. } H_R = H_o \cdot \left(\frac{H}{H_o} \right)_R$$

The equivalent retort time from the sucrose hydrolysis measurement is then given by -

$$\phi = \frac{pR_1 - pR_o}{H_R}$$

where pR_o and pR_1 are the values of pR before and after processing.

- (c) Calculation of H_o from measurement of sucrose hydrolysis in agitated tubes.

Significant sucrose hydrolysis takes place during the heating and cooling periods in the determinations of sucrose hydrolysis rate in agitated tubes at retort temperature. The specific sucrose hydrolysis rate is plotted against time (or point number) and the equivalent retort time (ϕ) calculated as outlined in section (i) above. The rate of hydrolysis at retort temperature is then given by :

$$H_R = \frac{pR_1 - pR_o}{\phi}$$

The specific hydrolysis rate $\left(\frac{H}{H_o} \right)_R$ at the mean retort temperature is determined from the mean height of the retort temperature specific hydrolysis rate curve, and the hydrolysis rate at 212.0°F (H_o) is then calculated by -

$$H_o = H_R \div \left(\frac{H}{H_o} \right)_R$$

This estimate of H_o is then used for the calculation of equivalent retort times from sucrose hydrolysis measurements as outlined in section (ii) above.

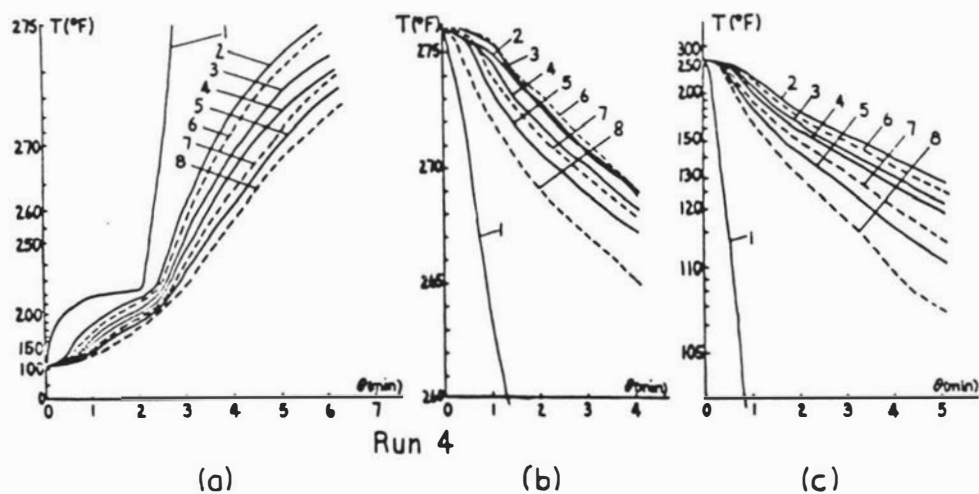
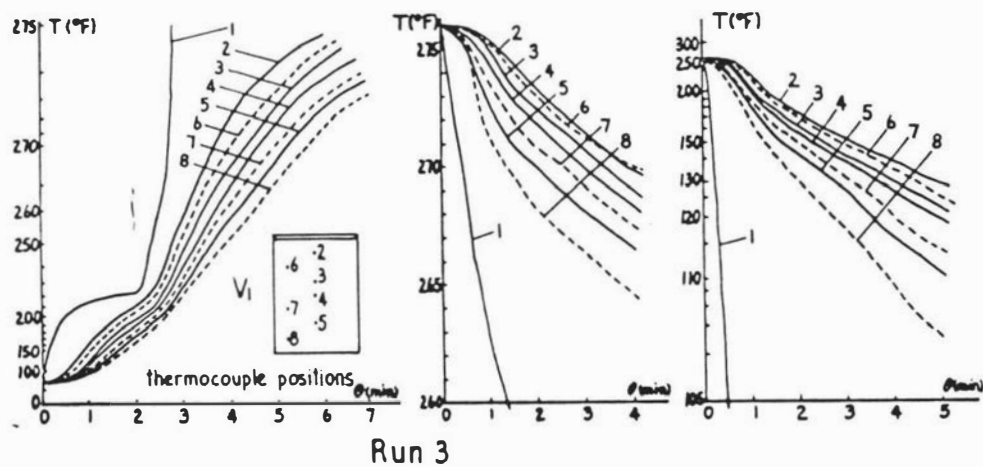
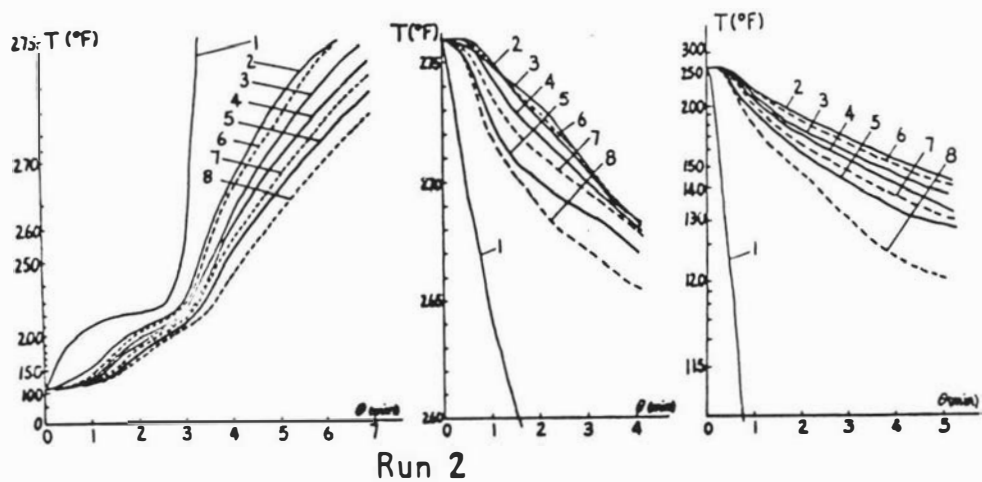


Fig. 27 Temperature distribution in static water-filled can: (a) heating, (b) air cooling, (c) water cooling.

RESULTS AND DISCUSSION

Static Cans

(a) Temperature distribution runs.

The results of the three runs with seven thermocouples in a single water-filled can are shown in figures 27a, 27b and 27c. Temperatures are plotted as $\log (T_R - T)$ vs θ , T vs θ , and $\log (T - T_0)$ vs θ , for the heating, air-cooling, and water-cooling periods respectively.

(i) Convection pattern.

It is seen that the temperature-time curves for points near the can wall (broken lines) and for points on the can axis (solid lines) are fairly evenly spaced, particularly in the heating part of the process. This implies that isothermal surfaces in a central core in the can are horizontal, and that a 'piston' of liquid is moving slowly down the centre region of the can. In the present case the piston is at least 2 in. diameter (of can diameter, 3.0 in.).

The downward velocity of the fluid core can be estimated from the temperatures if it is assumed that conduction is not significant within the piston. In the later stages of heating and in both periods of heating the fluid velocity is of the order of 2 in per min. These velocities tend to decrease as the temperature differences, between the inside and outside of the can, become small.

The general temperature distribution agrees well with that of Jackson and Olson (1939). The lower temperatures that these workers observed at the axis were not observed in this study. It therefore appears that disturbance of the weak convection currents may have been significant in their work.

The deviations from the simple piston flow temperature distribution in the air cooling period are probably due to minor eddy currents. These have been observed by a number of other workers including Tani (1939), Fagerson and Esselen (1950) and Blaisdell (1963) especially in the initial phases of heating. The momentum of the liquid could also be important as the direction of the flow reverses.

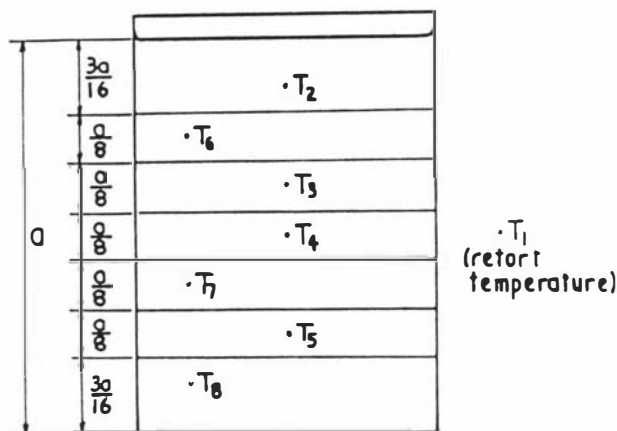


Fig.28 Temperature distribution for calculation of overall heat transfer coefficients.

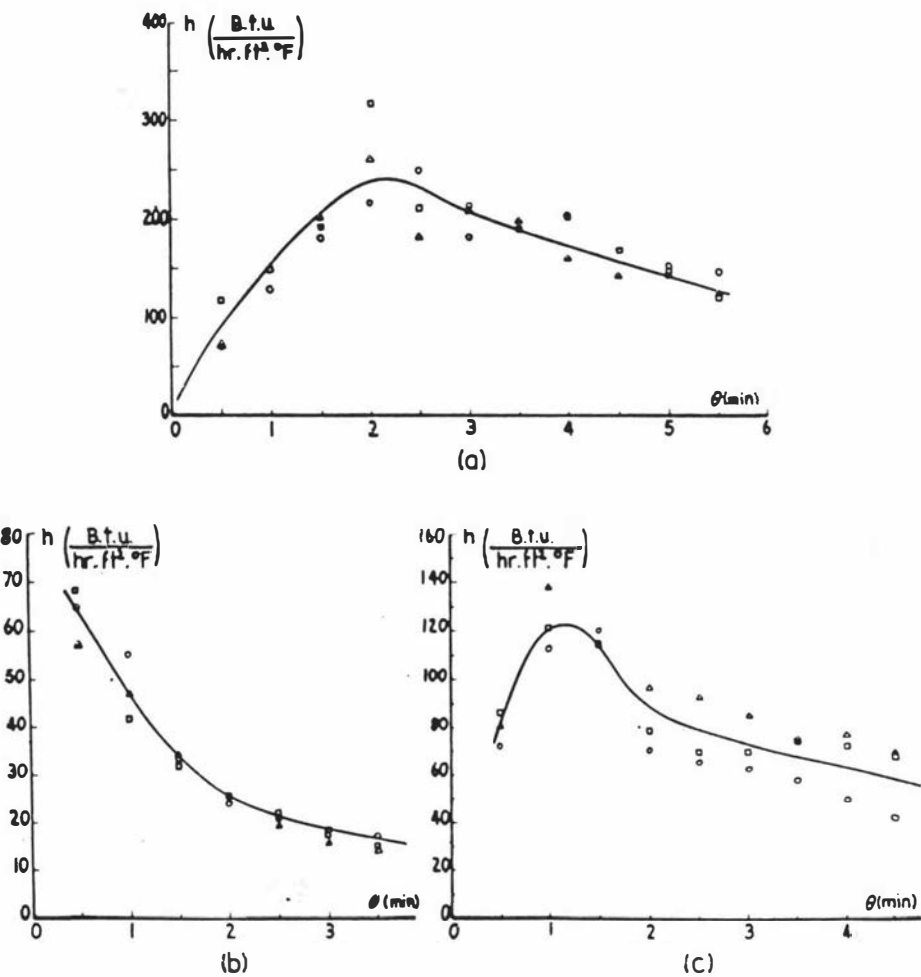


Fig 29 Overall heat transfer coefficients for static cans: (a) heating (b) air cooling (c) water cooling.

(ii) Heat transfer calculations.

A simplified temperature distribution based on the piston flow model has been assumed (see figure 28) and the total heat, Q , of the can calculated,

$$Q = \sum_n (m_n c_p T_n)$$

where m_n and T_n are the mass and temperature respectively, of element n as shown in figure 28, and c_p is the specific heat of the fluid.

An overall heat transfer coefficient, h , has been calculated from -

$$\frac{dQ}{d\theta} = h \sum_n (A_n \cdot \Delta T_n)$$

where A_n is the surface area of element n and ΔT_n is the difference between the retort temperature and the temperature of element n .

Newton's interpolation formula has been differentiated to give an equation for the calculation of the rate of heat transfer q -

$$q = \left(\frac{dQ}{d\theta} \right)_1 = \frac{1}{\Delta\theta} (\Delta Q_0 + \frac{1}{2} \Delta^2 Q_0)$$

The first and second forward differences ΔQ_0 and $\Delta^2 Q_0$ are based on the values of Q at θ_0, θ_1 and θ_2 . The time interval is $\Delta\theta$ and $\frac{dQ}{d\theta}$ is calculated at θ_1 .

Figures 29a, 29b and 29c show the variation of the overall heat transfer coefficient with time.

The increase in heat transfer coefficient in the first two minutes of heating (figure 29a) is due to the decreasing proportion of air in the retort and the consequent increase in outside heat transfer coefficient for heat transfer from the steam-air mixture to the wall. The fluid velocity appears to be relatively constant (about 4 in. per min.) during this venting period. The decrease in fluid velocity as retort temperature is approached probably explains the decrease in the heat transfer coefficient during the later stages of heating.

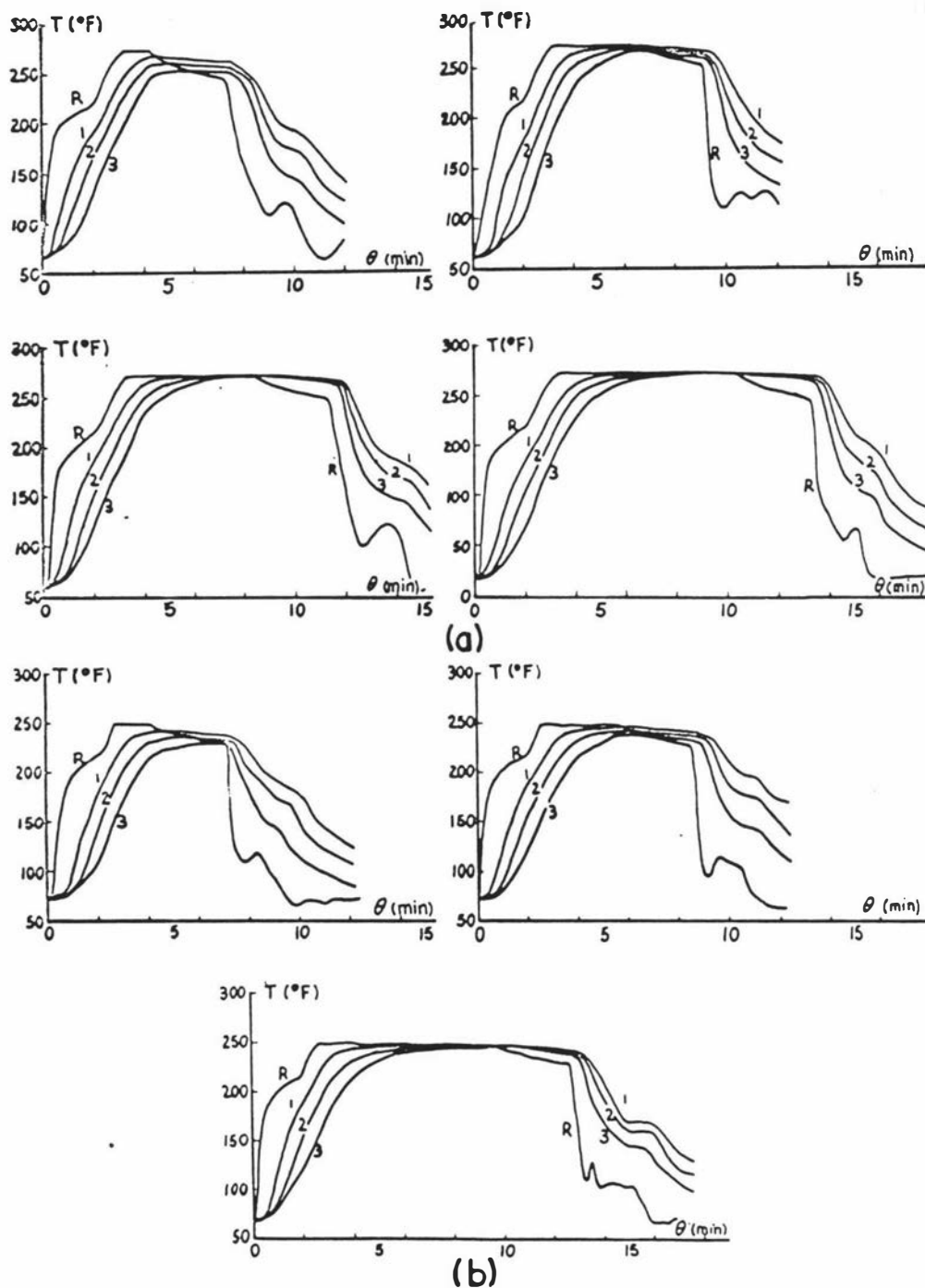


Fig. 30 Temperature vs time curves for static can runs: (a) 30 psig runs, (b) 15 psig runs.

The increasing proportion of air in the first stage of the cooling would tend to give a decrease in heat transfer coefficient. This has been observed in all runs (see figure 29b).

Figure 29c shows a maximum in the heat transfer coefficient vs time curve. This is almost certainly because approximately one minute is required to cover the can completely with water. The decrease in velocity, and the increase in viscosity with decrease of temperature will both decrease the heat transfer coefficient as the mean can temperature approaches the temperature of the cooling water.

Heat transfer coefficients as calculated above have the drawback that a temperature distribution within the can must be assumed before rates of heating can be calculated. Heat transfer coefficient based on the centre point temperature or on the average temperature may be more useful, e.g. in the calculation of equivalent time differences (see p 182).

(b) Sucrose hydrolysis runs

Temperature-time curves are shown for one can from each of the four runs at 30 psig and one for each of the three runs at 15 psig, in figures 30a and 30b respectively.

Hydrolysis rate and spore destruction rate curves have also been plotted for these runs. Two typical sets of rate vs time curves are shown in figure 31 to illustrate the effect of the greater activation energies of the bacterial systems. The temperature-time curves from which these rate curves are derived are also shown.

Tables 8a and 8b give the equivalent retort times calculated from the fixed point temperature data for the seven runs. The equivalent retort times calculated from sucrose hydrolysis measurements are also shown in tables 8a and 8b, (pp 120, 121).

(1) Equivalent point determination.

The validity of the application of the simple convection model to static can calculations can be assessed by comparing the sucrose hydrolysis equivalent retort time, as estimated by measurement of sucrose

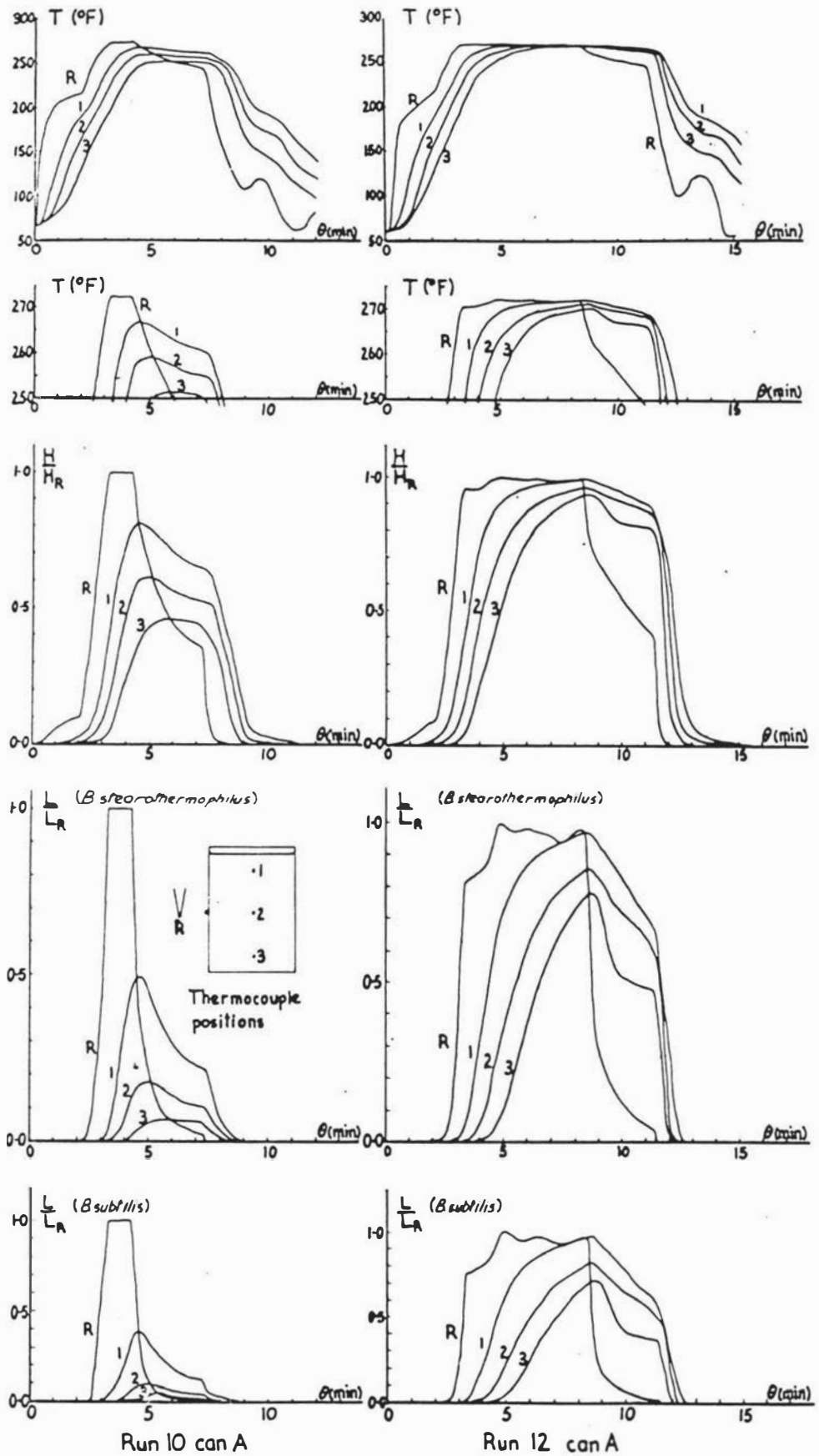


Fig.31 Temperature vs time, specific sucrose hydrolysis rate and specific spore destruction rate vs time curves for two typical static cans.

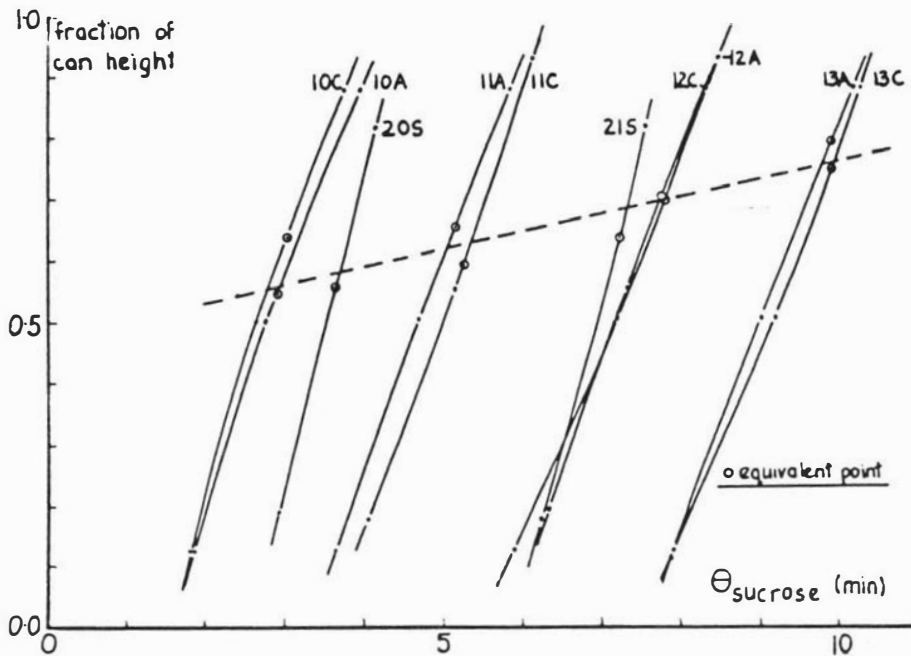


Fig. 32a Equivalent points : 30 psig static can runs.

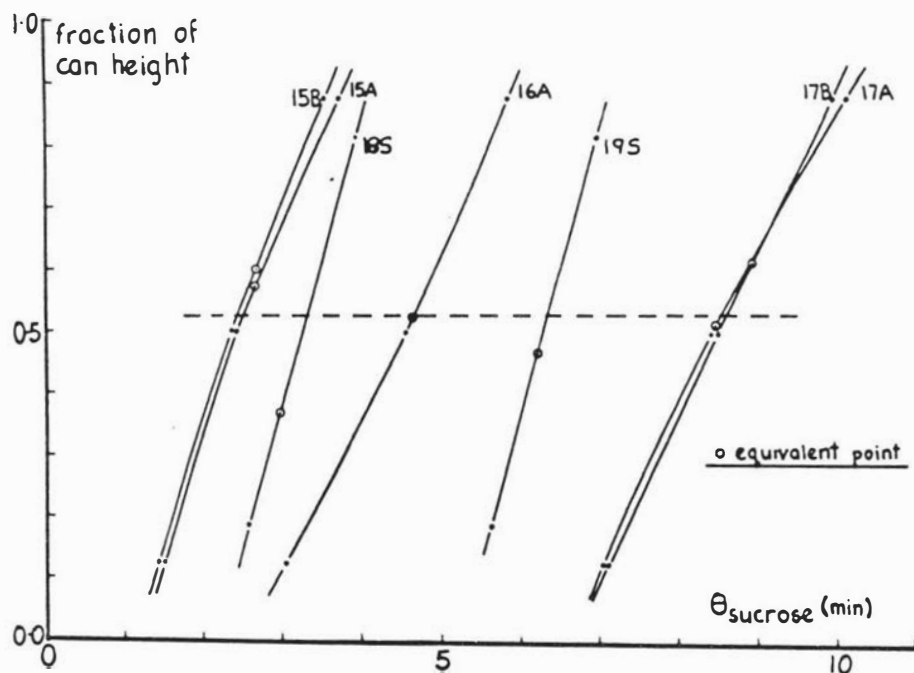


Fig. 32b Equivalent points : 15 psig static can runs.

hydrolysis, with that estimated from fixed point temperature data.

The equivalent retort times at the three points in the can are shown in figures 32a and 32b. Data from the four cans of sucrose solution in the sucrose, milk, and water comparison runs (see Table 10) are included in figures 32a and 32b.

If it is assumed that the fixed point equivalent retort time vs height of thermocouple above the bottom of the can curve is smooth (see figure 3c), an equivalent point can be found by interpolation. The equivalent point is such that the residual sucrose concentration at this point is equal to the average sucrose concentration in the can after processing. The equivalent points are shown in figures 32a and 32b.

It is seen that the equivalent point tends to move towards the top of the can as process time is increased in the 30 psig runs. No explanation could be found for this in terms of deviations from the convection pattern, as incomplete circulation in the can would cause the equivalent point to fall below the centre. This can be deduced from the equivalent retort time analysis of the piston flow convection model. The equivalent retort time for the whole can based on the extreme case of no circulation is 2.679 minutes, and the equivalent point is therefore approximately 0.3 of the can height above the bottom of the can.

A partial explanation of the rising equivalent point in the 30 psig runs was found when the agitated can experiments were proceeding. Consistent differences between calculated and measured equivalent retort times indicated that the specific sucrose hydrolysis rate vs temperature table used in the static can run calculations was in error. The error arose because too few data were taken to establish the rate of hydrolysis at high temperatures adequately. The equivalent retort times calculated from temperature data will not be affected greatly by the error, as they are ratios of two areas, both of which are calculated from the table. Because the error is small, the equivalent retort times have not been recalculated. The measured equivalent retort time is affected by the error, because -

$$\eta = \frac{A_p R}{H_R}$$

where

$$H_R = H_0 \left(\frac{H}{H_0} \right)$$

Table 8a : Equivalent Retort Times : Static cans, 30 psig runs

<u>Rm</u> and thermo- couple number		Process time (min.)	Equivalent retort times (min.)			
			from	from temperature data		
			sucrose hydrolysis	sucrose hydrolysis	<u>B. stearo-</u> <u>thermo-</u> <u>philus</u>	<u>B. subtilis</u>
<u>10</u>	R	1.0		3.45	1.77	1.64
	A1*		2.92	3.96	1.40	0.89
	A2			2.76	0.53	0.25
	A3			1.88	0.21	0.07
	B2		3.02	3.07	0.78	0.39
	C1		3.03	3.77	1.43	0.94
	C2			2.65	0.51	0.25
	C3			1.82	0.19	0.08
<u>11</u>	R	3.0		5.69	4.15	3.78
	A1		5.16	5.88	3.68	3.04
	A2			4.70	2.45	1.73
	A3			3.68	1.40	0.89
	B2		5.26	4.83	2.46	1.80
	C1		5.27	6.16	4.10	3.51
	C2			5.17	2.88	2.27
	C3			4.06	1.75	1.18
<u>12</u>	R	5.0		7.57	5.94	5.62
	A1		7.81	8.50	6.86	6.47
	A2			7.35	5.18	4.60
	A3			6.25	3.80	3.13
	B2		7.82	7.21	5.04	4.35
	C1		7.83	8.36	6.67	6.20
	C2			7.24	5.12	4.49
	C3			5.90	7.45	2.74
<u>13</u>	R	7.0		9.59	7.96	7.70
	A1		9.97	10.24	8.42	7.86
	A2			9.03	6.74	6.07
	A3			7.93	5.46	4.73
	B2		10.01	9.31	7.27	6.72
	C1		9.99	10.35	8.80	8.50
	C2			9.21	7.23	6.63
	C3			7.97	5.50	4.84

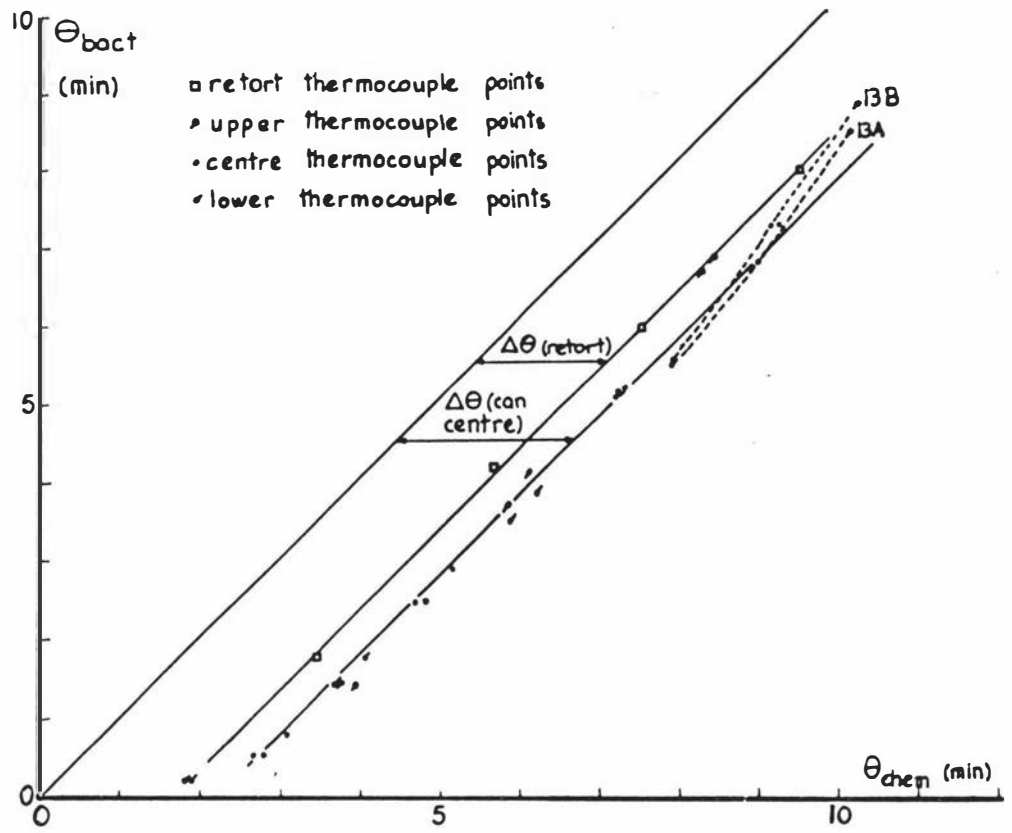
Table 8b : Equivalent Retort Times : Static cans, 15 psig runs

<u>Rm</u> and thermo- couple number	Process time (min.)	Equivalent retort times (min.)			
		from	from	temperature	data
		sucrose	sucrose	<u>B. stearo-</u>	<u>B. subtilis</u>
		hydrolysis	hydrolysis	<u>thermo-</u> <u>philus</u>	
<u>15</u>	R	1.5	3.93	2.38	2.11
	A1 *	2.65	3.72	1.35	0.86
	A2		2.41	0.47	0.22
	A3		1.50	0.16	0.05
	B1	2.68	3.52	1.26	0.80
	B2		2.39	0.47	0.22
	B3		1.41	0.13	0.04
<u>16</u>	R	3.0	5.60	4.06	3.78
	A1	4.63	5.82	3.44	2.76
	A2		4.56	1.84	1.21
	A3		3.04	0.83	0.14
<u>17</u>	R	7.0	9.03	8.32	7.80
	A1	8.90	10.11	8.14	7.31
	A2		8.40	5.56	4.53
	A3		7.02	4.21	3.27
	B1	8.49	9.96	7.98	7.08
	B2		8.50	5.99	5.04
	B3		7.06	4.27	3.38

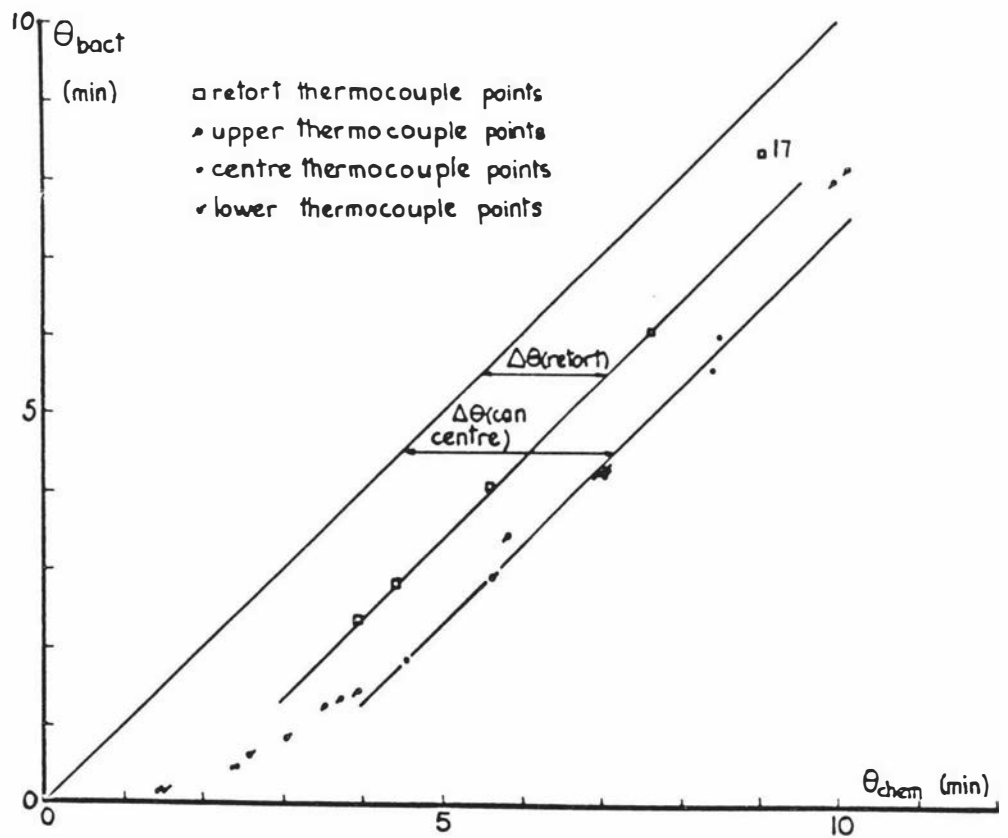
* Thermocouples 1, 2, 3 are on the axis of a 301 x 409 can, 3.5 in., 2.0 in., and 0.5 in. above the bottom respectively, except for cans 11C and 12A (thermocouples 3.7 in., 2.2 in., and 0.7 in., above the bottom of the can).

The effect of using the corrected specific sucrose hydrolysis rate vs temperature table is to increase the estimate of $\left(\frac{H}{H_0}\right)_R$ by about 3% at 270°F, and so to reduce the estimate of Θ by the same amount. This moves the equivalent point towards the can centre. Unfortunately no sucrose solution was available from these runs to check the estimates of $\left(\frac{H}{H_0}\right)_R$ and H_0 .

The 15 psig runs are not greatly affected by the error in the specific sucrose hydrolysis vs temperature table as the correction is only appreciable at temperatures greater than 250°F. While a certain



(i) 30 psig runs



(ii) 15 psig runs

Fig. 33a Equivalent retort time correlations for *B. stearothermophilus* (static cans)

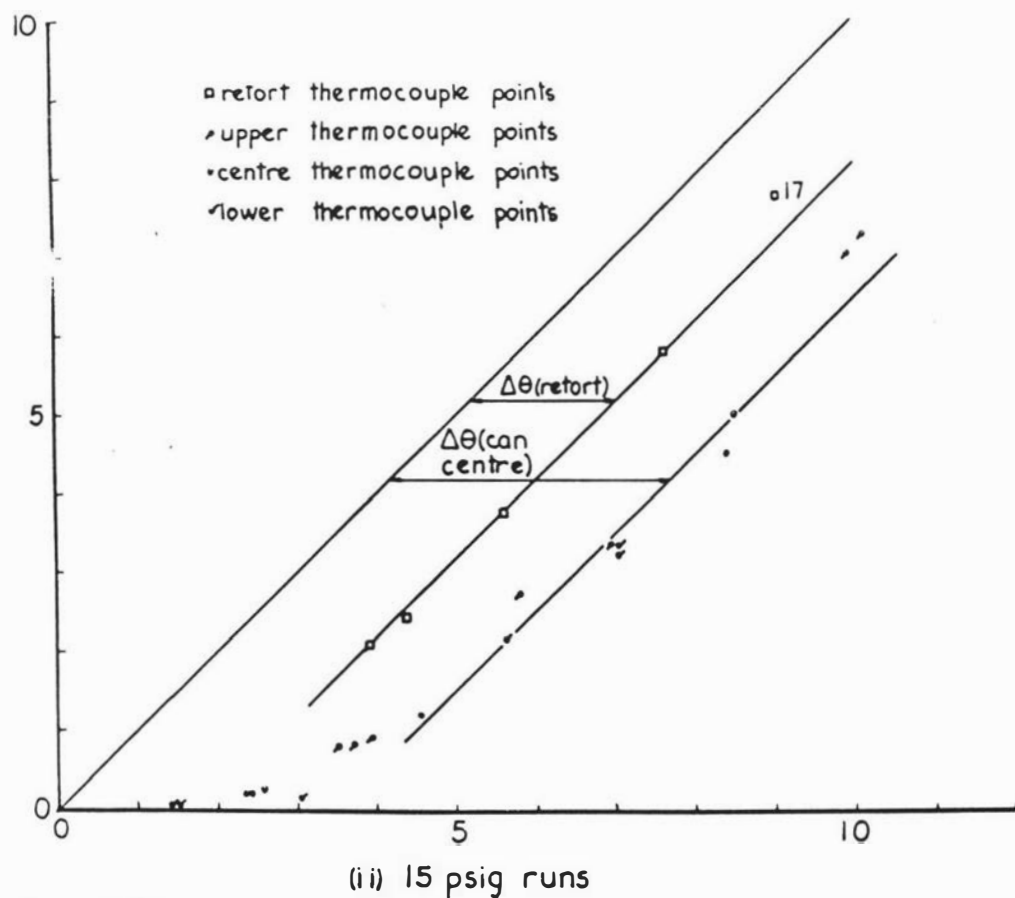
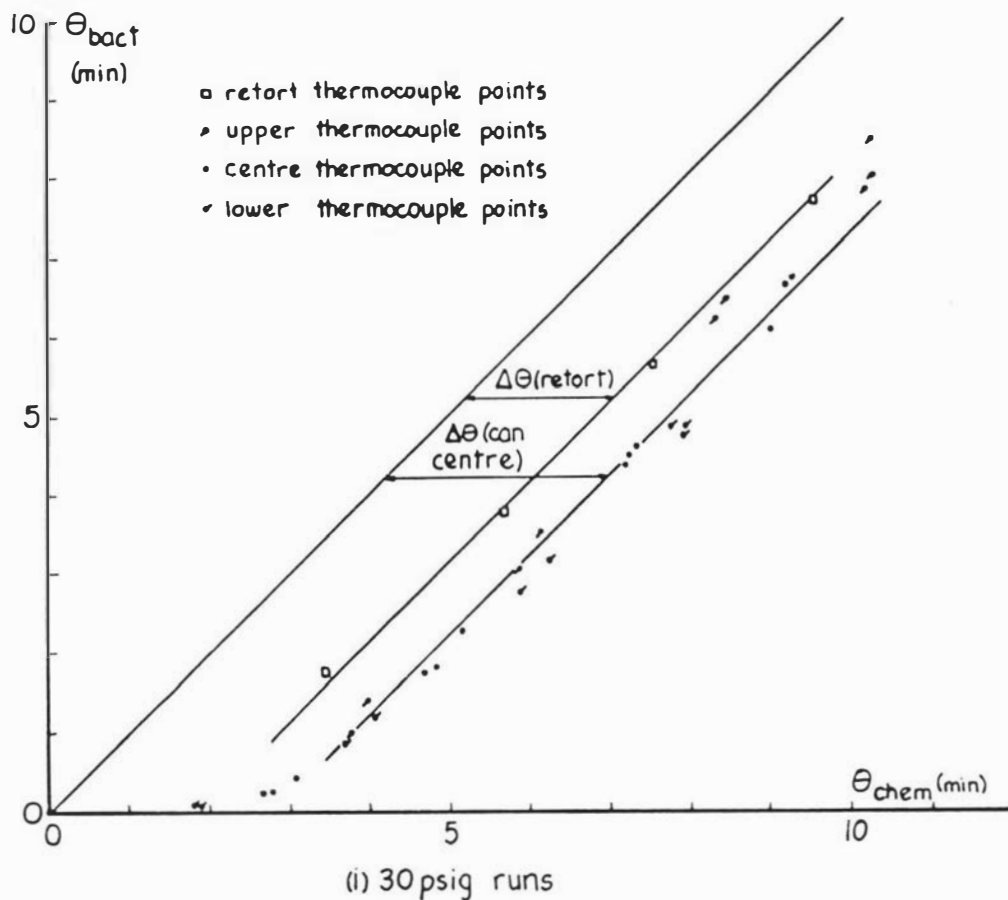


Fig.33b Equivalent retort time correlations for *B. subtilis* (static cans)

amount of scatter in is observed in the equivalent points for the 15 psig runs, there is no definite trend towards the top of the can. The effect of scatter of the equivalent points is discussed in the next section.

(ii) Equivalent retort time correlation (θ_{baot} vs θ_{chem}).

Figure 31 shows temperature vs time curves, and hydrolysis rate and spore destruction rate vs time curves for two typical stationary cans (can 10A, 1.0 min. at 30 psig; can 12A, 5.0 min. at 30 psig).

Although the ordinate scales of the rate graphs are different, it can be seen that the height of the can thermocouple curves, relative to the retort thermocouple curves, decreases with increasing activation energy. Comparison of the area under each can thermocouple curve, and the area under the retort thermocouple curve while the retort is at processing pressure, shows that the equivalent retort time for any point decreases as the activation energy increases.

The temperature and rate vs time curves for the 15 psig runs are slightly different in shape, but show the same general trends as the 30 psig runs.

The curves also illustrate the difference between total lethal effect of heat calculated at the coldest point, and that calculated at the centre point. It is seen that processes calculated on the basis of the temperatures at the coldest point may result in an unnecessarily severe heat treatment, especially in high temperature short time processes where all can temperatures do not approach closely the temperature of the retort.

For purposes of prediction of bacterial destruction from chemical reaction data, the equivalent retort times (Tables 8a, 8b) for spore destruction (θ_{baot}) were plotted against the equivalent retort times for sucrose hydrolysis (θ_{chem}) as shown in figures 33a and 33b for B. stearothermophilus and B. subtilis respectively.

Equivalent retort times are plotted for all points in the can (upper thermocouples (P), centre thermocouples (•) and lower thermocouples (✓)) as well as the equivalent retort times calculated from

the retort temperature. The equivalent retort times for a hypothetical can following retort temperature exactly are included because they can be calculated from temperature data which is relatively easy to obtain. These equivalent retort times may prove useful in prediction of the $\theta_{chem} : \theta_{bact}$ correlation for the can centres and are easier to obtain than direct values of θ_{chem} and θ_{bact} .

The retort temperature in run 17 fell rather more rapidly than the retort temperature in the other 15 psig runs in the air cooling period. This appears to be the reason for the somewhat irregular position of the retort point for this run in figures 33a (ii) and 33b (ii).

Figures 33a and 33b show that the θ_{bact} vs θ_{chem} correlation is of the form -

$$\theta_{bact} = \theta_{chem} - \Delta\theta$$

for all processes of commercial interest, where $\Delta\theta$ or "equivalent time difference" is a constant, the value of which depends on the time-temperature function obtaining in the can, and on the activation energies of the chemical and bacterial systems. Deviations from linearity occur only at very short process times (1.0 or 1.5 min. at retort temperature). These are not likely to be used in processing of unagitated cans of convection heating products.

As process time is increased beyond the maximum shown here, both the bacterial and chemical equivalent retort times will increase by the same amount as temperatures at all points in the can are equal to retort temperature.

The equivalent retort time points (figure 33) calculated from data of the upper thermocouples are above the line and points from lower thermocouples are, in general, below the line based on the centre points. Hence if uncertainty exists as to the exact position of the equivalent point in the can, the position of the θ_{chem} vs θ_{bact} line will also be uncertain.

The three points for each can may be connected, as shown for cans 13A and 13B in figure 33a (i). From these lines it may be deduced

that an uncertainty in the position of the equivalent point of ± 1 in. in a 4 inch high can represents an uncertainty in θ_{bact} of approximately ± 0.3 min. If θ_{bact} is calculated from temperature data alone (i.e. with no measurement of θ_{chem}) the uncertainty of ± 1 in. in the equivalent point gives an uncertainty in θ_{bact} of approximately ± 1.2 min.

The above analysis assumes that the sucrose hydrolysis equivalent point is the same as the spore destruction equivalent point. If the temperature data used in the development of the convection model are considered it is seen that the extreme case of no convection in the can gives an equivalent point 0.23 of the can height above the bottom of the can, which is 0.07 of the can height below the sucrose equivalent point. In general the bacterial and chemical equivalent points will be closer than the extreme case considered here. Smaller values of D_{bact} than that used here (1.0 min.) will also tend to move the equivalent point away from the centre point towards the coldest point, if the circulation of the fluid in the can does not give uniform equivalent retort times for all elements.

(iii) Equivalent time differences.

If a correlation of the form $\theta_{bact} = \theta_{chem} - \Delta\theta$ is to be useful in process evaluation where temperatures cannot be measured directly, a means of estimating $\Delta\theta$ must be found.

For example, if heat penetration characteristics such as heat transfer coefficients are known for a given product, then it will be possible to calculate temperature-time curves. Hence θ_{chem} and θ_{bact} and hence $\Delta\theta$ can be calculated. The calculated time-temperature curves could well be adequate for prediction of $\Delta\theta$ even if they are not precise enough for actual evaluation of the process under consideration.

Relationships between equivalent time differences for different organisms will also be extremely useful, as θ_{bact} for any organism can then be calculated from θ_{bact} from some other organism. This avoids having to carry out a complete calculation for the second organism as is necessary with traditional process calculation methods.

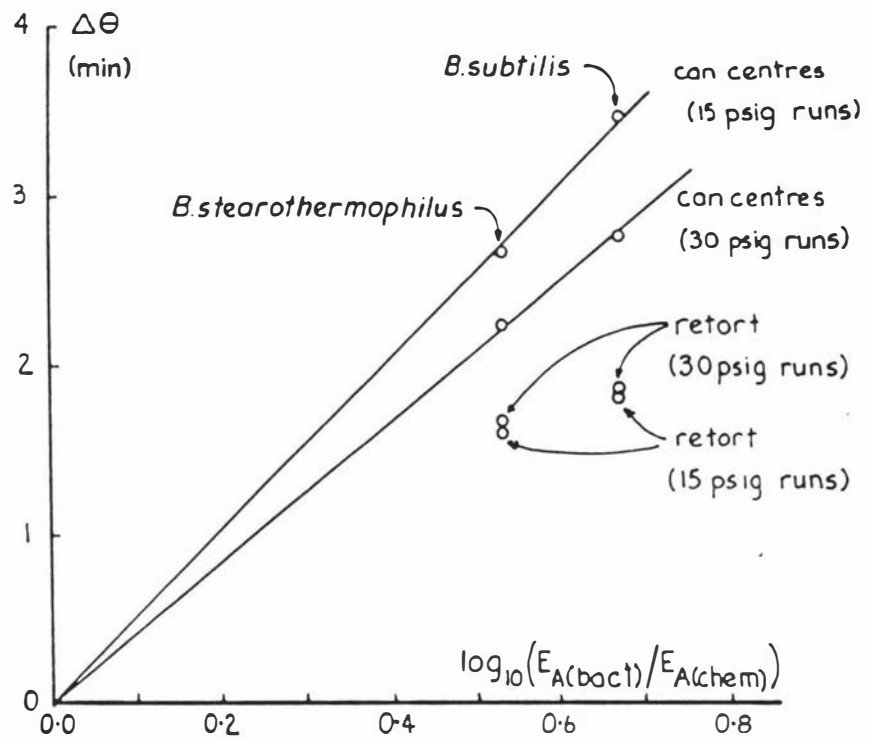


Fig. 34 Equivalent time differences vs activation energy for static can runs.

The equivalent time differences for the two organisms and two processing pressures pressures are shown in Table 9.

Table 9 : Equivalent Time Differences : Static Can Runs

Organism	Equivalent Time Differences (min.)			
	retort temperature curve		can temperature curve	
	15 psig	30 psig	15 psig	30 psig
<u>B. stearo-thermophilus</u>	1.60	1.65	2.68	2.25
<u>B. subtilis</u>	1.82	1.87	3.50	2.78

These equivalent time differences are plotted against $\log \left[E_A \text{ (baot)} / E_A \text{ (chem)} \right]$ in figure 34. The can points are adequately described by a straight line through the origin, but the retort points are not. Too few data have been obtained in this study to indicate whether this plot will be of general use in predicting $\Delta\theta$ for one organism from $\Delta\theta$ for another. It does not appear that the equivalent time differences calculated from the retort temperature curves are sufficient to calculate the equivalent time differences for the cans. The relationship between the equivalent retort times for cans and for the hypothetical can following retort temperature is further discussed in the section on Equivalent Time Difference Analysis (p 160).

(c) Milk, water, and sucrose solution comparison.

Temperature-time data from cans containing milk, water and sucrose solution have been used to plot the specific sucrose hydrolysis rate vs time curves. The rate vs time curves have been integrated and the sucrose hydrolysis equivalent retort times calculated for the three liquids. These equivalent retort times are shown in table 10. Spore destruction equivalent retort times have also been calculated for the

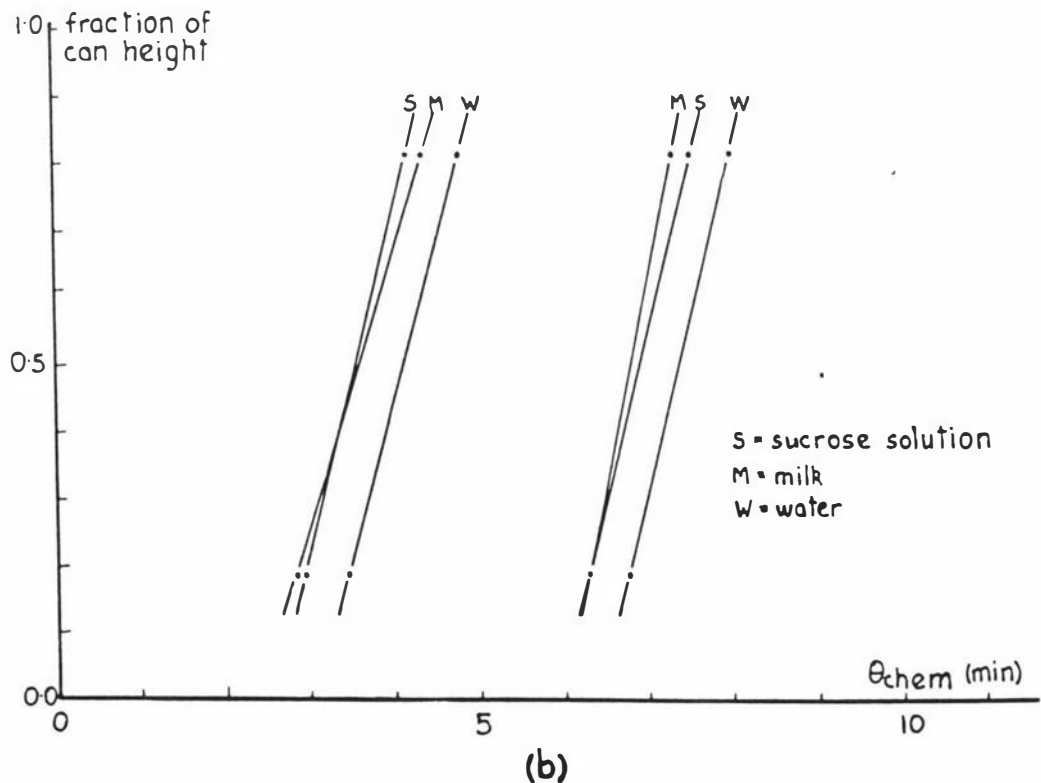
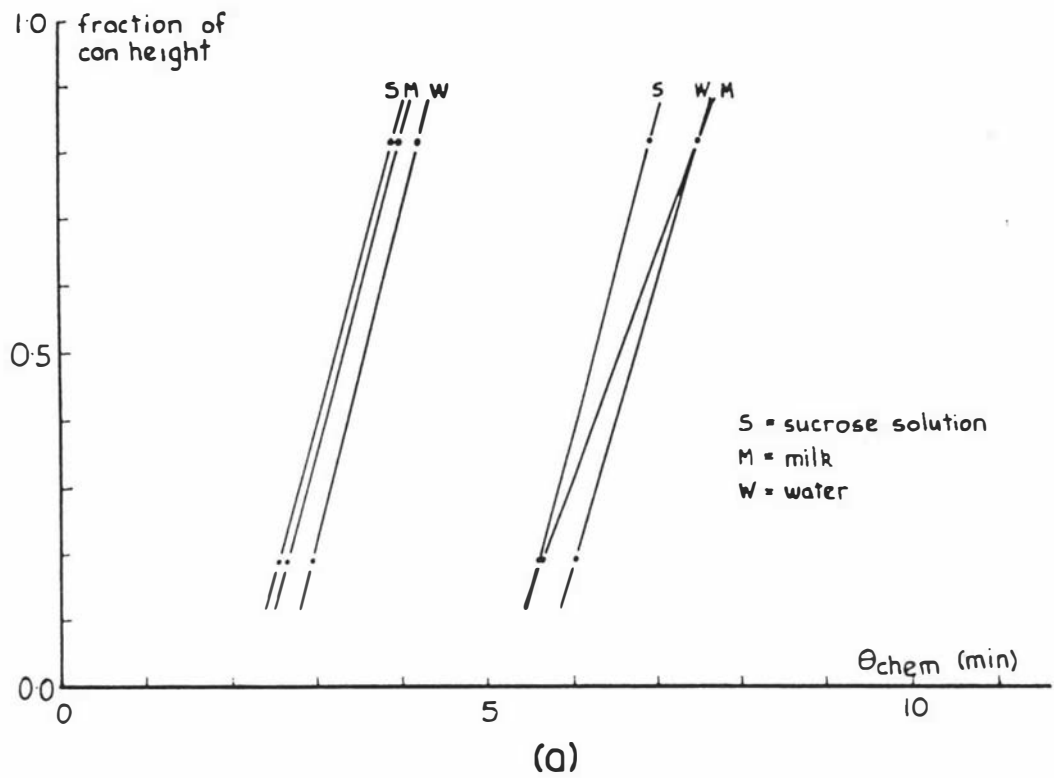


Fig.35 Comparison of milk, sucrose solution and water. Equivalent retort time vs position of thermocouple: (a) 15 psig runs, (b) 30 psig runs.

cans of sucrose solution for runs 18 and 19, and these are included in table 10, and in figures 33a (11) and 33b (11).

The sucrose hydrolysis equivalent retort times are plotted against height of thermocouple (above bottom of can) in figure 35. Equivalent retort times for the cans of milk and sucrose solution are in general nearly equal, but the equivalent retort times calculated from the temperature-time data from the water filled cans are greater than those times calculated from data from cans of milk or sucrose solution. (The upper thermocouple point from the milk filled can in run 19 is derived from a temperature-time curve which is somewhat unusual. The difference between the temperature-time curves for the upper and lower thermocouples is much greater than that observed for any of the other cans (including cans filled with sucrose solution).

These limited data indicate that measurements of θ_{chem} on an artificial system (sucrose solution in this case) can be considered to apply to a real product (such as milk) if the physical properties (e.g. viscosity) are of similar magnitude. The viscosities of milk and the 0.75 molar sucrose solution are both approximately twice that of water over the temperature range for which data are available (Jenness and Patton, 1959; Perry, 1950).

Agitated Cans

(a) Temperature distribution runs.

A number of preliminary runs with several thermocouples in each can were carried out, with water filled cans rotated radially and tangentially, and axially and paraxially (figure 21). Speeds in the range 70-110 rpm were used.

Differences in temperature within the can were only observed for axially and paraxially rotated cans. The temperature distribution in both tangentially and radially rotated cans was extremely uniform, and single thermocouples were therefore used for all heat penetration measurements with the exception of run 28 in which two cans had two thermocouples. Axial and paraxial rotation have not been studied in this investigation.

Table 10 : Equivalent Retort Times - Milk, water and sucrose solution
in static cans

Run and thermo- couple number	Process time and pressure	Equivalent retort times (min.)			
		sucrose hydrolysis (experi- mental)	sucrose hydrolysis (calculated)	<u>B. stearo- thermo- philus</u>	<u>B. subtilis</u>
<u>18</u>	R	2 min.			
	*S1	15 psig	3.50	4.40	2.83
	S2			3.94	2.47
				2.58	0.93
	M1			0.61	0.24
	M2			4.01	
				2.65	
	W1			4.24	
	W2			2.98	
<u>19</u>	R	5 min.			
	S1	15 psig	6.73	7.62	6.06
	S2			6.98	5.82
				5.61	3.40
	M1			4.22	2.19
	M2			2.91	
				7.54	
				5.65	
	W1			7.53	
	W2			6.04	
<u>20</u>	R	2 min.			
	S1	30 psig	3.91	4.53	
	S2			4.16	
				2.94	
	M1			4.33	
	M2			2.83	
	W1			4.68	
	W2			3.46	
<u>21</u>	R	5 min.			
	S1	30 psig	7.43	7.72	
	S2			7.50	
				6.30	
	M1			7.29	
	M2			6.29	
	W1			7.98	
	W2			6.78	

* S = sucrose, M = milk, W = water

Thermocouples 1 and 2 are 3.25 and 0.75 in above can bottom respectively.

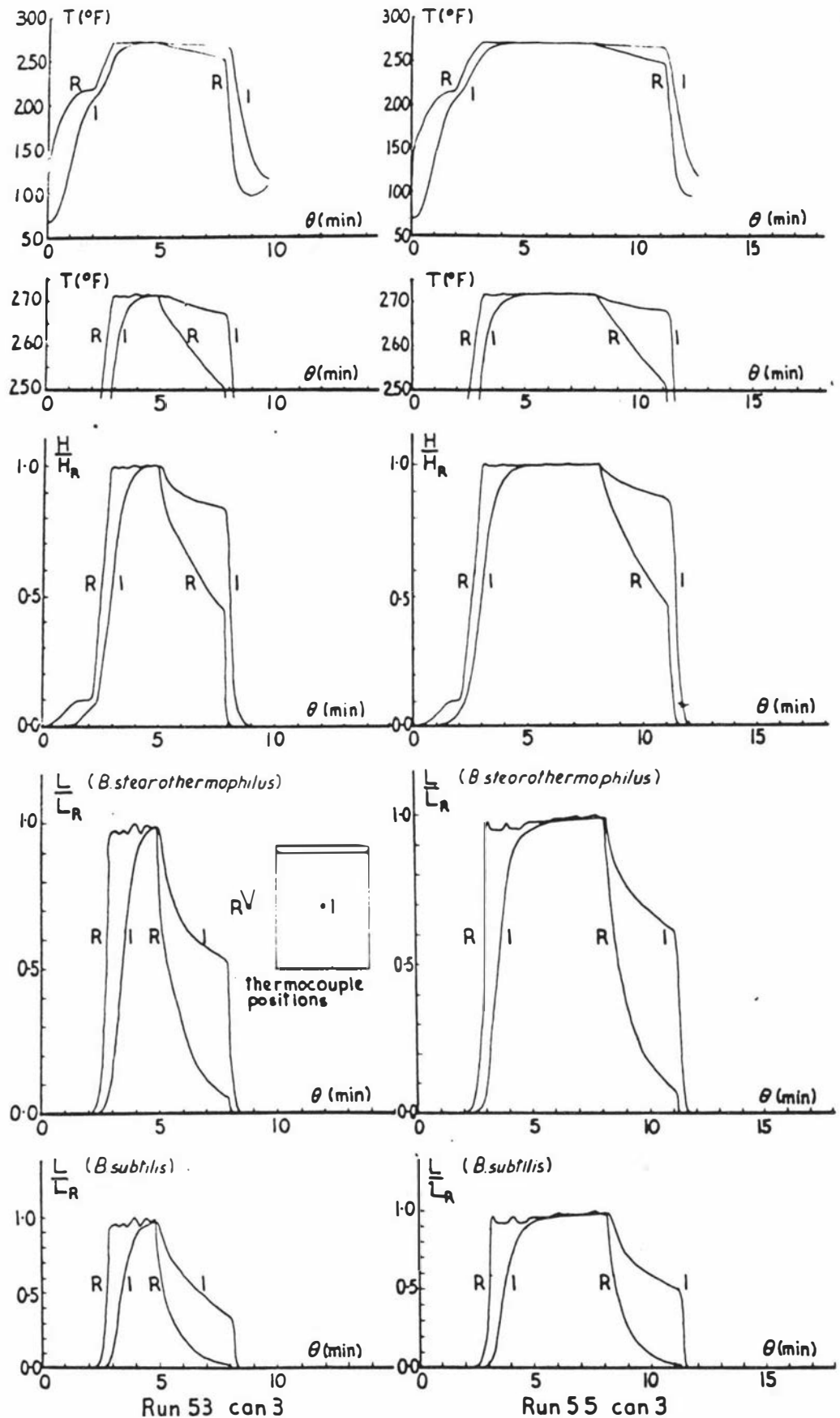


Fig.36 Temperature vs time, specific sucrose hydrolysis rate, and specific spore destruction rate vs time curves for two typical agitated cans.

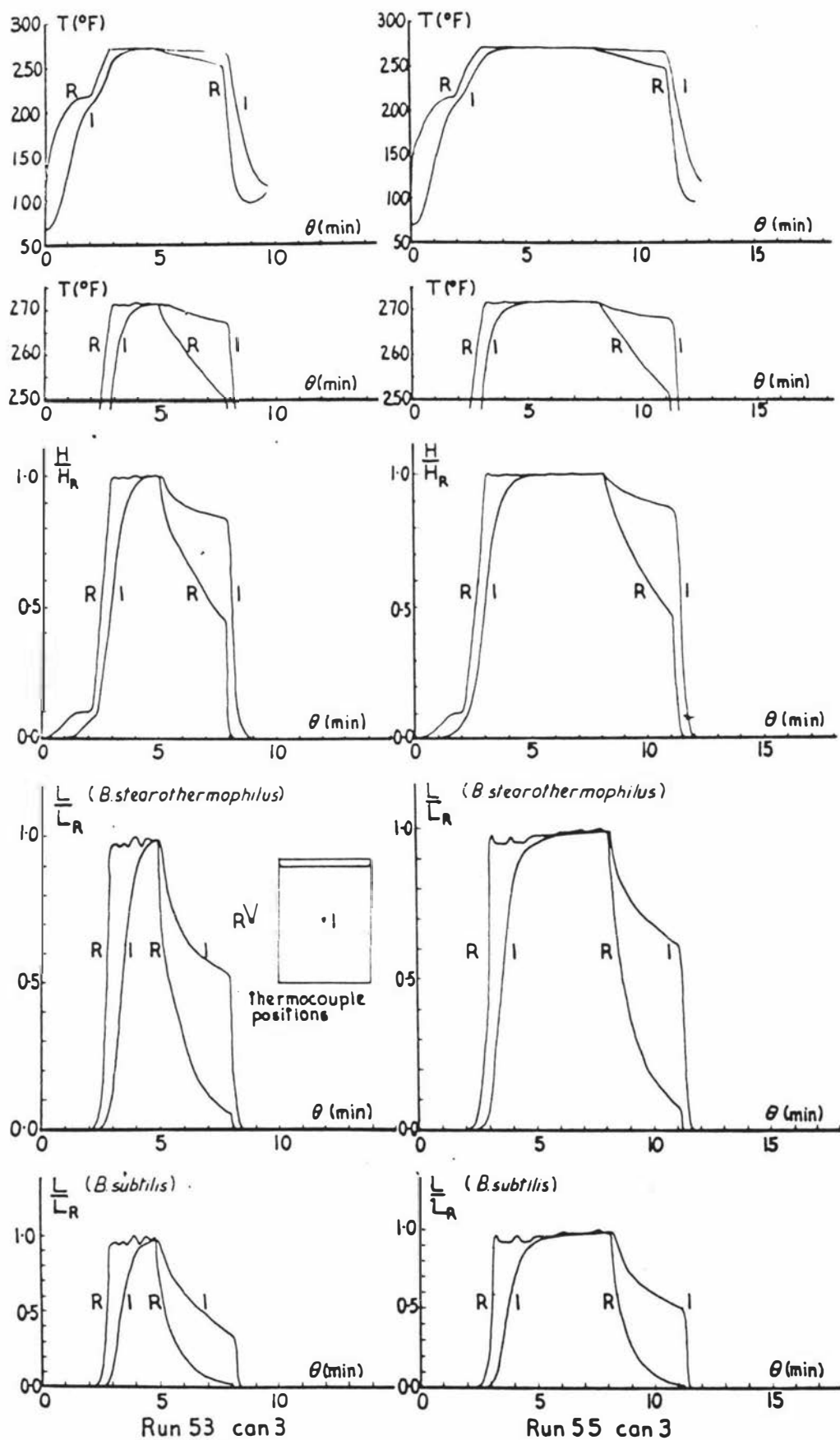


Fig.36 Temperature vs time, specific sucrose hydrolysis rate, and specific spore destruction rate vs time curves for two typical agitated cans.

(b) Sucrose hydrolysis runs.

The temperature-time curves are very similar for all the speeds of rotation, and for both the radially and tangentially rotated cans. At times greater than two minutes after processing pressure was reached, the can temperatures and the retort temperature were ⁱⁿ distinguishable.

Two typical temperature-time curves are shown in figures 36a and 36b. (The specific sucrose hydrolysis rate curves and the spore destruction rate curves for the same processes are also shown. The equivalent retort times and equivalent time differences calculated from the rate vs time curves are discussed in sections (ii) and (iii) below.)

(1) Heat transfer coefficients.

To enable a comparison of the relative rates of heating of agitated and static cans to be made, heat transfer coefficients have been calculated for four 30 psig sucrose hydrolysis runs, viz: runs 50, 51, 45, and 53, rotated at 72, 80, 96, and 108 rpm respectively. Average heat transfer coefficients based on these runs have been used to calculate time-temperature curves for a number of processes and can sizes, in an analysis of the equivalent time difference concept (see Equivalent Time Difference Analysis, pp 157, 158).

1. Calculation of overall heat transfer coefficients, (Fig. 37).

Graphical interpolation of the raw temperature data was used to prepare tables of temperature vs time. These tables were used in the calculation of rate of change of can temperature, and hence of overall heat transfer coefficients, for four runs at 30 psig. The runs used for heat transfer coefficient calculation were numbers 50, 51, 45, and 53, rotated at 72, 80, 96, and 108 rpm respectively.

The equation :

$$\frac{dT}{d\theta} = \frac{T_{n+1} - T_n}{\theta_{n+1} - \theta_n} = \frac{T_{n+1} - T_n}{\Delta\theta}$$

was used to estimate the mean rate of change of temperature in the interval θ_n to θ_{n+1} . T_n and T_{n+1} are the can temperatures at times

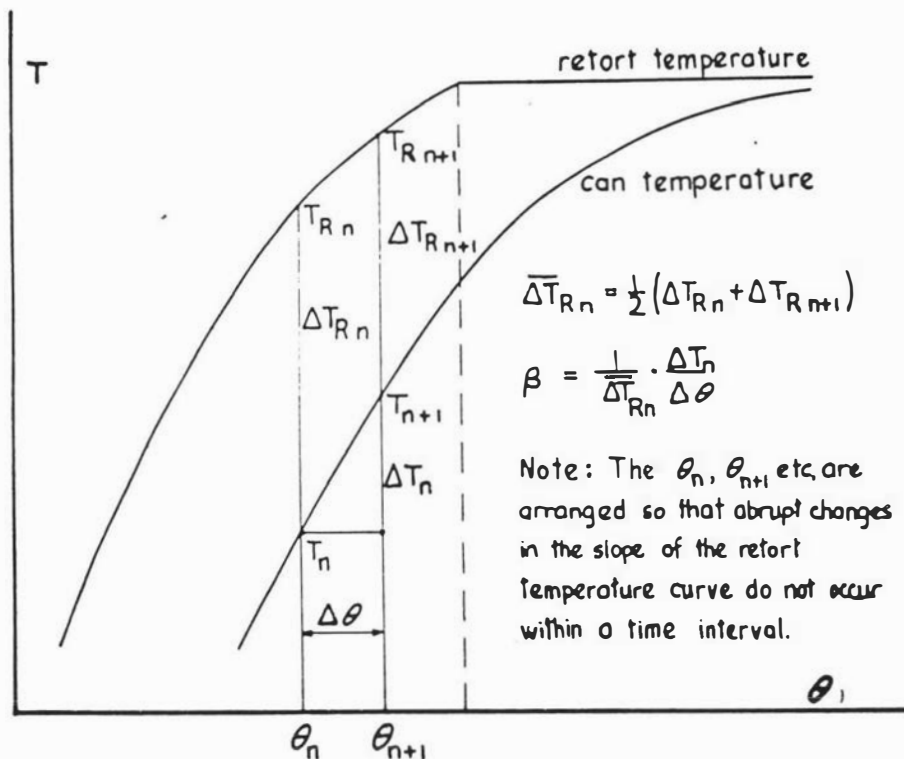


Fig. 37 Calculation of β i.e. rate of change of temperature (per unit temperature difference).

θ_n and θ_{n+1} respectively, and $\Delta\theta$ is the time interval. Time intervals of 30-40 seconds were used in the air cooling phase, and 15-20 seconds in the other phases of heating and cooling.

An arithmetic mean was used to estimate the mean temperature difference (ΔT_n) during the interval θ_n to θ_{n+1} :

$$\text{i.e., } \Delta T_n = \frac{1}{2} ((T_{Rn} - T_n) + (T_{Rn+1} - T_{n+1}))$$

where T_{Rn} and T_{Rn+1} are the retort temperatures at times θ_n and θ_{n+1} respectively.

The mean rate of change of temperature per unit temperature difference (β) is then given by:

$$\beta = \frac{1}{\Delta T} \frac{dT}{d\theta} = \frac{T_{n+1} - T_n}{\Delta\theta \cdot \Delta T_n}$$

The overall heat transfer coefficient (h) is given by:

$$h = \frac{m \cdot c_p}{A} \cdot \frac{1}{\Delta T} \frac{dT}{d\theta}$$

The effective surface area (A) of a 301 x 409 can is 0.380 ft² (internal height = 4 $\frac{5}{16}$ in., internal diameter = 3 in.), and the mass of sucrose solution (m) is 499 gm (1.10 lb.). The specific heat (c_p) of the sucrose solution is estimated from data of Guoker and Ayres (1937) to be 0.854 cal/gm.

The heat transfer coefficient for the system used is therefore given by:

$$h = 1.49 \frac{1}{\Delta T} \frac{dT}{d\theta} \frac{\text{Btu}}{\text{hr.ft}^2 \cdot ^\circ\text{F}}$$

where the time θ is in minutes.

2. Comparison of agitated can and static can overall heat transfer coefficients.

The values of the overall heat transfer coefficients for the four cans in each run have been averaged and plotted against time in figure 38.

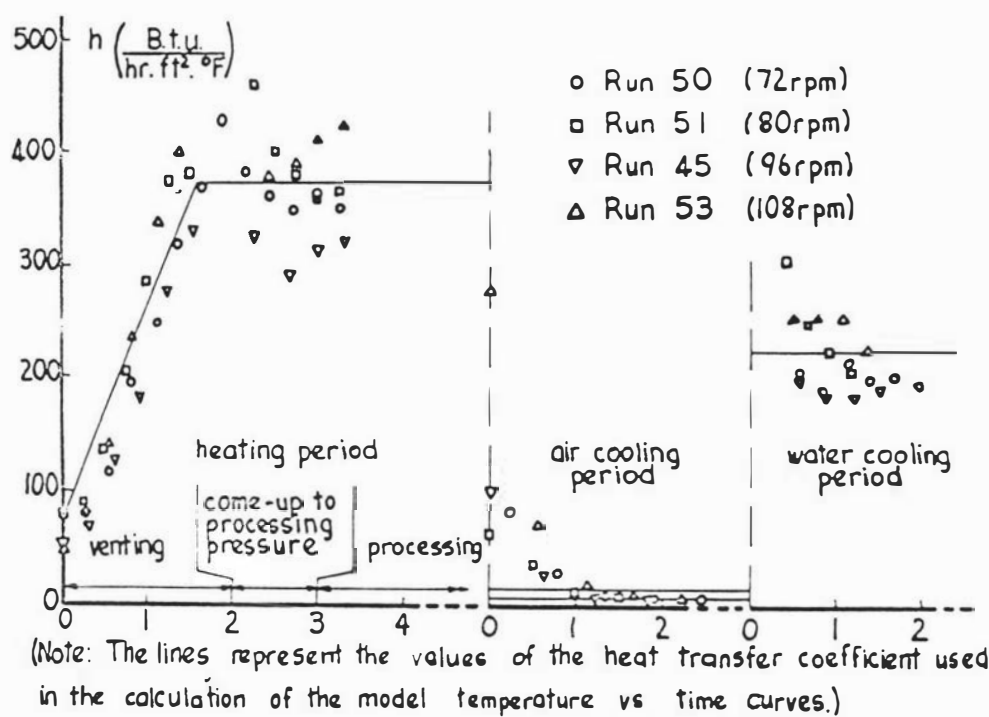


Fig.38 Overall heat transfer coefficients for four typical agitated cans.

The heat transfer coefficients for sucrose solution in the 301 x 409 cans are generally higher than those obtained for water in static cans. The maximum heat transfer coefficient for the heating of the agitated cans is about 370 B.t.u./hr.ft².°F; for unagitated cans it is about 200 B.t.u./hr.ft².°F. The heat transfer coefficients during the air phase of the cooling cycle are of the same order for the rotating and static cans, indicating that the outside film heat transfer coefficient may be the factor limiting heat transfer in this phase. During the water cooling period, the heat transfer coefficient for rotating cans is again higher than that for static cans (200-250 B.t.u./hr.ft².°F for agitated cans, and 100-120 B.t.u./hr.ft².°F for static cans).

(ii) Comparison of calculated and measured sucrose hydrolysis equivalent retort times.

Table 11 shows the equivalent retort times calculated from sucrose hydrolysis measurements and the sucrose hydrolysis equivalent retort times calculated from temperature data. Cans 1 and 3 are radially rotated cans, and cans 2 and 4 are tangentially rotated.

Table 11a : Measured and calculated sucrose hydrolysis equivalent retort times : 30 psig rotating can runs.

<u>Speed (rpm),</u> <u>can number</u>	<u>Process time = 2 min</u>		<u>Process time = 5 min</u>	
	<u>measured</u>	<u>calculated</u>	<u>measured</u>	<u>calculated</u>
<u>72</u>	1	5.06		
	2	5.20	8.47	8.30
	3	5.05	8.47	8.32
	4	5.11	8.39	8.22
		5.17	8.52	8.27
<u>80</u>	1	4.89		
	2	5.00	7.88	8.11
	3	5.03	8.10	8.23
	4	5.03	8.01	8.16
		4.95	8.12	8.09
<u>96</u>	1	4.98		
	2	5.23	8.12	8.34
	3	5.07	8.13	8.45
	4	5.09	8.29	8.13
		5.11	8.19	8.25
<u>108</u>	1	5.00		
	2	5.13	8.15	8.07
	3	5.00	8.36	8.24
	4	5.09	8.10	8.13
		5.18	8.36	8.22

Table 11b : Measured and calculated sucrose hydrolysis retort times :
15 psig rotating can runs

<u>Speed (rpm),</u>		<u>Process time = 2 min</u>		<u>Process time = 5 min</u>	
<u>can number</u>		<u>measured</u>	<u>calculated</u>	<u>measured</u>	<u>calculated</u>
<u>72</u>	1	5.06	5.07	7.66	7.80
	2	5.07	5.15	7.86	7.98
	3	5.02	5.11	7.71	7.91
	4	4.87	4.85	7.74	7.95
<u>80</u>	1	4.75	4.81	7.83	8.01
	2	4.99	4.96	7.95	7.97
	3	4.96	4.93	7.81	7.97
	4	4.91	4.82	7.90	7.98
<u>96</u>	1	4.96	5.05	7.99	8.22
	2	5.03	5.05	8.03	8.05
	3	5.07	5.15	7.96	7.90
	4	5.07	5.11	8.05	8.09
<u>108</u>	1	5.09	5.17	8.15	8.13
	2	5.27	5.29	8.27	8.21
	3	5.15	5.18	8.25	8.19
	4	5.23	5.22	8.27	8.20

Table 11c : Measured and calculated sucrose hydrolysis equivalent retort times : Miscellaneous rotating can runs

<u>Rm</u>	<u>Time</u>	<u>Pressure</u>	<u>Speed</u>	<u>Can</u>	<u>Equivalent retort time (min)</u>	
<u>number</u>	<u>(min)</u>	<u>(psig)</u>	<u>(rpm)</u>	<u>number</u>	<u>measured</u>	<u>calculated</u>
38	2 (long slow come-up)	30	80	1	6.15	6.17
				2	6.13	6.16
				3	5.85	5.98
				4	5.84	5.97
40	2 (long slow come-up)	30	80	1	6.90	6.75
				2	-	6.86
				3	6.79	6.78
				4	6.90	6.93
46	2	30	126	1	5.32	5.23
				2	5.45	5.37
				3	5.34	5.29
				4	5.39	5.32

The average difference between the calculated and measured equivalent retort times is only 0.38% with few differences greater than 2%. The standard deviation of the differences is 1.47%, whence Student's t with 74 degrees of freedom is 2.23. The difference between calculated and measured equivalent retort times is therefore significant at about the 3% probability level.

From the analysis of variance of the effect of different types of can, the component of variance arising from the polarimeter readings was found to be 0.0009 degrees², which corresponds to a standard deviation of 0.03°. Two polarimeter readings are required in the calculation of both the measured and calculated equivalent retort times, and the standard deviation or variance of the difference between the measured and calculated equivalent retort times arising from this cause can therefore be calculated for the two process times and two processing pressures. The mean differences between the calculated and measured equivalent retort times are not significant (Student's t -test) in terms of errors arising from the measurement of angle of polarization, and hence the assumption of the convection model in which the fluid is completely mixed can be considered valid in process calculations.

(iii) Bacterial equivalent retort times and equivalent time differences.

Tables 12a and 12b show the equivalent retort times calculated from temperature data and equivalent time differences for the rotating can runs.

An analysis of variance has been carried out to evaluate the magnitudes and significances of the effects of the various factors influencing the equivalent time differences. Table 13 shows the equivalent time differences used for this analysis. Where large corrections for "offset" (p 109) in temperature measurements have been made, the equivalent retort times have been replaced by a mean calculated from the equivalent time differences for the same speed, organism, time of processing and type of rotation. Because a preliminary analysis showed

Table 12a : Calculated equivalent retort times (t_{chem} and t_{bact}) and equivalent time differences (Δt) : Agitated can runs at 30 psig.

<u>Rm</u> <u>number</u> speed, time at T_R	Thermo- couple number	Sucrose Solution	<u>B. stearo- thermophilus</u>			<u>B. subtilis</u>	
		t_{chem} (min.)	t_{bact} (min.)	Δt (min.)	t_{bact} (min.)	Δt (min.)	
<u>28</u>	R	4.69	3.08	1.61	2.84	1.85	
72 rpm 2 min.	1	5.27	3.91	1.36	3.54	1.73	
	2a	4.87	3.59	1.28	3.26	1.61	
	2b**	5.01	3.94	1.07	3.82	1.19	
	3	5.06	3.73	1.33	3.41	1.65	
	4a,b	5.21	3.68	1.53	3.54	1.67	
<u>38*</u>	R	5.70	3.74	1.96	3.26	2.44	
80 rpm 2 min.	1	6.17	4.55	1.62	4.10	2.07	
	2	6.16	4.65	1.51	4.17	1.99	
	3	5.98	4.31	1.67	3.80	2.18	
	4	5.97	4.28	1.69	3.73	2.24	
<u>40*</u>	R	6.36	4.15	2.21	3.69	2.67	
80 rpm 2 min.	1	6.75	4.70	2.05	4.33	2.42	
	2	6.86	5.03	1.83	4.56	2.30	
	3	5.78	5.02	1.76	4.63	2.15	
	4	6.93	5.18	1.75	4.82	2.11	
<u>44</u>	R	4.57	3.08	1.49	2.81	1.76	
80 rpm 2 min.	1	4.91	3.51	1.40	3.20	1.71	
	2	4.97	3.97	1.00	3.72	1.25	
	3	5.04	3.91	1.13	3.67	1.37	
	4	4.95	3.97	0.98	3.66	1.29	
<u>45</u>	R	4.61	3.03	1.58	2.80	1.81	
96 rpm 2 min.	1	4.99	3.67	1.32	3.39	1.60	
	2	5.22	4.14	1.08	3.84	1.14	
	3	5.09	3.89	1.20	3.58	1.51	
	4	5.11	3.86	1.25	3.60	1.51	
<u>46</u>	R	4.65	3.06	1.59	2.81	1.84	
126 rpm 2 min.	1	5.23	3.95	1.28	3.59	1.64	
	2	5.37	4.18	1.19	3.98	1.39	
	3	5.29	4.08	1.21	3.78	1.58	
	4	5.32	4.12	1.20	3.94	1.38	

continued ...

* slow come-up

** extra point 2b not used in analysis of variance

Table 12a continued :

<u>Run number</u> speed, time at T_R	<u>Thermo- couple number</u>	<u>Sucrose Solution</u>	<u>B. stearo- thermophilus</u>		<u>B. subtilis</u>	
		θ_{chem} (min.)	θ_{baot} (min.)	$\Delta\theta$ (min.)	θ_{baot} (min.)	$\Delta\theta$ (min.)
<u>50</u>	R	7.80	6.23	1.57	5.93	1.87
	1	8.22	7.10	1.12	6.79	1.43
72 rpm	2	8.25	7.09	1.16	6.81	1.44
5 min.	3	8.33	7.24	1.09	6.93	1.40
	4	8.19	6.86	1.33	6.41	1.78
<u>51</u>	R	7.63	6.13	1.50	5.87	1.76
	1	8.11	7.00	1.11	6.71	1.40
80 rpm	2	8.23	7.26	0.97	6.95	1.28
5 min.	3	8.16	6.96	1.20	6.65	1.51
	4	8.09	6.87	1.22	6.49	1.60
<u>52</u>	R	7.81	6.18	1.63	5.89	1.92
	1	8.34	7.43	0.91	6.98	1.36
96 rpm	2	8.45	7.20	1.25	7.18	1.27
5 min.	3**	8.13	7.23	0.90	6.73	1.40
	4	8.25	7.41	0.84	7.25	1.00
<u>53</u>	R	4.69	3.13	1.56	2.84	1.85
	1	5.04	3.65	1.39	3.32	1.72
108 rpm	2	5.20	3.87	1.33	3.59	1.61
2 min.	3	5.09	3.72	1.37	3.56	1.53
	4	5.18	3.91	1.27	3.59	1.59
<u>54</u>	R	7.65	6.15	1.50	5.85	1.80
	1	8.07	6.67	1.40	6.28	1.79
108 rpm	2	8.24	7.07	1.17	6.73	1.51
5 min.	3	8.13	6.82	1.30	6.41	1.72
	4	8.22	7.01	1.21	6.71	1.51
<u>55</u>	R	7.84	6.16	1.68	5.87	1.97
	1	8.30	7.05	1.25	6.73	1.57
72 rpm	2	8.32	6.97	1.35	6.77	1.55
5 min.	3	8.22	6.91	1.31	6.56	1.56
	4	8.27	6.95	1.32	6.66	1.61

** Equivalent retort times corrected for offset (see pp 88 and 109)

Table 12b : Calculated equivalent retort times (Θ_{chem} and Θ_{bact}) and equivalent time differences ($\Delta\Theta$) : Agitated can runs at 15 psig.

<u>Rm</u> <u>number</u>	Thermo- couple number	Sucrose Solution	<u>B. stearo-</u> <u>thermophilus</u>		<u>B. subtilis</u>	
		Θ_{chem} (min.)	Θ_{bact} (min.)	$\Delta\Theta$ (min.)	Θ_{bact} (min.)	$\Delta\Theta$ (min.)
<u>57</u> 72 rpm 2 min.	R	4.64	3.09	1.55	2.80	1.84
	1	5.07	3.85	1.22	3.51	1.56
	2	5.15	3.91	1.24	3.55	1.60
	3	5.11	3.72	1.39	3.46	1.65
	4**	4.93	3.39	1.54	2.96	1.97
<u>58</u> 72 rpm 5 min.	R	7.62	6.15	1.47	5.83	1.79
	1	7.80	6.42	1.38	6.12	1.68
	2**	8.08	7.07	1.01	7.23	0.85
	3	7.91	6.82	1.09	6.53	1.38
	4	7.95	6.97	0.98	6.53	1.42
<u>59</u> 80 rpm 2 min.	R	4.57	3.03	1.51	2.75	1.82
	1	4.81	3.36	1.45	3.01	1.80
	2	4.96	3.68	1.28	3.38	1.58
	3	4.93	3.77	1.16	3.42	1.51
	4**	4.82	3.48	1.34	3.06	1.76
<u>61</u> 80 rpm 5 min.	R	7.18	5.71	1.47	5.54	1.64
	1	7.91	6.42	1.49	5.95	1.96
	2	7.96	6.44	1.52	5.88	2.08
	3	7.85	6.46	1.39	5.77	2.08
	4	7.98	6.51	1.47	6.10	1.88
<u>62</u> 96 rpm 2 min.	R	4.67	3.09	1.58	2.80	1.87
	1	4.98	3.65	1.33	3.05	1.93
	2	5.09	3.85	1.24	3.46	1.53
	3**	4.64	3.18	1.46	2.89	1.75
	4	4.75	3.33	1.42	2.92	1.83
<u>63</u> 96 rpm 5 min.	R	7.74	6.13	1.61	5.84	1.90
	1	8.08	6.69	1.39	6.24	1.84
	2**	7.96	6.60	1.36	6.00	1.96
	3	8.16	7.08	1.08	6.61	1.65
	4	8.04	6.57	1.47	6.23	1.81

continued ...

** Equivalent retort times corrected for offset (see pp 88 and 109)

Table 12b continued :

<u>Rm</u> <u>number</u> <u>speed,</u> <u>time</u> <u>at T_R</u>	Thermo- couple number	Sucrose Solution	<u>B. stearo-</u> <u>thermophilus</u>			<u>B. subtilis</u>	
		Θ_{chem} (min.)	Θ_{bact} (min.)	$\Delta\Theta$ (min.)	Θ_{bact} (min.)	$\Delta\Theta$ (min.)	
<u>64</u> 108 rpm 2 min.	R	4.67	3.19	1.48	2.87	1.80	
	1	5.17	3.90	1.27	3.53	1.64	
	2	5.29	4.11	1.18	3.82	1.47	
	3	5.18	3.87	1.31	3.56	1.62	
	4	5.22	3.97	1.25	3.72	1.50	
<u>65</u> 108 rpm 5 min.	R	7.78	6.27	1.51	5.92	1.86	
	1	8.13	6.85	1.28	6.58	1.55	
	2	8.21	7.04	1.17	6.76	1.45	
	3	8.19	6.98	1.27	6.62	1.57	
	4	8.20	7.20	1.00	6.71	1.49	
<u>69</u> 80 rpm 5 min.	R	7.78	6.23	1.55	5.92	1.86	
	1	8.01	6.96	1.05	6.62	1.39	
	2	7.97	6.81	1.16	6.26	1.71	
	3**	7.97	7.10	0.87	6.80	1.17	
	4	7.98	6.83	1.15	6.37	1.61	
<u>70</u> 96 rpm 2 min.	R	4.74	3.17	1.57	2.87	1.87	
	1	5.05	3.95	1.10	3.57	1.48	
	2	5.05	3.86	1.19	3.49	1.56	
	3	5.15	4.09	1.06	3.78	1.37	
	4	5.11	3.97	1.14	3.59	1.52	
<u>71</u> 96 rpm 5 min.	R	7.73	6.23	1.50	5.89	1.84	
	1	8.22	7.00	1.22	6.73	1.49	
	2	8.05	7.00	1.05	6.57	1.48	
	3	7.90	6.69	1.21	6.49	1.41	
	4	8.09	6.96	1.13	6.61	1.48	

** Equivalent retort times corrected for offset (see pp 88 and 109)

Note : Equivalent retort times have been calculated from the time-temperature data from the retort thermocouple (thermocouple R); thermocouples 1 and 3 are in radially rotated cans, and thermocouples 2 and 4 are in tangentially rotated cans.

that the main effect of pressure was insignificant, the mean equivalent time differences used to replace doubtful values have been calculated over both pressures. These are marked with an asterisk (*) in table 13.

Table 13 : Analysis of Variance : Equivalent Time Differences for Agitated Can Rms.

Cause	Symbol	Condition
Pressures	P ₁ , P ₂	(15 psig, 30 psig)
Organisms	B ₁ , B ₂	(<u>B.stearothermophilus</u> , <u>B.subtilis</u>)
Processing times	T ₁ , T ₂	(2min, 5min at retort temperature)
Types of rotation	R ₁ , R ₂	(radial,tangential rotation)
Speeds of rotation	S ₁ , S ₂ , S ₃ , S ₄	(72, 80, 96 and 108 rpm)

~ Equivalent time differences in hundredths of a minute.

		S ₁		S ₂		S ₃		S ₄		
		B ₁	B ₂	B ₁	B ₂	B ₁	B ₂	B ₁	B ₂	
P ₁	T ₁	R ₁	122	156	145	180	110	148	127	164
			139	165	116	151	106	137	131	162
		R ₂	124	160	128	158	119	156	118	147
			135*	163*	109*	137*	114	152	125	150
	T ₂	R ₁	138	168	105	139	122	149	128	155
			109	138	112*	143*	121	141	127	157
		R ₂	122*	153*	116	171	105	148	117	145
			98	142	115	161	113	148	100	149
P ₂	T ₁	R ₁	136	173	140	171	132	160	139	172
			133	165	113	137	120	151	137	153
		R ₂	128	161	100	125	108	114	133	161
			153	167	98	129	125	151	127	159
	T ₂	R ₁	125	157	111	140	91	136	140	172
			131	156	120	151	90	140	131	179
		R ₂	135	155	97	128	101*	132*	117	151
			132	161	122	160	84	100	121	151

* doubtful values replaced by means.

The sums of squares, degrees of freedom and mean squares arising from the various significant causes are shown in table 14. The significance level of each cause is also shown.

Table 14 : Analysis of variance : Summary of significant effects.

Cause	Sum of squares	Degrees of freedom	Mean Square	Significance level p(%)
B	32036.1	1	32036.1	$p \ll 0.1$
S	6927.6	3	2309.2	$p < 0.1$
R	1437.8	1	1437.8	$p < 0.1$
T	1603.2	1	1603.2	$p < 0.1$
P x S	2585.0	3	861.7	$p < 0.1$
PxSxT	1373.2	3	457.7	$0.1 < p < 1$
SxRxT	1652.4	3	550.8	$p < 0.1$
Residual	11390.8	112	101.7	
TOTAL	59006.1	127	464.6	

1. Effect of type of organism (B).

As expected this effect is by far the most significant. The greater slope of the rate of destruction vs reciprocal temperature curve of B. subtilis gives greater equivalent time differences for all combinations of speed (S), type of rotation (R), length of process (T) and process pressure (P). The mean equivalent time difference for B. stearothermophilus for all runs is 1.20 min. and for B. subtilis it is 1.52 min.

The type of organism does not occur in any significant interaction. The effect of type of organism is, therefore, the same for all combinations of pressure (P), speed (S), type of rotation (R) and time of processing (T). This was as expected, as the equivalent retort times for sucrose hydrolysis and the two organisms are all calculated from the same time-temperature data.

Static can data indicate that the equivalent time difference for one type of organism can be calculated from that of another type if the activation energies of both spore destruction reactions are known.

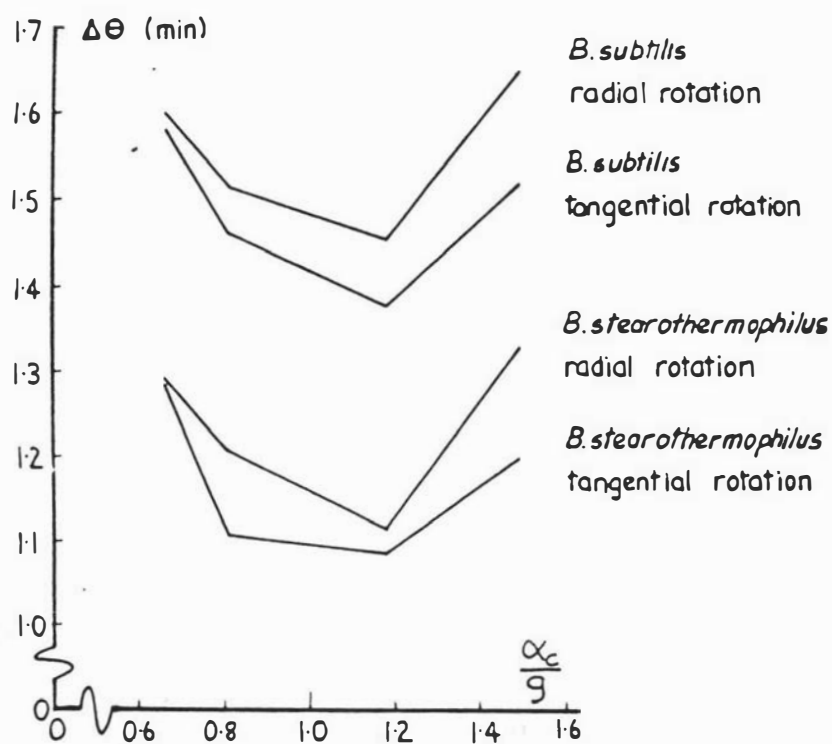


Fig.39 Effect of speed of rotation (plotted as relative acceleration at the can centre) on equivalent time difference.

The linear relationship of figure 34 gives the equation -

$$\frac{\Delta\theta_2'}{\Delta\theta_1'} = \frac{\log (E_{A \text{ bact}(2)} / E_{A \text{ chem}})}{\log (E_{A \text{ bact}(1)} / E_{A \text{ chem}})} \quad \dots \dots \dots (1)$$

where $\Delta\theta_2'$ represents the equivalent time difference for B. subtilis as calculated from the B. stearothermophilus equivalent time difference ($\Delta\theta_1'$).

Equivalent time differences for B. subtilis have been calculated from B. stearothermophilus data for 59 agitated cans (i.e. all data of table 13 except those marked with an asterisk).

The mean of the differences ($\Delta\theta_2' - \Delta\theta_1'$) is 0.0105 minutes, and the estimate of the standard deviation of the differences is 0.108 minutes. The probability of a mean greater than 0.0105 minutes arising from random sampling of an infinite population of zero mean and standard deviation of 0.108 minutes, is about 46% (Student's t with 58 degrees of freedom is 0.742). The mean difference is therefore not significantly different from zero. Hence equation (1) can be used to calculate equivalent time differences for one organism from equivalent time differences of another.

2. Effect of speed of rotation (S).

The effect of speed is the next most highly significant after the effect of type of organism. The exact effect of speed is not clear, as this effect occurs in all the significant interactions, i.e. the effect of speed is significantly dependent on the processing pressure (P x S interaction), and also on the combinations of pressure and processing time (P x S x T interaction) and on the combinations of type of rotation and time of processing (S x R x T interaction).

In general, however, the speeds of 80 and 96 rpm give lower equivalent time differences than do the extreme speeds. For example if the mean equivalent time differences for the four combinations of spore type (B) and type of rotation (R), are plotted against speed (S), each set of mean equivalent time differences shows a minimum (figure 39).

The equivalent retort time can be considered as a measure of the degree of "squareness" of a process. For a "square" process in which negligible time is taken to heat the material to maximum temperature and to cool it to some sub-lethal temperature, the equivalent time difference is zero. Hence the lower an equivalent retort time is, the nearer the process is to square. If the retort process itself is square, then the equivalent time difference is a measure of the rapidity of heating and cooling and hence of the heat transfer rate.

If the retort process is not square then a low equivalent time difference may not necessarily indicate a high heat transfer rate. The relative importance of the various phases of the process and the heat transfer rates in each phase are discussed on pages 167-171.

In this study, the processes used are by no means square, with the most important deviations from "squareness" occurring in the early part of the cooling. It is shown, however, in the section on the effect of can size and type of process (p 169), that the processes used here are such that an increase in heat transfer rate gives a decrease in the equivalent time difference. The work of Cliffoorn et al (1950) and Conley et al (1951) who observed maximum rates of heating at speeds which give an acceleration at the can centre equal to the acceleration due to gravity is therefore confirmed by the data obtained in this investigation.

3. Effect of type of rotation (R).

This effect is not as significant as the effect of speed, although still significant at the 0.1% probability level. As with speed, the effect of type of rotation was not apparent from examination of the raw data.

The data obtained indicate that in the speed range studied, the time-temperature curves obtained in tangentially rotated cans (R_2) are more nearly square than the radially rotated cans (R_1) (figure 39). Inspection of figure 39 indicates that the difference between types of rotation tends to increase slightly as the speed is increased.

It is doubtful whether this trend is real as the $R \times S$ interaction is only significant at about the 15% probability level. The mean equivalent time difference for radially rotated cans is 1.39 min. and that for tangentially rotated cans is 1.32 min.

4. Effect of length of process (T).

The highly significant effect of length of process on equivalent time difference was unexpected, as theoretical considerations indicate that the equivalent time difference should be independent of process length for all processes in which the temperature of the material in the can approaches retort temperature closely. For example, consider a process such that cooling begins $\Delta\theta$ minutes after the can temperature reaches that of the retort. Both the bacterial and chemical equivalent retort times are $\Delta\theta$ minutes greater than those for a process in which the cooling phase is begun as soon as the can temperature reaches that of the retort. The equivalent time differences of the two processes will be the same, provided that the processes are identical in all respects except the length of time the can is held at retort temperature. Data from the static can runs indicate that the equivalent time difference is independent of the length of process even for some processes in which cooling is begun before the can temperature reaches that of the retort.

The data obtained in these experiments give mean equivalent time differences of 1.39 min. for the short processes (2 min.) and 1.32 min. for the long processes. The probability of a difference between the mean equivalent time differences of 0.07 min. arising from experiments in which processing time has no effect is less than 0.1%.

The most likely source of this difference between long and short runs is variation in the can temperature vs time curves. For example, slow cooling in the air cooling phase will tend to give a lower equivalent time difference. A comparison of lethal rate curves for long and short processes indicated that the longer processes had a larger

proportion of relatively slow cooling curves than did the shorter processes. These relatively slower cooling curves frequently corresponded to lower than average equivalent time differences.

The reason for the higher proportion of slower cooling cans in the longer runs is not known. It may be associated with changes in the viscosity of the sucrose solution as the hydrolysis reaction proceeds. This could result in different heat transfer rates during the cooling phase for the two different process times. Slight leakage of the can fittings has been observed during some runs. Any loss of fluid will alter the volume of the headspace. Different lengths of process could have different effects on the amount of leakage, and hence on the heat transfer rate in the cooling period.

Differences between the come-up rates and between the cooling rates of the retort of different runs cannot be discounted as a source of variation in the can temperature vs time curves. This source of variation is probably not of great importance in these experiments, as the length of process is not likely to affect the retort come-up rates or the retort cooling rates.

Small non-random errors may occur in the measurement and calculation of the equivalent retort times. For example, the mean rates of sucrose hydrolysis and spore destruction at retort temperature (on which all equivalent retort times are based) are calculated from temperature curves which often fluctuate over several tenths of a degree during the process. An error of 0.1°F in the estimate of mean retort temperature (which could easily arise from small systematic thermocouple errors) leads to an error in the equivalent time difference of 0.06 to 0.08 min. for typical 5 minute processes, and an error of 0.01 to 0.02 min. in the equivalent time difference for 2 min. processes. Hence it is seen that if the measurement or calculation of mean retort temperature gives an estimate which is consistently too high or too low, then a significant difference between the equivalent time differences for long and short processes would occur.

A highly significant effect of length of process can, therefore,

indicate either that the heating and cooling curves are not completely independent of length of process, or that significant systematic errors are present in either the measurement of temperatures or the calculation of equivalent retort times.

Because the proposed $\theta_{chem} : \theta_{bact}$ correlation

viz: $\theta_{bact} = \theta_{chem} - \Delta\theta$, is such that $\Delta\theta$ is independent of length of the process, it can be argued that any variation due to different process times should be included with the residual variation due to all other random or undetermined errors. If this is done, both significant three-factor interactions are eliminated from the analysis of variance, and the significant levels of the three main effects (type of spore (B), speed of rotation (S), and type of rotation (R)) are not significantly changed by the increase in the estimate of residual variance from 0.00997 min^2 to 0.001131 min^2 . The two-factor interaction (process pressure (P) x speed of rotation (S)) also remains significant at the 0.1% probability level. This would then imply that the effect of speed on equivalent time difference depends only on the processing pressure, and that the effect of the factors type of spore (B) and type of rotation (R) are not dependent in any way on any other factor or combination of factors.

Equivalent Time Difference Analysis

Theoretical considerations, and experiments on both static and agitated cans have indicated that the correlation for estimation of spore destruction from measurements of chemical reaction is of the form -

$$\theta_{bact} = \theta_{chem} - \Delta\theta$$

The equivalent time difference $\Delta\theta$ has been shown to be a function of various processing parameters such as speed and type of agitation (if any), type of organism, characteristics of the chemical reaction, etc.

The equivalent time difference concept has been examined in some detail, and the relative contributions made by the different phases of the process to the equivalent time difference are discussed. A range of processes has been used as a basis for this discussion, with temperature-time curves calculated for three different sizes of can. Heat transfer data based on the temperature-time curves obtained in the agitated can experiments has been used for the calculation of model temperature-time curves. The discussion can also be applied to static cans, with some slight modification to take account of the different type of convection.

(a) The specific rate difference function.

Because the activation energies of chemical reactions are lower than spore destruction activation energies, the specific chemical reaction rate $\frac{H}{H_R}$ is greater than the specific spore destruction rate $\frac{L}{L_R}$ at all temperatures below retort temperature T_R . The chemical reaction and spore destruction rates are H and L respectively, and subscript R refers to the rate of chemical reaction or spore destruction at retort temperature.

The equivalent retort times θ_{chem} and θ_{bact} are given by -

$$\theta_{chem} = \int_{\theta_0}^{\theta_1} \frac{H}{H_R} d\theta$$

and -

$$\theta_{bact} = \int_{\theta_0}^{\theta_1} \frac{L}{L_R} d\theta$$

Hence -

$$\Delta\theta = \theta_{chem} - \theta_{bact}$$

$$= \int_{\theta_0}^{\theta_1} \left(\frac{H}{H_R} - \frac{L}{L_R} \right) d\theta$$

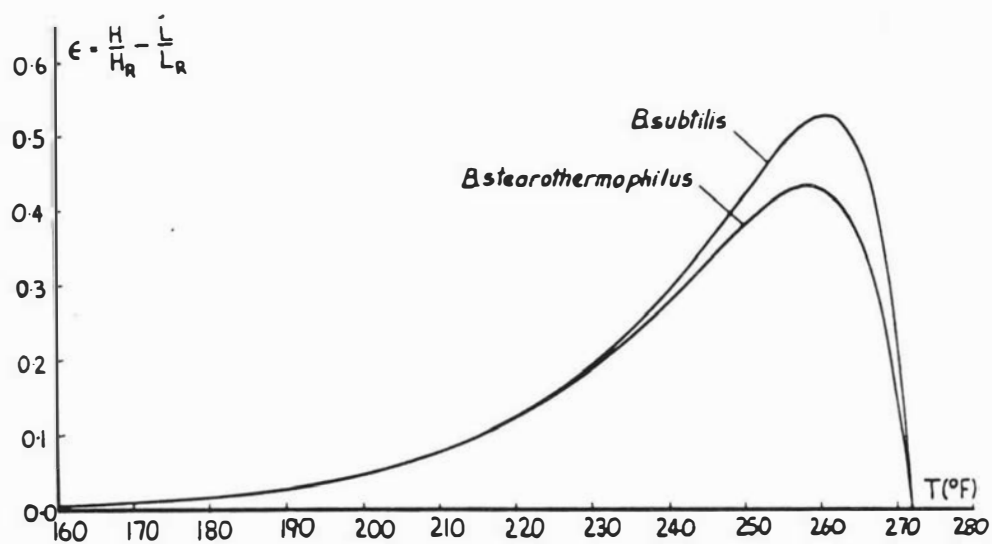


Fig 40 Specific rate difference vs temperature for *B. subtilis* and *B. stearothermophilus*.

The integrand $\left(\frac{H}{H_R} - \frac{L}{L_R} \right)$ is termed the specific rate difference function.

The equivalent time difference can now be defined as the integral (with respect to time θ) of the specific rate difference.

The specific rate differences for B. stearothermophilus and B. subtilis relative to sucrose hydrolysis are plotted against temperature in figure 40. The retort temperature is 272°F.

The curves of figure 40 show clearly that temperatures within about 30°F of retort temperature are likely to make a much greater contribution to the equivalent time differences than temperatures below this range. The slopes of the specific rate difference vs temperature curves in the range 265-272°F are higher than the slopes at lower temperatures. Hence small changes in temperature in the range immediately below retort temperature will have a larger effect on the equivalent time differences than small changes of temperature below 265°F.

The temperatures in the air cooling phase of the agitated can runs are in the range 265-272°F. Hence if the cooling in this phase is slower than usual (see p:150) a lower equivalent retort time than usual will be obtained.

The derivation and application of the specific rate difference function are shown graphically in figure 41. A typical process is shown in figure 41a, and the specific rate vs time curves for chemical reaction and spore destruction are shown in figure 41b.

The specific rate difference curves are plotted in figure 41c. The area underneath each section of the curve is the same as those between the heating and cooling sections of the specific rate curves (figure 41b). The effect of any variation of temperature can be visualized much more readily on the specific rate difference vs time graph (figure 41c) than it can on the specific rate vs time graph (figure 41b).

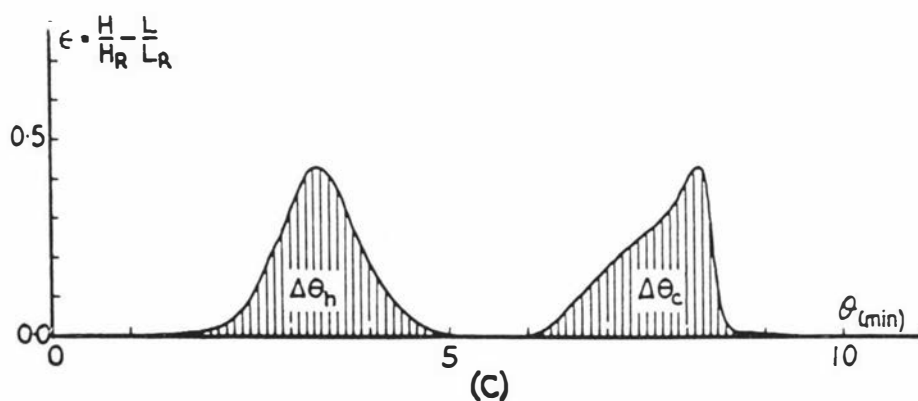
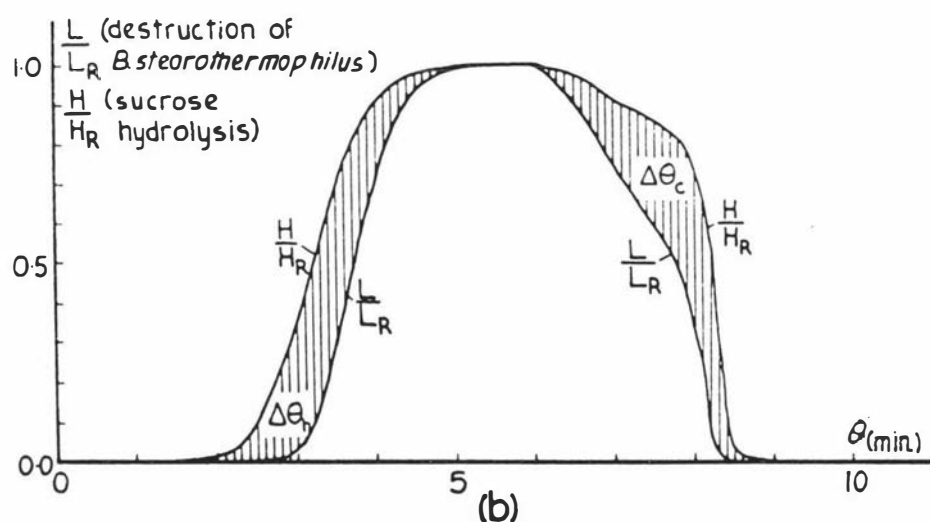
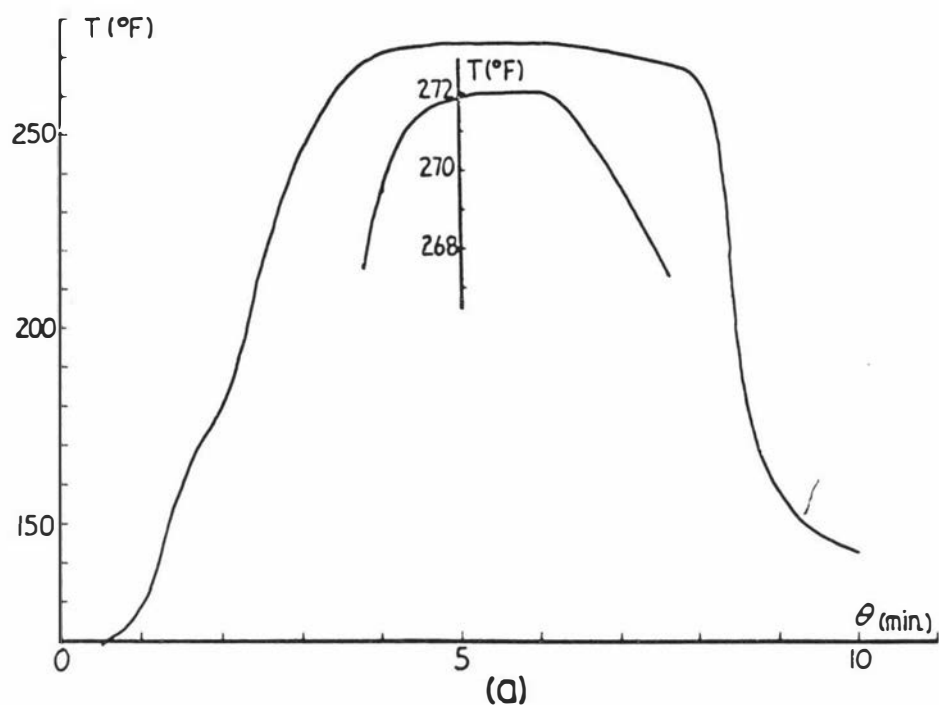


Fig.41 Derivation of the specific rate difference function; (a) a typical temperature vs time curve; (b) specific chemical reaction rate and specific spore destruction rate vs time curves; (c) specific rate difference vs time curves.

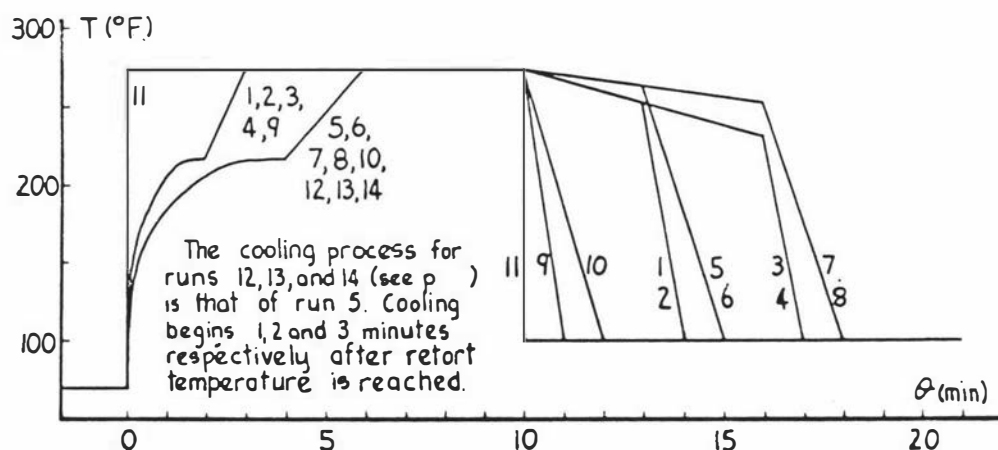


Fig. 42 Processes used for calculation of the model temperature vs time curves.

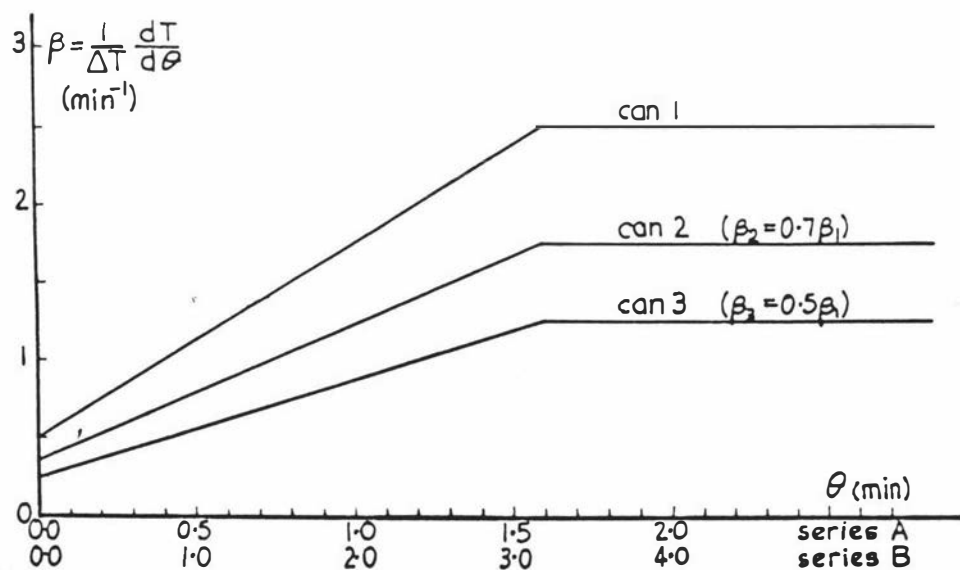


Fig. 43 Rate of change of can temperature per unit temperature difference for the heating period.

(b) Calculation of the model can temperature vs time curves.

(i) The model processes.

The processes used for calculation of the can temperature vs time curves are shown in figure 42.

The retort temperature is 272°F.

Two series of processes are used. The rate of change of retort temperature in series A (runs 1,2,3, 4 and 9) is twice that of series B (runs 5,6,7,8 and 10). Series A is based on the heating and cooling curves obtained in the experimental retort used in this study. Series B is used to study the effect of slower heating and cooling rates, which would be obtained in larger retorts with greater thermal inertia than the small experimental retort.

All phases of the process are linear except the initial venting phase. The venting phase of series A is based on one of the agitated can runs (number 51). In series B this phase is spread over four minutes instead of two minutes.

Because the air cooling phase can make a large contribution to the equivalent time difference, three durations of air cooling are used.

The temperature of the cooling water is taken as 100°F, which is approximately the final temperature of the first fill of cooling water in the experimental retort used in the present work.

(ii) Rates of heat transfer to the model cans.

Rates of change of can temperature per unit temperature difference ($\frac{1}{\Delta T} \frac{dT}{d\theta} = \frac{h \cdot A}{m c_p} = \beta$) are shown in figure 43 for the heating phase of the process. The values of β for a 301 x 409 can (i.e. β_1) approximate those obtained in the agitated can runs. Two values of β_1 are used in the air cooling phase, as differences between identical cans were often observed in the agitated can runs. The values of β_1 are 0.10 min⁻¹ (runs 1, 3, 5 and 7) and 0.05 min⁻¹ (runs 2, 4, 6 and 8). The value of β_1 in the water cooling phase is 1.50 min⁻¹.

Two larger sizes of can are considered such that $\beta_2 = 0.70 \beta_1$ and $\beta_3 = 0.50 \beta_1$. If it is assumed that the overall heat transfer coefficient h is independent of can size (Schultz and Olson, 1938), then the values of β_2 and β_3 would apply to 406 x 607 cans and 601 x 814 cans respectively, or to cans of the same surface to volume ratio.

(iii) Method of calculation of the temperature vs time curves for the model cans.

The method is essentially the reverse of that used to calculate values of β from the temperature vs time data of runs 50, 51, 45 and 53 (p. 135).

The rate of change of can temperature per unit temperature difference (β) is defined by -

$$\beta = \frac{1}{\Delta T} \frac{dT}{d\theta} = \frac{T_{n+1} - T_n}{\Delta\theta \cdot \Delta T_n}$$

where $\Delta T_n = \frac{1}{2} (T_{Rn} - T_n) + (T_{Rn+1} - T_{n+1})$

This leads to -

$$T_{n+1} - T_n = \frac{\beta \Delta\theta (T_{Rn} + T_{Rn+1} - 2 T_n)}{2 + \beta \Delta\theta}$$

$$= \gamma (T_{Rn} + T_{Rn+1} - 2 T_n)$$

where $\gamma = \frac{\beta \Delta\theta}{2 + \beta \Delta\theta}$

These formulae have been used to calculate the model can temperature vs time curves. The time interval ($\Delta\theta$) was 0.2 minutes, and temperatures were calculated to 0.01°F to avoid accumulation of rounding off errors.

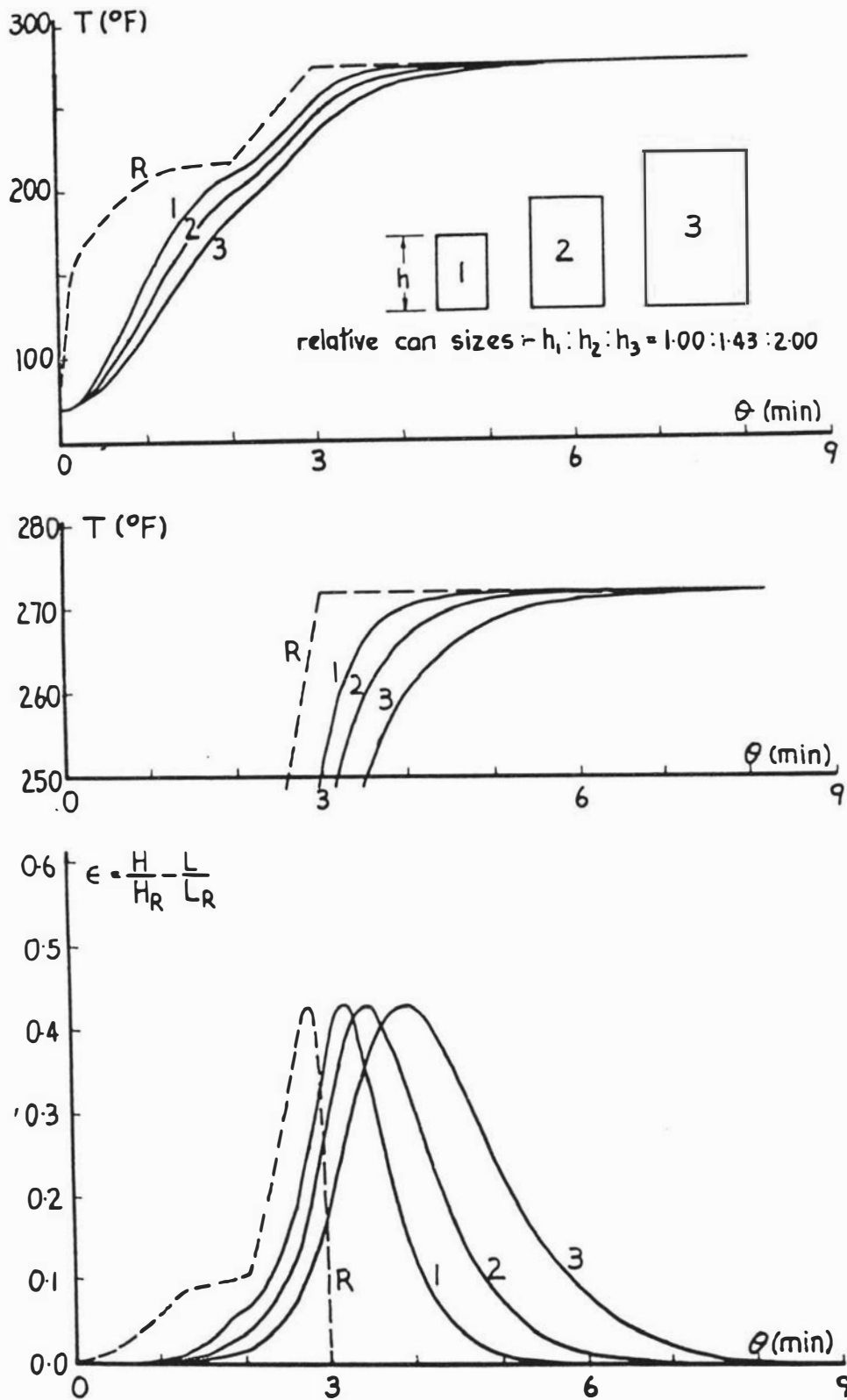


Fig. 44 Typical temperature vs time and specific rate difference vs time curves for heating.

(o) Equivalent time differences for the model cans.

The equivalent time differences calculated from the model temperature vs time curves by graphical integration of the specific rate difference vs time functions are shown for the two organisms B.stearothermophilus and B.subtilis in table 15.

Typical temperature vs time curves and specific rate difference vs time curves (from which the equivalent time differences are calculated) are shown in figure 44 (heating) and figure 45 (cooling). Specific rate difference vs time curves for one organism only (B.stearothermophilus) are shown, as the B.subtilis and B.stearothermophilus specific rate difference curves are very similar in general form. The B.subtilis curves have higher maxima than the B.stearothermophilus curves. In the heating period the B.subtilis maxima occur later than the B.stearothermophilus maxima, and vice versa in the cooling period.

Retort temperature vs time curves are also shown in figures 44 and 45 (broken lines), along with specific rate difference vs time curves calculated from these temperature vs time curves. The specific rate difference vs time curves based on retort temperature are quite different in form from the specific rate difference curves for the cans, especially during the air cooling phase where the heat transfer coefficients are low and can temperatures are such that specific rate differences are very sensitive to changes of temperature. Because the specific rate difference curves based on can and retort temperatures are not at all similar in form, it is not possible to use equivalent time differences based on retort temperature vs time curves to predict equivalent time differences for cans.

(i) Effect of type of organism on equivalent time difference.

The B.subtilis equivalent time differences are always greater than the B.stearothermophilus equivalent time differences. That this must be so can be deduced from figure 40 in which the specific rate differences are plotted against temperature. The specific rate difference for B.stearothermophilus is less than that for B.subtilis for all temperatures

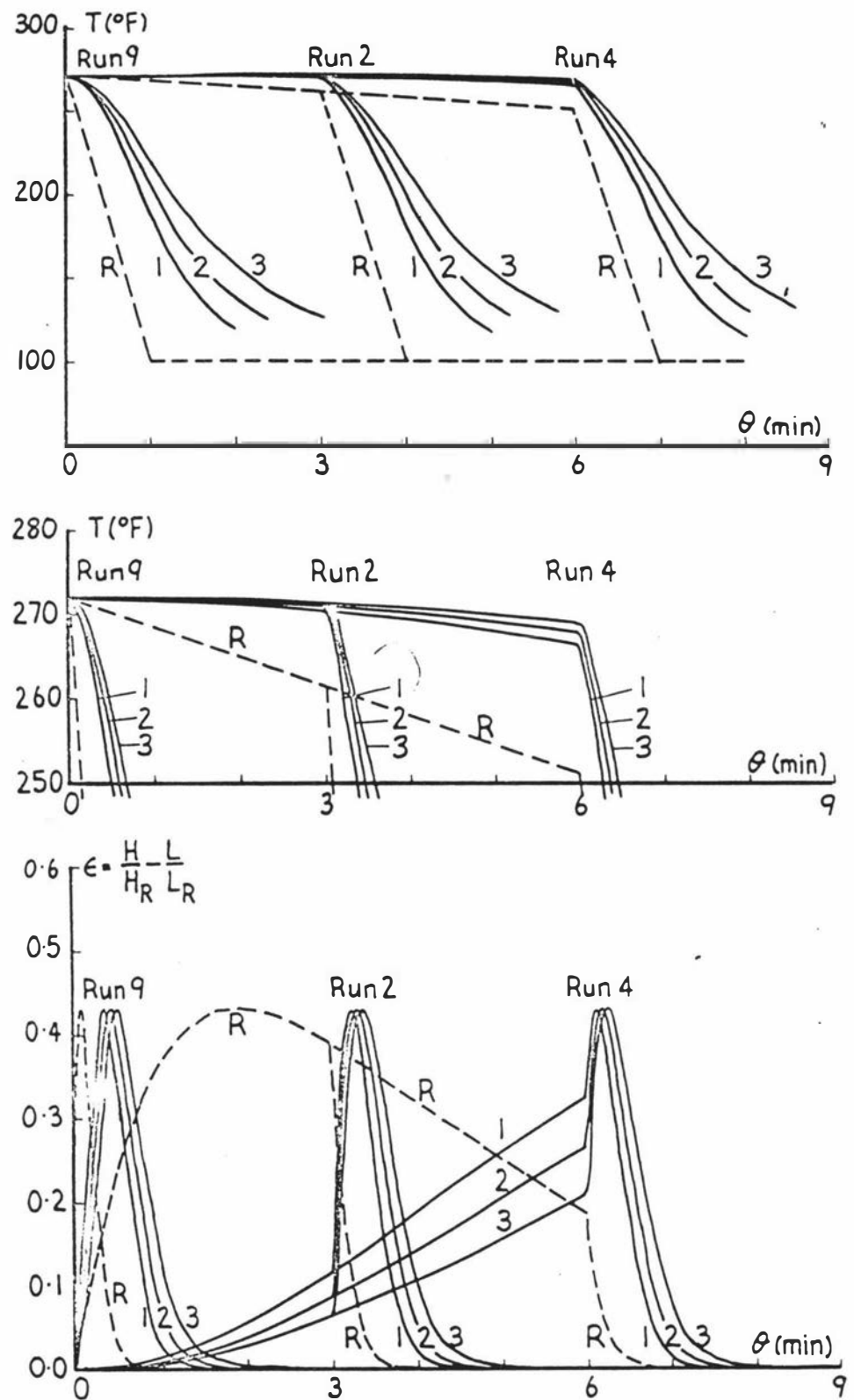


Fig.45 Typical temperature vs time and specific rate difference vs time curves for cooling.

Table 15 : Effect of Can Size and Type of Process on Bacterial Equivalent Time Differences.

		Equivalent Time Differences (min.)					
Rm No.	Can No.	<u>B. stearothermophilus</u>			<u>B. subtilis</u>		
		heating	cooling	total	heating	cooling	total
<u>1</u>	R	0.382	1.110	1.492	0.414	1.353	1.767
	1	0.572	0.461	1.033	0.699	0.606	1.305
	2	0.734	0.439	1.173	0.911	0.569	1.480
	3	0.978	0.431	1.409	1.224	0.557	1.781
<u>2</u>	R	0.382	1.110	1.492	0.414	1.353	1.767
	1	0.572	0.349	0.921	0.699	0.451	1.150
	2	0.734	0.347	1.081	0.911	0.447	1.358
	3	0.978	0.367	1.345	1.224	0.459	1.683
<u>3</u>	R	0.382	1.924	2.306	0.414	2.214	2.628
	1	0.572	1.414	1.986	0.699	1.869	2.568
	2	0.734	1.245	1.979	0.911	1.662	2.573
	3	0.978	1.098	2.076	1.224	1.476	2.700
<u>4</u>	R	0.382	1.924	2.306	0.414	2.214	2.628
	1	0.572	1.002	1.574	0.699	1.359	2.058
	2	0.734	0.856	1.590	0.911	1.167	2.078
	3	0.978	0.761	1.739	1.224	1.033	2.257
<u>5</u>	R	0.774	1.015	1.789	0.840	1.297	2.137
	1	0.878	0.463	1.341	1.014	0.585	1.599
	2	0.987	0.477	1.464	1.165	0.591	1.756
	3	1.154	0.511	1.665	1.391	0.622	2.013
<u>6</u>	R	0.774	1.015	1.789	0.840	1.297	2.137
	1	0.878	0.403	1.281	1.014	0.485	1.499
	2	0.987	0.429	1.416	1.165	0.511	1.676
	3	1.154	0.474	1.628	1.391	0.558	1.949
<u>7</u>	R	0.774	2.220	2.994	0.840	2.715	3.555
	1	0.878	1.101	1.979	1.014	1.470	2.484
	2	0.987	0.978	1.965	1.165	1.284	2.449
	3	1.154	0.909	2.063	1.391	1.185	2.576
<u>8</u>	R	0.774	2.220	2.994	0.840	2.715	3.555
	1	0.878	0.779	1.657	1.014	1.035	2.049
	2	0.987	0.718	1.705	1.165	0.931	2.096
	3	1.154	0.689	1.843	1.391	0.885	2.376
<u>9</u>	R	0.382	0.101	0.483	0.414	0.113	0.527
	1	0.572	0.221	0.793	0.699	0.249	0.948
	2	0.734	0.255	0.989	0.911	0.291	1.202
	3	0.978	0.297	1.275	1.224	0.345	1.569
<u>10</u>	R	0.774	0.202	0.976	0.840	0.224	1.064
	1	0.878	0.359	1.237	1.014	0.391	1.405
	2	0.987	0.385	1.372	1.165	0.442	1.607
	3	1.154	0.434	1.588	1.391	0.503	1.894
<u>11</u>	R	0.000	0.000	0.000	0.000	0.000	0.000
	1	0.469	0.082	0.551	0.592	0.090	0.682
	2	0.678	0.117	0.795	0.853	0.129	0.982
	3	0.936	0.164	1.100	1.202	0.180	1.382

continued

Table 15 : continued

Run No. Can No.	Equivalent Time Differences (min.)					
	<u>B.stearothermophilus</u>			<u>B.subtilis</u>		
	<u>heating</u>	<u>cooling</u>	<u>total</u>	<u>heating</u>	<u>cooling</u>	<u>total</u>
<u>12</u> 3	0.825	1.488	2.313	0.931	1.911	2.842
<u>13</u> 3	1.050	0.865	1.915	1.245	1.121	2.366
<u>14</u> 3	1.122	0.625	1.747	1.354	0.785	2.139

less than retort temperature, and hence the equivalent time difference for B.subtilis must be greater than that of B.stearothermophilus. If the control of the process was such that the temperature of the retort was allowed to rise above the nominal retort temperature for an appreciable length of time, the B.subtilis equivalent time difference could be less than the B.stearothermophilus equivalent time difference if these were based on the nominal retort temperature, instead of the actual maximum temperature. This is because the B.subtilis specific rate difference is less than the B.stearothermophilus specific rate difference at temperatures greater than retort temperature.

The use of equation (1), (p 147) in the calculation of B.subtilis equivalent time differences (i.e. $\Delta\theta'_2$) from B.stearothermophilus equivalent time differences (i.e. $\Delta\theta_1$), gives values of $\Delta\theta'_2$ which tend to be greater than the actual B.subtilis equivalent time difference $\Delta\theta_2$. An analysis similar to that described on page 147 gives a mean difference (i.e. $\Delta\theta'_2 - \Delta\theta_2$) of 0.0332 minutes, and an estimate of the standard deviation of 0.0646 minutes. This difference is significant at the 1% probability level (Students' $t = 2.91$ with 32 degrees of freedom). It therefore appears that equation (1) is not satisfactory for calculation of equivalent time differences for one organism from the equivalent time differences of another.

The estimates of B.subtilis equivalent time differences tend to be greater than the actual B.subtilis equivalent time differences.

The estimated equivalent retort time for B.subtilis is therefore less than the actual equivalent retort time, and processes calculated on basis of the estimated equivalent time difference ($\Delta\theta_2'$) will be safe, i.e. the actual reduction in spore numbers will be greater than that indicated by the estimated equivalent retort time. If B.stearothermophilus equivalent time differences are estimated from B.subtilis equivalent time differences, then the actual spore reduction will be less than that indicated by data calculated by equation (1). The difference between actual and estimated equivalent time differences (and hence between actual and estimated equivalent retort times) is small in terms of total process time, and a correction, or 'safety factor', to be added to the estimate of the equivalent time difference, may be quite satisfactory for process calculations. This correction would be based on the standard deviation (σ) of the difference between estimated and actual equivalent time differences for a range of processes. The standard deviation (σ) of the differences, $\Delta\theta_2' - \Delta\theta_2$, for the range of model processes and can sizes considered is less than the standard deviation of the differences $\Delta\theta_2' - \Delta\theta_2$ for the agitated can runs (model cans, $\sigma = 0.065$ min.; experimental agitated cans, $\sigma = 0.108$ min.).

(11) Effect of can size and type of process on equivalent time difference.

The effect of can size on equivalent time difference is dependent on the type of process, and hence these two effects are discussed together.

The temperature-time functions $T = F(\theta)$, for the model cans are solutions of the equation -

$$\frac{1}{T_R - T} \frac{dT}{d\theta} = \frac{UA}{mc_p} = \beta \quad \dots\dots\dots (2)$$

where U is the overall heat transfer coefficient, A is the surface area of the container, m and c_p are the mass and specific heat of the material

in the can, and β is the rate of change of temperature per unit temperature difference. The can temperature is T , and T_R , which is a function of time θ , is the retort temperature.

The time θ , can be transformed to θ' , where $\theta' = \frac{\theta A}{mc_p}$; equation (2) then becomes -

$$\frac{1}{T_R - T} \frac{dT}{d\theta'} = U \quad \dots \dots \dots (3)$$

The solution of equation (3) i.e. $T = F'(\theta')$ is, therefore, the same for all sizes of can if U is independent of can size (see Schultz and Olson, 1938) and if the retort temperature T_R is the same function of transformed time θ' for all can sizes. The only temperature-time function to satisfy this condition is a step change in retort temperature, i.e. a "square" process which is approximately that obtained in some forms of continuous cooker-cooler (e.g. the spiral and reel type).

The specific rate difference function (ϵ) is a function of temperature only, for any pair of chemical and bacterial systems. Hence the specific rate difference vs transformed time function (i.e. ϵ vs θ') is independent of can size.

The equivalent time difference is given by :

$$\begin{aligned} \Delta\theta &= \int_{\theta_0}^{\theta_1} \epsilon d\theta \\ &= \frac{mc_p}{A} \int_{\theta'_0}^{\theta'_1} \epsilon d\theta' \end{aligned}$$

where θ'_0 and $\theta'_1 = \frac{A}{mc_p} \cdot \theta_0$ and $\frac{A}{mc_p} \cdot \theta_1$ respectively.

If θ_0 and θ_1 are such that the specific rate difference ϵ is zero at θ'_0 and θ'_1 for all can sizes (i.e. if the final temperature of all cans and the retort temperature are indistinguishable), the

integral -

$$\int_{\theta'_0}^{\theta'_1} \epsilon d\theta'$$

does not depend on the can size. The equivalent time difference is, therefore, proportional to $\frac{V_0}{A}$, and hence to the ratio of can volume to surface area for a step or "square" process.

The case also arises in which the retort temperature increases slowly from sublethal temperatures to retort temperature.

Consider the case in which the retort temperature T_R is defined by -

$$T_R = T_0 + k\theta$$

Equation (2) then gives -

$$\frac{dT}{d\theta} = \beta(T_0 + k\theta - T)$$

The general solution of this equation is -

$$T - T_0 = Ae^{-\beta\theta} + k\theta - \frac{k}{\beta}$$

If the initial can temperature is T_0 , this gives -

$$T - T_0 = k\theta - \frac{k}{\beta}(1 - e^{-\beta\theta})$$

which gives -

$$T - T_0 = k\theta - \frac{k}{\beta}$$

when θ is large.

Because low temperatures make no significant contribution to the equivalent time difference, the can temperature vs time curves will be substantially parallel to the retort temperature vs time curves, and hence to each other, from the time the spore destruction and chemical reaction rates become significant, until the retort reaches its final temperature. The temperatures of the larger cans lag behind those of the smaller cans, and the specific rate vs time curves of the different sizes of can are therefore identical in shape for much of the process. In the phase of heating in which the temperature vs time curves for the different sizes of can are not parallel, the contributions to equivalent time differences

are approximately proportional to the ratio of can volume to surface area.

Similarly, temperature vs time curves for slow linear cooling can be shown to be approximately parallel after the initial phase in which the exponential term (i.e. the transient) is significantly large. Hence the equivalent time differences for slow cooling are also nearly independent of can size.

The model processes illustrate the effects of type of process and can size on equivalent time difference. Figures ⁴⁴~~54~~ and ⁴⁵~~46~~ show typical temperature vs time and specific rate difference vs time curves.

1. Effect of total length of heating and cooling periods.

The most important effect of type of process is that of the total length of the heating and cooling periods (irrespective of can size) on the equivalent time difference. The equivalent time differences of the cans in each set of runs (9,1,3), (9,2,4), (10,5,7), (10,6,8) and (11,9,10) can be compared. In each set the slower retort heating and cooling rates give greater equivalent time differences. Series A and series B runs with the same length of air cooling phase cannot strictly be compared as the different rates of cooling of the retort in this period have an effect that tends to offset the effect of longer total heating and cooling time. In runs 2 and 5, and in runs 4 and 7, however, the temperature-time curves in the air cooling phase are almost identical. The effect of total length of heating and cooling phase is not obscured by the effect of the different retort-cooling rates. Again, the effect of longer total length of heating and cooling phase is to increase the equivalent time difference.

2. Effect of can size : square process.

The effect of can size has been shown above to be dependent on the type of process. Run 11 is a square process in which U , the overall heat transfer coefficient is independent of temperature. The abscissae

of the temperature vs time curves, and of the specific rate difference vs time curves at any given value of the ordinate (~~see figures 44 and 45~~) are in the proportion $\frac{1}{\beta_1} : \frac{1}{\beta_2} : \frac{1}{\beta_3}$ (i.e. $\frac{V_1}{S_1} : \frac{V_2}{S_2} : \frac{V_3}{S_3}$) for the three can sizes 1, 2 and 3, i.e. the temperature vs transformed time curves (i.e. T vs θ'), and the specific rate difference vs transformed time curves (i.e. ϵ vs θ') are identical for the three can sizes, as shown above (p 165). The can volume and can surface area are V and S respectively. As expected, the equivalent ~~retort times~~^{time differences} for run 11 in table 15 also show the same proportionality to $\frac{V}{S}$.

3. Effect of can size : non-square process

The retort temperature vs time curves for the non-square processes (runs 1-10) are by no means linear as assumed in the analysis above (p 166). However, the can temperature vs time curves are nearly parallel for the three sizes of can in both the heating and cooling periods. The slopes of the can temperature vs time curves (see figure 44) are approximately equal to that of the retort temperature vs time curve, especially in the period immediately before the retort temperature reaches its maximum. The effect of can size on the equivalent time difference in the heating phase (see table 15) is less for the slower heating runs (series B, runs 5,6,7,8 and 10) than it is for the faster heating runs (series A, runs 1,2,3,4 and 9). This is because length of the period in which the can temperature vs time curves are approximately parallel is relatively longer in the slower heating runs.

The situation in the cooling phase is not so clear as there is an abrupt change of slope in the model retort temperature vs time curves and a large increase in the overall heat transfer coefficient as the cooling water is introduced. The can temperatures pass slowly through the range in which the faster cooling cans have higher specific rate differences, and then pass very quickly through the temperature range in which the faster cooling cans have lower specific rate differences. The net result is that the faster cooling cans tend to have greater equivalent time differences for the cooling phase, especially

for those processes which have the longer air cooling periods.

Because the temperatures in the air cooling phase are in the range in which the rate of change of specific rate difference with respect to temperature is large (see figure 40) the effect of heat transfer coefficient is appreciable. Runs 1 and 2, 3 and 4, 5 and 6, and 7 and 8 (see figure 43) are identical, except that the overall heat transfer coefficient in the air cooling phase of the odd numbered runs is twice that in the even numbered runs. In all these runs the greater heat transfer coefficient in the air cooling phase gives the larger equivalent time differences for the cooling phase.

The effect of can size on the equivalent time difference is the sum of the effects of the heating and cooling periods. For a square or step process, the equivalent time differences are proportional to the ratio of can volume to surface area $\frac{V}{S}$. The effect of can size in the non-square processes is less than in the square process, especially where the air cooling phase is relatively long. For some processes with long air cooling periods, the effect of can size is small, and sometimes is negative, i.e. the equivalent time difference decreases with an increase in can size.

4. Effect of length of process.

The equivalent retort time correlations for static cans indicate that equivalent time differences for runs in which the maximum temperature is indistinguishable from that of the retort can be applied without serious error to processes in which the maximum can temperature is near, but not equal, to the retort temperature.

Three model temperature vs time curves have been constructed for this case. These are based on the largest size of can, and the heating and cooling curves are those of run 5. Cooling is started 1, 2 and 3 minutes after the retort reaches maximum temperature (272.0°F), at which times the can temperatures are 266.00°F, 270.04°F and 271.56°F respectively. Equivalent time differences are shown in table 15 for the three runs (numbers 12, 13 and 14 respectively for the 1, 2 and 3 minute processes).

In all cases the equivalent time differences are greater than those for run 5 can 3 in which sufficient time is allowed for the can temperature to reach that of the retort. The contribution to equivalent time difference made by the heating period is reduced, as the cooling is begun before the specific rate difference becomes zero (as in run 5). The contribution to equivalent time difference made by the cooling period is increased as the temperatures in the air cooling phase are lower, giving greater specific rate differences. The increase in the cooling curve contribution to the equivalent time difference more than offsets the lower equivalent time difference for the heating phase, giving greater overall equivalent time differences.

It, therefore, appears that the equivalent time difference is a function of maximum temperature obtained in the can, and is in general constant only for processes in which the maximum can temperature is indistinguishable from that of the retort. The apparently linear equivalent retort time correlations for the 15 psig and 30 psig static can runs are probably due to a fortuitous choice of processes in which the effect of beginning the cooling while the can temperature is still rising is not great. The overall coefficients of heat transfer to agitated and static cans are approximately equal in the air cooling phase, and hence the increase in contribution to the equivalent time difference made by this phase will be of the same order for the two types of process. Static can heat transfer coefficients in the heating, and water cooling, phases are about half those for the agitated cans, and the rate of change of temperature in the static cans will be less than in the agitated cans. Hence the contributions to the equivalent time difference in the heating and water cooling periods of static cans are greater than those of agitated cans, and the relative effect of the air cooling phase will be less in the static can runs than it is in the agitated can runs.

The effect of beginning the cooling while the can temperature is still rising may explain the anomalous effect of process time (T) in the agitated can runs. If the cooling in the short (i.e. 2 min.) run was, in

fact, begun just before the can temperature stopped rising, the equivalent time differences for the short runs would be slightly higher than those for the long (i.e. 5 min.) processes where the can temperature has for all practical processes reached that of the retort. Comparison of the equivalent time differences of run 14 can 3 and run 5 can 3 shows that a difference between retort temperature and can temperature at the beginning of the cooling period of 0.44°F leads to an increase in equivalent time difference of 0.08 min. for B.stearothermophilus, and 0.13 min. for B.subtilis. The observed differences in equivalent time differences in the agitated can experiments were 0.09 min. and 0.05 min. respectively.

- (d) Application of equivalent time difference analysis conclusions to real processes.

The model processes discussed here are somewhat artificial, in that linear heating and cooling curves with abrupt changes of slope are only approximations to those observed in practice. The overall heat transfer coefficients are based on a limited number of runs of one type. In particular, the retort temperature and the heat transfer coefficient in the air cooling phase may not be representative of a very wide range of processes. For example, much greater thermal load in a commercial retort could well affect the rate of change of retort temperature in the air cooling phase (and hence the specific rate differences and equivalent time differences).

However, the model temperature vs time functions cover quite a range of types of process, and the broad conclusions from the equivalent time difference analysis should be applicable to real processes. These conclusions can be listed as follows :-

1. The equivalent time differences for organisms whose spore destruction reactions are characterised by high activation energies are greater than organisms with relatively low activation energies. Approximate calculation of equivalent time differences of an organism appears

possible with the equation -

$$\frac{\Delta \theta_2}{\Delta \theta_1} = \frac{\log (E_{A \text{ bact}(2)} / E_{A \text{ chem}})}{\log (E_{A \text{ bact}(1)} / E_{A \text{ chem}})}$$

2. Slower rates of heating and cooling of the retort give larger equivalent time differences.
3. The effect of an increase in can size is generally to increase the equivalent time difference. The effect of can size is greatest for a square process where the equivalent time difference is proportional to the ratio of can volume to surface area. Can size does not have as great an effect on equivalent time difference in processes with finite rates of heating and cooling of the retort. The effect of can size decreases as the length of the total heating and cooling periods increases. In some cases, particularly processes with long air cooling periods, the effect of an increase in the can size may be to reduce the equivalent time difference slightly.
4. The most important source of variation in equivalent time differences is the air cooling period. Hence smaller differences between the equivalent time differences of similarly processed cans, as well as greater uniformity of processing, will be obtained by the use of processes in which the duration of the air cooling period is as short as possible.

FURTHER DEVELOPMENT OF THE

CHEMICAL ANALOGUE

FURTHER DEVELOPMENT OF THE CHEMICAL ANALOGUE

INTRODUCTION

Experiments and theoretical considerations have both shown that the equivalent retort time correlation is dependent on the temperature-time functions obtained in the can during the heating and cooling phases of the process.

For a single element of material in a container, it has been shown that the equivalent retort time correlation depends on the temperature-time function if only one chemical reaction is used. If two chemical reactions with different activation energies are used, it is still necessary to know the form of the temperature-time function. Hence measurements or calculations of temperatures within the can must be made.

Where the effect of heat on all elements of material in the can is not identical, as in static convection or conduction, a knowledge of the effect of heat on all elements is necessary for the prediction of equivalent retort times from chemical measurements.

Because of this dependence on temperature-time functions (which are sometimes quite difficult to obtain) the possibility of an analogue which is independent of temperature-time functions was investigated. This section is, therefore, a discussion of methods of calculation of spore destruction from chemical measurements with particular reference to the degree of dependence of these methods on a knowledge of temperature-time functions. In particular, a chemical analogue which can be applied to any process with unknown can temperatures is sought.

MULTIPLE REACTION SYSTEMS

Temperature vs time curves of best fit

A number of chemical reactions (with non-equal activation energies) can be used, and chemical equivalent retort times determined for each system.

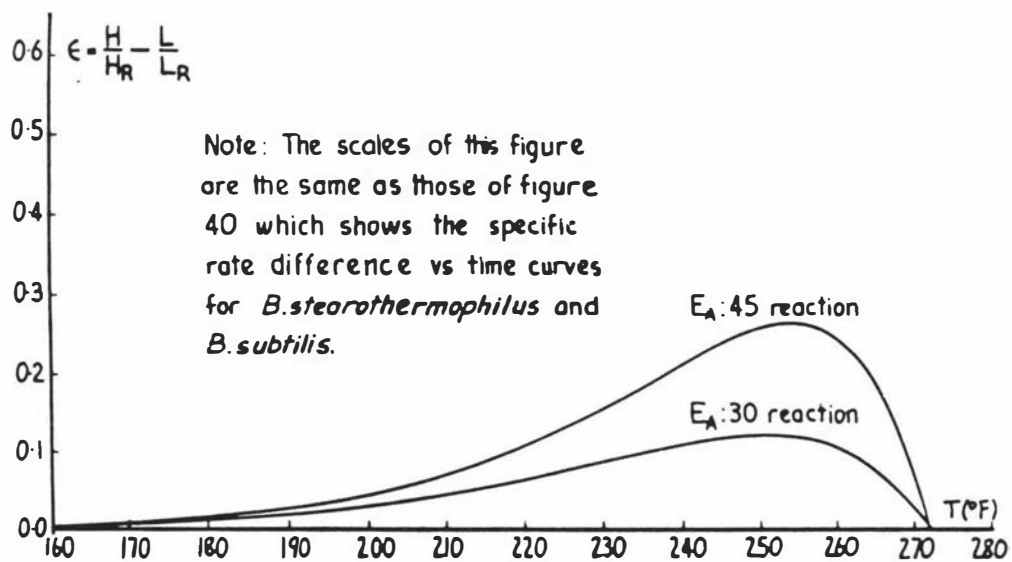


Fig.46, Specific rate difference vs temperature for the $E_A:30$ and $E_A:45$ reactions.

A temperature vs time curve of best fit (i.e. a hypothetical time-temperature function which gives chemical equivalent retort times identical to those observed) can then be used to extrapolate from chemical data to bacterial equivalent retort times.

These hypothetical curves need not necessarily resemble closely the temperature vs time curves to which they are equivalent. It has been shown earlier (p 45), that apparently dissimilar temperature vs time curves can be equivalent for the calculation of bacterial equivalent retort times from measurements on chemical systems.

The development of a chemical analogue which is independent of any knowledge of the form of the temperature-time functions obtained in the can, therefore requires an investigation into the number of chemical reaction systems necessary to define a curve of best fit which is satisfactory for the calculation of bacterial equivalent retort times.

Method

In this study, prediction of bacterial equivalent retort times from measurements on two, and on three chemical reactions, with different activation energies, has been investigated. Because suitable chemical reactions with the required activation energies and rate constants were not readily available, hypothetical reactions with activation energies of 30 and 45 Kcal/mole have been used. These are referred to as the $E_A:30$ and the $E_A:45$ reactions.

The equations :

$$\log_{10} \frac{K}{K_R} = 11.803 \left(1.3667 - \frac{10^3}{T} \right)$$

and

$$\log_{10} \frac{K}{K_R} = 11.704 \left(1.3667 - \frac{10^3}{T} \right)$$

have been used to calculate specific reaction rates for the $E_A:30$ and $E_A:45$ reactions respectively. The rate of reaction at T ($^{\circ}\text{R}$) is K , and that at retort temperature ($272.0^{\circ}\text{F} = 731.7^{\circ}\text{R}$) is K_R . These specific reaction rates have been used to prepare tables of specific rate difference

(with respect to sucrose hydrolysis) vs time. These tables are presented in Appendix VIII.

All specific rate differences and equivalent time differences (for chemical and bacterial systems) are with respect to the sucrose hydrolysis reaction :

$$\text{i.e. } \epsilon_{\text{bact}} = \frac{L}{L_R} - \frac{H}{H_R},$$

$$\epsilon_{\text{chem}} = \frac{K}{K_R} - \frac{H}{H_R},$$

$$\Delta \Theta_{\text{bact}} = \Theta_{\text{sucrose}} - \Theta_{\text{bact}},$$

$$\text{and } \Delta \Theta_{\text{chem}} = \Theta_{\text{sucrose}} - \Theta_{\text{chem}}.$$

where ϵ is the specific rate difference, H, L and K are the rates of sucrose hydrolysis, spore destruction and hypothetical chemical reaction. Equivalent retort times are denoted by Θ , and the equivalent time differences by $\Delta \Theta$. Subscript R refers to retort temperature, while subscripts bact, chem, and sucrose refer to the bacterial systems, the hypothetical chemical reactions ($E_A:30$, and $E_A:45$) and the sucrose hydrolysis reaction, respectively.

Equivalent time differences have been calculated for the range of model processes used in the study of the equivalent time difference concept (pp 157,158). Table 16 shows the equivalent time differences for the heating and cooling periods, and the total equivalent time difference, for both reactions.

(a) Two reaction systems.

(i) Temperature vs time curves of best fit.

A curve of best fit based on two chemical reactions must be defined in terms of two parameters, with all other necessary parameters required to define the can temperature vs time curve being defined in terms of these two. For example, if the two parameters are f_h (the reciprocal of the slope of the semilogarithmic heating curve (p 18) and

Table 16 : Effect of Can Size and Type of Process on Equivalent Time Differences for Chemical Reactions with Activation Energies of 30 kcal/mole and 45 kcal/mole.

Run no.	can no.	Equivalent Time Differences (min.)					
		E_A : 30 reaction			E_A : 45 reaction		
		heating	cooling	total	heating	cooling	total
<u>1</u>	R	0.156	0.299	0.455	0.290	0.658	0.948
	1	0.178	0.109	0.287	0.368	0.263	0.631
	2	0.210	0.117	0.327	0.450	0.259	0.709
	3	0.266	0.123	0.389	0.886	0.267	0.853
<u>2</u>	R	0.156	0.299	0.455	0.290	0.658	0.948
	1	0.178	0.096	0.274	0.368	0.206	0.574
	2	0.210	0.101	0.311	0.450	0.212	0.662
	3	0.266	0.112	0.378	0.586	0.237	0.823
<u>3</u>	R	0.156	0.604	0.760	0.290	1.279	1.569
	1	0.178	0.323	0.501	0.368	0.767	1.135
	2	0.210	0.285	0.495	0.450	0.672	1.122
	3	0.266	0.256	0.522	0.586	0.606	1.192
<u>4</u>	R	0.156	0.604	0.760	0.290	1.279	1.569
	1	0.178	0.223	0.401	0.368	0.534	0.902
	2	0.210	0.198	0.408	0.450	0.467	0.917
	3	0.266	0.185	0.451	0.586	0.428	1.014
<u>5</u>	R	0.312	0.257	0.569	0.586	0.571	1.157
	1	0.315	0.136	0.451	0.610	0.292	0.902
	2	0.333	0.145	0.473	0.663	0.308	0.971
	3	0.357	0.158	0.515	0.745	0.331	1.076
<u>6</u>	R	0.312	0.257	0.569	0.586	0.571	1.157
	1	0.315	0.126	0.441	0.610	0.261	0.871
	2	0.328	0.138	0.466	0.665	0.280	0.943
	3	0.357	0.151	0.508	0.745	0.313	1.058

continued ...

Table 16 cont.

Run no.		Equivalent Time Differences (min.)					
		E_A : 30 reaction			E_A : 45 reaction		
		heating	cooling	total	heating	cooling	total
<u>7</u>	R	0.312	0.574	0.886	0.586	1.322	1.908
	1	0.315	0.258	0.573	0.610	0.608	1.218
	2	0.328	0.241	0.569	0.663	0.552	1.215
	3	0.357	0.229	0.586	0.745	0.552	1.297
<u>8</u>	R	0.312	0.574	0.886	0.586	1.322	1.908
	1	0.315	0.199	0.514	0.610	0.439	1.049
	2	0.328	0.188	0.516	0.663	0.416	1.079
	3	0.357	0.192	0.549	0.745	0.416	1.161
<u>9</u>	R	0.156	0.036	0.192	0.290	0.070	0.360
	1	0.178	0.070	0.248	0.368	0.149	0.517
	2	0.210	0.084	0.294	0.450	0.170	0.620
	3	0.266	0.100	0.366	0.586	0.199	0.785
<u>10</u>	R	0.312	0.073	0.385	0.586	0.144	0.730
	1	0.315	0.113	0.428	0.610	0.225	0.835
	2	0.328	0.126	0.454	0.663	0.253	0.916
	3	0.357	0.143	0.500	0.745	0.288	1.033
<u>11</u>	R	0.000	0.000	0.000	0.000	0.000	0.000
	1	0.123	0.032	0.155	0.279	0.061	0.340
	2	0.177	0.046	0.223	0.402	0.087	0.489
	3	0.252	0.065	0.317	0.567	0.122	0.689
<u>12</u>	3	0.297	0.367	0.664	0.585	0.845	1.430
<u>13</u>	3	0.340	0.225	0.565	0.697	0.504	1.201
<u>14</u>	3	0.352	0.179	0.531	0.730	0.384	1.114

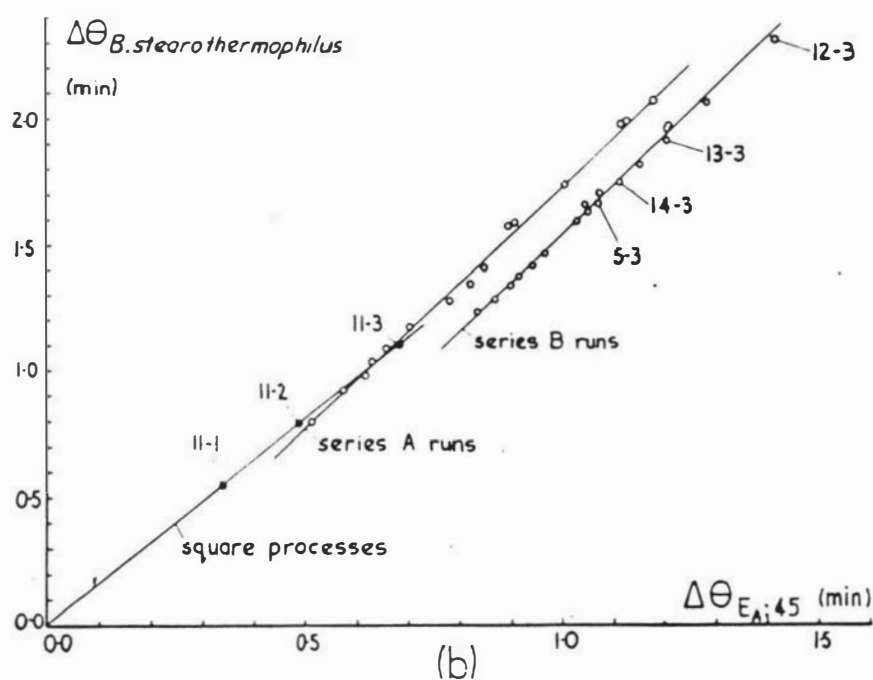
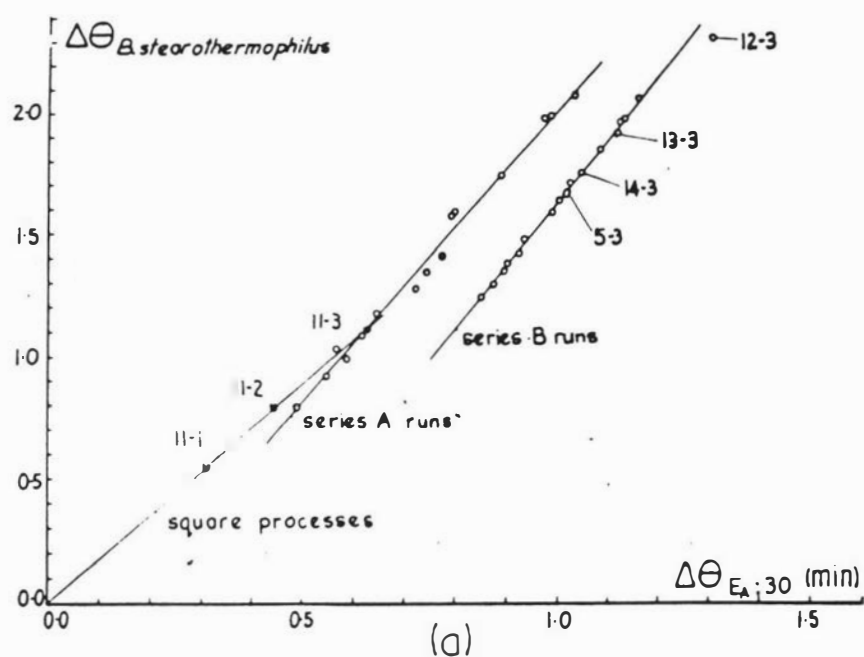


Fig. 47 Equivalent time difference correlations for two reaction systems.

(a) $\Delta\theta_{B.stearothermophilus}$ vs $(\theta_{sucrose} - \theta_{E_A:30})$.

(b) $\Delta\theta_{B.stearothermophilus}$ vs $(\theta_{sucrose} - \theta_{E_A:45})$.

g (the difference between the maximum can temperature and that of the retort) are used, then values of other parameters such as the shape and slope of the cooling curve, initial temperature, etc. must be assumed to be invariant, or defined in terms of f_h and g.

A number of types of curve can be used to fit the chemical data. In general the two parameter systems have proved inadequate for calculation of bacterial equivalent retort times from measurements on chemical systems.

(ii) Equivalent time difference correlations.

Although it has been shown that measurements on two chemical reactions are not sufficient to make possible the calculation of bacterial equivalent retort times from chemical equivalent retort times, correlations involving two chemical reactions have been plotted (figures 4.7a and 4.7b). These figures show the equivalent time difference for B. stearothermophilus plotted against the equivalent time differences for the $E_A:30$ and the $E_A:45$ reactions. The corresponding correlations for B. subtilis (which are quite similar in general form to the B. stearothermophilus curves) are not shown.

In each figure the data for the non-square runs can be represented by two distinct straight lines. The upper line represents the data of runs 1, 2, 3, 4 and 9 (i.e. series A) which are based on the heating and cooling rates obtained in the experimental retort used in this study. The lower line represents the data of series B (runs 5, 6, 7, 8 and 10) in which the heating and cooling rates of the retort are half the corresponding rates of series A. Within each set of data, the effects of length of air cooling phase, overall heat transfer coefficient in the air cooling phase, and size of can are relatively unimportant. The maximum error in the bacterial equivalent time difference (and hence in the equivalent retort time) predicted from the chemical equivalent time difference is less than 0.07 min. (4 sec.) if the $E_A:30$ reaction is used, and is less than 0.05 min. (3 sec.) if the $E_A:45$ reaction is used.

If the magnitudes of these errors are representative of the orders of the errors to be expected from real processes, then relatively crude heat transfer data can be used to calculate temperature vs time curves from retort temperature data for the process being investigated. Chemical and bacterial equivalent time differences on these can temperature vs time curves can be used to establish the relationship between the chemical and bacterial equivalent time differences. Measurements on two chemical systems within the can will determine the chemical equivalent time difference for the given product and process. Thus the bacterial equivalent time difference and hence the bacterial equivalent retort time (i.e. the total lethal effect of heat) can be determined.

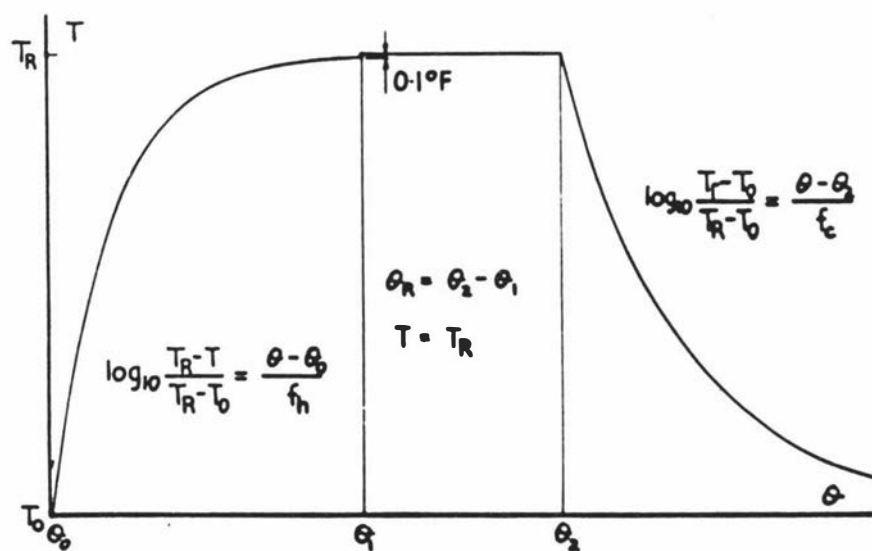
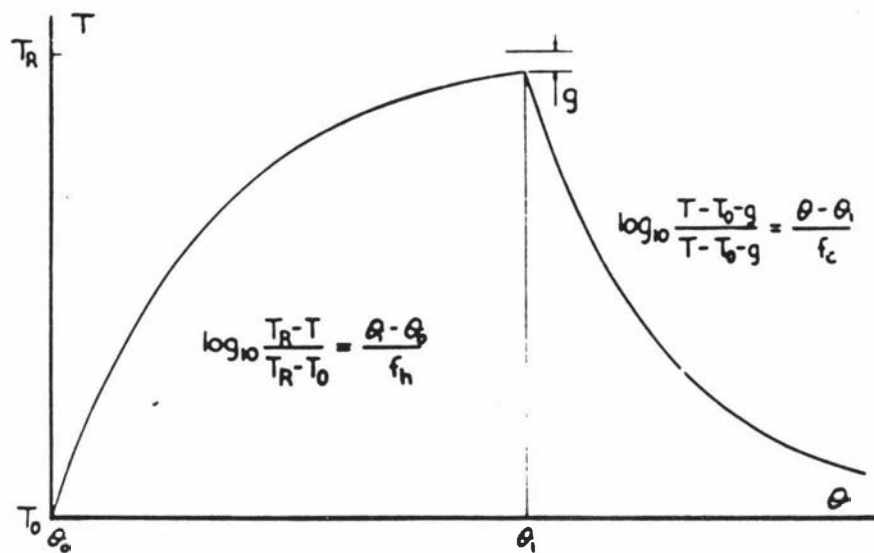
The data from the square process (i.e. run 11) lie on a straight line which passes through the origin. The points are marked 11-1, 11-2 and 11-3 in figures 47a and 47b. The linearity of the three points and the origin arises because both the chemical and bacterial equivalent time differences for the three can sizes are proportional to the respective ratios of can volume to surface area $\frac{V}{S}$. Hence, for a square process, temperature vs time curves for one size of can only, are required to define the line relating the bacterial and chemical equivalent time differences.

The data from the runs in which the can temperature did not reach retort temperature are also shown in figures 47a and 47b (points 12-3, 13-3 and 14-3). The point for run 12 can 3, in which the can temperature at the beginning of the cooling period is 6.0 degrees below the retort temperature, lies below the line. Hence the correlation between the chemical and the bacterial equivalent time differences may prove to be non-linear. The correlation can still be determined by calculating temperature vs time curves for processes of length similar to that being investigated, and hence measurements on two chemical systems can be used to determine the total lethal effect of heat.

(b) Three reaction systems.

(1) Types of best fit curves.

Two types of curve of best fit have been used for the calculation of bacterial equivalent retort times from chemical data in this



investigation. Type I, which is shown graphically in figure 48a is based on three parameters f_h , f_c and g , and type II (figure 48b) on the parameters f_h , f_c and Θ_r , where f_h and f_c are the reciprocal slopes of the semi-logarithmic heating and cooling curves respectively, and g is the difference between the maximum can temperature (T) and that of the retort (T_R). The holding time Θ_r is a period in which the can temperature is the same as the retort temperature. This period is arbitrarily assumed to begin when the can contents reach a temperature 0.1°F below that of the retort.

The equations relating the chemical reaction data (i.e. equivalent retort times), and the three parameters are given below, along with the method of solution of these equations. The methods of calculation of the various functions or constants required in the solution of the equations are also outlined.

1. Type I curve of best fit.

Bacterial and chemical equivalent retort times (Θ) are given by the equation -

$$\Theta = \Theta_h + \Theta_c \dots\dots\dots (1)$$

where Θ_h and Θ_c are the respective contributions to equivalent retort time of the heating and cooling phases of the process represented by the curve of best fit.

Because Θ_h and Θ_c are proportional to f_h and f_c respectively for a given maximum can temperature $T_R - g$, Θ_h and Θ_c in equation (1) may be replaced by af_h and bf_c respectively.

Equation (1) is then

$$\Theta = af_h + bf_c$$

where the coefficients a and b are functions of g only, for any given chemical or bacterial system. The use of the subscripts A, B and C for reference to the three chemical reactions (which in this study are sucrose

hydrolysis and the hypothetical reactions with activation energies of 30 and 45 kcal/mole respectively), and S for reference to the destruction of bacterial spores leads to the equations :

$$\theta_A = a_A f_h + b_A f_o \dots\dots\dots (2)$$

$$\theta_B = a_B f_h + b_B f_o \dots\dots\dots (3)$$

$$\theta_C = a_C f_h + b_C f_o \dots\dots\dots (4)$$

$$\text{and } \theta_S = a_S f_h + b_S f_o \dots\dots\dots (5)$$

Equations (2), (3) and (4) are solved for f_h and f_o in pairs, using trial values of g to determine the coefficients a and b . Values of f_h , f_o and g which satisfy equations (2), (3) and (4) are used to determine θ_S by substitution in equation (5).

Values of a and b for a range of values of g can be calculated by graphical or numerical integration of the specific rate vs time curves based on the respective semilogarithmic heating and cooling curves. Alternatively a and b can be determined using the equations :

$$a = \log_{10} e \cdot -E_1 \left(-B \left(\frac{1}{u_g} - 1 \right) \right) + e^B E_1 \left(-\frac{B}{u_g} \right) \dots\dots\dots (6)$$

and

$$b = \log_{10} e \cdot e^{B(1 - \frac{1}{u_o})} \overline{E_1} \left(\frac{B}{u_o} \frac{u_g - u_o}{u_g} \right) - e^B E_1 \left(-\frac{B}{u_g} \right) \dots\dots (7)$$

where

$$B = \frac{E_A}{RT_R} \text{ and } u = \frac{T}{T_R}$$

Subscripts g and o refer to the temperatures at the end of the heating period ($T = T_R - g$), and the temperature T_o of the cooling water. Two terms which occur in the full form of equation (7) are omitted. These arise from the lower limit (where all rates of reaction and spore destruction are very low) and are negligible for values of B , u_g , and u_o of interest in the present context.

The functions $-Ei(-x)$ and $\overline{Ei}(x)$ are known as exponential integrals. They are defined by :

$$-Ei(-x) = \int_x^{\infty} \frac{e^{-u}}{u} du \quad (x > 0)$$

$$\text{and} \quad \overline{Ei}(x) = \lim_{y \rightarrow 0+0} Ei(x \pm iy) \pm i\pi$$

(x and y real).

These functions have been tabulated, e.g. Korn and Korn (1961) and Jahnke and Emde (1945).

The derivation of equations (6) and (7) is shown in Appendix IX. Appendix X gives values of a and b for the sucrose hydrolysis reaction (activation energy in the range 212-272°F assumed constant and equal to 22.34 kcal/mole). Values of Δa and Δb for the other chemical and bacterial systems are also shown, where Δa_N and Δb_N are given by :

$$\Delta a_N = a_A - a_N$$

$$\text{and} \quad \Delta b_N = b_A - b_N$$

Subscript A refers to the sucrose hydrolysis reaction and subscript N to the other systems. The range of g in the table is 10.0°F to 0.01°F. Retort temperature is 272.0°F and the temperature of the cooling water is 67°F ($u_0 = 0.72$).

2. Type II curve of best fit.

For a type II best fit curve, the bacterial and chemical equivalent retort times are given by the equation :

$$\Theta = \Theta_h + \Theta_r + \Theta_c$$

where Θ_h , Θ_r and Θ_c are the respective contributions to equivalent retort time of the heating, holding and cooling periods of the process represented by the curve of best fit.

As in type I, the contributions ϑ_h and ϑ_o can be replaced by af_h and bf_o respectively, giving -

$$\vartheta = af_h + \vartheta_r + bf_o$$

Use of the subscripts A, B, C and S, as above, leads to the equations :

$$\vartheta_A = a_A f_h + \vartheta_r + b_A f_o \quad \dots\dots\dots (8)$$

$$\vartheta_B = a_B f_h + \vartheta_r + b_B f_o \quad \dots\dots\dots (9)$$

$$\vartheta_C = a_C f_h + \vartheta_r + b_C f_o \quad \dots\dots\dots (10)$$

$$\text{and } \vartheta_S = a_S f_h + \vartheta_r + b_S f_o \quad \dots\dots\dots (11),$$

$$\begin{aligned} \text{whence } \Delta\vartheta_B &= \vartheta_A - \vartheta_B \\ &= \Delta a_B f_h + \Delta b_B f_o \quad \dots\dots\dots (12) \end{aligned}$$

$$\begin{aligned} \text{and } \Delta\vartheta_C &= \vartheta_A - \vartheta_C \\ &= \Delta a_C f_h + \Delta b_C f_o \quad \dots\dots\dots (13) \end{aligned}$$

Because the high temperature limits of the type II heating and cooling curves are invariant, the values of a and b (and hence of Δa and Δb) are constant for each chemical and bacterial system. The values for the different systems are marked with an asterisk in the table of Appendix X, (p 269).

The solution of the equations for the type II curve of best fit is much simpler than that for the type I best fit curve. A single pair of linear simultaneous equations with constant coefficients (viz., equations (12) and (13) above) are solved for f_h and f_o . The value of ϑ_r is found by substitution in one of the equations (8), (9) or (10). Substitution of f_h , f_o and ϑ_r in equation (11) yields the equivalent retort time for spore destruction.

Alternatively equations (8), (9) and (10) may be solved for θ_h , θ_r and f_0 in terms of θ_A , θ_B and θ_C . Substitution into equation (11) yields, after simplification, an equation of the form -

$$\theta_S = p \theta_A - q \theta_B + r \theta_C \dots\dots\dots (14)$$

which can be used to calculate bacterial equivalent retort times directly from the chemical equivalent retort times. For B.stearothermophilus and B.subtilis the equations are -

$$\theta_S = 1.2801 \theta_A - 3.4408 \theta_B + 3.1607 \theta_C$$

and

$$\theta_S = 2.5426 \theta_A - 6.4005 \theta_B + 4.8579 \theta_C$$

respectively.

If equivalent time differences only are known (as in the calculations on the model processes), the bacterial equivalent time differences ($\Delta\theta_S$) can be calculated using the equation -

$$\Delta\theta_S = -q \Delta\theta_B + r \Delta\theta_C \dots\dots\dots (15)$$

This gives

$$\Delta\theta_S = -3.4408 \Delta\theta_B + 3.1607 \Delta\theta_C$$

and

$$\Delta\theta_S = -6.4005 \Delta\theta_B + 4.8579 \Delta\theta_C$$

for B.stearothermophilus and B.subtilis respectively.

An advantage of this direct method (apart from its extreme simplicity) is the ease with which the error in θ_S , due to errors in estimation of θ_A , θ_B and θ_C , can be calculated.

(11) Comparison of the two types of best fit curve as methods of calculation of spore destruction.

Tables 17a and 17b show the equivalent time differences and equivalent retort times, and the relevant parameters of the best fit curves. In table 17a (runs 1-11) equivalent retort times and lengths of the holding periods are not shown, as the equivalent time differences have

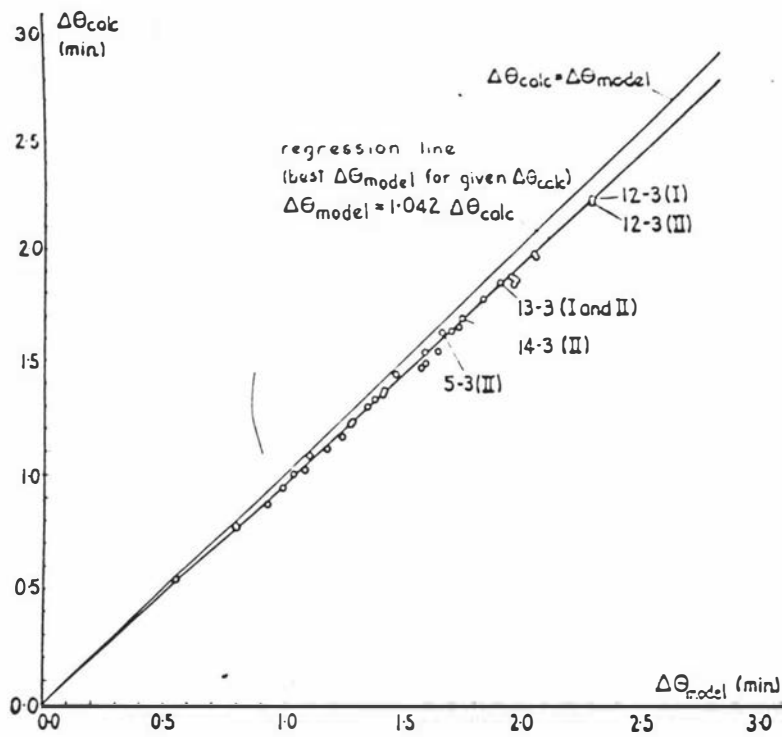
Table 17a : Equivalent time differences and parameters of the curves of best fit : Runs 1 - 11.

Run, can	No.	f_h (min)	f_o (min)	Equivalent time difference, $\Delta\theta$ (min.)			
				<u>B. stearothermophilus</u>		<u>B. subtilis</u>	
				type II	model	type II	model
<u>1</u>	1	1.399	6.91	1.007	1.033	1.228	1.305
	2	1.423	9.14	1.116	1.173	1.351	1.480
	3	1.858	9.65	1.358	1.409	1.654	1.784
<u>2</u>	1	0.848	10.24	0.871	0.921	1.035	1.150
	2	1.142	10.28	1.022	1.081	1.225	1.358
	3	1.704	10.13	1.301	1.345	1.579	1.683
<u>3</u>	1	3.017	7.75	1.864	1.986	2.307	2.568
	2	2.991	7.56	1.842	1.979	2.282	2.573
	3	3.306	6.87	1.971	2.076	2.450	2.700
<u>4</u>	1	2.304	7.03	1.471	1.574	1.815	2.058
	2	2.332	7.25	1.494	1.590	1.843	2.078
	3	2.584	7.97	1.653	1.739	2.039	2.257
<u>5</u>	1	0.661	22.36	1.299	1.341	1.495	1.599
	2	1.122	20.24	1.442	1.464	1.690	1.756
	3	1.544	19.62	1.629	1.665	1.931	2.013
<u>6</u>	1	0.457	23.27	1.236	1.281	1.409	1.499
	2	0.872	21.69	1.377	1.416	1.598	1.676
	3	1.465	19.79	1.596	1.628	1.888	1.949
<u>7</u>	1	2.076	19.16	1.878	1.979	2.249	2.484
	2	2.156	18.31	1.682	1.965	2.260	2.449
	3	2.472	16.97	1.985	2.063	2.399	2.576
<u>8</u>	1	1.114	22.78	1.547	1.657	1.806	2.049
	2	1.563	19.54	1.635	1.705	1.939	2.096
	3	1.886	19.12	1.781	1.843	2.126	2.376
<u>9</u>	1	0.724	9.60	0.780	0.793	0.924	0.948
	2	0.980	10.46	0.948	0.989	1.130	1.202
	3	1.446	11.33	1.222	1.275	1.471	1.569
<u>10</u>	1	0.267	23.91	1.167	1.237	1.317	1.405
	2	0.803	21.48	1.333	1.372	1.554	1.607
	3	1.299	20.55	1.545	1.588	1.819	1.894
<u>11</u>	1	0.742	3.83	0.541	0.551	0.660	0.682
	2	1.065	5.53	0.778	0.795	0.948	0.982
	3	1.409	8.65	1.087	1.100	1.318	1.382

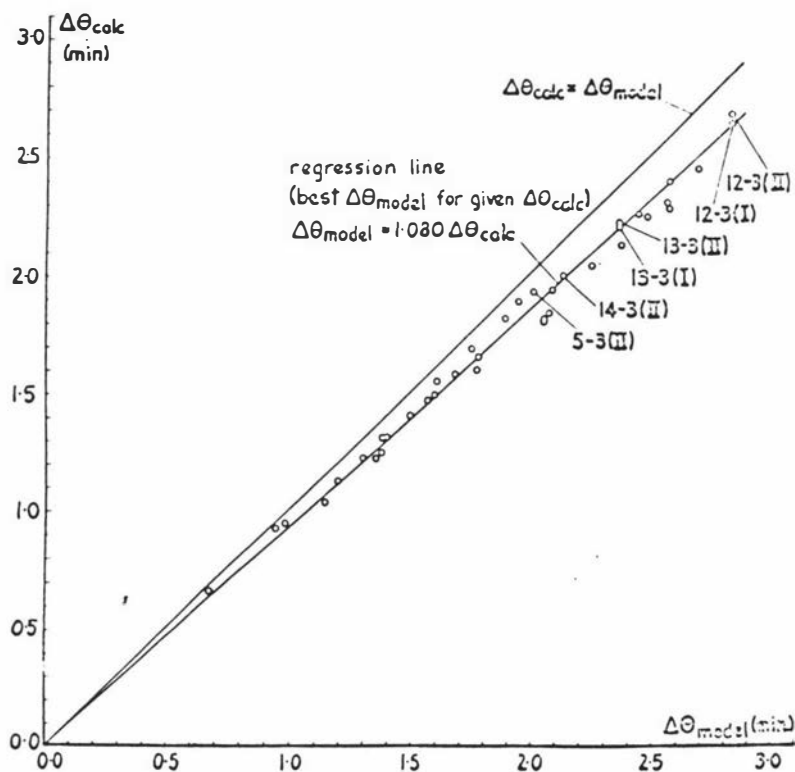
Table 17b : Equivalent time differences, equivalent retort times and parameters of the best fit curves : Runs 12-14.

		model	type I	type II
		T vs θ curve	best fit curve	best fit curve
<u>Run 12 can 3</u>				
f_h	(min)	-	3.119	2.724
f_o	(min)	-	18.29	19.81
g	($^{\circ}\text{F}$)	6.00	1.45	0.54
θ_r	(min)	-	-	- 1.994
<u>B. stearothermophilus</u>				
θ	(min)	2.313	2.215	2.235
$\Delta\theta$	(min)	1.916	2.014	1.994
<u>B. subtilis</u>				
θ	(min)	2.842	2.644	2.697
$\Delta\theta$	(min)	1.387	1.585	1.532
<u>Run 13 can 3</u>				
f_h	(min)	-	2.064	2.047
f_o	(min)	-	18.75	18.89
g	($^{\circ}\text{F}$)	1.56	0.10	0.0995
θ_r	(min)	-	-	0.025
<u>B. stearothermophilus</u>				
θ	(min)	1.915	1.854	1.852
$\Delta\theta$	(min)	3.666	3.727	3.729
<u>B. subtilis</u>				
θ	(min)	2.366	2.222	2.218
$\Delta\theta$	(min)	3.215	3.359	3.363
<u>Run 14 can 3</u>				
f_h	(min)	-	*	1.671
f_o	(min)	-	*	19.64
g	($^{\circ}\text{F}$)	0.44	< 0.01	0.0074
θ_r	(min)	-	*	1.887
<u>B. stearothermophilus</u>				
θ	(min)	1.747	*	1.692
$\Delta\theta$	(min)	4.929	*	4.982
<u>B. subtilis</u>				
θ	(min)	2.139	*	2.013
$\Delta\theta$	(min)	4.537	*	4.663

* A solution is not possible as the minimum value of g in the table of Appendix X is 0.01 $^{\circ}\text{F}$.



(a)



(b)

Fig. 49 Comparison of calculated and model equivalent time differences (a) *B. stearothermophilus* (b) *B. subtilis*.

been calculated directly from the heating and cooling curves of model processes of unspecified length. Table 17b shows data for the runs 12-14, in which cooling was begun before the can temperature reached that of the retort. Equivalent retort times, as well as equivalent time differences, are shown, along with the relevant parameters of the best fit curves (i.e. f_h , f_o and θ_r or g). In both tables equivalent time differences of the model process are shown for comparison. Table 17b also includes equivalent retort times calculated from the model curve.

Calculated equivalent time differences (ordinates) are plotted against the model equivalent times (abscissae) in figures 49a (B.stearo-thermophilus) and 49b (B.subtilis).

1. The best fit curves.

A qualitative examination of the model temperature vs time curves and the curves of best fit has been made. It is apparent that for processes in which relatively large contributions to equivalent time difference are made by temperatures near that of the retort (say within about 15°F), the slope of the heating part of the curve of best fit will be relatively low. The value of f_h will hence be relatively high, and the contribution to equivalent time difference by this part of the best fit curve will be large. Similarly, processes in which lower temperatures give relatively large contributions to equivalent time difference will give rise to relatively large values of f_o for the curve of best fit.

The temperature in the model processes during the air cooling phase are in the range which gives large contributions to equivalent time differences. The runs with the longest air cooling periods give higher values of f_h . Figure 42 (p 156) shows that there are four sets of runs which are identical except for the length of the air cooling phase. These are runs 9, 1 and 3, runs 9, 2 and 4, runs 10, 5 and 7, and runs 10, 6 and 8. In each set the value of f_h increases with the length of the process, while the value of f_o remains approximately constant.

The effect of rate of change of retort temperature for the model processes is also shown in table 17a. The values of f_h for runs 1, 2, 3, 4 and

9 (i.e. series A) are in the range 7-11 min., while runs 5, 6, 7, 8 and 10 (series B) are in the range 17-24 min. In series B the rate of change of retort temperature is lower than in series A, and hence the longer times are spent at lower temperatures. This effect appears to be almost independent of differences in process occurring at high temperatures.

In both type I and type II curves of best fit, the cooling curve used falls rapidly from maximum temperature to sublethal temperatures. The contribution to equivalent time difference of the cooling curve with unit slope (i.e. coefficient b of equations (2) to (5) and equations (8) to (11)) is about one order of magnitude less than the corresponding quantity (i.e. coefficient a) for the heating curve of unit slope. The model temperature vs time curves are such that the contributions to equivalent time difference of the heating and cooling sections of the best fit curve are of the same order. Hence the values of f_c are about one order of magnitude greater than the values of f_h . This again emphasises the fact that a curve of best fit may be the equivalent of some other temperature vs time curve, for purposes of calculation of spore destruction, without being at all similar to it in general shape.

The parameters g (type I curve of best fit) and ϕ_r (type II curve) are both measures of the length of the process. When the can temperatures are very close to retort temperature (say $g < 0.1^\circ\text{F}$), a tenfold decrease in g represents an increase in overall process length equal to f_h . Similarly an increase (or decrease) in overall process length increases (or decreases) the value of ϕ_r . If g is small (say $< 0.1^\circ\text{F}$), the change in ϕ_r is equal to the change in process length.

Table 17b shows the values of g and ϕ_r for runs 12-14. As the process length is increased the values of g and ϕ_r for the type I and type II curves of best fit show the expected trends, with the values of g decreasing, and the values of ϕ_r increasing.

An unexpected feature of the type I curve of best fit is that the values of g for the best fit curve are much less than those of the model temperature vs time curves from which they are derived. In the type II curves of best fit, the temperature on the heating curve (extrapolated if necessary) at the instant when cooling begins can be calculated.

The values of g for type II curves are shown in table 17b. Again they are considerably less than the values of g for the model curves.

It is not known why the curve of best fit gives values of g which are lower than expected. It is probably because the types of best fit curve assumed do not allow the model temperature vs time curves to be fitted very closely. Other curves of best fit based on three parameters could be used which give a closer fit to the model curves. It is expected that the more closely fitting curves would give values of g closer to those actually obtaining in the can.

The two types of best fit curve used here are such that for small g (say $g < 0.1^{\circ}\text{F}$) the curves of best fit are almost identical. Important differences between the curves are expected only when g is greater than about 1.0°F . The values of f_h and f_o for runs 12 and 13 (table 17b) show this behaviour clearly. There is close agreement between the two values of f_h , and between the two values of f_o , of run 13 in which the value of g for the curves of best fit is 0.10°F . The values of f_h and f_o for run 12 do not show this close agreement.

The value of Θ_r of run 12 can be seen to have the "impossible" value of -1.994 min. This negative value arises because the sum of the contributions to equivalent retort time of the heating and cooling periods is greater than the equivalent retort time of the model curve. The result is a curve of best fit in which the cooling period begins before the heating period is complete. Contributions to equivalent time difference are hence being made by both the heating and cooling parts of the curve of best fit during the negative holding time. The bacterial equivalent retort times predicted using this "impossible" curve of best fit are discussed below.

2. Equivalent time differences and equivalent retort times.

All bacterial equivalent time differences calculated using three parameter curves of best fit are less than those based on the model curves (see tables 17a and 17b, and figures 49a and 49b), and it hence appears that the two types of best fit curve as used here are not equivalent to the model curves when used for calculation of spore destruction.

Because the equivalent time differences predicted from the chemical analogue are less than the equivalent time differences calculated directly from the model temperature-time functions, the bacterial equivalent retort times based on the chemical analogue will tend to be high. The error in spore destruction is hence on the unsafe side.

The discrepancy between calculated and model equivalent time differences is probably because the curves of best fit do not allow the model temperature vs time curves to be fitted closely. It may be possible to modify the three parameter curves of best fit to allow a closer fit to the actual curves (particularly in the early stages of cooling) and so get a more reliable prediction of equivalent time difference.

The differences between the model and calculated equivalent time differences are not great, and the equivalent time differences calculated from a type I curve of best fit do not appear to be significantly different from the type II equivalent time differences. The points representing the very short runs are marked in figures 49a and 49b with the run and can numbers, and the type of best fit curve used.

The most important observation is that the scatter of the results as plotted in figures 49a and 49b is small (i.e. ± 0.5 min. or 2.5% for B. stearothermophilus and ± 0.10 min. or 5% for B. subtilis equivalent time differences), even though the analogue is not completely independent of the temperature-time function obtaining in the can. If it can be shown that this dependence of the analogue on the can temperature-time function is the same for a wide range of processes, can sizes, etc., then the analogue can be used to predict bacterial equivalent retort times.

(iii) Modification of the analogue.

Two methods of eliminating the difference between the calculated and model equivalent time differences (see figures 49a and 49b) can be used. One possibility, the modification of the best fit curve to enable the can temperature vs time curve to be fitted more closely has been proposed. The second method, which is somewhat simpler involves

modification of some of the constants in the equations of the analogue.

Figures 49a and 49b show that for the range of model processes considered, the data can be represented by a straight line through the origin without serious error.

$$\text{i.e. } \Delta \theta_S = k \Delta \theta_{S \text{ calc.}} \quad (16)$$

where k is a constant of proportionality.

The equations which have been developed for the calculation of bacterial equivalent time differences from chemical measurements are :

$$\Delta \theta_{S \text{ calc.}} = \Delta a_S f_h + \Delta b_S f_c \quad (17)$$

and

$$\Delta \theta_{S \text{ calc.}} = -q \Delta \theta_B + r \Delta \theta_C \quad (18)$$

For any given system of three reactions the coefficients Δa_S and Δb_S in equation (17) and the coefficients q and r in equation (18) depend only on the characteristics of the organism and the retort temperature on which the equivalent time differences and equivalent retort times are based.

Equation (16), with equations (17) and (18) respectively gives -

$$\begin{aligned} \Delta \theta_S &= k \Delta \theta_{S \text{ calc.}} \\ &= k \Delta a_S f_h + k \Delta b_S f_c \\ &= \Delta a'_S f_h + \Delta b'_S f_c \quad (19) \end{aligned}$$

$$\begin{aligned} \text{and } \Delta \theta_S &= -kq \Delta \theta_B + kr \Delta \theta_C \\ &= -Q \Delta \theta_B + R \Delta \theta_C \quad (20) \end{aligned}$$

where $\Delta a'_S$, $\Delta b'_S$, Q and R are constants equal to $k \Delta a_S$, $k \Delta b_S$, kq and kr respectively. These constants can be tabulated for a range of bacterial activation energies and retort temperatures.

If the reciprocal slopes f_h and f_o are to retain their meaning, the modification of equation (17) to give equation (19) can only be regarded as a somewhat arbitrary modification of the present analogue. This is because the bacterial equivalent time difference is calculated from a curve of the same form as the curve of best fit, but with decreased slopes of the heating and cooling curves, i.e. the heating and cooling curve slopes respectively are $\frac{1}{kf_h}$ and $\frac{1}{kf_o}$ instead of $\frac{1}{f_h}$ and $\frac{1}{f_o}$.

Equation (20), which was derived via equation (16) from equation (18), can be regarded as a modification of the shape of the curve of best fit. Although the equation of this modified best fit curve is not known, it is such that an analysis similar to that leading to the equation -

$$\theta_S = P \theta_A - Q \theta_B + R \theta_C \quad \dots\dots\dots (14) \text{ (p 189)}$$

will give the equation-

$$\theta_S = P \theta_A - Q \theta_B + R \theta_C \quad \dots\dots\dots (21)$$

where P is given by -

$$P - Q + R = 1 \quad \dots\dots\dots (22)$$

(see footnote below)

Regression equations (for the best estimate of $\Delta\theta_S$ for a given $\Delta\theta_{S \text{ calc.}}$) have been calculated by the method of least squares for the B.stearothermophilus and B.subtilis data. Values of the constant k of equation (16) are 1.0424 and 1.0802 respectively.

Equation (21) then becomes -

$$\theta_S = 1.2920 \theta_A - 3.5867 \theta_B + 3.2947 \theta_C \quad \dots\dots\dots (23)$$

Equation (22) is derived from consideration of an element of food which heats instantaneously to retort temperature and cools instantaneously to sublethal temperatures. All equivalent retort times θ_A , θ_B , θ_C and θ_S are equal. Equation (21) then becomes -

$$\theta_S = P \theta_S - Q \theta_S + R \theta_S$$

which gives -

$$P - Q + R = 1$$

and

$$\theta_S = 2.6663 \theta_A - 6.9138 \theta_B + 5.2475 \theta_C \dots\dots\dots (24)$$

for B.stearothermophilus and B.subtilis respectively.

- (iv) Error in equivalent retort time due to error in measurement of retort temperature.

Because an average retort temperature has been calculated for each run in the experimental work and a precisely known retort temperature has been assumed in the calculations on model processes, the effect of error in retort temperature has been minimized or eliminated.

In practice however, the equivalent retort times would be based on the rates of chemical reaction and spore destruction at the nominal retort temperature. A number of factors can cause this nominal retort temperature to be different from that actually obtaining in the retort, e.g. variation of temperature within the retort arising from inadequate venting, errors in temperature and pressure measurement and/or control, etc. Hence the effect of an error in retort temperature on the predicted equivalent retort time has been investigated.

Bacterial equivalent retort times are given by :

$$\hat{\theta}_S = P \theta_A - Q \theta_B + R \theta_C \dots\dots\dots (25)$$

and

$$\theta'_S = P \theta'_A - Q \theta'_B + R \theta'_C \dots\dots\dots (26)$$

where the equivalent retort times θ_A , θ_B , θ_C and θ_S are based on the nominal retort temperature (T_R) and the equivalent retort times

θ'_A , θ'_B , θ'_C and θ'_S are based on the actual retort temperature T'_R .

The error in θ_S is defined by -

$$\delta \theta_S = \hat{\theta}_S - \theta_S$$

where θ_S is the actual bacterial equivalent retort time (based on the nominal retort temperature) and $\hat{\theta}_S$ is the estimate of θ_S obtained using the incorrect retort temperature.

If δT is small ($\delta T = T'_R - T_R$), then -

$$\theta'_A = \theta_A + (1 + a_A \delta T) \dots \dots \dots (27)$$

$$\theta'_B = \theta_B + (1 + a_B \delta T) \dots \dots \dots (28)$$

$$\theta'_C = \theta_C + (1 + a_C \delta T) \dots \dots \dots (29)$$

$$\text{and } \theta'_S = \theta_S (1 - a_S \delta T) \dots \dots \dots (30)$$

where a_A , a_B etc. are the slopes of the rate of chemical reaction vs temperature or spore destruction rate vs temperature curves. The values of a_A , a_B , a_C , a_S for B.stearothermophilus and a_S for B.subtilis are 0.038, 0.051, 0.076, 0.125 and 0.173 $^{\circ}\text{F}^{-1}$ respectively.

Substitution for θ'_A , θ'_B and θ'_C in equation (26) gives -

$$\begin{aligned} \hat{\theta}_S &= P\theta'_A - Q\theta'_B + R\theta'_C \\ &+ (P a_A \theta'_A - Q a_B \theta'_B + R a_C \theta'_C) \delta T \\ &= \theta'_S + (P a_A \theta'_A - Q a_B \theta'_B + R a_C \theta'_C) \delta T \\ &= \theta_S + (P a_A \theta'_A - Q a_B \theta'_B + R a_C \theta'_C - a_S \theta_S) \delta T \end{aligned}$$

Therefore

$$\begin{aligned} \delta \theta_S &= \hat{\theta}_S - \theta_S \\ &= (P a_A \theta'_A - Q a_B \theta'_B + R a_C \theta'_C - a_S \theta_S) \delta T \end{aligned} \dots \dots \dots (27)$$

For B.stearothermophilus equation (27) is -

$$\delta \theta_S = (0.049 \theta'_A - 0.183 \theta'_B + 0.250 \theta'_C - 0.125 \theta_S) \delta T \dots \dots \dots (28)$$

and for B.subtilis the error $\delta \theta_S$ is given by -

$$\delta \theta_S = (0.101 \theta'_A - 0.353 \theta'_B + 0.399 \theta'_C - 0.173 \theta_S) \delta T \dots \dots \dots (29)$$

Equations (28) and (29) have been used to calculate the error in θ_S for runs 12, 13 and 14. Errors (expressed as percentages of θ_S) are shown

in table 18, for an actual temperature of 272.0°F and a nominal temperature of 273.0°F .

Table 18 : Errors in bacterial equivalent retort time due to error in measurement of retort temperature.

<u>Run</u> and can no.	<u>12</u> 3	<u>13</u> 3	<u>14</u> 3
<u>B. stearothermophilus</u>	-0.9	-1.7	-2.0
<u>B. subtilis</u>	-0.3	-3.4	-4.1

Error in temperature = $+1.0^{\circ}\text{F}$

Errors in bacterial equivalent retort times are expressed as percentages.

In traditional methods of process calculation an error of $+1^{\circ}\text{F}$ in retort temperature will give rise to errors of approximately -12.5% and -17.3% for B. stearothermophilus and B. subtilis respectively. The error in bacterial retort time due to error in retort temperature is less in the chemical analogue method than it is in traditional process calculations, because the alternating signs of equation (21) tend to cancel out the error.

(v) Integration with respect to volume.

Much of the discussion above applies only to single elements of food, or to containers in which the whole volume of food can be treated as a single element for the purposes of spore destruction calculations. In some products, such as conduction heating packs, it may be possible to estimate the lethal effect of heat on each element of food before integrating with respect to volume. In many other foods, however, this may not be possible, and the lethal effect of heat for the whole container may then have to be evaluated on the basis of mass average chemical measurements made on the well mixed bulk. The actual overall equivalent retort time $\bar{\theta}_g$ (based on the actual number of viable spores remaining in the container after processing) may not be identical to the equivalent retort time $\hat{\theta}_g$ calculated on the basis of chemical measure-

ments made on the well mixed bulk (i.e. $\bar{\theta}_A$, $\bar{\theta}_B$ and $\bar{\theta}_C$). Hence the equivalence of the actual overall equivalent retort time $\bar{\theta}_S$ and the chemical analogue overall equivalent retort time $\hat{\theta}_S$ has been investigated.

For any element of food, r , the bacterial equivalent retort time θ_{Sr} is given by :

$$\theta_{Sr} = P \theta_{Ar} - Q \theta_{Br} + R \theta_{Cr}$$

where θ_{Ar} , θ_{Br} and θ_{Cr} are the chemical equivalent retort times for the three reactions of element r .

The actual overall equivalent retort time θ_S is given by -

$$\bar{\theta}_S = -D_S \log \left[\frac{1}{n} \sum_{r=1}^n \log^{-1} \left(-\frac{\theta_{Sr}}{D_S} \right) \right] \dots\dots\dots (30)$$

$$= -D_S \log \left[\frac{1}{n} \sum_{r=1}^n \log^{-1} \left(-\frac{1}{D_S} (P \theta_{Ar} - Q \theta_{Br} + R \theta_{Cr}) \right) \right] \dots\dots\dots (31)$$

where n is the total number of elements of food considered and D is the decimal reduction time. Equation (30) is derived from equation (9) p 52, in which the integration with respect to volume is replaced by a summation over all n . Equations (32), (33) and (34) below are derived from equation (8) p 52, in a similar manner.

The chemical analogue overall equivalent retort time $\hat{\theta}_S$ is evaluated by the equation :

$$\hat{\theta}_S = P \bar{\theta}_A - Q \bar{\theta}_B + R \bar{\theta}_C.$$

The overall chemical equivalent retort times $\bar{\theta}_A$, $\bar{\theta}_B$ and $\bar{\theta}_C$ are given by the equations :

$$\bar{\theta}_A = -D_A \log \left[\frac{1}{n} \sum_{r=1}^n \log^{-1} \left(-\frac{\theta_{Ar}}{D_A} \right) \right] \dots\dots\dots (32)$$

$$\bar{\theta}_B = -D_B \log \left[\frac{1}{n} \sum_{r=1}^n \log^{-1} \left(-\frac{\theta_{Br}}{D_B} \right) \right] \dots\dots\dots (33)$$

$$\bar{\theta}_C = -D_C \log \left[\frac{1}{n} \sum_{r=1}^n \log^{-1} \left(-\frac{\theta_{Cr}}{D_C} \right) \right], \dots\dots\dots (34)$$

whence -

$$\begin{aligned} \hat{\theta}_S = & -PD_A \log \left[\frac{1}{n} \sum_{r=1}^n \log^{-1} \left(-\frac{\theta_{Ar}}{D_A} \right) \right] \\ & + QD_B \log \left[\frac{1}{n} \sum_{r=1}^n \log^{-1} \left(-\frac{\theta_{Br}}{D_A} \right) \right] \\ & - KD_C \log \left[\frac{1}{n} \sum_{r=1}^n \log^{-1} \left(-\frac{\theta_{Cr}}{D_C} \right) \right] \dots\dots\dots (35) \end{aligned}$$

Because the operations $\log$ and $\log^{-1}$ are not linear the actual overall equivalent retort time $\bar{\theta}_S$ and the chemical analogue overall equivalent retort time $\hat{\theta}_S$ as given by equations (31) and (35) respectively are not necessarily equivalent.

The differences between $\hat{\theta}_S$ and $\bar{\theta}_S$ will need to be investigated quantitatively before a three reaction analogue can be applied to products in which the lethal effect of heat on all elements is not identical. A method using model systems and calculated temperature vs time curve will probably be the best way of investigating the integration with respect to volume.

As the number of temperature vs time curves will be large in any extensive study, digital computation methods will almost certainly be required for both generation of the temperature vs time curves and integration of specific rate with respect to time, and with respect to volume.

CONCLUSIONS

AND

POTENTIAL APPLICATIONS OF THE CHEMICAL ANALOGUE

CONCLUSIONS

Theoretical Considerations

The conditions under which chemical reactions can be used to estimate spore destruction in a container of food depend on the activation energies and the decimal reduction times of the bacterial and chemical systems, and on the "heat-penetration" characteristics of the processed food.

If the activation energies of the bacterial and chemical systems are equal then the extent of a chemical reaction can be used as a direct measure of the extent of spore destruction in any small element of material, or in any container of material in which the temperature throughout is uniform at all instants. The chemical concentration change can be used as a measure of the spore reduction ratio for a container in which the instantaneous temperature distribution is not uniform, only if the bacterial and chemical decimal reduction times are equal, or if both the residual chemical reactant concentration and the spore reduction ratio are not functions of position in the can.

If the activation energies of the bacterial and chemical systems are not equal, then the residual chemical reactant concentration can be used to estimate the spore reduction ratio for any element of material only if the form of the temperature-time function for that element is known. The residual chemical reactant concentration can only be used as a measure of the mean spore reduction ratio for a whole container if the temperature-time functions of all elements of the material being processed are such that

$$\frac{\Theta_{\text{chem}}}{D_{\text{chem}}} = \frac{\Theta_{\text{bact}}}{D_{\text{bact}}}$$

is the same for all elements of volume. The equivalent retort time (Θ) of a process is the time required at retort temperature to bring about the same change in chemical reactant (or bacterial spore) concentration as does the process; D is the decimal reduction time, and the subscripts chem and bact refer to the chemical and bacterial systems respectively.

It is also shown that the mean residual chemical reactant concentration (or residual spore concentration) calculated from temperature data which has been measured at points fixed with respect to the container, is not identical to that occurring in the can if convective movement of the processed material takes place. However, a consideration of convective currents in the container (using simplified convection models for two types of convection) indicates that relationships do exist between the residual chemical reactant concentrations (or residual spore concentration) calculated using fixed point temperature data, and those actually obtained in convection heating products.

The Experiments

The acid hydrolysis of sucrose in buffered solution was chosen as the chemical reaction in this investigation.

(a) Static cans.

The convection model proposed for the static cans was not confirmed conclusively by the limited number of static can runs carried out. The deviations from the expected behaviour can be explained only in part by experimental errors. More work will be required to confirm or reject the validity of the model.

The relationship between the bacterial and chemical equivalent retort times is of the form -

$$\tau_{\text{bact}}^{\text{eq}} = \tau_{\text{chem}}^{\text{eq}} - \Delta\theta \quad \dots\dots\dots (1)$$

where $\Delta\theta$, the equivalent time difference, is a constant for any given process and pair of bacterial and chemical systems. The equivalent time difference is independent of the length of the process except for extremely short runs.

A logarithmic relationship appears to exist between the equivalent time differences and the activation energies, of different bacterial systems, i.e.

$$\frac{\Delta\theta_2}{\Delta\theta_1} = \frac{\log E_{A \text{ bact}} (2) - \log E_{A \text{ chem}}}{\log E_{A \text{ bact}} (1) - \log E_{A \text{ chem}}} \quad \dots\dots\dots (2)$$

It does not appear that any useful relationship exists between equivalent time differences calculated from the retort temperature vs time curve, and the equivalent time differences for the cans, i.e. the value of $\Delta\theta$ for a container cannot be determined from retort temperature vs time curves alone.

If the chemical reaction technique is used with temperature measurements, the uncertainty in equivalent retort time is about one quarter of the uncertainty which arises if temperature measurements alone are used.

It also appears that measurements on a model system (e.g. sucrose solution) can be applied to a real system (e.g. milk) if the physical properties (especially viscosity) are similar. If the physical properties are not similar (e.g. water and sucrose solution), significant errors arise.

(b) Agitated cans.

The convection model of complete mixing was confirmed by a comparison of the actual residual sucrose concentration and that calculated from temperature measurements. Differences between the actual and calculated equivalent retort times were seldom greater than 3%, and the mean difference was less than 0.4%.

Again the relationship between the chemical and bacterial equivalent retort times is of the form -

$$\theta_{\text{baot}} = \theta_{\text{chem}} - \Delta\theta$$

The equivalent time difference, $\Delta\theta$, was calculated for two different types of organism for all cans of a series of runs, with cans agitated in two different ways at four different speeds. Two lengths of process and two processing pressures were used.

The effect of type of organism on $\Delta\theta$ is very highly significant. The organism with the greater activation energy gives greater equivalent time differences than an organism with a lower activation energy. The

relationship between activation energy and equivalent time differences can be applied to the data of all agitated can runs without serious error.

It appears that the effect of processing pressure on Θ is not significant. This may be due to a fortuitous choice of process. Further work will be required to show whether this is so or not.

The effect of speed is to give the lowest equivalent time differences at speeds giving centrifugal acceleration, at the can centre, approximately equal to the acceleration due to gravity. The processes are such that a relatively low equivalent time difference is indicative of a high heat transfer rate, and hence this work confirms that of Clifcorn et al, (1950), and Conley et al, (1951).

Two types of rotation were studied. The difference between the equivalent time differences of tangentially rotated cans, and those of the radially rotated cans is small, but quite significant. No explanation of this effect has been found.

The effect of length of process is also quite significant, which is contrary to the effect expected from theoretical considerations. A number of possible reasons for this effect have been discussed. Further work will be needed, as examination of the experimental results does not give much indication of the cause of the anomaly.

A comparison of heat transfer coefficients for the agitated and static can runs indicates that the inside film heat transfer coefficient is the rate controlling factor in the static cans in the heating and in the cooling periods. The importance of the inside film heat transfer coefficient is much less in the air cooling periods of the processes.

Analysis of the equivalent time difference concept

This analysis uses model temperature vs time curves, calculated for a range of processes and can sizes using heat transfer coefficients based on the agitated can runs. The most important conclusion is that both type of process and the size of can have an important effect on equivalent time difference.

It is seen that an increase in can size generally increases the equivalent time difference. If the process is square (i.e. if the heating and cooling of the retort are both step changes in temperature), the equivalent time difference is proportional to the can volume-to-surface ratio. For processes with finite rates of heating and cooling of the retort the increase in equivalent time difference with increase in can size is somewhat less than proportional to the can volume-to-surface ratio.

The magnitude of the equivalent time difference tends to increase with an increase in the overall length of the heating and cooling periods of the retort.

It is seen that the most important phase of a process is the early part of the cooling period. In this period small variations in temperature have greater effects on both the equivalent time difference and the equivalent retort time. It is hence advantageous from the point of view of uniformity of processing, as well as from the point of view of precision of estimation of spore reduction ratios from chemical measurements, to keep the air cooling period as short as possible.

The analysis also shows that organisms with greater activation energies must have equivalent time differences greater than those organisms with lower activation energies. However, the quantitative relationship between activation energy and equivalent time difference (i.e. equation (2) above) is not explained. In fact, it appears that the relationship is not applicable, as it stands, to the data from the wider range of processes considered. The errors introduced by the use of the equation are small, and it should be possible to modify the relationship if it is found necessary to apply it to a wide range of processes.

Multiple Reaction Systems

The prediction of bacterial equivalent retort times using measurements on multiple reaction systems has been studied using the model temperature vs time curves which were calculated for the analysis of the equivalent time difference concept. Two hypothetical reactions, with

activation energies of 30 and 45 kcal/mole, were used along with the sucrose hydrolysis reaction ($E_A = 22.35$ kcal/mole).

If two reactions only are used (e.g. sucrose hydrolysis and the $E_A:30$ reaction) the bacterial equivalent retort time or equivalent time difference cannot be predicted satisfactorily without some knowledge of the temperature-time function or of heat transfer rate data. It is shown that this heat transfer rate data may be quite satisfactory for use with a two reaction system even if it is not precise enough for the direct calculation of equivalent retort times (as in traditional process calculation procedures).

If three reactions are used, then no heat transfer rate or can temperature vs time data is required for satisfactory prediction of bacterial equivalent retort times from measurements on chemical systems.

The two types of curve of best fit used to fit the chemical data, give predictions of bacterial equivalent retort time which are not significantly different.

An expression derived from the most widely applicable of these two types of best fit curve allows the bacterial equivalent retort time to be calculated directly, and has the added advantage that the error in the estimate of the bacterial equivalent retort time due to any uncertainties in the measurement of chemical equivalent retort times is very readily calculated.

Other sources of error have been considered (e.g. error in the measurement of retort temperature) and the three reaction analogue of spore destruction is shown to be much less affected by these errors than are traditional process calculation methods.

It is not known whether mean residual chemical reactant concentrations can be used to estimate mean residual spore concentrations for the whole container. However, definitive equations have been set up, and a method of investigation of this aspect of the three reaction analogue (using digital computation) has been suggested.

General Conclusions

The two major conclusions which can be drawn from this work are -

- (a) Chemical reaction systems can be used to evaluate the effect of product movement in a container on the total effect of heat on the product; and
- (b) Chemical reactions, used singly, in pairs, or in groups of three, can be used to estimate the total lethal effect of heat on the bacterial population of containers of food material. Various quantities of temperature-time data are required along with the chemical data of each method.

POTENTIAL APPLICATIONS OF THE CHEMICAL ANALOGUE

A number of applications of chemical reaction techniques arise directly from the methods discussed in this work. Among these are the following -

(a) Method for checking process calculation assumptions.

Single, double or triple reaction systems can be used to check the validity of various assumptions made in traditional process, calculation methods, e.g. the effect of product movement within the can, especially in products which heat partly by convection and partly by conduction. Products of this type include those with solid portions in liquid such as some canned fruits (in syrup) and vegetables (in brine) as well as soups and juices which exhibit "broken heating curves" as the material forms a gel.

Actual products, or model systems using for example carboxymethyl-cellulose to form a gel with some suitable reaction system, could be used to study the distribution or lethal effect of heat within a container heating by conduction. In this case samples could be taken from various parts of the material and analysed.

(b) The evaluation of new or modified processes.

The chemical reaction technique - especially the three reaction chemical analogue - could prove very useful in evaluating the total effect of heat of a process, particularly for continuous equipment in which measurements of can temperature are impossible. If chemical systems can be found which can be used in the actual food product, then the effect of changes in formulation of the product and variations between individual cans can be investigated.

(c) Trouble shooting and control techniques.

The chemical analogue in one of its different forms can be used to assist in evaluation of processing problems, such as uneven retort

heating (due to "air pockets") or fluctuations of pressure during a run. The method is much more sensitive to small changes in temperature than traditional procedure in which temperatures only are measured.

(d) Evaluation of effect of heat on vitamin losses etc.

Because the chemical analogue can be applied with confidence to systems which behave essentially as chemical reactions, the effect of heat on loss of nutritive value, changes in colour, flavour etc., can be readily evaluated. The chemical analogue technique will probably be most useful in comparison of processes which are equivalent from a bacterioid point of view, but which may have widely different effects on nutritive value and other heat sensitive factors.

In addition to the applications mentioned above, there are a number of other possible uses.

(e) Evaluation of the effect of heat in continuous flow systems.

In constant temperature flow systems the residence time distribution is important. Wang et al (1964) have observed that the actual spore destruction in a continuous flow system is less than that calculated assuming plug flow. If the temperature vs time curve of the processed material is not constant, e.g. as it passes through heat exchangers, then the residence time-temperature distribution becomes important. The chemical analogue technique, using a suitable convection model to take account of the residence time distribution and the heating and cooling curves of the equipment, will enable flow processes to be evaluated.

(f) Low temperature applications.

Some recent interest has been shown in the development of a device to measure the average temperature of chilled and frozen products during transport, and a device proposed for this purpose has measured an arithmetic mean temperature.

Because rate of spoilage of foodstuffs is more likely to be

described by an Arrhenius type of expression ~~rather~~ than a linear function of temperature, it is felt that measurement of suitable chemical reactions would give a better estimate of the effective mean temperature than a linear averaging device.

The chemical analogue technique could well be adapted to this application. The results would be expressed as an "effective mean temperature" rather than an equivalent time at some given temperature.

SYMBOLS AND DEFINITIONS

REFERENCES

AND

APPENDICES

SYMBOLS AND DEFINITIONS

A	A constant Concentration of component A Total surface area of can Angle of rotation of polarized light
A_0, A_1	Concentrations of component A at times t_0 and t_1 respectively
$\bar{A}$	Mass average concentration of component A in the can
a	A coefficient ($= \rho_h / f_h$) Radius of can
B	A constant ($= E_A / R T_R$) Symbol for type of organism Barometric height in mm. of mercury
B'	A constant ($= E_A / R T_0$)
b	A constant A coefficient ($= \rho_c / f_0$)
C	A constant Concentration of surviving organisms
C_a	Total concentration of acetate ion plus unionized acetic acid in solution
C_i, C_s	Concentrations of invert sugar and sucrose respectively (gm / 100 ml)
C_n	A constant
c	A constant ($= 2.303 / f_h$)
c_p	Specific heat

c_{pL}	Specific heat of liquid
D	Decimal reduction time Diameter of wire
D_A, D_N	Decimal reduction times of components A and N respectively
E_A	Activation energy
E'	A constant ($= E_A/R$)
$Ei(-x), \overline{Ei}(x)$	The exponential integral functions
F	"The number of minutes required to destroy an organism at 250°F" - Ball "The equivalent time in minutes at 250°F of all heat considered, with respect to its capacity to destroy spores and vegetative cells of a particular organism" - Stumbo A factor A function of time
F_c	The F value of all lethal heat received by the geometrical centre of the can during a process
F_λ	The F value of all lethal heat received by any point other than the geometrical centre of the can during a process
F_1	A factor used in calculation of $Ei(-x)$
f	A subscript used to denote the fixed point basis of calculation of mass average spore survival ratio Reciprocal of slope of a semilogarithmic heating or cooling curve
f_h	Reciprocal slope of a semilogarithmic heating curve

f_o	Reciprocal slope of a semilogarithmic cooling curve
G	A function of time
g	Acceleration due to gravity A factor involving Planck's and Boltzmann's constants The difference between the maximum can temperature and that of the retort
H	Rate of sucrose hydrolysis ($= \partial p_R / \partial \theta$)
H_o	Rate of sucrose hydrolysis at 212°F
H_R	Rate of sucrose hydrolysis at retort temperature
h	Heat transfer coefficient
I	Subscript denoting "indicated can temperature"
i	Square root of minus one
j	Lag factor for a semilogarithmic heating or cooling curve
K	Rate of hypothetical reaction at temperature T (see definition of H)
K_a	Dissociation constant of acetic acid
K_R	Rate of hypothetical reaction at retort temperature T_R
k	Slope of the $\Delta^{\theta} S$ model vs $\Delta^{\theta} S$ calc curve Rate of chemical reaction or spore destruction at any temperature, T ($= \partial \log N / \partial \theta)_T$) A constant Thermal conductivity
k_R	Rate of chemical reaction or spore destruction at retort temperature

k_L	Thermal conductivity of liquid
k_T	Rate of chemical reaction at T^0 absolute
k'	A constant ($= k [H^+]$)
L	Lethal rate (rate of destruction of spores) i.e. "reciprocal of the thermal death time (TDT)" - Ball, or "reciprocal of the decimal reduction time, D." - Stumbo Length of polarimeter tube
L_g	Lethal rate at temperature T_g
m	A temperature difference ($m+g = T_R - T_C$) Mass Subscript denoting moving element basis of calculation of mass average spore survival ratio
m_n	Mass of element n
N	Number of spores per unit volume
$\bar{N}$	Mean number of surviving spores per unit volume averaged over the whole container
N_0, N	Initial and final numbers of spores per unit volume respectively
Nu	Nusselt number ($= hD / k_L$)
n	An integer Total number of elements of volume
n_1	Number of surviving spores per layer
P	Symbol for pressure of processing A constant ($= k P$)
P_h, P_c	Ball's notation for his "percent sterility" function (heating and cooling phases of the process respectively)

Pr	Prandtl number ($= \alpha_{pL} \rho / k_L$)
p	A coefficient An integer ($0 < p < q$) Significance level
P_n	A parameter in the equation for $U(x, \rho)$
pR	Negative logarithm of the sucrose concentration reduction ratio ($= -\log_{10}(S_1/S_0)$)
Q	Total heat A constant ($= kq$)
q	Rate of heat transfer Number of time intervals in a process ($q_{\Delta \theta} = \theta_1 - \theta_0$)
q_n	A parameter in the series for $U(x, \rho)$
K	Universal gas constant A constant ($= kr$) Symbol for retort thermocouple Symbol for type of rotation
Re	Reynold's number ($= Du \rho_L / \mu$)
r	A coefficient An integer ($0 < r < n$)
r_n	A parameter in the series for $U(x, \rho)$
S	Surface area of can Sucrose concentration Symbol for speed
s	An integer ($0 < s < q$)
TDT	Thermal death time
T	Temperature Symbol for time of processing

T_c	Temperature of cooling water
T_{oc}	Temperature at which all rates of spore destruction and chemical reaction are negligible
T_g	Maximum can temperature ($= T_R - g$)
T_o	Initial can temperature
T	Can temperature at time
T_L	Liquid temperature
T_n	Temperature of element n in can
T_n, T_{n+1}	Can temperature at times θ_n, θ_{n+1} , respectively
T_R	Retort temperature
T_R'	An estimate of retort temperature
T_{Rn}, T_{Rn+1}	Retort temperature at times θ_n, θ_{n+1} , respectively
T_W	Temperature of thermocouple wire
t	Temperature in degrees centigrade
U_Δ	"Number of minutes required to destroy organism at retort temperature" - Ball; or "The equivalent, in minutes at retort temperature, of all lethal heat received by some designated point in the container" - Stumbo
	Overall heat transfer coefficient
U	A transformed temperature difference, i.e. error due to conduction of heat along a thermocouple wire ($= (T_L - T_W) / (T_R - T_o)$)
U_L	A transformed temperature difference giving temperature of liquid surrounding the thermocouple wire ($= (T_L - T_o) / (T_R - T_o)$)

U_o	Overall heat transfer coefficient
$\bar{U}_n (\theta)$	Eigenfunction transform of a transformed temperature difference
$\dot{\bar{U}}_n (\theta)$	Differential of $\bar{U}_n (\theta)$ with respect to time
u	A variable in the definition of the exponential integral functions A transformed temperature ($= T/T_R$ or T/T_o) (T , T_R , and T_o are absolute temperatures) Velocity of liquid past a thermocouple wire
u_o	Transformed temperature ($= (T_R - T_o) / T_R$) (T_R and T_o are absolute temperatures)
u_g	Transformed temperature ($= (T_R - g) / T_R$) (T_R is an absolute temperature)
u'	Transformed temperature based on T_o instead of T_R ($= T/T_o$, where T and T_o are absolute temperatures)
V	Volume of can
v	Volume
x	A variable Distance from can axis
y	A variable
$y_n (x), y_m (x)$	Eigenfunctions
$y'_n (x)$	First differential of $y_n (x)$ with respect to x
$y''_n (x)$	Second differential of $y_n (x)$ with respect to x

- z "Slope of thermal death time curve" - Ball
(Mathematically equal to the reciprocal of the slope of the thermal death time curve); or
"Degrees fahrenheit required for the thermal destruction curve to traverse one log cycle. Mathematically, equal to the reciprocal of the slope of the thermal destruction curve" - Stumbo
- α A parameter
A constant ($= \sqrt{4 U_0 / k d}$)
- $\alpha_A, \alpha_B, \alpha_C$ Slopes of the rate of reaction vs temperature curves for the reactions -
A $\rightarrow$ products,
B $\rightarrow$ products, and
C $\rightarrow$ products, respectively
- α_S Slope of the rate of spore destruction vs temperature curve
- α_0 Centrifugal acceleration at centre of the can
- β Rate of change of can temperature (per unit temperature difference ($= (1/\Delta T) \cdot (dT / d\theta)$))
A constant ($= \sqrt{\rho c_p / k}$)
- γ A parameter used in calculation of model temperature vs time curves ($= \beta \Delta T / (2 + \beta \Delta \theta)$)
- Δ A difference
First forward difference operator
- Δ^2 Second forward difference operator
- $\Delta\theta$ Equivalent time difference, i.e. the difference between the equivalent retort time for chemical reaction and that for spore destruction ($= \theta_{chem} - \theta_{bact}$) or the difference between the equivalent retort times for two chemical reaction systems of different energies ($= \theta_{chem} (1) - \theta_{chem} (2)$)

$\Delta\theta_1, \Delta\theta_2$	Equivalent time differences for two organisms, with activation energies of $E_{A \text{ baot (1)}}$ and $E_{A \text{ baot (2)}}$ respectively
$\Delta\theta_2'$	Estimate of $\Delta\theta_2$ using $\Delta\theta_1$ and activation energy data
$\Delta\theta$	A time interval
δT	An error in retort temperature ($= T_R' - T_R$)
$\delta\theta$	An error in the estimate of θ_S
e	Specific rate difference ($= H/H_R - L/L_R$ or $H/H_R - K/K_R$)
z (zeta)	Ball's early notation for decimal reduction time
θ	Equivalent retort time, i.e. time required at retort temperature to accomplish the same relative change in spore numbers or chemical reactant concentration as the process being considered.
$\theta_A, \theta_B, \theta_C$	Equivalent retort times for the reactions - $A \rightarrow \text{products,}$ $B \rightarrow \text{products, and}$ $C \rightarrow \text{products, respectively}$
θ_S	Equivalent retort time for destruction of spores
$\theta_{Ar}, \theta_{Br}, \theta_{Cr}, \theta_{Sr}$	Values of $\theta_A, \theta_B, \theta_C$ and θ_S respectively for element r
$\bar{\theta}_A, \bar{\theta}_B, \bar{\theta}_C, \bar{\theta}_S$	Mass average values of $\theta_A, \theta_B, \theta_C$ and θ_S respectively for the whole container
θ_r	Length of the holding time in a type II curve of best fit
θ_h, θ_c	Contribution of heating and cooling phases respectively of process of best fit (types I and II curve of best fit)
θ'	Equivalent retort time based on nominal retort temperature T'

$\hat{\sigma}_S$	An estimate of σ_S using an incorrect estimate of T_R (i.e. T_R')
$\hat{\mu}_S$	An estimate of the mass average bacterial equivalent retort time $\bar{\tau}_S$ using mass average chemical equivalent retort times $\bar{\tau}_A$, $\bar{\tau}_B$ and $\bar{\tau}_C$
τ	Time
θ_0, θ_1	Time at the beginning and end, respectively, of a process
θ_h, θ_c	Times during the heating and cooling periods, respectively, of a process
λ_n	A parameter $\left(= \frac{n^2 \pi^2}{4\alpha^2} + \alpha^2 \right)$
μ	Viscosity of liquid in can
ρ	Density
ρ_L	Density of liquid
σ	Standard deviation

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APPENDIX I

Comparison of Mass Average Survival Ratios, Calculated using Fixed Point and Moving Element Temperature Data

In traditional methods of process calculation, the total lethal effect of heat is calculated using temperature obtained at points fixed with respect to the container. In many products the material heats by convection, and the microorganisms the process is designed to destroy move about in the container, and may be subjected to temperature histories quite different in form from those measured at fixed points.

In this analysis, a simplified process is set up in which the positions and temperatures of n moving elements are known. The total lethal effect of heat is calculated for each moving element, and the mass average spore survival ratio $\left(\frac{\bar{N}}{N_0}\right)_m$ for the whole can is then obtained by averaging over all elements of volume.

Because the positions of all elements are known, the temperatures at n points in the can (corresponding to the n moving elements at any instant) are known. These temperatures are used to calculate the mass average spore survival ratio $\left(\frac{\bar{N}}{N_0}\right)_f$ on the assumption that no product movement takes place. The moving element spore survival ratio $\left(\frac{\bar{N}}{N_0}\right)_m$ and the fixed point spore survival ratio $\left(\frac{\bar{N}}{N_0}\right)_f$ are then compared.

The container of food is divided into n elements of equal volume. The process is considered to consist of q short time intervals (of length $\delta\theta$), and the temperatures of all elements are considered to be constant during each time interval. The absolute temperature of element r during the interval θ_p to θ_{p+1} (where $\theta_{p+1} = \theta_p + \delta\theta$) is denoted by $T_{r,p}$, and the temperature of element s during the interval θ_{p+1} to θ_{p+2} is given by $T_{s,p+1}$, etc.

If $N_{r,p}$ denotes the concentration of spores in element r at time θ_p , and $N_{r,p+1}$ denotes the concentration at time θ_{p+1} , then the reduction in the interval θ_p to θ_{p+1} is $N_{r,p+1}/N_{r,p}$.

For bacterial systems in which the destruction of spores is first order, $\log_e \frac{N_{r,p+1}}{N_{r,p}} = -k(T_{r,p}) \delta \theta$,

where $k(T_{r,p})$ is the rate constant for destruction of spores at temperature $T_{r,p}$.

$$\text{Hence } \frac{N_{r,p+1}}{N_{r,p}} = \exp(-k(T_{r,p}) \delta \theta)$$

The Arrhenius equation gives -

$$k(T_{r,p}) = A \exp\left[-\frac{E'}{T_{r,p}}\right]$$

$$\text{where } E' = \frac{E_A}{R}$$

Hence -

$$\frac{N_{r,p+1}}{N_{r,p}} = \exp\left[-A \delta \theta \exp\left(-\frac{E'}{T_{r,p}}\right)\right].$$

If the initial uniform spore concentration is N_0 , then the residual spore concentration in element r at the end of the process (i.e. at time θ_q) is given by -

$$\begin{aligned} N_{r,q} &= N_0 \prod_{p=0}^{q-1} \frac{N_{r,p+1}}{N_{r,p}} \\ &= N_0 \prod_{p=0}^{q-1} \exp\left[-A \delta \theta \exp\left(-\frac{E'}{T_{r,p}}\right)\right] \\ &= N_0 \exp\left[-A \delta \theta \sum_{p=0}^{q-1} \exp\left(-\frac{E'}{T_{r,p}}\right)\right] \end{aligned}$$

..... (1)

The mass average spore survival ratio is then given by -

$$\left(\frac{\bar{N}}{N_0}\right)_m = \frac{1}{n} \sum_{r=1}^n \exp \left[-A \delta \theta \sum_{p=0}^{q-1} \exp \left(\frac{-E'}{T_{r,p}} \right) \right] \dots \dots \dots (2)$$

The effect of product movement can be evaluated by consideration of the simple process in which all elements of fluid remain stationary for the entire process, except for elements k and l which are interchanged during the interval θ_s to θ_{s+1} . The mass average spore survival ratio based on the fixed point temperature data (i.e. $\frac{\bar{N}}{N_0}_f$) is then calculated from the same temperature data as used for the calculation of $\frac{\bar{N}}{N_0}_m$, except that $T_{k,s}$ replaces $T_{l,s}$ and vice versa.

If each of the n fixed points at which the temperatures are measured take the number of the moving element corresponding to it in the first time interval (i.e. θ_0 to θ_1) then for all fixed points except points k and l .

$N'_{r,q} = N_{r,q}$ where $N'_{r,q}$ is the residual spore concentration in element r calculated on the fixed point basis.

For element k -

$$\begin{aligned} N'_{k,s} &= N_{k,s} \\ &= N_0 \exp \left[-A \delta \theta \sum_{p=0}^{s-1} \exp \left(\frac{-E'}{T_{k,p}} \right) \right] \end{aligned}$$

whence -

$$\begin{aligned} N'_{k,s+1} &= N_0 \exp \left[-A \delta \theta \sum_{p=0}^{s-1} \exp \left(\frac{-E'}{T_{k,p}} \right) \right. \\ &\quad \left. + A \delta \theta \exp \left(\frac{-E'}{T_{l,s}} \right) \right] \end{aligned}$$

The residual spore concentration ($N'_{k,q}$) at point k is then given by -

$$\begin{aligned}
 N'_{k,q} &= N_0 \exp \left[-A \delta \theta \sum_{\substack{p=0 \\ p \neq s}}^{q-1} \exp \left(\frac{-E'}{T_{k,p}} \right) \right. \\
 &\quad \left. - A \delta \theta \exp \left(\frac{-E'}{T_{1,s}} \right) \right] \\
 &= N_0 \exp \left[-A \delta \theta \sum_{p=0}^{q-1} \exp \left(\frac{-E'}{T_{k,p}} \right) \right. \\
 &\quad \left. + A \delta \theta \exp \left(\frac{-E'}{T_{k,s}} \right) - A \delta \theta \exp \left(\frac{-E'}{T_{1,s}} \right) \right] \\
 &\dots\dots\dots (3)
 \end{aligned}$$

Similarly the residual spore concentration at point 1 (i.e. $N'_{1,q}$) is given by -

$$\begin{aligned}
 N'_{1,q} &= N_0 \exp \left[-A \delta \theta \sum_{p=0}^{q-1} \exp \left(\frac{-E'}{T_{1,p}} \right) \right. \\
 &\quad \left. + A \delta \theta \exp \left(\frac{-E'}{T_{1,s}} \right) - A \delta \theta \exp \left(\frac{-E'}{T_{k,s}} \right) \right] \\
 &\dots\dots\dots (4)
 \end{aligned}$$

The mass average spore survival ratio based on fixed point temperature data (i.e. $\left(\frac{\bar{N}}{N_0} \right)_f$) can be expressed in a form similar to the equation for $\left(\frac{\bar{N}}{N_0} \right)_m$ i.e. equation (2). The expression, however, is rather large, and does not facilitate the comparison of the two quantities $\left(\frac{\bar{N}}{N_0} \right)_m$ and $\left(\frac{\bar{N}}{N_0} \right)_f$. Instead the difference between the two spore survival ratios, which depends only on the residual spore concentration in elements k and 1 , is considered.

This difference is given by -

$$\begin{aligned} \left(\frac{\bar{N}}{\bar{N}_0} \right)_m - \left(\frac{\bar{N}}{\bar{N}_0} \right)_f &= \frac{1}{n \bar{N}_0} (N_{k,q} + N_{l,q}) \\ &- \frac{1}{n \bar{N}_0} (N'_{k,q} + N'_{l,q}). \end{aligned}$$

The difference will be zero if -

$$\Delta = (N_{k,q} + N_{l,q}) - (N'_{k,q} + N'_{l,q}) = 0.$$

Equations (1) (with $r=k$) and (3) above give -

$$\begin{aligned} N'_{k,q} &= N_{k,q} F \\ \text{where} \quad F &= \exp \left[A \delta \theta \exp \left(\frac{-E'}{T_{k,s}} \right) \right. \\ &\quad \left. - A \delta \theta \exp \left(\frac{-E'}{T_{l,s}} \right) \right] \end{aligned}$$

Similarly equations (1) (with $r=l$) and (4) give -

$$N'_{l,q} = N_{l,q} \frac{1}{F}.$$

$$\begin{aligned} \text{Thus -} \quad \Delta &= N_{k,q} + N_{l,q} - N_{k,q} F - N_{l,q} \frac{1}{F} \\ &= N_{k,q} (1-F) - N_{l,q} \left(\frac{1-F}{F} \right) \\ &= \left(N_{k,q} - N_{l,q} \frac{1}{F} \right) (1-F) \end{aligned}$$

Hence Δ is zero if $F=1$ or if $F = \frac{N_{l,q}}{N_{k,q}}$

The first condition obtains if $T_{1,s} = T_{k,s}$.

The second condition obtains if $N_{1,q}$, $N_{k,q}$, $T_{k,s}$ and $T_{1,s}$ are such that -

$$\begin{aligned} N_{k,q} \exp \left[A \delta \eta \exp \left(\frac{-E'}{T_{k,s}} \right) \right] \\ = N_{1,q} \exp \left[A \delta \eta \exp \left(\frac{-E'}{T_{1,s}} \right) \right] \end{aligned}$$

Because the $T_{1,s}$, $T_{k,s}$ etc. are independent of each other, Δ is not necessarily equal to zero. Hence the mass average spore survival ratios calculated on the two bases (i.e. fixed point and moving element) are not necessarily identical.

In this analysis only, one pair of elements have been interchanged. Any desired convection pattern can be approximated to by multiple interchanges of pairs of elements, and hence the non-equivalence of the two bases of calculation of mass average spore survival ratio as shown above can be extended to a general process.

The analysis can also be applied to chemical reactions, if N , the concentration of spores is replaced by C the concentration of a chemical reactant.

APPENDIX II

Calculation of Equivalent Retort Time for Linear Processes

Equivalent retort time is defined (see p 42) as the integral (with respect to time) of specific spore destruction rate or specific chemical reaction rate;

$$\begin{aligned} \text{i.e.} \quad \tau &= \int_{\theta_0}^{\theta_1} \frac{k}{k_R} d\theta \\ &= \int_{\theta_0}^{\theta_1} \frac{B(1 - \frac{1}{u})}{e} d\theta \end{aligned}$$

The simplest expression of a linear process is -

$$u = \frac{\theta}{a},$$

whence $\frac{B}{u} = \frac{a}{\theta}.$

A change of variable in the integral such that

$$x = \frac{aB}{\theta}$$

leads to -

$$\tau = -aBe^B \int_{x_0}^{x_1} \frac{e^{-x}}{x^2} dx$$

where $x_0 = \infty$

and $x_1 = \frac{B}{u_1}$

This gives -

$$\begin{aligned}
 \Theta &= aBe^B \left[\frac{e^{-x}}{x} \right]_{\frac{B}{u_1}}^{\frac{B}{u_1}} + aBe^B \int_{\infty}^{\frac{B}{u_1}} \frac{e^{-x}}{x} dx \\
 &= au_1 e^{B(1 - \frac{1}{u_1})} + aBe^B \text{Ei}(-\frac{B}{u_1}) \\
 &= au_1 e^{B(1 - \frac{1}{u_1})} (1 - F_1) \dots\dots\dots (1)
 \end{aligned}$$

The function $-\text{Ei}(-x)$ is known as the exponential integral.

Values of this function are tabulated (e.g. Jahnke and Emde (1945), Korn and Korn (1961) for $x < 15$. For $x > 15$ equation (1) above is used. The value of F_1 is tabulated for $15 < x < 40$, and for $x > 40$ it is calculated from the semi-convergent series

$$F_1 = 1 - \frac{1!}{x} + \frac{2!}{x^2} - \frac{3!}{x^3} + \dots\dots\dots$$

APPENDIX III ACalculation of pR vs A Table

For sucrose

$$\alpha_{20}^D = 66.462 + 0.0087 C_s - 0.000235 C_s^2$$

For invert sugar (the equimolar mixture of glucose and fructose)

$$\alpha_{20}^D = - (19.415 + 0.07065 C_i - 0.00054 C_i^2)$$

$$\text{and } \alpha_t^D = \alpha_{20}^D + (0.238 + 0.0014 C_i) (t-20)$$

(Kaye and Laby (1959))

For sucrose we have -

$$\alpha_t^D = \alpha_{20}^D (1 + 0.000184 (t-20))$$

(Honig (1963))

The respective concentrations of sucrose and invert sugar (in gm/100 ml) are C_s and C_i , and α_t^D is the specific rotation of the solution (sodium D line of the spectrum) at a temperature of $t^\circ\text{C}$.

$$0.750 \text{ M sucrose solution} = 25.673 \text{ gm/100 ml.}$$

$$0.750 \text{ M invert sugar} = 27.024 \text{ gm/100 ml.}$$

$$\text{Therefore } C_i = 27.024 \left(1 - \frac{C_s}{25.673} \right) \dots\dots\dots (1)$$

At 25°C we have -

$$\begin{aligned} 100 \frac{A}{L} &= 66.532 C_s + 0.0087 C_s^2 - 0.000235 C_s^3 \\ &- 18.000 C_i - 0.0635 C_i^2 + 0.00054 C_i^3 \\ &\dots\dots\dots (2) \end{aligned}$$

Solution of equations (1) and (2) for a 200 mm polarimeter tube leads to -

$$A = -10.4452 + 1.7571 C_s - 0.032663 C_s^2 - 0.041730 C_s^3$$

Values of A have been calculated for values of C_s between 0 and 26 gm/100 ml and, by interpolation, a table of C_s against A has been prepared. From this table, the table of pR (= $-\log_{10} C_s/C_{s0}$) against A has been calculated. Because the calculation is rather laborious the pR vs A table is presented herein.

APPENDIX IVCalculation of the Acetic acid - Sodium acetate Buffer

Sodium, acetate, hydrogen and hydroxyl ions (Na^+ , Ac^- , H^+ , and OH^- respectively) and undissociated acetic acid (HAc) are present in the buffer solution. The hydrogen ion concentration is given approximately* by -

$$[\text{H}^+] = \frac{[\text{HAc}] K_a}{[\text{Ac}^-]} \quad \dots\dots\dots (1)$$

where K_a is the dissociation constant of the acid, and square brackets denote concentration.

Electrical neutrality of the solution gives the relationship -

$$[\text{H}^+] + [\text{Na}^+] = [\text{Ac}^-]$$

because the hydroxyl ion concentration $[\text{OH}^-]$ in acid solution is negligibly small.

Hence -

$$[\text{H}^+] = \frac{(C_a - [\text{H}^+] - [\text{Na}^+]) K_a}{[\text{H}^+] + [\text{Na}^+]} \quad \dots\dots\dots (2)$$

where C_a is the total acetate concentration in the solution.

Interaction of the can with the unbuffered solution had the effect of increasing the pH, i.e. the interaction is equivalent to the addition of hydroxyl ions to the solution.

- * This analysis is approximate in that equation (1) only applies strictly in dilute solutions. Deviations from this simple form, along with variation of the dissociation constant K_a with temperature are almost certainly the reason for the observed non-linearity of the $\log \text{H}/\text{H}_0$ vs $1/T$ curve.

The addition of δM gm-ions of hydroxyl ion per litre (as NaOH) has the effect of increasing the sodium ion concentration by δM gm-ions per litre. The concentration of hydroxyl ions remains negligibly small.

The effect on hydrogen ion concentration of the addition of M gm-ions of hydroxyl ion per litre is therefore given by -

$$\delta[H^+] = -\frac{d[H^+]}{d[Na^+]} \delta M \quad \dots\dots\dots (3)$$

Differentiation of equation (1) with respect to $[Na^+]$ leads to -

$$\frac{d[H^+]}{d[Na^+]} = -\frac{\frac{[H^+]}{2[H^+]} + \frac{K_a}{[Na^+] + K_a}}{\dots\dots\dots (4)}$$

The rate of hydrolysis of sucrose is directly proportional to the hydrogen ion concentration. Hence if the maximum tolerable change in the rate of hydrolysis is 1%, then $\delta[H^+] = -3.16 \cdot 10^{-6}$ gm-ion/litre. ($[H^+] = 3.16 \cdot 10^{-4}$ gm-ion/litre at pH 3.5).

Changes in the pH of unbuffered sucrose solution in laquered cans are equivalent to the addition of approximately 1.3×10^{-4} gm-moles of NaOH per litre.

$$\text{i.e. } \delta M = 1.3 \cdot 10^{-4} \text{ gm-ions/litre.}$$

Hence -

$$\frac{d[H^+]}{d[Na^+]} = -\frac{\delta[H^+]}{\delta M} = -\frac{3.16 \cdot 10^{-6}}{1.3 \cdot 10^{-4}} = -2.43 \cdot 10^{-2}$$

Substitution of the values of $[H^+]$, K_a (K_a for acetic acid = $1.82 \cdot 10^{-5}$ gm-moles/litre) and $\frac{d[H^+]}{d[Na^+]}$ in equations (2) and (4) give -

$$C_a = 0.231 M$$

$$\text{and } [Na^+] = 0.132 M$$

A total acetate concentration of 0.250 M was chosen. The corresponding sodium ion concentration is 0.0143 M.

All buffer was prepared in a concentrated form, and diluted 1 part in 8 (by volume) before use. The concentrations in the stock buffer solution were -

acetic acid	2.00 M, and
sodium hydroxide	0.1144 M

The buffered sucrose solutions were made up by weight. The quantities required per litre of solution are -

256.7 gm	sucrose
127.5 gm	buffer
<u>714.8 gm</u>	<u>water</u>
1099.0 gm	total

The alternative method of preparing the buffer from acetic acid and sodium acetate was not used as the end point of the titration of sodium acetate with hydrochloric acid (Kolthoff and Steager (1954) Vol. II, p.152 using thymol blue as indicator) is not very sharp, even with concentrations up to 1N.

APPENDIX V

SPECIFIC SUCROSE HYDROLYSIS RATE

(RATE AT 212°F = 1.00)

T (°F)	0	1	2	3	4	5	6	7	8	9
120	0.00	0	0	0	1	1	1	1	1	1
130	0.01	1	1	1	1	1	1	1	1	2
140	0.02	2	2	2	2	2	2	3	3	3
150	0.03	3	4	4	4	4	5	5	5	6
160	0.06	6	7	7	8	8	9	9	10	10
170	0.11	12	12	13	14	15	16	16	17	18
180	0.19	21	22	23	24	26	27	28	30	32
190	0.33	35	37	39	41	43	45	48	50	53
200	0.56	59	62	65	68	71	75	79	82	87
210	0.91	95	100	105	110	115	121	127	132	139
220	1.45	152	159	166	174	182	190	198	207	217
230	2.26	236	247	257	269	281	292	305	318	332
240	3.46	360	375	391	407	424	442	460	478	498
250	5.18	539	560	583	606	630	654	680	706	734
260	7.62	791	827	853	885	919	953	989	1025	1064
270	11.03	1143	1185	1228	1272	1318	1365	1414	1464	1515

APPENDIX VIASolution of the Equation for Heating of the Thermocouple Junction by Conduction along the Wire.

The derivation of the partial differential equation for heat conduction along a wire is shown in figure 14 (p 82). This equation is -

$$\left(\frac{\partial^2 U(x, \theta)}{\partial x^2} \right)_{\theta} - \alpha^2 (U(x, \theta) - U_L(\theta)) = \beta^2 \left(\frac{\partial U(x, \theta)}{\partial \theta} \right)_x \dots \dots \dots (1)$$

where $U(x, \theta)$ is the temperature of the wire at time θ and position x .

The condition that the temperature of the wire at time $\theta = 0$ is equal to the initial temperature of the fluid T_0 , gives -

$$U(x, 0) = 0$$

The boundary conditions obtaining at each end of the wire (i.e. $T = T_R$ for all time θ greater than zero) gives -

$$U(\pm a, \theta) = 1$$

The temperature of the fluid heating the thermocouple wire is assumed to approach retort temperature exponentially, i.e.

$$U_L(\theta) = 1 - e^{-\alpha \theta}$$

The method of solution of equation (1) (due to J. Gamlen) uses eigenfunction transforms. In this solution a bar ($-$) is used to denote the eigenfunction transform of a function, and primes ($'$) and dots ($\dot{}$) are used to denote differentials with respect to position x and time θ respectively.

The eigenfunctions of the problem

$$y_n''(x) + (\lambda_n - \alpha^2) y_n(x) = 0 \quad \dots\dots\dots (2)$$

$$(y(-a) = y(a) = 0)$$

are

$$y_n(x) = \sin \sqrt{\lambda_n - \alpha^2} \cdot (x + a)$$

where

$$\sqrt{\lambda_n - \alpha^2} = \frac{n\pi}{2a}$$

i.e.

$$\lambda_n = \frac{n^2\pi^2}{4a^2} + \alpha^2$$

These eigenfunctions form a base for analytic functions in the interval $-a$ to a .

Hence

$$U(x, \theta) = C + \sum_1^{\infty} a_n y_n(x)$$

The boundary condition, $U(\pm a,) = 1$, gives $C = 1$ as the $y_n(x)$ vanish at $x = \pm a$,

i.e.

$$U(x, \theta) = 1 + \sum_1^{\infty} a_n y_n(x) \quad \dots\dots\dots (3)$$

These eigenfunctions are orthogonal,

$$\text{i.e.} \quad \int_{-a}^a y_n(x) y_m(x) dx = 0 \quad (m \neq n)$$

and

$$\int_{-a}^a y_n(x) y_m(x) dx = a \quad (m = n)$$

Multiplication of equation (3) by $y_n(x)$ followed by integration with respect to x between $-a$ and a gives -

$$\int_{-a}^a U(x, \theta) y_n(x) dx = \int_{-a}^a y_n(x) dx + a_n \int_{-a}^a y_n^2(x) dx$$

whence

$$\begin{aligned} a_n &= \frac{1}{a} \int_{-a}^a U(x, \theta) y_n(x) dx - \frac{1}{a} \int_{-a}^a y_n(x) dx \\ &= \frac{1}{a} \int_{-a}^a U(x, \theta) y_n(x) dx - \frac{1}{a} \int_{-a}^a \sin \frac{n\pi}{2a} (x+a) dx \\ &= \frac{1}{a} \int_{-a}^a U(x, \theta) y_n(x) dx + \frac{2}{n\pi} \left[\cos \frac{n\pi}{2a} (x+a) \right]_{-a}^a \\ &= \frac{1}{a} \int_{-a}^a U(x, \theta) y_n(x) dx + \frac{2}{n\pi} (\cos n\pi - 1). \end{aligned}$$

Hence

$$a_n = \frac{1}{a} \int_{-a}^a U(x, \theta) y_n(x) dx \quad \text{for all even } n$$

and

$$a_n = \frac{1}{a} \int_{-a}^a U(x, \theta) y_n(x) dx - \frac{4}{n\pi} \quad \text{for all odd } n.$$

Therefore

$$U(x, \theta) = 1 + \frac{1}{a} \sum_1^{\infty} \bar{U}_n(\theta) y_n(x) - \sum_{\text{odd } n}^{\infty} \left(\frac{4}{n\pi} \right) y_n(x) \dots (4),$$

where

$$\bar{U}_n(\theta) = \int_{-a}^a U(x, \theta) y_n(x) dx.$$

An ordinary differential equation in $\bar{U}_n(\theta)$ can now be obtained.

$$\begin{aligned}
\int_{-a}^a \frac{\partial^2 U(x, \theta)}{\partial x^2} y_n(x) dx &= \left[y_n(x) \frac{\partial U(x, \theta)}{\partial x} \right]_{-a}^a - \int_{-a}^a \frac{\partial U(x, \theta)}{\partial x} y_n'(x) dx \\
&= 0 - \left[U(x, \theta) y_n'(x) \right]_{-a}^a \\
&\quad + \int_{-a}^a U(x, \theta) y_n''(x) dx \\
&= \left[y_n'(x) \right]_{-a}^a - (\lambda_n - \alpha^2) \int_{-a}^a U(x, \theta) y_n(x) dx
\end{aligned}$$

because $U(\pm a, \theta) = 1$ and $y_n''(x) = -(\lambda_n - \alpha^2) y_n(x)$.

Therefore

$$\begin{aligned}
\int_{-a}^a \left(\frac{\partial^2 U(x, \theta)}{\partial x^2} - \alpha^2 U(x, \theta) \right) y_n(x) dx \\
= \left[y_n'(x) \right]_{-a}^a - \lambda_n \bar{u}_n(\theta) \quad \dots\dots\dots (5)
\end{aligned}$$

Equation (5) with equation (1) then gives -

$$\begin{aligned}
\int_{-a}^a \beta^2 \frac{\partial U(x, \theta)}{\partial \theta} y_n(x) dx - \int_{-a}^a \alpha^2 U_L(\theta) y_n(x) dx \\
= \left[y_n'(x) \right]_{-a}^a - \lambda_n \bar{u}_n(\theta).
\end{aligned}$$

$$\begin{aligned}
\text{Now } \int_{-a}^a \beta^2 \frac{\partial U(x, \theta)}{\partial \theta} y_n(x) dx &= \beta^2 \frac{d}{d\theta} \bar{u}_n(\theta) \\
&= \beta^2 \dot{\bar{u}}_n(\theta),
\end{aligned}$$

$$\text{and } \int_{-a}^a \alpha^2 U_L(\theta) y_n(x) dx = \alpha^2 U_L(\theta) \int_{-a}^a y_n(x) dx$$

Therefore

$$\beta^2 \dot{\bar{u}}_n(\theta) - \alpha^2 u_L(\theta) \int_{-a}^a y_n(x) dx = \left[y_n'(x) \right]_{-a}^a - \lambda_n \bar{u}_n(\theta)$$

i.e.

$$\begin{aligned} \dot{\bar{u}}_n(\theta) + \frac{\lambda_n}{\beta^2} \bar{u}_n(\theta) &= \frac{1}{\beta^2} \left[\frac{d}{dx} \sin \frac{n\pi}{2a} (x+a) \right]_{-a}^a \\ &\quad + \frac{\alpha^2}{\beta^2} u_L(\theta) \int_{-a}^a \sin \frac{n\pi}{2a} (x+a) dx \\ &= - \left[\frac{2a}{n\pi} \frac{\alpha^2}{\beta^2} u_L(\theta) + \frac{n\pi}{2a\beta^2} \right] \left[\cos \frac{n\pi}{2a} (x+a) \right]_{-a}^a \end{aligned}$$

Because $\left[\cos \frac{n\pi}{2a} (x+a) \right]_{-a}^a$ is equal to 0 for all even n

and is equal to -2 for all odd n , two differential equations in $\bar{u}_n(\theta)$ are obtained.

These equations are -

$$\dot{\bar{u}}_n(\theta) + \frac{\lambda_n}{\beta^2} \bar{u}_n(\theta) = 0 \quad (\text{for } n \text{ even}) \quad \dots\dots\dots (6)$$

and

$$\begin{aligned} \dot{\bar{u}}_n(\theta) + \frac{\lambda_n}{\beta^2} \bar{u}_n(\theta) &= \frac{n\pi}{a\beta^2} + \frac{4a\alpha^2}{n\pi\beta^2} u_L(\theta) \\ &= \frac{n\pi}{a\beta^2} + \frac{4a\alpha^2}{n\pi\beta^2} - \frac{4a\alpha^2}{n\pi\beta^2} e^{-c\theta} \end{aligned}$$

i.e.

$$\dot{\bar{u}}_n(\theta) + p_n \bar{u}_n(\theta) = q_n - r_n e^{-c\theta} \quad (\text{for } n \text{ odd}) \quad \dots\dots\dots (7)$$

where

$$p_n = \frac{\lambda_n}{\beta^2} = \frac{n^2\pi^2}{4a^2\beta^2} + \frac{\alpha^2}{\beta^2}$$

$$q_n = \frac{n\pi}{a\beta^2} + \frac{4a\alpha^2}{n\pi\beta^2}$$

and

$$r_n = \frac{4a\alpha^2}{n\pi\beta^2}.$$

Equation (6) gives -

$$\bar{U}_n(\theta) = C e^{-P_n \theta}$$

The initial condition $U(x, 0) = 0$ gives $\bar{U}_n(0) = 0$

Hence $C = 0$ and $\bar{U}_n(\theta) = 0$ for all even n

Equation (7) gives -

$$\frac{d}{d\theta} (e^{P_n \theta} \bar{U}_n(\theta)) = q_n e^{P_n \theta} - r_n e^{(P_n - c)\theta}$$

Hence

$$e^{P_n \theta} \bar{U}_n(\theta) = \frac{q_n}{P_n} e^{P_n \theta} - \frac{r_n}{P_n - c} e^{(P_n - c)\theta} + C$$

Again

$$\bar{U}_n(0) = 0$$

This gives $C = \frac{r_n}{P_n - c} - \frac{q_n}{P_n}$

whence

$$\bar{U}_n(\theta) = \frac{q_n}{P_n} - \left(\frac{r_n}{P_n - c} \right) e^{-c\theta} + \left(\frac{r_n}{P_n - c} - \frac{q_n}{P_n} \right) e^{-P_n \theta}$$

for all odd n .

Substitution for $\bar{U}_n(\theta)$ in equation (4) gives -

$$U(x, \theta) = 1 + \frac{1}{a} \sum_{\substack{n=1 \\ (\text{odd } n)}}^{\infty} \left(\frac{q_n}{P_n} - \left(\frac{r_n}{P_n - c} \right) e^{-c\theta} + \left(\frac{r_n}{P_n - c} - \frac{q_n}{P_n} \right) e^{-P_n \theta} \right) \sin \frac{n\pi}{2a} (x+a)$$

$$= \frac{1}{a} \sum_{\substack{n=1 \\ (\text{odd } n)}}^{\infty} \frac{4g}{n\pi} \sin \frac{n\pi}{2a} (x+a) \dots \dots \dots (8).$$

Equation (8) could be used to calculate the temperature of the wire at any time θ and position x , and hence the error due to heat conduction (i.e. $U_\Delta(x, \theta)$) could be calculated.

Alternatively an expression can be derived from which the error may be calculated directly.

An analysis similar to that leading to equation (4) gives the expression -

$$u_{\Delta}(x, \theta) = \frac{1}{a} \sum_1^{\infty} \bar{u}_{n\Delta}(\theta) y_n(x)$$

where $\bar{u}_{n\Delta}(\theta) = \bar{u}_n(\theta) - \bar{u}_{nL}(\theta)$

(The value of the constant is zero in this case as the initial temperatures of the wire and fluid are equal, giving $u_{\Delta}(x, 0) = 0$ and hence $\bar{u}_{n\Delta}(0) = 0$.)

Now

$$u_L(\theta) = 1 - e^{-c\theta}$$

Therefore

$$\begin{aligned} \bar{u}_{nL}(\theta) &= \int_{-a}^a (1 - e^{-c\theta}) y_n(x) dx \\ &= (1 - e^{-c\theta}) \int_{-a}^a \sin \frac{n\pi}{2a} (x+a) dx \end{aligned}$$

Hence, when n is even

$$\bar{u}_{nL}(\theta) = 0$$

and when n is odd

$$\bar{u}_{nL}(\theta) = \frac{4a}{n\pi} (1 - e^{-c\theta})$$

Thus

$$u_{\Delta}(x, \theta) = \frac{1}{a} \sum_{\substack{n=1 \\ (\text{odd } n)}}^{\infty} \left(\frac{q_n}{p_n} - \frac{r_n}{p_n - c} \right) (e^{-c\theta} - e^{-p_n\theta}) \sin \frac{n\pi}{2a} (x+a)$$

..... (9)

because $\frac{4a}{n\pi} = \frac{q_n}{p_n}$.

Substitution for p_n , q_n and r_n in equation (9) gives

$$u_A(x, \theta) = \frac{4}{\pi} \sum_{\substack{n=1 \\ (\text{odd } n)}}^{\infty} \left[\frac{1}{n} \left(\frac{n^2 \pi^2 - 4a^2 c \beta^2}{n^2 \pi^2 + 4a^2 \alpha^2 - 4a^2 c \beta^2} \right) \times \left(e^{-c\theta} - e^{-\frac{1}{\beta^2} \left(\frac{n^2 \pi^2}{4a^2} + \alpha^2 \right) \theta} \right) \sin \frac{n\pi}{2a} (x+a) \right]$$

If the transient term

$$\text{i.e. } e^{-\frac{1}{\beta^2} \left(\frac{n^2 \pi^2}{4a^2} + \alpha^2 \right) \theta}$$

(which is much less than $e^{-c\theta}$ for large values of θ) is neglected, the error can be expressed as a function of the unaccomplished temperature difference, $1 - u_L(\theta) = e^{-c\theta}$,

$$\text{i.e. } \frac{u_A(x, \theta)}{1 - u_L(\theta)} = \frac{4}{\pi} \sum_{\substack{n=1 \\ (\text{odd } n)}}^{\infty} \frac{1}{n} \left(\frac{n^2 \pi^2 - 4a^2 c \beta^2}{n^2 \pi^2 + 4a^2 \alpha^2 - 4a^2 c \beta^2} \right) \sin \frac{n\pi}{2a} (x+a) \quad \dots \dots \dots (10)$$

APPENDIX VI B

Calculation of Heat Conduction Error in Thermocouple Wire

(a) Calculation of the Parameters.

Values of the parameters α^2 , β^2 , c and a of equation (10) Appendix (p 258) are required for calculation of the heat conduction error.

(i) Calculation of α^2

$$\alpha^2 = \frac{4 U_o}{k d}$$

where U_o is the overall heat transfer coefficient (based on the diameter of the wire d) for transfer of heat from the fluid to the wire, and k is the thermal conductivity of the wire material (i.e. copper or constantan).

The film heat transfer coefficient of h has been calculated from the equation of Davis (1924), i.e.

$$Nu = 0.86 .Re^{0.43} .Pr^{0.3}$$

for flow of liquids past a single cylinder ($0.2 < Re < 200$). Nu , Re and Pr are the Nusselt, Reynolds and Prandtl numbers respectively.

$$Nu = \frac{hD}{k_L}$$

$$Re = \frac{Du \rho_L}{\mu}$$

$$\text{and } Pr = \frac{C_{pL} \mu}{k_L}$$

where D is the diameter of the cylinder, and k_L , ρ_L , μ and c_{pL} are the thermal conductivity, density, viscosity and specific heat respectively, of the liquid. The velocity of the liquid past the wire is u .

The liquid properties are measured at the mean film temperature, which is taken as 250°F . The velocity of the fluid is deduced from temperature distribution within the static water-filled cans (see figure 27, p 111). A value of $u = 17\text{ft/hr}$ is used in these calculations.

The overall heat transfer coefficient U_o is calculated from the film coefficient h and heat flow through a thick-walled tube (i.e. the nylon insulation) to the thermocouple wire. The overall heat transfer coefficient is based on the diameter of the wire (0.011 in.) rather than the outside diameter of the insulation (0.020 in.).

(ii) Calculation of β^2

$$\beta^2 = \frac{c_p \rho}{k}$$

where c_p , ρ , k are the specific heat, density, and thermal conductivity of the wire material.

(iii) Calculation of c

The value of c is deduced from the temperature distribution in a static can (see figure 27).

$$\text{i.e. } c = 2.303 \left(\frac{1}{f} \right)$$

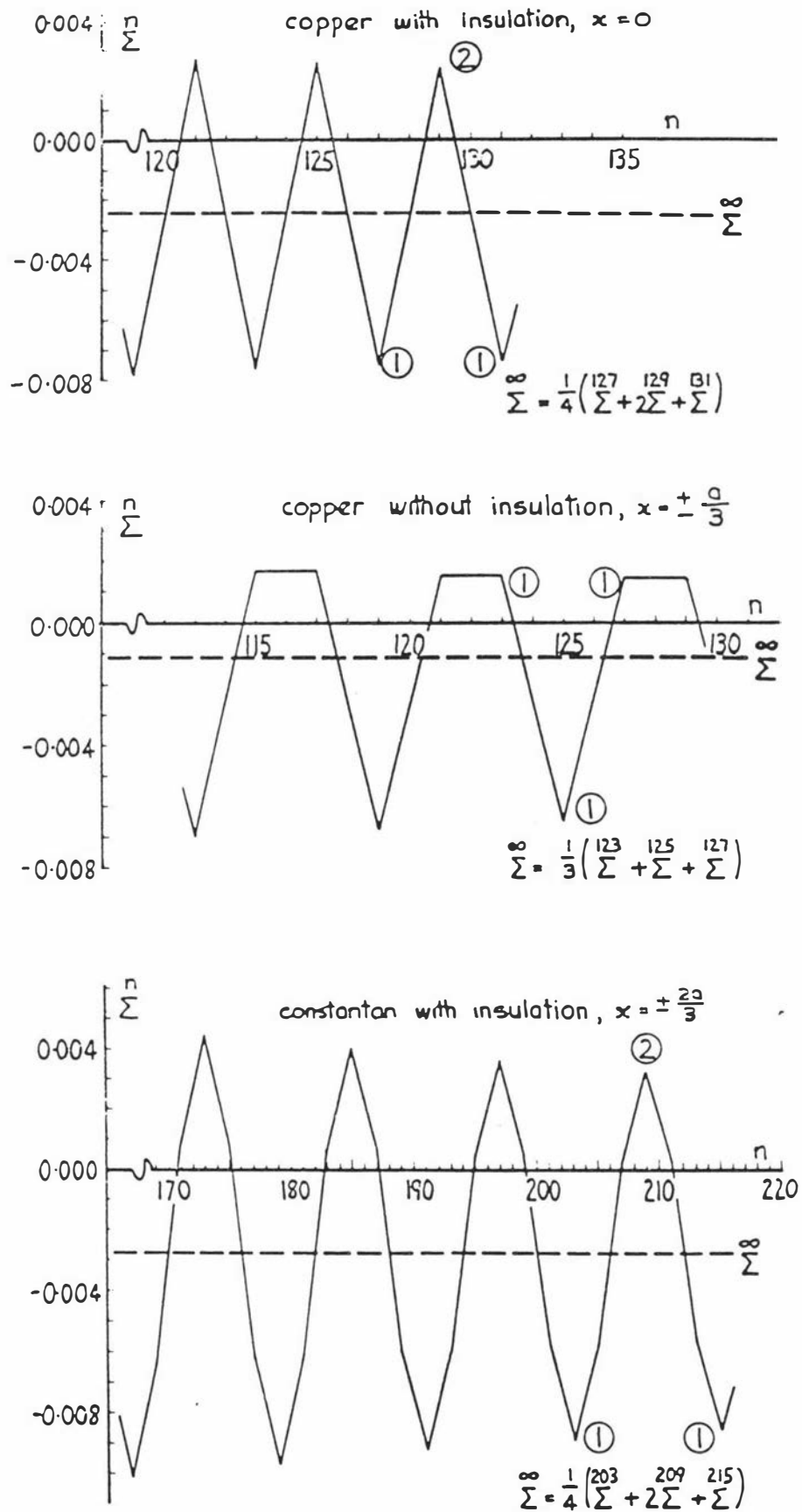
where $\frac{1}{f}$ is the slope of the semilogarithmic heating curve. A value of $f = 2.0 \text{ min.}$ is used in these calculations.

(iv) Calculation of a

$$2a = \text{diameter of the can} = 3 \text{ in.}$$

$$\text{Hence } a = 0.125 \text{ ft.}$$

The values of the parameters α^2 , β^2 , c and a are shown in table 18 for the three cases.



The circled figures are the weights given to each point in the summations.

Fig. 50 Method of summation of the slowly converging series for the heat conduction error.

Table 18 : Values of Parameters for Calculation of Heat Conduction Error.

Type of wire and insulation	α^2 ft ⁻²	β^2 hr.ft ⁻²	α hr ⁻¹	α ft
copper with insulation	5900	0.236	70	0.125
copper without insulation	10200	0.236	70	0.125
constantan with insulation	121000	3.33	70	0.125

(b) Calculation of the heat conduction error.

Arithmetical details of the calculation of the terms of the series (i.e. equation (10) p 258) and the summation to n terms are not shown.

Because the series converges very slowly, weighted means of the sums to n_1 , n_2 and n_3 terms have been used for calculation of the sum to infinity. These calculations are shown graphically in figures 50a, 50b and 50c, for three typical sets of data.

APPENDIX VII

LETHAL RATE (DECIMAL REDUCTIONS PER MINUTE)
BACILLUS STRAROTHERMOPHILUS (STRAIN TH24 IN MILK)

T (°F)	0	1	2	3	4	5	6	7	8	9
200	0.000	0	0	0	1	1	1	1	1	1
210	0.001	2	2	2	2	3	3	4	4	5
220	0.006	7	8	9	11	12	14	16	19	22
230	0.025	29	33	38	44	50	58	67	76	88
240	0.100	116	132	151	173	199	227	260	297	340
250	0.389	443	505	578	661	750	859	975	*111	*126
260	1.44	164	187	212	241	274	311	353	401	456
270	5.18	585	664	753	849	966	*110	*124	*140	*158
280	17.9									

* denotes a change of decimal point

LETHAL RATE (DECIMAL REDUCTIONS PER MINUTE)
BACILLUS SUBTILIS (STRAIN 786 IN MILK)

T (°F)	0	1	2	3	4	5	6	7	8	9
210	0.00	0	0	0	0	0	1	1	1	1
220	0.01	1	2	2	2	3	4	4	5	7
230	0.08	10	12	14	17	21	25	31	37	45
240	0.54	66	79	95	114	139	167	201	242	291
250	3.50	417	499	604	726	865	*104	*124	*149	*178
260	21.2	255	303	362	431	514	613	729	871	*104
270	124	146	174	207	245	292	348	410	484	575
280	682	805								

* denotes a change of decimal point

APPENDIX VIII

SUCROSE HYDROLYSIS - $E_A:30$ REACTION
 SPECIFIC RATE DIFFERENCE ($T_R = 272^{\circ}\text{F}$)

$T (^{\circ}\text{F})$	0	1	2	3	4	5	6	7	8	9
120	0.000	0	0	0	0	0	0	0	0	0
130	0.001	1	1	1	1	1	1	1	1	1
140	0.001	1	1	1	1	2	2	2	2	2
150	0.002	2	2	3	3	3	3	3	4	4
160	0.004	4	4	4	5	5	5	6	6	7
170	0.007	7	8	8	8	9	9	10	10	11
180	0.012	12	13	13	14	15	16	16	17	18
190	0.019	20	21	22	23	24	25	26	27	28
200	0.030	31	33	34	35	36	38	40	41	43
210	0.045	46	48	50	52	54	56	58	60	62
220	0.064	67	69	71	73	75	77	79	82	84
230	0.087	89	91	93	96	99	101	103	105	107
240	0.109	110	112	114	115	117	119	120	120	121
250	0.121	121	121	120	119	118	116	114	111	109
260	0.105	100	96	90	84	77	69	60	50	40
270	0.028	14	0							

SUCROSE HYDROLYSIS - $E_A:45$ REACTION
 SPECIFIC RATE DIFFERENCE ($T_R = 272^\circ\text{F}$)

T ($^\circ\text{F}$)	0	1	2	3	4	5	6	7	8	9
120	0.000	0	0	0	0	0	0	0	0	0
130	0.001	1	1	1	1	1	1	1	1	1
140	0.001	1	1	1	1	2	2	2	2	2
150	0.002	3	3	3	3	3	4	4	4	5
160	0.005	5	6	6	7	7	8	8	8	9
170	0.009	10	10	11	12	12	13	13	14	15
180	0.016	17	18	19	20	21	22	23	24	25
190	0.027	29	30	32	33	35	37	39	41	43
200	0.045	47	49	52	54	57	59	62	65	68
210	0.071	74	77	81	85	88	92	96	99	104
220	0.108	113	117	122	127	132	136	141	146	152
230	0.157	163	169	174	180	186	191	196	202	208
240	0.214	219	224	230	235	240	245	249	252	256
250	0.259	262	264	265	266	266	264	262	258	254
260	0.248	240	232	220	207	192	173	153	129	103
270	0.073	38	0							

APPENDIX IXCalculation of Equivalent Retort Times for Linear
Semilogarithmic Processes

It has been shown (p 42) that equivalent retort time θ is given by -

$$\theta = \int_{\theta_0}^{\theta_1} e^{B(1-\frac{1}{u})} d\theta \quad \dots\dots\dots (1)$$

where -

$$B = \frac{E_A}{RT_R}$$

and -

$$u = \frac{T}{T_R}$$

Linear semilogarithmic heating and cooling curves can be expressed as -

$$1-u = e^{-\theta}$$

and $u-1 = e^{-\theta}$ respectively,

where $\theta = \log_{10} f_h = 1/\log_{10} e \cdot f_h$

or $\theta = \log_{10} f_0 = 1/\log_{10} e \cdot f_0$

Hence for heating and cooling the temperature-time function is

$$1-u = a e^{-\theta}$$

where $a = +1$ for heating

and $a = -1$ for cooling.

This gives -

$$u = 1 - a e^{-\theta}$$

$$\text{and } du = -a(1-u)d\theta$$

$\dots\dots\dots (2)$

Hence -

$$c\theta = \int_{u_0}^{u_1} \frac{B(1 - \frac{1}{u})}{1-u} du$$

Putting $B(1 - \frac{1}{u}) = x$ then leads to -

$$c\theta = - \int_{x_0}^{x_1} \frac{Be^x}{x(B-x)} dx \quad \dots\dots\dots (3)$$

Simplification of equation (3) gives -

$$\begin{aligned} c\theta &= - \int_{x_0}^{x_1} \frac{e^x}{x} dx - \int_{x_0}^{x_1} \frac{e^x}{B-x} dx \\ &= - \int_{x_0}^{x_1} \frac{e^x}{x} dx + \int_{B-x_0}^{B-x_1} \frac{e^{-x}}{x} dx \\ &= - \int_{x_0}^{x_1} \frac{e^x}{x} dx + e^B \int_{B-x_0}^{B-x_1} \frac{e^{-x}}{x} dx \quad \dots\dots\dots (4) \end{aligned}$$

For heating,

$$x_0 = B(1 - \frac{1}{u_0}) = -\infty$$

$$\text{and } x_1 = B(1 - \frac{1}{u_g}) = -B(\frac{1}{u_g} - 1)$$

where the initial temperature of the material is taken as zero absolute

(i.e. $u_0 = 0$), and $T_R - g$ is the final temperature (i.e. $u_g = (T_R - g)/T_R$)

Hence, for heating -

$$\begin{aligned} \Theta_h &= \log_{10} e \cdot f_h \left(\int_{-\infty}^{-B(\frac{1}{u_g} - 1)} \frac{e^x}{x} dx - e^B \int_{\frac{B}{u_g}}^{\infty} \frac{e^{-x}}{x} dx \right) \\ &= \log_{10} e \cdot f_h \left(-\text{Ei}(-B(\frac{1}{u_g} - 1)) + e^B \text{Ei}(-\frac{B}{u_g}) \right) \end{aligned} \quad \dots\dots\dots (5)$$

Because the cooling curve approaches the temperature of the cooling water (T_c) asymptotically, the parameters B , u and Θ of equation (4) are based on T_c rather than T_R when this equation is applied to cooling;

$$\begin{aligned} \text{i.e. } B' &= \frac{E_A}{RT_c} \\ u' &= \frac{T}{T_c} \\ \text{and } \Theta'_c &= \Theta_c e^{B(1 - \frac{1}{u_c})} \end{aligned} \quad \dots\dots\dots (6)$$

where the prime (') is used to distinguish the parameters based on T_c from those based on T_R .

$$\text{Thus } x_0 = B' \left(1 - \frac{1}{u'_g} \right)$$

$$\text{where } u'_g = (T_R - g)/T_c.$$

The cooling phase may be considered complete when a temperature is reached at which all rates of chemical reaction and spore destruction are negligible. If T_{oo} is some such temperature, then -

$$\begin{aligned} u'_{oo} &= \frac{T_{oo}}{T_c} \\ \text{and } x_1 &= B' \left(1 - \frac{1}{u'_{oo}} \right). \end{aligned}$$

In terms of the parameters based on T_R

$$x_0 = B \left(\frac{1}{u_0} - \frac{1}{u_g} \right) \dots\dots\dots (7)$$

$$\text{and } x_1 = B \left(\frac{1}{u_0} - \frac{1}{u_{\infty}} \right). \dots\dots\dots (8)$$

Equation (4) (with parameters ϕ'_0 , B' and u' replacing ϕ , B and u , respectively) and equations (6), (7), and (8) lead to the equation for ϕ_0

i.e.

$$\begin{aligned} \phi_0 = \log_{10} e \cdot f_0 \cdot e^{B(1 - \frac{1}{u_0})} & \left(\overline{\text{Ei}} \left(B \left(\frac{1}{u_0} - \frac{1}{u_g} \right) \right) - \overline{\text{Ei}} \left(B \left(\frac{1}{u_0} - \frac{1}{u_{\infty}} \right) \right) \right) \\ & + \log_{10} e \cdot f_0 \cdot e^B \left(\text{Ei} \left(-\frac{B}{u_{\infty}} \right) - \text{Ei} \left(-\frac{B}{u_g} \right) \right) \dots\dots\dots (9) \end{aligned}$$

Both terms involving u_{∞} are negligible for values of B , u_g and u_0 of interest in the present context, and can hence be eliminated from equation (9) yielding the equation -

$$\begin{aligned} \phi_0 = \log_{10} e \cdot f_0 \cdot e^{B(1 - \frac{1}{u_0})} & \left(e^{\overline{\text{Ei}} \left(B \left(\frac{1}{u_0} - \frac{1}{u_g} \right) \right)} - e^B \text{Ei} \left(-\frac{B}{u_g} \right) \right) \\ & \dots\dots\dots (10) \end{aligned}$$

Equations (5) and (10) with $f_h = f_0 = 1$ min. give equations (6) and (7) (p 186) respectively, for the calculation of the parameters a and b .

APPENDIX X

Coefficients a , b , Δa , and Δb for calculation of parameters for type I curve of best fit.

g (°F)	sucrose hydrolysis		$E_A : 30$ reaction		$E_A : 45$ reaction		<u>B. stearo-</u> <u>thermophilus</u>		<u>B. subtilis</u>	
	a	b	Δa	Δb	a	b	Δa	Δb	Δa	Δb
10.0	3074	4233	785	1546	1689	2872	2472	3738	2778	4011
9.0	3394	4387	824	1564	1789	2918	2654	3826	3011	4122
8.0	3762	4547	862	1586	1891	2965	2808	3911	3263	4232
7.0	4199	4714	903	1597	2002	3007	3060	3993	3542	4339
6.0	4721	4884	945	1611	2117	3045	3237	4067	3847	4440
5.0	5363	5061	989	1623	2253	3079	3533	4134	4184	4533
4.5	5745	5152	1011	1628	2302	3094	3662	4164	4365	4575
4.0	6180	5242	1035	1633	2369	3107	3798	4195	4554	4615
3.5	6684	5336	1055	1638	2436	3120	3940	4220	4754	4652
3.0	7276	5342	1083	1641	2505	3131	4087	4243	4965	4686
2.8	7543	5471	1093	1642	2533	3135	4147	4252	5052	4699
2.6	7834	5510	1104	1643	2562	3139	4208	4260	5141	4711
2.4	8150	5549	1112	1645	2596	3142	4271	4267	5231	4722
2.2	8497	5588	1123	1646	2621	3146	4335	4275	5323	4732
2.0	8880	5627	1134	1647	2651	3148	4399	4281	5417	4733
1.8	9304	5667	1143	1648	2680	3152	4465	4287	5512	4751
1.6	9784	5708	1153	1650	2710	3155	4532	4293	5610	4759
1.4	10332	5748	1165	1650	2740	3157	4598	4299	5709	4766
1.2	10969	5789	1176	1651	2771	3159	4667	4303	5811	4774
1.0	11729	5830	1187	1651	2804	3160	4737	4306	5915	4779
0.8	12666	5872	1198	1651	2835	3162	4808	4309	6021	4783
0.6	13883	5912	1209	1651	2868	3162	4881	4312	6131	4787
0.40	15611	5953	1220	1652	2900	3163	4954	4313	6243	4790
0.30	16845	5973	1225	1652	2917	3163	4992	4313	6299	4791
0.20	18594	5994	1230	1652	2932	3163	5029	4313	6356	4792
0.10	21589*	6008	1236*	1652	2949*	3163	5068*	4313	6415*	4792
0.08	22555	6011	1237	1652	2954	3163	5076	4313	6427	4792
0.06	23365	6013	1238	1652	2957	3163	5083	4313	6438	4792
0.04	23604	6016	1239	1652	2960	3163	5090	4313	6450	4792
0.03	26807	6017	1240	1652	2962	3163	5093	4313	6456	4792
0.02	28566	6018	1240	1652	2964	3163	5097	4313	6461	4792
0.01	31575	6020*	1241	1652	2966	3163*	5102	4313*	6468	4792*

The units of a and Δa are 0.0001 min.; units of b and Δb are 0.00001 min.

For purposes of interpolation the curves a vs $\log g$, Δa vs $\log g$, b vs g , and Δb vs g may be assumed linear.

APPENDIX XINomenclature of Can Sizes

The system of nomenclature used is that employed in the industry, in which the can is identified by a statement of its dimensions (over-all ~~height~~ ^{diameter} by over-all ^{height} ~~diameter~~).

The left hand digit in each dimension is the number of whole inches and the two right hand digits give the additional fraction of the dimension expressed as sixteenths of an inch.

For example, a 307 x 409 can is $3 \frac{7}{16}$ in. in diameter and $4 \frac{9}{16}$ in. in height, while a 208 x 006 can is $2 \frac{1}{2}$ in. by $\frac{3}{8}$ in.