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A DEVELOPMENT OF AN ELECTRICAL ANALOGUE FOR
THERMAL PROCESSING

A thesis presented in partial fulfilment of the
requirement for the degree

MASTER OF TECHNOLOGY
in Biotechnology

At Massey University
Palmerston North
New Zealand

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1973

ACKNOWLEDGEMENTS

The writer wishes to express his gratitude for the generous assistance and guidance which he received throughout this work, without which this study would have been impossible.

The writer would like to thank Professor R.L. Earle for his continual teaching and guidance throughout this study.

To Mr. R.E. Hendtlass, Chemistry, Biochemistry and Biophysics Department, whose suggestions and contribution of the electrical circuits is deeply appreciated.

Thanks are also due to the staff of the Food Science and Biotechnology Faculty, Massey University, for their aid.

TABLE OF CONTENTS

	Page
I. SUMMARY	1
II. INTRODUCTION	
A. THERMAL PROCESSING IN GENERAL	3
B. PROBLEMS IN FORMULATING AND MANIPULATING PROCESSING CONDITION	4
C. THE OBJECTIVE OF THIS STUDY	5
III. LITERATURE SURVEY	
A. KINETICS OF THERMAL PROCESSING	6
1. Reaction Rate Equation	6
2. Temperature Dependency of Reaction Rate Constant	8
B. THERMAL PROCESSING EVALUATION	13
C. ANALOGUE SYSTEM FOR THERMAL PROCESSING	15
IV. THEORY	
A. GENERATION OF REACTION RATE FOLLOWING THE ARRHENIUS EQUATION	17
1. Thermistor Sensor	17
2. Generation of a Primary Reaction Rate Following the Arrhenius Equation	18
3. Modification of the Primary Reaction Rate Constant	19
B. INTEGRATION OF THE GENERATED REACTION RATE ...	20
C. CORRELATION OF ANALOGUE OUTPUT VOLTAGE v_0 WITH PROGRESS OF IRREVERSIBLE REACTION IN THERMAL PROCESSING	22
1. Irreversible Unimolecular First-order Reactions	22
2. Irreversible Bimolecular Second-order Reactions	24
3. Irreversible Trimolecular Third-order Reactions	27

	Page
4. Irreversible Reaction with Empirical Rate Equation of the n th Order	30
5. The Relationship of the Ratio of Frequency Factor and the Ratio of Reaction Rate Constants at a Constant Temperature	31
V. APPARATUS	
A. REGULATED POWER SUPPLY FOR THE ANALOGUE SYSTEM .	33
B. ELECTRICAL ANALOGUE SYSTEM	33
1. Primary Reaction Rate Generator	33
2. Analogue Multiplier	34
3. Analogue Integrator	34
C. THERMAL PROCESSING REACTOR	35
D. MEASURING EQUIPMENT	36
1. Voltmeter	36
2. Potentiometer and Thermocouple	36
3. Potentiometric Recorders	36
VI. PROCEDURE	
A. ARRANGEMENT OF APPARATUS FOR EXPERIMENTAL TESTING OF THE ANALOGUE SYSTEM	43
B. DETERMINATION OF GENERATED PRIMARY REACTION RATE v_1 AT VARIOUS TEMPERATURE T	43
C. DETERMINATION OF GENERATED SECONDARY REACTION RATE v_2 AT VARIOUS TEMPERATURE T	44
D. TESTING OF THE ANALOGUE INTEGRATOR	44
E. APPLICATION OF THE ELECTRICAL ANALOGUE IN THERMAL PROCESSING	45
VII. RESULTS	50
VIII. DISCUSSION OF RESULTS	
A. TESTING OF THE ANALOGUE SYSTEM	64
1. Generation of the Primary Reaction Rate v_1 .	64
2. Generation of the Reaction Rate v_2 with Application of the Analogue Multiplier	64
3. The Analogue Integrator	65

	Page
B. THE ANALOGUE SYSTEM IN THERMAL PROCESSING	67
IX. CONCLUSIONS	88
APPENDIX	90
BIBLIOGRAPHY	101

LIST OF TABLES

	Page
Table VII.1	Results of Primary Reaction Rate v_1 Generated by the Analogue 51
Table VII.2	Results of Reaction Rate v_2 Generated by Application of Analogue Multiplier (n=2) 52
Table VII.3	Results of Reaction Rate v_2 Generated by Application of Analogue Multiplier (n=4) 53
Table VII.4	Results of Reaction Rate v_2 Generated by Application of Analogue Multiplier (n=6) 54
Table VII.5	Results of Reaction Rate v_2 Generated by Application of Analogue Multiplier (n=8) 55
Table VII.6	Results of Reaction Rate v_2 Generated by Application of Analogue Multiplier (n=10) 56
Table VII.7	Results of Reaction Rate v_2 Generated by Application of Analogue Multiplier (n=12) 57
Table VII.8	Results of Reaction Rate v_2 Generated by Application of Analogue Multiplier (n=16) 58
Table VIII.1	Summary of Results in Reaction Rate Generation by the Analogue 70

		Page
Table VIII.2	Measured Output Voltage Changes of Integrator at Various Input Voltages ...	71
Table VIII.3	Comparison of Progress of the Thermal Sterilization Detected by the Analogue and that by the Temperature-time Profile	72
Table VIII.4	Comparison of Progress of the Thermal Destruction of the Chemical Species Detected by the Analogue and that by the Temperature-time Profile	73
Table A.1	Characteristics of Copper-constantan Thermocouple	91
Table A.2	Relationship of Inverse Absolute Temperature at Hot Junction and Electrical Potential of the Copper-constantan Thermocouple	92
Table C.1	Pertinent Values Associated with Analysis of Experimental Reaction Rates Generated by the Analogue	98

LIST OF FIGURES

	Page
Figure V.1	Circuit Diagram of the Voltage Regulated Power Supply 38
Figure V.2	Circuit Diagram of the Primary Reaction Rate v_1 Generator 39
Figure V.3	Circuit Diagram of an Analogue Multiplier 40
Figure V.4	Circuit Diagram of the Analogue Integrator 41
Figure V.5	Diagram of Wiring Through the Door of the Autoclave 42
Figure VI.1	Arrangement of Apparatus for Testing the Analogue 49
Figure VII.1	Results of Analogue Integrator Testing 59
Figure VII.2	Output Voltage from the Analogue System in Following the Progress of the Sterilization of a Microorganism ... 60
Figure VII.3	Temperature and Time Profile in the Vicinity of the Sensor of the Analogue in a Microbial Sterilization 61
Figure VII.4	Output Voltage from the Analogue System in Following the Progress of the Thermal Destruction of the Chemical Species 62

	Page
Figure VII.5	Temperature and Time Profile in the Vicinity of the Sensor of the Analogue in a Chemical Destruction Reaction 63
Figure VIII.1	Plot of the Primary Reaction Rate Generated by the Analogue According to the Arrhenius Equation ($n=1$) 74
Figure VIII.2	Plot of the Reaction Rate Generated by the Analogue According to the Arrhenius Equation ($n=2$) 75
Figure VIII.3	Plot of the Reaction Rate Generated by the Analogue According to the Arrhenius Equation ($n=4$) 76
Figure VIII.4	Plot of the Reaction Rate Generated by the Analogue According to the Arrhenius Equation ($n=6$) 77
Figure VIII.5	Plot of the Reaction Rate Generated by the Analogue According to the Arrhenius Equation ($n=8$) 78
Figure VII.6	Plot of the Reaction Rate Generated by the Analogue According to the Arrhenius Equation ($n=10$) 79
Figure VIII.7	Plot of the Reaction Rate Generated by the Analogue According to the Arrhenius Equation ($n=12$) 80
Figure VIII.8	Plot of the Reaction Rate Generated by the Analogue According to the Arrhenius Equation ($n=16$) 81

	Page
Figure VIII.9	Relationship between Temperature Coefficient of Generated Reaction Rate and Integer Multiple n 82
Figure VIII.10	Measured Output Voltage Changes of Integrator at Various Input Voltages 83
Figure VIII.11	Reaction Rate and Time Profile in the Vicinity of the Sensor of the Analogue in a Thermal Sterilization 84
Figure VIII.12	Progress of the Thermal Sterilization Detected by the Analogue and that by Temperature and Time Measurement 85
Figure VIII.13	Reaction Rate and Time Profile in the Vicinity of the Sensor of the Analogue in a Thermal Destruction of a Chemical Species 86
Figure VIII.14	Progress of the Thermal Destruction of the Chemical Species Detected by the Analogue and that by Temperature and Time Measurement 87
Figure A.1	Characteristics of Copper-constantan Thermocouple 93
Figure A.2	Relationship of Inverse Absolute Temperature at Hot Junction and Electrical Potential of the Copper- constantan Thermocouple 94

I. SUMMARY

The objective of this study was to investigate some general principles in thermal processing and some methods for following this processing experimentally. The emphasis of the investigation was to develop a simple electrical analogue system for following the progress of a single stage irreversible thermal processing reaction.

Documented data and principles of the kinetics of thermal processing of biological material showed that such process reaction could be approximated by the kinetic model of a single stage irreversible reaction. Temperature dependency of the thermal processing rate could also be approximated by the Arrhenius equation.

Functional principles of electrical analogue computers were applied to develop the electrical analogue system. The structure and mode of operation of this system is described. The relationship between the output voltage of the analogue system and the progress of the thermal processing are derived for different known thermal processing reactions, following the kinetic model of a single stage irreversible reaction.

The performance of the electrical analogue system in this study was tested. The results indicated that the electrical analogue system so constructed could approximate the function described in theory. Non-ideality of the electrical circuitry, however, restricted the application of the electrical analogue system for its qualitative value only. The parameter governing

the temperature dependence of an irreversible reaction rate could be generated with error of approximately $\pm 4.55\%$. The error associated with application of the analogue integrator for integrating the generated reaction rate was approximately $\pm 7.25\%$. The overall error in application of the analogue system for detecting thermal processing varied with the time span of processing cycle, and processing effect achieved at temperatures other than the set temperature of processing.

II. INTRODUCTION

A. THERMAL PROCESSING IN GENERAL

Thermal processing implies application of thermal energy at suitable thermal potential, namely temperature to a reacting system. Thermal effects on chemicals, biochemicals and biological materials have long been recognised. Existence of these effects has been used to the advantages of many industries. Thermal activation of chemical reactions and biochemical reaction constitutes a very fundamental process in chemical and biochemical technology. Polymerisation reactions, hydrolysing reactions, oxidation and reduction reactions are few examples of many important processing reactions which may involve thermal processing.

In active living tissue, many metabolic reactions can proceed appreciably at room temperature, causing undesirable alteration in the tissue. Low temperature storage has the basic objective of arresting the various reactions which may cause spoilage and which proceed at higher temperatures. With active proteins like enzymes and living tissue, denaturation and functional inactivation can occur rapidly at processing temperatures. Sterilization of microorganisms, pasteurisation of milk are specific examples of this type of thermal processing.

Many reactions may occur simultaneously during a thermal processing. Each of these reactions occurs to a varying extent, depending upon the reaction rate constant. Among the reactions in thermal processing, there is at least one desirable reaction which is the objective of the processing. Some of the remaining

reactions and very often all of them may be undesirable, causing deleterious effects on organoleptic properties and nutritive properties. Minimal processing to meet its objective is also required by economical consideration.

Temperature and time are the two variables which when combined determine the extent of thermal processing. Particular processing conditions can be selected to favour desirable reaction according to the basis of high-temperature short-time processing or low-temperature long-time processing.

B. PROBLEMS IN FORMULATING AND MANIPULATING PROCESSING CONDITION

Effective means of formulating processing condition and evaluating processing results must be available, to minimize a thermal processing at its lowest necessary level. Certain analytical methods of formulating processing condition have been developed in the fields of thermobacteriology (39, 10), biochemical engineering (1), and food technology (25, 9). Consideration of heat transfer must be included in these analytical methods, in order to account for the thermal processing effect achieved during heating and cooling periods as step changes in temperature are not possible in practice. Accurate data on the heat transfer properties and conditions for a specific reacting system must be available. Very often assumptions on the mode of heat transfer and the mode of process operation have also to be made. Uncontrolled or unknown changes in the plant and its operation which could arise from design or constructional tolerances or from operator variability, could lead to large variations in the process characteristics. For example; variations

in heat flow patterns, deposition of scale on heat transfer surface, and changes in thermal properties of materials.

Thermal processing condition may be very accurately formulated in terms of temperature and time, for example by a process working pressure and the holding time at this pressure. These two parameters specifying a thermal process do not easily allow correction to be made by operator whenever unexpected failure of processing system occurs.

Thermal processing may result in readily detectable physical changes. Such changes are useful in following the progress of processing, provided access to the material being processed is possible. Very often biochemical and biological changes are the only results from thermal processing. Incubation requirement and time lag in evaluating results may make it inconvenient to examine the adequacy of a proposed process or to explore the manipulation of a processing condition to meet its specification.

C. THE OBJECTIVE OF THIS STUDY

The object of this study was to develop an electrical analogue system to monitor the progress of a thermal processing reaction, throughout a small region, with the reaction rate constant following the Arrhenius equation.

III. LITERATURE SURVEY

A. KINETICS OF THERMAL PROCESSING

Reaction kinetics have formed a quantitative basis for analysing thermal processing. So it is necessary to survey the kinetic principles which can be applied to thermal processing.

1. Reaction Rate Equation

In the review on the chemistry of protein denaturation by Neurath et al. (29), large numbers of experimental results on thermal denaturation of protein were observed to follow first order reaction kinetics.

From a number of investigations, Rahn (33) established that the thermal destruction of microbial spores proceeded, in many instances, as first order reaction.

Wood (43) surveyed many experimental results of thermal inactivation on cellular constituents, viruses, bacteria and yeasts. He concluded that the denaturation of proteins and inactivation of enzymes were first order. Some exceptions were explained by changes taking place in the environment, during the course of heat treatment.

The kinetics of thermal denaturation of bovine plasma was observed by Levy and Warner (24) to be first order for pH below 4, using isoelectric precipitation as the criterion of denaturation. This demonstrated the existence of a pseudo first order reaction, similar to the case of acid hydrolysis of sucrose in dilute aqueous solution.

Stumbo (39) discussed the problems of assuming death of microorganism to be first order. Factors causing apparent deviations from the logarithmic order were explained. The reaction rate equation for thermal destruction of microorganism was given as:

$$-\frac{dc}{dt} = kc$$

where c = concentration of microorganisms

k = proportionality constant or specific reaction rate

t = time

In thermobacteriology, however, another parameter is often used instead of the specific reaction rate. The parameter is decimal reduction time, D . The definition of decimal reduction time was the time required to destroy 90% of the microbial content. Katzin et al. (21) showed the relation between the decimal reduction time and the specific reaction rate to be:

$$D = \frac{2.3}{k}$$

where k = specific reaction rate.

This first order reaction rate equation has been adopted by many investigators proposing methods of formulating and evaluating heat sterilization of microorganisms. Deindoerfer and Humphrey (10) assumed a first order reaction rate equation in proposing an analytical method for calculating heat sterilization time on fermentation media. A study was made by Teixeira et al. (40) on computer optimisation of nutrient retention in the thermal processing of conduction-heated foods, in which a first order reaction rate equation was applied in the basic program.

A general reaction rate equation was discussed by Levenspiel (22). The rate of a reaction involving reacting components W, X...Z can be approximated by an equation:

$$r_W = k c_W^w c_X^x \dots c_Z^z, \quad w + x + \dots + z = n$$

where r_W = the rate of reaction of component W

k = reaction rate constant

$c_W, c_X \dots c_Z$ = concentrations of components W, X...and Z respectively.

$w, x \dots z$ and n = the order of reaction, namely

w th order with respect to W

x th order with respect to X

z th order with respect to Z

and n th order over-all

Methods for determining the order of a reaction were discussed by Glasstone (16).

2. Temperature Dependency of Reaction Rate Constant

The reason for thermal processing is the temperature dependence of the reaction rate constant. By increasing the temperature the reactions can occur within processing times that can be easily achieved. Different parameters describing the dependence of reaction rate constants on temperature have arisen in various different fields of work, often because of independent development and variations in particular requirements. The following is a survey of some such parameters and their relationship.

Data on thermal resistance of microorganisms was studied by Bigelow (7). Thermal death time data were plotted on logarithmic scale against corresponding temperature on linear

scale. The curve was subsequently known as thermal death time curve.

The "F" value together with the "z" value were applied by Ball (4, 5) in characterizing the thermal death time curve. The definition of the z value was given as temperature increment in degrees Fahrenheit for a tenfold decrease in thermal death time. The F value was defined as the time in minutes required to sterilize a particular microorganism at 250°F.

A large amount of data on thermal resistance of microorganisms has since been gathered in the literature by using the thermal death time curve. Such data on putrefactive anaerobe P.A. 3679 and thermophilic anaerobe T.A. 3814 were reported by Reed et al. (35).

The concept of Q_{10} has been used widely to express temperature dependency of chemical reactions as well as biological reactions. Application of the Q_{10} concept to indicate temperature dependency for thermal destruction of microorganisms was demonstrated by Rahn (34). The definition of Q_{10} adopted was the quotient indicating how much more rapidly death proceeds at a temperature 10 degree C higher than that at a given temperature, T degree C. Relationship of Q_{10} and z value was derived as:

$$z = \frac{18}{\log_{10} Q_{10}}$$

Some data of temperature dependency for thermal destructions of vitamins in foods were reported by Greenwood et al. (18) and Jackson et al. (20), using Q_{10} concept. Ball and

Olson (5) discussed application of Q_{10} data for predicting organoleptic properties of foods, during thermal processing.

Non-linearity in the plot of $\log_{10} D$ against temperature on linear scale was observed by Gillespy (14). It was also noted that the plot of $\log_{10} D$ against the reciprocal of temperature on the same data was more linear. The plot of $\log_{10} D$ against the reciprocal of temperature was made according to the Arrhenius equation for chemical reaction. The Arrhenius equation can be defined as:

$$k = A \exp \left(- \frac{E}{RT} \right)$$

where k = reaction rate constant at absolute temperature T .

A = parametric constant which is often referred to as frequency factor.

E = activation energy of the reaction.

R = the universal gas constant.

The approximate relationship between $\frac{E}{R}$ and z , measured over limited temperature T_1 and T_2 was shown by Gillespy to be:

$$z = 2.303 T_1 T_2 \left(\frac{R}{E} \right)$$

Thermal resistance characteristics of Clostridium sporogenes (P.A. 3679) in phosphate buffer, over the temperature range of 105-120°C, were reported by Amaha (2). The results conformed with Gillespy's observation.

Analysis of thermal resistance data of P.A. 3679 and Clostridium botulinum by the Arrhenius equation was presented by

Levine (23), and many subsequent data on temperature dependency of thermal destruction of microorganisms have been reported in this manner.

Wang (42) studied the kinetics of death of Bacillus stearothermophilus spore (FS 7954) at elevated temperature, in a flow system. The results were analysed according to the Arrhenius equation. The activation energy and the frequency factor were reported to be 83.6 kcal/gm mole and $10^{47.2} \text{ min}^{-1}$ respectively. The temperature dependence of the spore destruction was also correlated by the thermal death time curve, but serious errors were observed in extrapolating low temperature results to high temperatures.

The collision theory of reaction or rate process was discussed by Glasstone, Laidler and Eyring (15). Mechanical and statistical consideration of collision between reacting gas molecules was the basis of this theory. According to the collision theory, the specific rate of reaction between two species W and X, assuming the standard state to be one molecule per cc, was given as:

$$k = Z \exp \left(- \frac{E}{RT} \right) \text{ cc molecule}^{-1} \text{ sec}^{-1}$$

where Z = collision frequency or collision number

k = reaction rate at temperature T

E = activation energy

R = the universal gas constant

T = absolute temperature

The collision frequency itself was temperature dependent, and was described by the equation:

$$Z = s_{W,X}^2 \left(8 k_B T \frac{m_W + m_X}{m_W m_X} \right)^{\frac{1}{2}}$$

where $s_{W,X}$ = the mean free path between A and B

k_B = Boltzman constant

m_W and m_X = the actual mass of subscribed molecules.

Subsequent modification to this theory was made by introducing a factor P which was described as "steric" or "probability" factor to account for slower gas reaction rates in practice.

The absolute reaction rate theory was also discussed in which the existence of equilibrium between an "activated complex" molecule and reactants in a reaction or rate process was assumed. Decomposition of activated complex along the reaction coordinate gave rise to rate of reaction. Application of relationships between the equilibrium constant and the thermodynamic properties of the activated complex to the rate of reaction resulted in equation:

$$\begin{aligned} k &= \frac{k_B T}{h} \exp \left(- \frac{\Delta G^*}{RT} \right) \\ &= \frac{k_B T}{h} \exp \left(+ \frac{\Delta S^*}{R} \right) \exp \left(- \frac{\Delta H^*}{RT} \right) \end{aligned}$$

where k = reaction rate constant

k_B = Boltzman constant

h = Planck's constant

T = absolute temperature

ΔG^* = standard free energy change from reactant to activated complex

ΔS^* = standard entropy change from reactant to activated complex.

ΔH^* = standard enthalpy change from reactant to activated complex.

Application of the absolute reaction rate theory to discuss reaction mechanisms in protein denaturation was cited by Eyring and Stern (11). Interpretation and correlation of parameters describing reaction rate constant by the Arrhenius equations, the collision theory and the absolute reaction rate theory was noted by Neurath et al. (29).

Temperature dependency of reaction rate constant according to different reaction rate theory was summarized by Levenspiel (22) in the following expression:

$$k = T^m \exp\left(-\frac{E}{RT}\right); \quad 0 \leq m \leq 1$$

where k = reaction rate constant

T = absolute temperature

E = activation energy

R = the universal gas constant

m = constant

= 0 when Arrhenius equation was applied

= $\frac{1}{2}$ when collision theory of reaction was applied

= 1 when the absolute reaction rate theory was applied.

B. THERMAL PROCESSING EVALUATION

Thermal processing can be evaluated from analysis of the fractional conversion achieved. Actual methods of analysis may vary with the nature and the kinetics of the reaction taking

place. Application of kinetic principles, however, permits thermal processing to be evaluated from valid records of processing condition. The following is survey of some techniques available for such evaluation.

Thermal processing condition is generally expressed in terms of temperature and time. The employment of a standard method in temperature recording was discussed by Miller (27).

A graphical method of determining the adequacy of thermal sterilization process was described by Bigelow et al. (6). The method was based on the temperature and time data at the region of slowest heating. Conversion of the temperature and time data to the thermal death time (TDT) and time data, was carried out according to the thermal death time curve of the microorganism concerned. The sterilizing rate at a particular temperature was equated to the reciprocal of the corresponding thermal death time. The area under the sterilizing rate curve was estimated as $\int_0^{t'} \frac{1}{\text{TDT}} dt$ which must be at least one to indicate adequacy of sterilization.

A simplified procedure for thermal process evaluation was proposed by Patashnik (31). Instead of using the lethality concept, the concept of process equivalence in terms of minutes at 250°F (F value) was used. The temperature and time data of the slowest heating region was expressed in terms of $\frac{F}{t}$ and time (t) by the equation:

$$\frac{F}{t} = \frac{1}{\text{antilog}_{10} \left(\frac{250-T}{z} \right)}$$

Integration of $\frac{F}{t}$ with respect to time was carried out to give the total F value of a process. For adequate processing, the F value must be at least equivalent to the thermal death time at 250°F for the microorganism upon which the process was based.

Special temperature and time coordinate paper was constructed by Schultz and Olson (37), to permit convenient plotting of lethal rates. The temperature scale on the paper was set proportional to $\frac{F}{t}$ or $\frac{1}{TDT}$ value of the corresponding temperature. The special coordinate paper referred to the sterilization with respect to Clostridium botulinum with the z parameter of 18°F and the F value of 2.45 minutes.

The concept of special coordinate paper may also be applied to thermal processing of other kinds with temperature dependency of reaction rate following any one of the known reaction rate theories. The temperature scale of the special coordinate paper may be constructed proportional to the reaction rate constant, k, at its corresponding temperatures.

C. ANALOGUE SYSTEM FOR THERMAL PROCESSING

A chemical analogue of thermal destruction of bacterial spore was developed by Packer (30). The analogue was a system of acid hydrolysis of sucrose, in buffer solution. Under identical thermal condition as the bacterial population in the sealed container of food material, the extent of sucrose hydrolysis was measured to indicate the total lethal effect of heat. The relationship between the extent of a chemical reaction and the degree of destruction of bacterial spore was cited to depend on the heat transfer characteristics of the material being processed,

and on the parametric constants describing the specific reaction rate in each system, namely z or Q_{10} or activation energy and decimal reduction time or the frequency factor in the Arrhenius equation. A similar analogue system in sealed glass tube was independently described by Herson (19).

An electromechanical analogue was developed by Sikyta and Mastner (38) as an automatic equipment for media sterilization. A platinum resistance thermometer was used as sensor to generate the thermal destruction coefficient of microbial spores, Bacillus stearothermophilus 1518. Integration of the thermal destruction coefficient to produce output indicating total sterilization effect was carried out by a servomechanical method. A so-called "extrapolator" was fitted on the analogue system to approximate the value of sterilization effect which will be produced during the cooling period.

IV. THEORY

A. GENERATION OF REACTION FOLLOWING THE ARRHENIUS EQUATION

1. Thermistor Sensor

Over a limited range of temperature, a negative temperature coefficient (NTC) thermistor has the electrical resistance characteristics (32) described by the equation:

$$r = D \exp \left(\frac{B}{T} \right) \quad (\text{IV.1})$$

where r = electrical resistance of an NTC thermistor

T = ambient absolute temperature of the thermistor

D & B = parametric constants of the thermistor.

A reaction rate constant following the Arrhenius equation may be written as:

$$k = A \exp \left(- \frac{E}{RT} \right) \quad (\text{IV.2})$$

where k = reaction rate constant

E = the activation energy

R = the universal gas constant

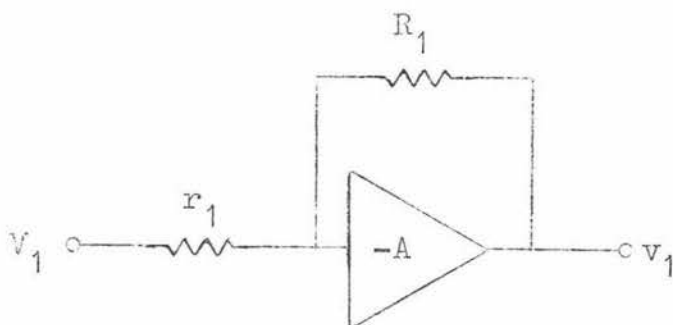
A = the frequency factor

T = absolute temperature of the reacting system.

The inverse of the electrical resistance of an NTC thermistor thus resembles the Arrhenius equation. If the inverse resistance of an NTC thermistor can be incorporated into the transfer function of an electrical circuit, the NTC thermistor may be used as a thermal sensor for generating voltage proportional to a reaction rate following the Arrhenius equation.

2. Generation of a Primary Reaction Rate Following the Arrhenius Equation

An electrical circuit may be constructed by using an operational amplifier such that its voltage transfer function is the negative ratio of two resistors in the circuit (26) as follows:



where V_1 = a constant input voltage

R_1 = a fixed feed back resistor

r_1 = an input resistor

v_1 = the output voltage

The output voltage v_1 is described by the equation:

$$v_1 = -V_1 \left(\frac{R_1}{r_1} \right) \quad (\text{IV.3})$$

When an NTC thermistor is used as the input resistor, substitution of equation IV.1 into equation IV.3 is possible giving:

$$v_1 = -V_1 \left(\frac{R_1}{D} \right) \exp \left(-\frac{B}{T} \right) \quad (\text{IV.4})$$

The output voltage v_1 , so generated is thus proportional to a primary reaction rate, following the Arrhenius equation. By comparing equation IV.4 with equation IV.2, the parametric constants in the generated reaction rate have the following numerical

magnitudes:

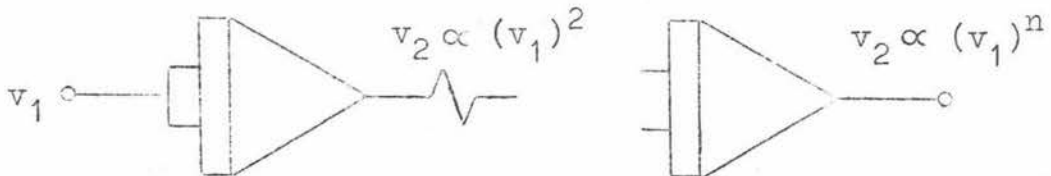
$$A = -V_1 \left(\frac{R}{D} \right) \quad (\text{IV.5})$$

$$\text{and } \frac{E}{R} = B \quad (\text{IV.6})$$

The magnitude of the generated frequency factor is $-V_1 \left(\frac{R}{D} \right)$ is under control by selecting suitable input voltage V_1 or suitable feed back resistor R_1 . The magnitude of the generated temperature coefficient B , is fixed according to the characteristics of the NTC thermistor. The term "primary" reaction rate is given according to its fixed value of temperature coefficient.

3. Modification of the Primary Reaction Rate for Suitable Temperature Coefficient

In order to gain some control on the parameter describing the temperature coefficient in the generated reaction rate, analogue multipliers are used to obtain the n th power of the primary reaction rate v_1 as follows:



The output voltage v_2 may be described by the equation:

$$v_2 = A_1 \exp \left(-\frac{nB}{T} \right) \quad (\text{IV.7})$$

where $n =$ a constant integer

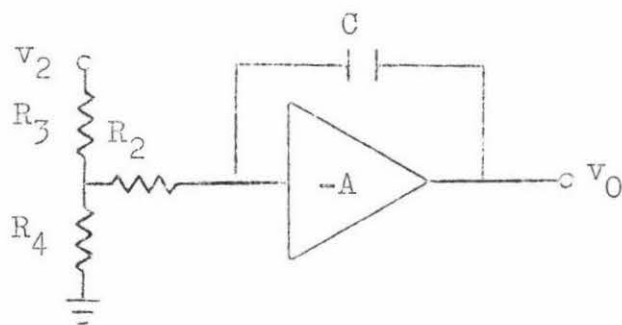
$A_1 =$ a constant

The output voltage v_2 is thus proportional to a secondary reaction rate generated by the analogue. The temperature coefficient in this secondary reaction rate is nB which can therefore be set to any required value by selection of a suitable thermistor with respect to its B parameter and manipulation of multipliers to give an integral multiplier of value n .

Application of analogue multipliers to modify the primary reaction rate for a suitable temperature coefficient appropriate to a particular reaction does not permit continuous value of temperature coefficient nB to be produced. Alternative method in modifying the primary reaction rate for a suitable temperature coefficient may be described as follows. A logarithmic circuit (41) may be used to take the logarithm of the generated reaction rate v_1 which can be further multiplied by appropriate constant n , and then finally antilogarithmic circuit may be used to obtain $(v_1)^n$. This logical path of modifying the primary reaction rate will permit reaction rate with continuous value of temperature coefficient, nB to be generated. The cost and complexity of logarithmic and antilogarithmic circuit with suitable operational voltage range however, is greater.

B. INTEGRATION OF THE GENERATED REACTION RATE

The secondary reaction rate constant v_2 may be integrated by an analogue integrator (12, 13, 26) as follows:



where R_2 , R_3 and R_4 = fixed resistance

C = a feedback capacitance

v_0 = output voltage from the integrator

The output voltage v_0 from the integrator can be described by the equation:

$$\begin{aligned}
 v_0 &= - \left(\frac{R_4}{R_3 + R_4} \right) \frac{1}{R_2 C} \int_0^{t'} v_2 dt \\
 &= - \frac{1}{K} \int_0^{t'} v_2 dt \quad \text{(IV.8)}
 \end{aligned}$$

where K = constant associated with the integration

$$= \left(\frac{R_3 + R_4}{R_4} \right) R_3 C \quad \text{(IV.9)}$$

t = time variable

t' = integration time limit

On substituting equation IV.7 into equation IV.8, the result obtained is:

$$v_0 = - \frac{A_1}{K} \int_0^{t'} \exp \left(- \frac{nB}{T} \right) dt \quad \text{(IV.10)}$$

Further substituting equation IV.2 into equation IV.10,

the result is:

$$v_0 = -\frac{A_1}{KA} \int_0^{t'} k dt \quad (\text{IV.11})$$

provided $nB = \frac{E}{R}$, irrespective of whatever the temperature and time relationship may be.

According to equation IV.11, the output voltage v_0 is thus a measure of progress of an irreversible process reaction with reaction rate following the Arrhenius equation. Correlation of output voltage v_0 from the analogue and progress of various irreversible process reaction will be discussed in the following section.

C. CORRELATION OF ANALOGUE OUTPUT VOLTAGE v_0 WITH PROGRESS OF IRREVERSIBLE REACTION IN THERMAL PROCESSING

Kinetics of irreversible reactions with different molecularity have been discussed by Levenspiel (22). The progress in each of such reaction is a function of initial composition, reaction rate k and reaction time t' . In a reacting system with known initial composition, the progress of a single stage irreversible reaction can be measured by $\int_0^{t'} k dt$ alone. As an electrical analogue system previously discussed can produce output voltage v_0 proportional to $\int_0^{t'} k dt$, the output voltage v_0 is thus a measure of progress of a single stage irreversible reaction.

1. Irreversible Unimolecular First-Order Reactions

The model of this reaction is:



The reaction rate is described by the equation:

$$- \frac{dc_W}{dt} = kc_W \quad (\text{IV.13})$$

where c_W = concentration of reacting species W

t = time variable

k = reaction rate following the Arrhenius equation.

Integration of equation IV.13 can be carried out giving:

$$- \int_{c_{W0}}^{c_{Wf}} \frac{dc_W}{c_W} = \int_0^{t'} k dt$$

$$\text{or } \ln \frac{c_{W0}}{c_{Wf}} = \int_0^{t'} k dt \quad (\text{IV.14})$$

where c_{W0} = initial concentration of reacting species W

c_{Wf} = final concentration of reacting species W

Substituting equation IV.11 into equation IV.14 gives:

$$\ln \frac{c_{W0}}{c_{Wf}} = - \frac{KA}{A_1} v_0 \quad (\text{IV.15})$$

For constant volume reaction, equation IV.15 may be written as:

$$\ln \frac{N_{W0}}{N_{Wf}} = - \frac{KA}{A_1} v_0 \quad (\text{IV.16})$$

where N_{W0} = initial content of reacting species W

N_{Wf} = final content of reacting species W

Occasionally, fractional conversion is used to express the progress of a process reaction. If fractional conversion X_W of a given reactant W at any time t is defined by the equation:

$$X_W = 1 - \frac{N_W}{N_{W0}} \quad (\text{IV.17})$$

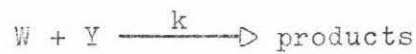
where N_W = content of reacting species W at any time t
Equation IV.17 can be substituted into equation IV.16 giving:

$$\ln (1 - X_{Wf}) = \frac{KA}{A_1} v_0 \quad (\text{IV.18})$$

where X_{Wf} = final fractional conversion of reacting species W at time t'

2. Irreversible Biomolecular Second-Order Reactions

When the reaction model follows the form:



the reaction rate equation is described by the equation:

$$\begin{aligned} -\frac{dc_W}{dt} &= -\frac{dc_Y}{dt} \\ &= k c_W c_Y \end{aligned} \quad (\text{IV.19})$$

where c_W, c_Y = concentration of two reacting species W and Y respectively

k = reaction rate

t = time variable

Applying the concept of fractional conversion, the amount of W or Y which has disappeared at any time t is:

$$c_{W0} X_W = c_{Y0} X_Y \quad (\text{IV.20})$$

where c_{W0}, c_{Y0} = initial concentration of W and Y respectively

X_W, X_Y = fractional conversion at any time t of W and Y respectively

$$\text{Let } M = \frac{c_{Y0}}{c_{W0}} \quad (\text{IV.21})$$

then equation IV.19 may be written as:

$$c_{W0} \frac{dX_W}{dt} = k c_{W0}^2 (1-X_W)(M-X_W) \quad (\text{IV.22})$$

The integrated form of equation IV.22 can be derived as:

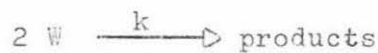
$$\ln \frac{M - X_{Wf}}{M(1-X_{Wf})} = c_{W0} (M-1) \int_0^{t'} k dt$$

provided $M \neq 1$

After substituting equation IV.11, it can be shown that:

$$\frac{1}{c_{W0} (M-1)} \ln \frac{M-X_{Wf}}{M(1-X_{Wf})} = - \frac{KA}{A_1} v_0 \quad (\text{IV.23})$$

In situations where the initial concentrations of reactants W and Y are the same (i.e. $M = 1$), the reaction model may be written as:



The reaction rate is described by the equation:

$$\begin{aligned} - \frac{dc_W}{dt} &= k c_W^2 \\ &= k c_{W0}^2 (1-X_W)^2 \end{aligned} \quad (\text{IV.24})$$

After integration, the result is:

$$\begin{aligned} \frac{1}{c_{Wf}} - \frac{1}{c_{W0}} &= \int_0^{t'} k dt \\ &= \frac{1}{c_{W0}} \frac{X_{Wf}}{1-X_{Wf}} \end{aligned}$$

Its relationship with the output voltage v_0 from the electrical analogue can be obtained by substituting equation IV.11, giving:

$$\frac{1}{c_{Wf}} - \frac{1}{c_{W0}} = - \frac{KA}{A_1} v_0 \quad (\text{IV.25})$$

Dependence of the integrated reaction rate expression on the stoichiometry of the reaction has been demonstrated by Levenspiel (22). Such dependence will therefore affect the equation describing the relationship between the output voltage v_0 from the electrical analogue and the progress of processing reaction. When the reaction model is:



which is first order with respect to both W and Y. The reaction rate equation becomes:

$$\begin{aligned} -\frac{dc_W}{dt} &= k c_W c_Y \\ &= k c_{W0}^2 (1-X_W)(M-2X_W) \end{aligned}$$

The integrated form of this reaction rate equation can be derived to be:

$$\frac{1}{c_{W0}(M-2)} \ln \frac{M-2X_{Wf}}{M(1-X_{Wf})} = \int_0^{t'} k dt$$

provided $M \neq 2$.

The corresponding relationship between analogue output voltage v_0 and the progress of this reaction becomes:

$$\frac{1}{c_{W0}(M-2)} \ln \frac{M-2X_{Wf}}{M(1-X_{Wf})} = -\frac{KA}{A_1} v_0 \quad (\text{IV.26})$$

when the initial composition of the reactants is at stoichiometric ratio (i.e. $M = 2$), equation IV.26 is indeterminate. It can be derived however, that

$$\frac{1}{c_{W0}} \frac{X_{Wf}}{1-X_{Wf}} = 2 \int_0^{t'} k dt$$

provided $M = 2$.

The corresponding relationship between analogue output

voltage v_0 and the progress of reaction is:

$$\frac{1}{c_{W0}} \frac{X_{Wf}}{1-X_{Wf}} = 2 \frac{KA}{A_1} v_0 \quad (\text{IV.27})$$

3. Irreversible Trimolecular Third-Order Reactions

If a model of this reaction is



the reaction rate equation will be:

$$-\frac{dc_W}{dt} = k c_W c_Y c_Z$$

where c_W , c_Y and c_Z = concentrations of reactants W, Y, and Z respectively.

k = reaction rate

t = time variable

In term of fractional conversion X_W of W, the reaction rate equation can be expressed as:

$$c_{W0} \frac{dX_W}{dt} = k c_{W0}^3 (1-X_W) \left(\frac{c_{Y0}}{c_{W0}} - X_W\right) \left(\frac{c_{Z0}}{c_{W0}} - X_W\right)$$

where c_{W0} , c_{Y0} and c_{Z0} = initial concentration of reactants W, Y and Z respectively

The integrated form of the reaction rate equation may be shown to be:

$$\begin{aligned} & \frac{1}{(c_{W0} - c_{Y0})(c_{W0} - c_{Z0})} \ln \frac{c_{W0}}{c_{Wf}} \\ & + \frac{1}{(c_{Y0} - c_{Z0})(c_{Y0} - c_{W0})} \ln \frac{c_{Y0}}{c_{Yf}} \\ & + \frac{1}{(c_{Z0} - c_{W0})(c_{Z0} - c_{Y0})} \ln \frac{c_{Z0}}{c_{Zf}} \end{aligned}$$

$$= - \int_0^{t'} k dt$$

where c_{Wf} , c_{Yf} and c_{Zf} = final concentration of reactants W, Y and Z respectively, after reacting time t' .

The corresponding relationship between the progress of this reaction and the analogue output voltage v_0 is obtained after substituting equation IV.11, and can be written as:

$$\begin{aligned} & \frac{1}{(c_{W0} - c_{Y0})(c_{W0} - c_{Z0})} \ln \frac{c_{W0}}{c_{Wf}} \\ & + \frac{1}{(c_{Y0} - c_{Z0})(c_{Y0} - c_{W0})} \ln \frac{c_{Y0}}{c_{Yf}} \\ & + \frac{1}{(c_{Z0} - c_{W0})(c_{Z0} - c_{Y0})} \ln \frac{c_{Z0}}{c_{Zf}} \\ & = - \frac{KA}{A_1} v_0 \end{aligned} \quad (IV.28)$$

For reaction model of the form:



with differential rate equation:

$$\begin{aligned} - \frac{dc_W}{dt} &= k c_W c_Y^2 \\ \text{or } \frac{dX_W}{dt} &= k c_{W0}^2 (1 - X_W) \left(\frac{c_{Y0}}{c_{W0}} - 2X_W \right)^2 \end{aligned}$$

the integrated form of the reaction rate equation can be derived as:

$$\frac{(2c_{W0} - c_{Y0})(c_{Y0} - c_{Yf})}{c_{Y0} c_{Yf}}$$

$$+ \ln \frac{c_{W_0} c_{Yf}}{c_{Y_0} c_{Wf}} = (2c_{W_0} - c_{Y_0})^2 \int_0^{t'} k dt$$

provided $\frac{c_{Y_0}}{c_{W_0}} \neq 2$

The corresponding relationship between the progress of reaction and the output voltage v_0 of the electrical analogue is:

$$\frac{(2c_{W_0} - c_{Y_0})(c_{Y_0} - c_{Yf})}{c_{Y_0} c_{Yf}} + \ln \frac{c_{W_0} c_{Yf}}{c_{Y_0} c_{Wf}} = -(2c_{W_0} - c_{Y_0})^2 \frac{KA}{A_1} v_0 \quad (\text{IV.29})$$

When $\frac{c_{Y_0}}{c_{W_0}} = 2$, it can be derived that:

$$\begin{aligned} \frac{1}{2} \frac{1}{c_{Wf}} - \frac{1}{2} \frac{1}{c_{W_0}} &= 8 \int_0^{t'} k dt \\ &= -8 \frac{KA}{A_1} v_0 \end{aligned} \quad (\text{IV.30})$$

For the reaction model:



with differential reaction rate equation:

$$- \frac{dc_W}{dt} = k c_W c_Y^2,$$

the integrated form of reaction rate equation can be derived as:

$$\frac{(c_{W_0} - c_{Y_0})(c_{Y_0} - c_{Yf})}{c_{Y_0} c_{Yf}} + \ln \frac{c_{W_0} c_{Yf}}{c_{Y_0} c_{Wf}} = (c_{W_0} - c_{Y_0})^2 \int_0^{t'} k dt$$

$$\text{provided } \frac{c_{Y_0}}{c_{W_0}} \neq 1$$

$$\text{or } \frac{1}{\frac{c_{W_f}}{2}} - \frac{1}{\frac{c_{W_0}}{2}} = 2 \int_0^{t'} k dt$$

$$\text{provided } \frac{c_{Y_0}}{c_{W_0}} = 1$$

After substituting equation IV.11, the result is:

$$\begin{aligned} & \frac{(c_{W_0} - c_{Y_0})(c_{Y_0} - c_{Y_f})}{c_{Y_0} c_{Y_f}} + \ln \frac{c_{W_0} c_{Y_f}}{c_{Y_0} c_{W_f}} \\ & = -(c_{W_0} - c_{Y_0})^2 \frac{KA}{A_1} v_0 \end{aligned} \quad (\text{IV.31})$$

$$\text{provided } \frac{c_{Y_0}}{c_{W_0}} \neq 1$$

$$\text{or } \frac{1}{\frac{c_{W_f}}{2}} - \frac{1}{\frac{c_{W_0}}{2}} = -2 \frac{KA}{A_1} v_0 \quad (\text{IV.32})$$

$$\text{provided } \frac{c_{Y_0}}{c_{W_0}} = 1$$

4. Irreversible Reaction with Empirical Rate Equation of the n th Order

The differential reaction rate is described by the equation:

$$-\frac{dc_W}{dt} = k c_W^n$$

where c_W = concentration of reacting species W

k = reaction rate

t = time variable

n = order of reaction

Integration can be carried out to obtain the reaction rate equation as:

$$c_{Wf}^{1-n} - c_{W0}^{1-n} = (n-1) \int_0^{t'} k dt$$

provided $n \neq 1$

where c_{W0}, c_{Wf} = initial and final concentration of W
 t' = reaction time

In terms of the fractional conversion X_W of W it can be shown that:

$$c_{W0}^{1-n} ((1-X_W)^{1-n} - 1) = (n-1) \int_0^{t'} k dt$$

provided $n \neq 1$

After substituting equation IV.11, the relationship of progress of such a reaction and the analogue output voltage v_0 can be obtained as:

$$\begin{aligned} c_{Wf}^{1-n} - c_{W0}^{1-n} &= (1-n) \frac{KA}{A_1} v_0 & \text{(IV.33)} \\ &= c_{W0}^{1-n} ((1-X_W)^{1-n} - 1) \end{aligned}$$

5. The Relationship of the Ratio of Frequency Factor and the Ratio of Reaction Rate Constants at a Constant Temperature

The ratio of frequency factors $\frac{A}{A_1}$ always appears in relationship between the output voltage of the electrical analogue and the progress of a reaction. Such frequency factors, namely A, that of actual reaction rate and A_1 , that of generated reaction rate, may not be conveniently obtained in practice. For example, data on the kinetics of thermal processing may be given in terms of reaction rate at a given temperature as is often the case in

thermobacteriology. Furthermore, the generated reaction rate at a given temperature can more easily be measured by a voltmeter while the generated frequency factor A_1 has to be calculated according to equation IV.7. Using the ratio of reaction rate constants at a constant temperature instead of the ratio of frequency factors may become convenient in many cases. The relationship of the ratio of frequency factors and the ratio of reaction rate constants at a constant temperature may be obtained from dividing equation IV.2 by equation IV.7 as:

$$\frac{A}{A_1} = \frac{k_T}{v_{2T}} \quad (\text{IV.34})$$

provided $\frac{E}{R} = nB$

where k_T = reaction rate at a given temperature
T

v_{2T} = generated reaction rate at a given
temperature T.

V. APPARATUS

A. REGULATED POWER SUPPLY FOR THE ANALOGUE SYSTEM

A voltage regulated power supply was constructed according to the circuit diagram in Figure V.1. The power supply so constructed forms two separated pairs of DC supply output terminals. Each pair of the DC supply output terminals could have variable electrical potential from approximately 5.5 to 16 volts by adjusting the associated 1 kilohm variable resistor. The ripple rejection in such voltage regulation was approximately 80 decibels. The output current available was approximately 1 ampere. Connection of the output terminals was arranged to indicate the positive, negative and ground terminals for application to the electrical analogue system. Electrical potential at the output terminal had +12 volts with respect to ground and that the negative output terminal had -12 volts with respect to ground.

B. ELECTRICAL ANALOGUE SYSTEM

1. Primary Reaction Rate Generator

A primary reaction rate generator was constructed according to the circuit diagram in Figure V.2. The sensor of the circuit was formed by two NTC thermistors incorporated. The NTC thermistors were placed as close together as possible such that similar thermal environment was sensed. The 1 kilohm variable resistor was incorporated for adjusting input voltage into the base of the transistor BC 307 such that control of constant input voltage V_1 according to equation IV.4 could be exercised. As the electrical resistance characteristic of the NTC thermistors in the circuit were not exactly identical, off-setting of the

operational amplifier was carried out within ± 1 millivolt with the sensor held at the middle of the significant temperature range of thermal processing. This was necessary to minimise deviation of gain from linearity while the electrical resistance of thermistors changed with temperature over the significant range during processing. Were the NTC thermistors to be chosen such that their electrical resistance characteristics were exactly identical, off-setting of the operational amplifier could be carried out with the sensor being held at any suitable temperature. According to the NTC thermistors chosen, maximum allowable temperature for application of the sensor was 200°C .

2. Analogue Multiplier

Four analogue multipliers were constructed, each of which had the structure shown in Figure IV.3. Off-setting of the integrated circuit OTA CA 3080 (that is adjusting the bias resistor to give zero output when there is zero input) was carried out according to the procedure described in its application data (36). The amplifier, using an integrated circuit uA 741, was incorporated to give low input impedance for direct connection to the next stage of the analogue multiplier as well as for maintaining a suitable voltage gain for further manipulation. Off-setting of each operational amplifier was carried out within ± 1 millivolt.

3. Analogue Integrator

An analogue integrator was constructed according to the circuit diagram in Figure IV.4. Off-setting of the integrator was carried out by adjusting the 10 kilohms trim pot for minimal

drift while the input terminal was grounded. The input voltage divider was provided to permit only a constant fraction of input voltage to be integrated. This would allow the output voltage from the analogue integrator to be held within the voltage of power supply when high input voltage of approximately 10 volts was integrated over the anticipated thermal processing time (no more than two hours). The reset switch placed across the capacitor was provided for discharging the capacitor prior to an integrating operation. The terminal "OUTPUT" was provided for application of voltmeter. The terminal $\frac{\text{"OUTPUT"}}{101}$ was provided for application of the potentiometric chart recorder during analogue system testing.

C. THERMAL PROCESSING REACTOR

An autoclave was used to supply thermal potential and energy to a conical flask of water containing the sensor of the analogue system. A "Danfoss" thermostat was fitted on the autoclave to control the supply of steam and hence the temperature in the chamber of the autoclave. The thermostat was an on-off switching type. It was capable of maintaining a constant temperature in the chamber of the autoclave within approximately $\pm 1^{\circ}\text{C}$. The wiring arrangement through the door of the autoclave was as shown in Figure IV.5. Sufficient water in the conical flask was provided to attenuate fluctuation of the temperature surrounding the sensors. Thermal convection of water in the flask also minimised the temperature difference arising from any difference in the location of the sensors. This was very important in testing the performance of the analogue because the temperature in the vicinity of the sensor of the analogue had to be sensed by thermocouple.

D. MEASURING EQUIPMENT

1. Voltmeter

A null detector and microvoltmeter (Keithley Instruments, model 155, serial number 88724) was used to measure voltage in off-setting the analogue circuit. It was also used in the experiments for measuring the voltage v_2 which represented the generated reaction rate according to equation IV.7. The accuracy of the voltage reading from the voltmeter was within $\pm 1\%$ of its full scale reading.

2. Potentiometer and Thermocouple

A copper constantan thermocouple was used to sense the temperature in the vicinity of the sensor. The thermoelectric characteristics of the thermocouple were observed to follow those described in the British Standard BS 1828. The hot junction of the thermocouple was placed within 3 mm of each thermistor of the analogue sensor. The cold junction of the thermocouple was maintained at 0°C by immersion in wet ice flake.

The millivolt output from the thermocouple was measured by a manually operated potentiometer (Cambridge Potable Potentiometer, type number 44228, serial number 438767). The accuracy of the voltage reading from such a potentiometer was approximately ± 0.003 millivolt, i.e. approximately $\pm 0.05^\circ\text{C}$ for the copper constantan thermocouple.

3. Potentiometric Recorders

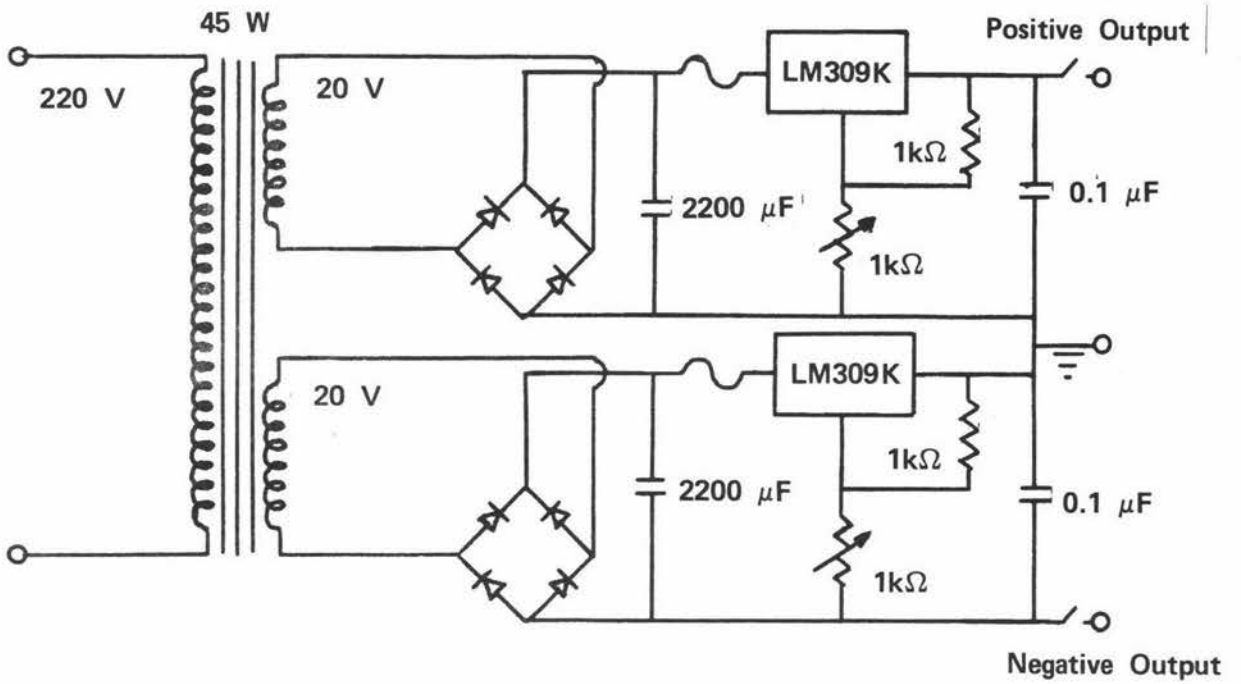
A potentiometric recorder (Sargent Recorder, model SRG, catalog number S 72180-17, serial number 2080008) was used to follow the output voltage development from the analogue system.

The accuracy of the voltage reading from the recorder was within $\pm 0.5\%$ of the full scale reading.

A potentiometric recorder (Venture Servoscribe, RE 511.20, serial number 3476) was also used to record the temperature and time profile in the vicinity of the thermistor. The variable voltage span was used to enlarge the scale of recorded temperature slightly. Calibration of the temperature scale on the recorder was made against the measurement obtained by using the Cambridge potentiometer. The accuracy of temperature reading from the recorder was approximately $\pm 0.5^{\circ}\text{C}$.

FIGURE V.1

CIRCUIT DIAGRAM OF THE VOLTAGE REGULATED POWER SUPPLY



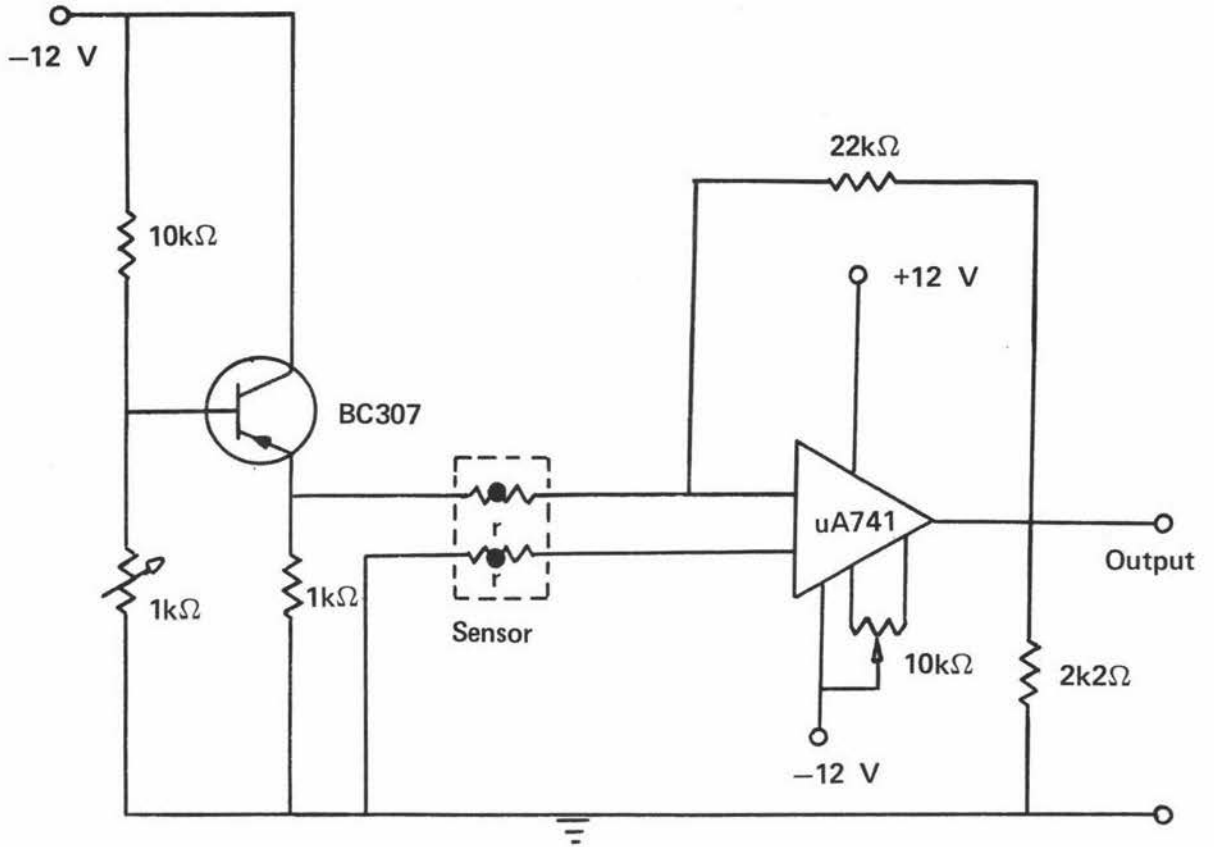
LM309K

= Integrated circuit of a voltage regulator (28)



= IN 4003 diode

FIGURE V.2

CIRCUIT DIAGRAM OF THE PRIMARY REACTION RATE v_1 GENERATOR

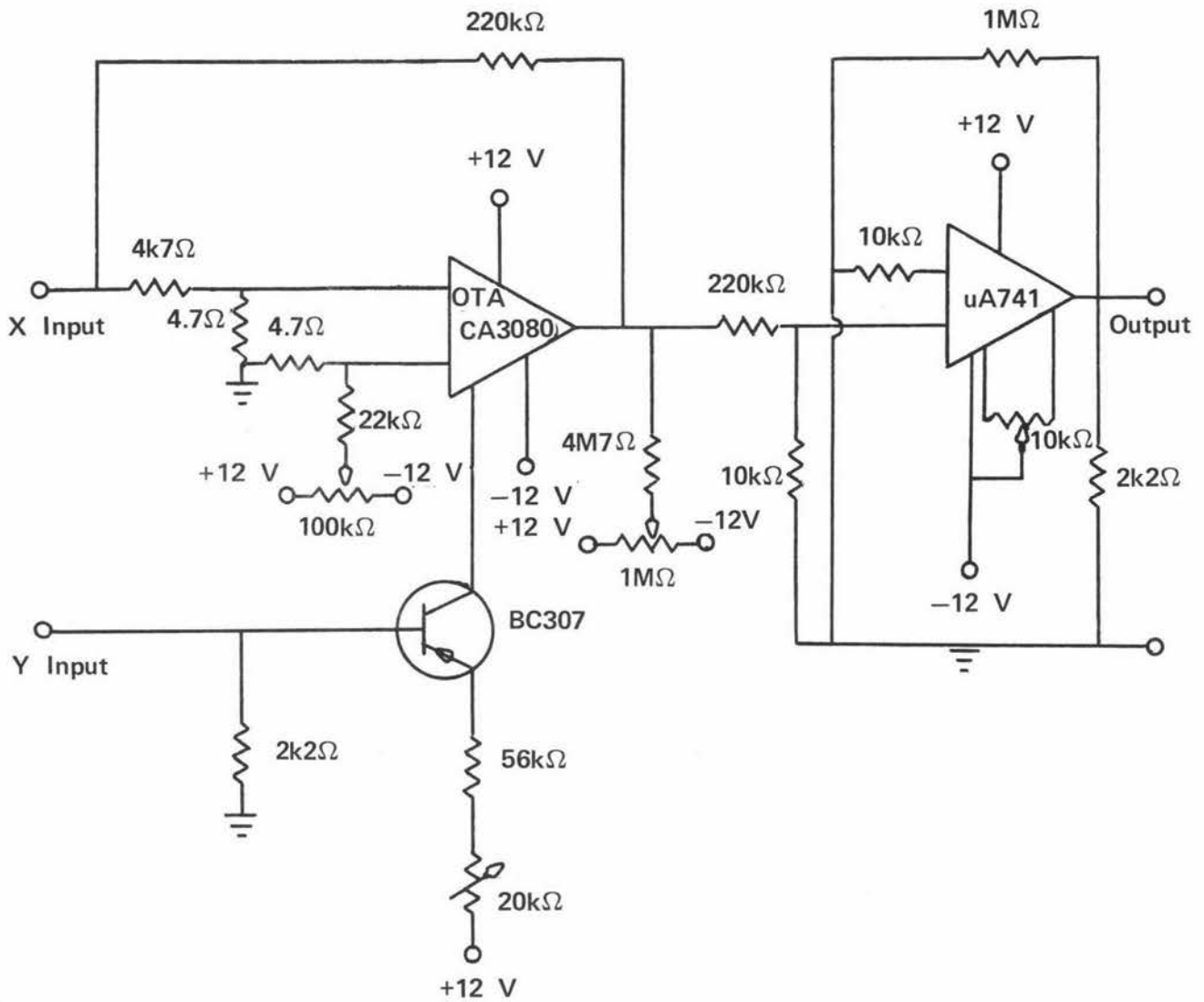
= Integrated circuit of an operational amplifier (12)



= NTC thermistor with $R_{25^{\circ}\text{C}}$ of 15,000 Ω and $B_{25^{\circ}\text{C}}$ of 3750 $^{\circ}\text{K}$ (32)

FIGURE V.3

CIRCUIT DIAGRAM OF AN ANALOGUE MULTIPLIER



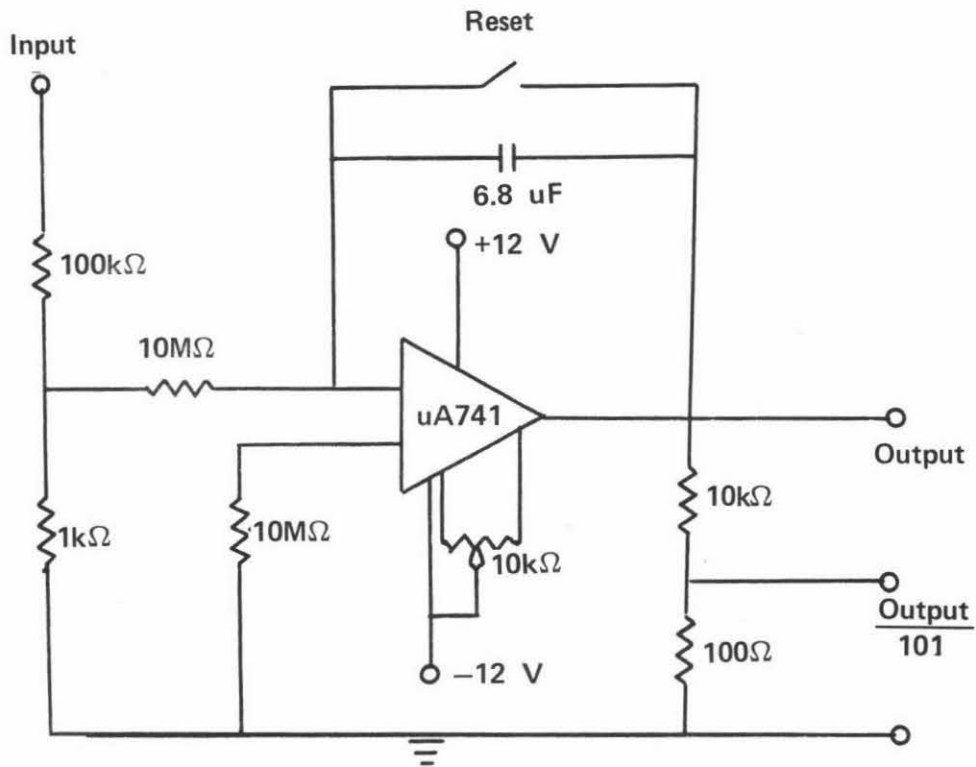
= Integrated circuit of an operational transconduction amplifier (36)



= Integrated circuit of an operational amplifier (12)

FIGURE V.4

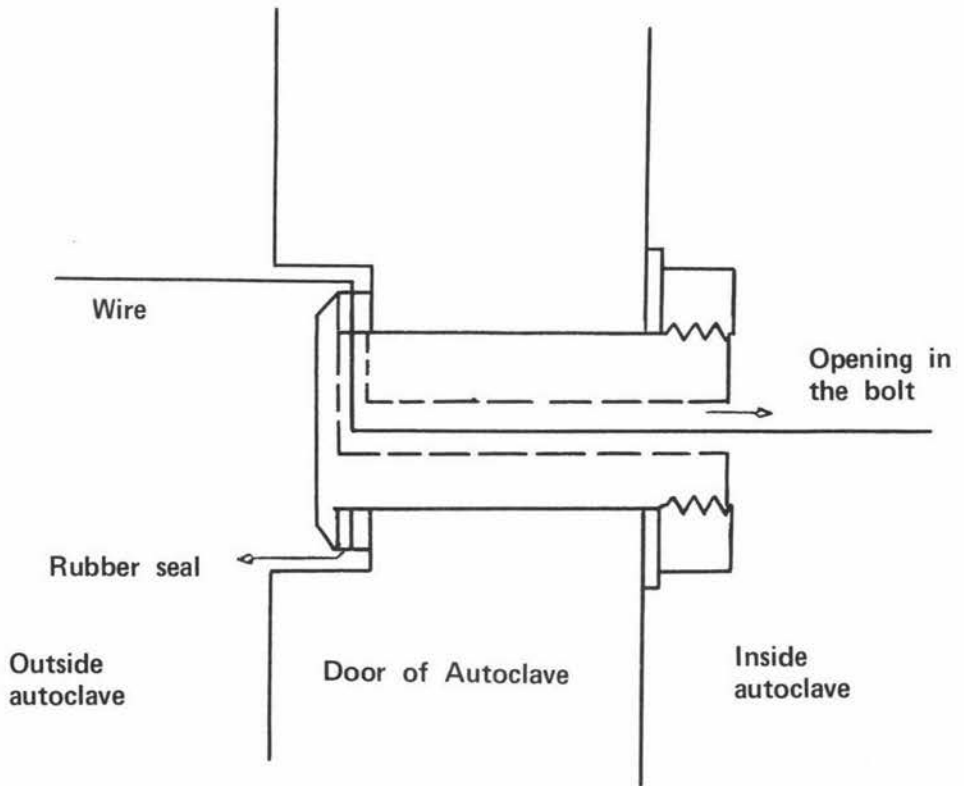
CIRCUIT DIAGRAM OF THE ANALOGUE INTEGRATOR



= Integrated circuit of an operational amplifier (12).

FIGURE V.5

DIAGRAM OF WIRING THROUGH THE DOOR OF THE AUTOCLAVE



VI. PROCEDURE

A. ARRANGEMENT OF THE APPARATUS FOR EXPERIMENTAL TESTING OF THE ANALOGUE SYSTEM

The apparatus was arranged as shown in Figure IV.1. The power supply was omitted from the block diagram for simplicity. The arrangement of the intermediate units of the analogue multiplier is omitted, the actual arrangement depending on specific requirements.

B. DETERMINATION OF THE GENERATED PRIMARY REACTION RATE v_1 AT VARIOUS TEMPERATURE T

The performance of the analogue in generating the primary reaction rate v_1 was determined by testing the validity of equation IV.4. Recording of the primary reaction rate v_1 at various temperature T was made over the range of temperature for thermal processing. In the experiments a temperature range from approximately 100°C to 120°C was considered.

Adjustment on the magnitude of the primary reaction rate v_1 was made for convenient reading on the voltmeter. The adjustment was made such that the primary reaction rate v_1 reading was approximately at maximum on a suitable scale of the voltmeter when the thermistors were at their highest expected temperature. The adjustment could be done on the 1 kilohm variable resistor in Figure V.2 to give a suitable voltage at the base of the transistor and hence suitable magnitude of the primary reaction rate v_1 according to equation IV.4.

Recording of the primary reaction rate v_1 and the corresponding temperature T in the vicinity of the thermistors was made as soon as the change of readings following the change of temperature in the autoclave was sufficiently small. Such records were taken during both the heating period and the cooling period.

The temperature in the vicinity of the thermistors was sensed by a copper-constantan thermocouple. Conversion of the millivolt output from the copper-constantan thermocouple to its corresponding inverse absolute temperature $\frac{1}{T}$ was made according to the Appendix A. The data on the primary reaction rate v_1 and corresponding inverse absolute temperature $\frac{1}{T}$ were subsequently used in the analysis to verify equation IV.4.

C. DETERMINATION OF GENERATED SECONDARY REACTION RATE CONSTANT v_2 AT VARIOUS TEMPERATURES T

The performance of the analogue multipliers for increasing the temperature coefficient of the primary reaction rate constant, was determined by testing the validity of equation IV.7 at various settings of integer n . The values of the secondary reaction rate and the corresponding inverse absolute temperature $\frac{1}{T}$ for each setting of integer n were obtained in the same way as that described in Section VI, B.

D. TESTING OF THE ANALOGUE INTEGRATOR

The performance of the analogue integrator for this purpose was determined by testing its conformity with equation IV.8. In this test various constant voltages were used instead of the

variable voltage v_2 representing the secondary reaction rate.

A potentiometric recorder was used to record the output voltage at various integrating times for each of the constant input voltages applied. Such records were necessary to show the linearity of the integrated output voltage in response to each constant input voltage. The rate of change of output voltage with time at various constant input voltages was measured for subsequent computation of the constant K associated with the integration according to equation IV.8.

E. APPLICATION OF THE ELECTRICAL ANALOGUE IN THERMAL PROCESSING

A thermal sterilization of an indicator microorganism in a flask of medium, at approximately 121°C , was used to demonstrate the procedure by which application of the electrical analogue system followed the progress of the processing reaction.

The kinetics of the thermal processing reaction was assumed to follow the irreversible unimolecular first-order reaction. The temperature dependency of the rate constant k was also assumed to follow the Arrhenius equation. The equations developed in Section IV. C.1 were applicable accordingly for correlating the output voltage v_0 from the analogue system and the progress of the processing reaction. In order to meet the requirement for the valid application of the equations developed in Section IV. C.1, the temperature coefficient of the generated reaction rate constant was set equal to the temperature coefficient of the process reaction rate (i.e. $nB = \frac{E}{R}$). The thermal resistance

data of the microorganism under the processing condition was assumed to be as follows:

$$\frac{E}{R} = 36,570^{\circ}\text{K} \quad \text{or} \quad z = 17.6^{\circ}\text{F}$$

$$k_{121^{\circ}\text{C}} = 11.5 \text{ min}^{-1} \quad \text{or} \quad D_{121^{\circ}\text{C}} = 0.2 \text{ min.}$$

The sensor of the analogue system was placed in the flask of medium at the region where progress of the thermal processing was followed. In the experiment the sensor of the analogue was placed approximately at the centre of the medium. The secondary reaction rate v_2 was set to 8 volts at 121°C . The setting was carried out through the 1 kilohm variable resistor shown in Figure V.2. An accurate reading of the secondary reaction rate v_2 at the setting temperature or at any other constant temperature T must be taken for interpretation of the results from the analogue system according to equation IV.15 and equation IV.34.

The generated secondary reaction rate v_2 could not be obtained accurately below 100 millivolts because of imperfection in circuitry off-setting and drifting with temperature. Setting for a high voltage reading of the secondary reaction rate v_2 at the processing temperature was necessary to minimise the significance of the error of the generated reaction rate v_2 at lower temperatures. For example, if the generated secondary reaction rate v_2 was set to 8 volts at the expected processing temperature (121°C), the magnitude of the generated secondary reaction rate v_2 below 100 millivolts would be below 1.25% of that at 121°C (8 volts). The highest possible value of the generated reaction rate v_2 was just under +12 volts. Allowance had to be made, however, for slight over-shooting of the process-

ing temperature during the operation.

Approximately 122°C was set on the thermostat controlling the temperature in the chamber of the autoclave. When thermal energy was applied the output voltage v_0 and the processing time were recorded by the potentiometric recorder to indicate the progress of the thermal processing.

The temperature and time profile in the vicinity of the thermistors was sensed by a copper-constantan thermocouple, the millivolt output of which was recorded by a potentiometric recorder for the graphical determination of the progress of the thermal processing.

The electrical analogue was also used to follow the progress of thermal destruction of a chemical species at 100°C in the middle of a flask of medium. In this case, the required thermal processing temperature could be achieved by boiling at the atmospheric pressure. A hot plate was used to supply the thermal energy for processing. Any tendency towards over-shooting of the processing temperature in this case was very well controlled by the constant atmospheric pressure, so that setting of the generated secondary reaction rate v_2 could be made closer to +12 volts with little allowance for over-shooting of the processing temperature. In the experiment, the generated secondary reaction rate v_2 , at the processing temperature (100°C) was set at 9 volts.

The process kinetics of the thermal destruction of the

chemical species was assumed to follow an irreversible unimolecular first-order reaction. The following parameters governing the thermal destruction rate of the chemical species were assumed:

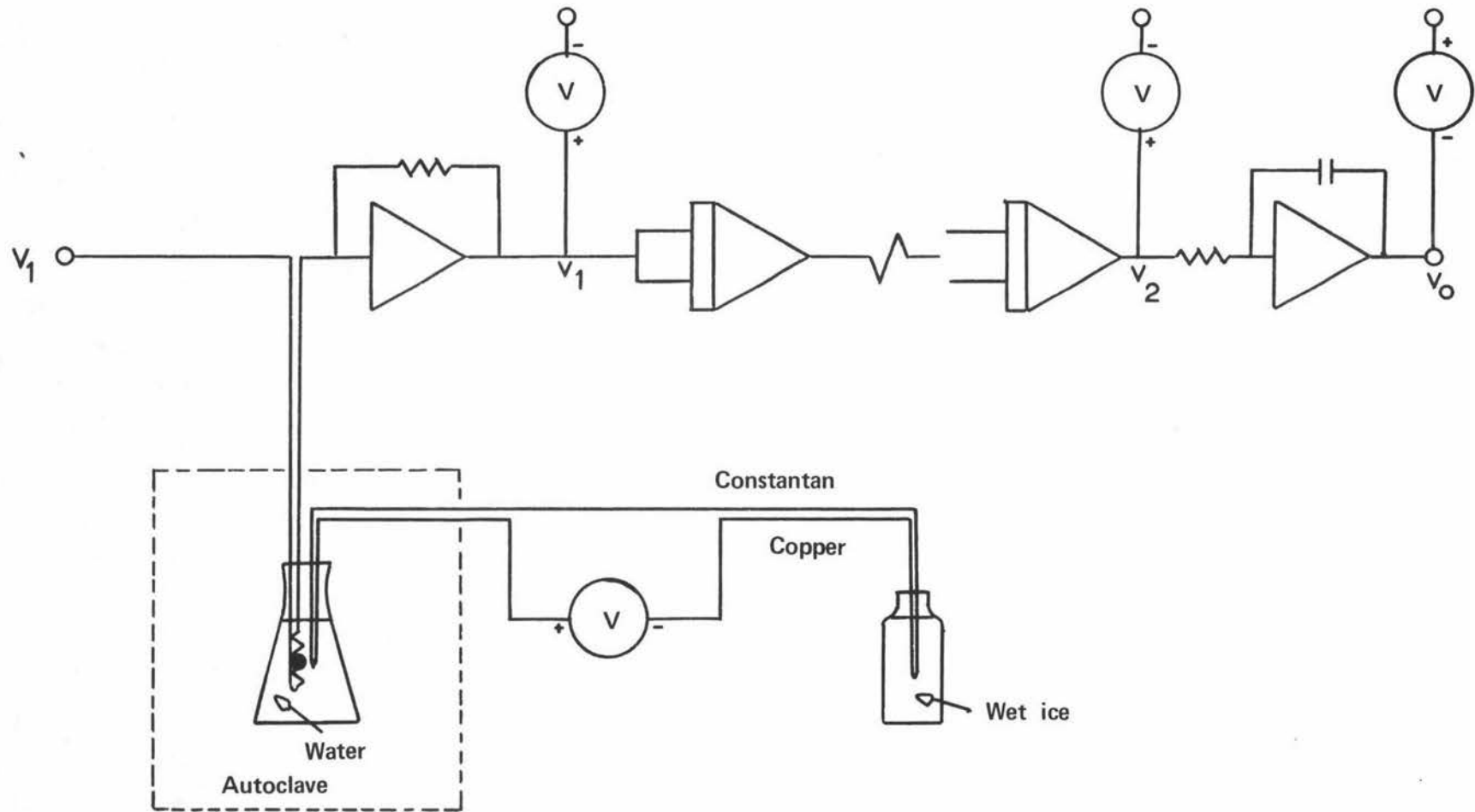
$$\frac{E}{R} = 7314^{\circ}\text{K}$$

$$k_{100^{\circ}\text{C}} = 1 \text{ min}^{-1}$$

The multipliers of the electrical analogue system were set to have the temperature coefficient nB of the generated secondary reaction rate v_2 , of 7314°K with $n = 2$. The output voltage v_0 from the electrical analogue and the temperature-time profile in the vicinity of the thermistor were recorded.

FIGURE VI.1

ARRANGEMENT OF APPARATUS FOR TESTING THE ANALOGUE



VII. RESULTS

The experimental results of the analogue in generating the primary reaction rate v_1 are collected in Table VII.1.

Table VII.2 to Table VII.8 are summaries of experimental results in generating the secondary reaction rate v_2 at various settings of the temperature coefficient.

The results of testing the performance of the analogue integrator are shown in Figure VII.1.

Figure VII.2 shows the recorded output voltage v_0 from the analogue system, indicating the progress of the thermal destruction of a microbial population. The thermal conditions in the vicinity of the sensor of the analogue system are shown in Figure VII.3.

Figure VII.4 is the recorded output voltage v_0 from the analogue system, indicating the progress of the thermal destruction of a chemical species. The corresponding thermal conditions in the vicinity of the sensor of the analogue system are shown in Figure VII.5.

TABLE VII.1

RESULTS OF PRIMARY REACTION RATE v_1 GENERATED
BY THE ANALOGUE

	Electrical Potential of Thermocouple (mV)	Primary Reaction Rate v_1 (V)	Inverse Absolute Temperature $1/T \times 10^3$ ($^{\circ}\text{K}^{-1}$)
HEATING	4.639	4.00	2.621
	4.979	4.75	2.571
	5.163	5.25	2.546
	5.292	5.62	2.528
COOLING	5.126	5.15	2.551
	4.892	4.60	2.584
	4.695	4.15	2.612
	4.428	3.55	2.652
	4.292	3.30	2.673

TABLE VII.2

RESULTS OF REACTION RATE v_2 GENERATED BY
APPLICATION OF ANALOGUE MULTIPLIER

The integer multiple, n of the temperature coefficient in the primary reaction rate is 2.

	Electrical Potential of Thermocouple (mV)	Reaction Rate v_2 (V)	Inverse Absolute Temperature $1/T \times 10^3$ ($^{\circ}\text{K}^{-1}$)
HEATING	4.388	3.05	2.658
	4.626	4.00	2.623
	4.833	5.10	2.592
	4.978	5.95	2.572
	5.148	7.15	2.548
	5.280	8.20	2.531
COOLING	5.131	7.05	2.550
	4.890	5.45	2.584
	4.682	4.35	2.614
	4.493	3.50	2.642
	4.300	2.83	2.672

TABLE VII.3

RESULTS OF REACTION RATE v_2 GENERATED BY
APPLICATION OF ANALOGUE MULTIPLIER

The integer multiple, n of the temperature coefficient in the primary reaction rate is 4.

	Electrical Potential of Thermocouple (mV)	Reaction Rate v_2 (V)	Inverse Absolute Temperature $1/T \times 10^3$ ($^{\circ}\text{K}^{-1}$)
HEATING	4.479	1.50	2.644
	4.512	1.68	2.639
	4.698	2.52	2.612
	4.818	3.25	2.595
	5.060	5.40	2.560
	5.206	7.40	2.540
	5.255	8.20	2.534
COOLING	5.100	5.90	2.555
	4.891	3.80	2.584
	4.663	2.35	2.617
	4.359	1.20	2.664

TABLE VII.4

RESULTS OF REACTION RATE v_2 GENERATED BY
APPLICATION OF ANALOGUE MULTIPLIER

The integer multiple, n of the temperature coefficient in the primary reaction rate is 6.

	Electrical Potential of Thermocouple (mV)	Reaction Rate v_2 (V)	Inverse Absolute Temperature $1/T \times 10^3$ ($^{\circ}\text{K}^{-1}$)
HEATING	4.308	0.48	2.671
	4.483	0.86	2.643
	4.571	1.18	2.630
	4.732	1.95	2.607
	4.933	3.60	2.578
	5.089	5.85	2.556
	5.155	7.15	2.547
	5.228	8.90	2.538
COOLING	5.166	7.40	2.546
	5.095	5.90	2.555
	5.002	4.50	2.568
	4.850	2.87	2.590
	4.620	1.40	2.623
	4.320	0.55	2.669

TABLE VII.5

RESULTS OF REACTION RATE v_2 GENERATED BY
APPLICATION OF ANALOGUE MULTIPLIER

The integer multiple, n of the temperature coefficient in the primary reaction rate is 8.

	Electrical Potential of Thermocouple (mV)	Reaction Rate v_2 (V)	Inverse Absolute Temperature $1/T \times 10^3$ ($^{\circ}\text{K}^{-1}$)
HEATING	4.374	0.195	2.660
	4.568	0.460	2.631
	4.678	0.760	2.615
	4.768	1.10	2.602
	4.907	2.00	2.582
	5.090	4.10	2.556
	5.206	6.50	2.540
	5.260	8.00	2.534
COOLING	5.221	7.00	2.539
	5.131	4.95	2.550
	4.984	2.78	2.570
	4.734	1.00	2.606
	4.620	0.62	2.623
	4.538	0.42	2.636
	4.355	0.18	2.663

TABLE VII.6

RESULTS OF REACTION RATE v_2 GENERATED BY
APPLICATION OF ANALOGUE MULTIPLIER

The integer multiple, n of the temperature coefficient in the primary reaction rate is 10.

	Electrical Potential of Thermocouple (mV)	Reaction Rate v_2 (V)	Inverse Absolute Temperature $1/T \times 10^3$ ($^{\circ}\text{K}^{-1}$)
HEATING	4.455	0.175	2.647
	4.560	0.295	2.632
	4.678	0.565	2.615
	4.771	0.870	2.601
	4.838	1.50	2.585
	4.985	2.45	2.570
	5.061	3.50	2.560
	5.159	5.30	2.547
5.247	8.80	2.535	
COOLING	5.192	6.70	2.542
	5.102	4.40	2.554
	5.030	3.05	2.564
	4.940	1.90	2.577
	4.815	1.00	2.595
	4.751	0.720	2.604
	4.620	0.370	2.623
	4.545	0.265	2.635

TABLE VII.7

RESULTS OF REACTION RATE v_2 GENERATED BY
APPLICATION OF ANALOGUE MULTIPLIER

The integer multiple, n of the temperature coefficient in the primary reaction rate is 12.

	Electrical Potential of Thermocouple (mV)	Reaction Rate v_2 (V)	Inverse Absolute Temperature $1/T \times 10^3$ ($^{\circ}\text{K}^{-1}$)
HEATING	4.565	0.162	2.631
	4.652	0.265	2.618
	4.780	0.585	2.599
	4.885	1.12	2.585
	4.995	2.30	2.569
	5.085	3.70	2.557
	5.158	5.75	2.546
	5.212	7.70	2.540
	5.250	9.30	2.535
COOLING	5.221	8.00	2.538
	5.169	5.90	2.545
	5.078	3.55	2.558
	4.967	2.15	2.573
	4.810	0.810	2.595
	4.682	0.345	2.614
	4.605	0.195	2.625

TABLE VII.8

RESULTS OF REACTION RATE v_2 GENERATED BY
APPLICATION OF ANALOGUE MULTIPLIER

The integer multiple, n of the temperature coefficient in the primary reaction rate is 16

	Electrical Potential of Thermocouple (mV)	Reaction Rate v_2 (V)	Inverse Absolute Temperature $1/T \times 10^3$ ($^{\circ}\text{K}^{-1}$)
HEATING	4.925	0.570	2.579
	4.960	0.790	2.574
	5.020	1.30	2.566
	5.105	2.70	2.554
	5.165	4.30	2.546
	5.200	6.00	2.541
	5.225	7.20	2.538
COOLING	5.140	3.50	2.548
	5.070	2.05	2.559
	4.980	1.00	2.571
	4.910	0.540	2.581
	4.770	0.130	2.601

FIGURE VII.1.

RESULTS OF ANALOGUE INTEGRATOR TESTING

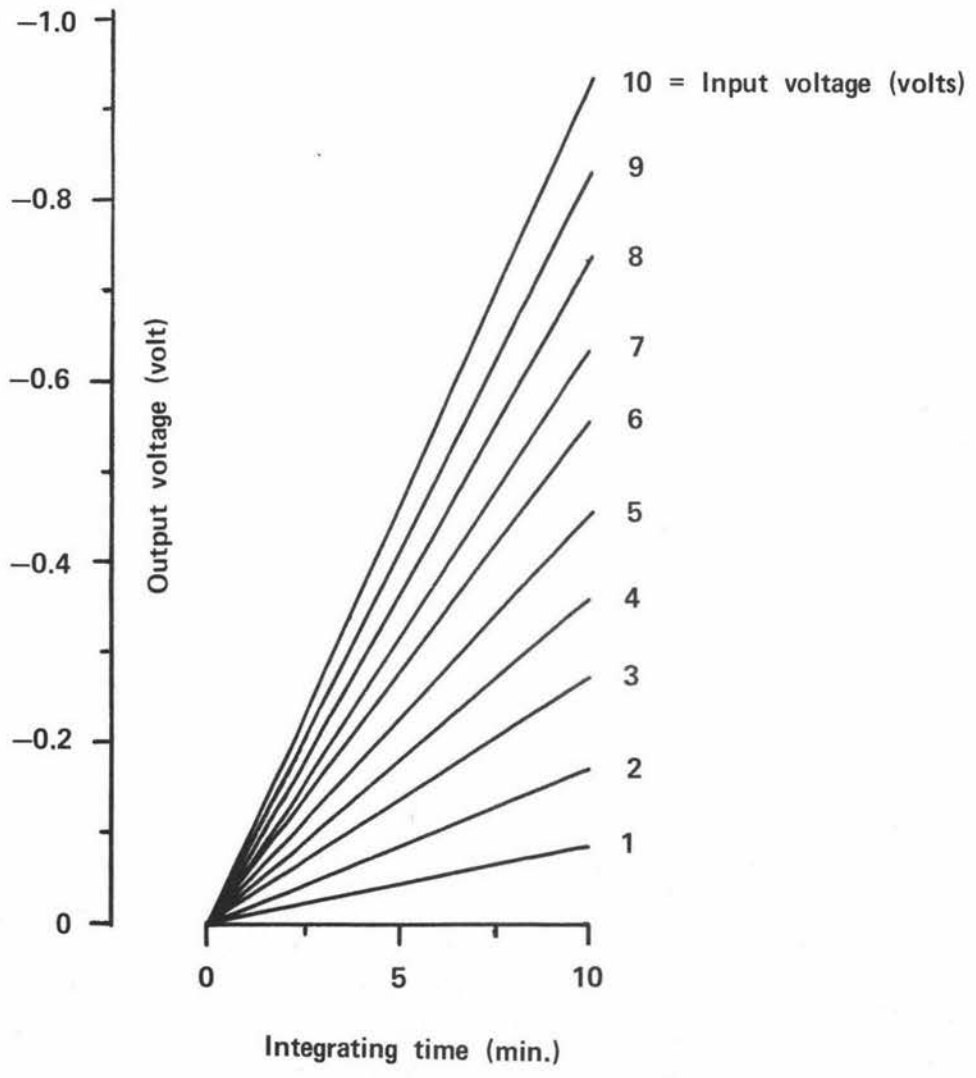


FIGURE VII.2

OUTPUT VOLTAGE FROM THE ANALOGUE SYSTEM IN FOLLOWING THE
PROGRESS OF THE STERILIZATION OF A MICROORGANISM

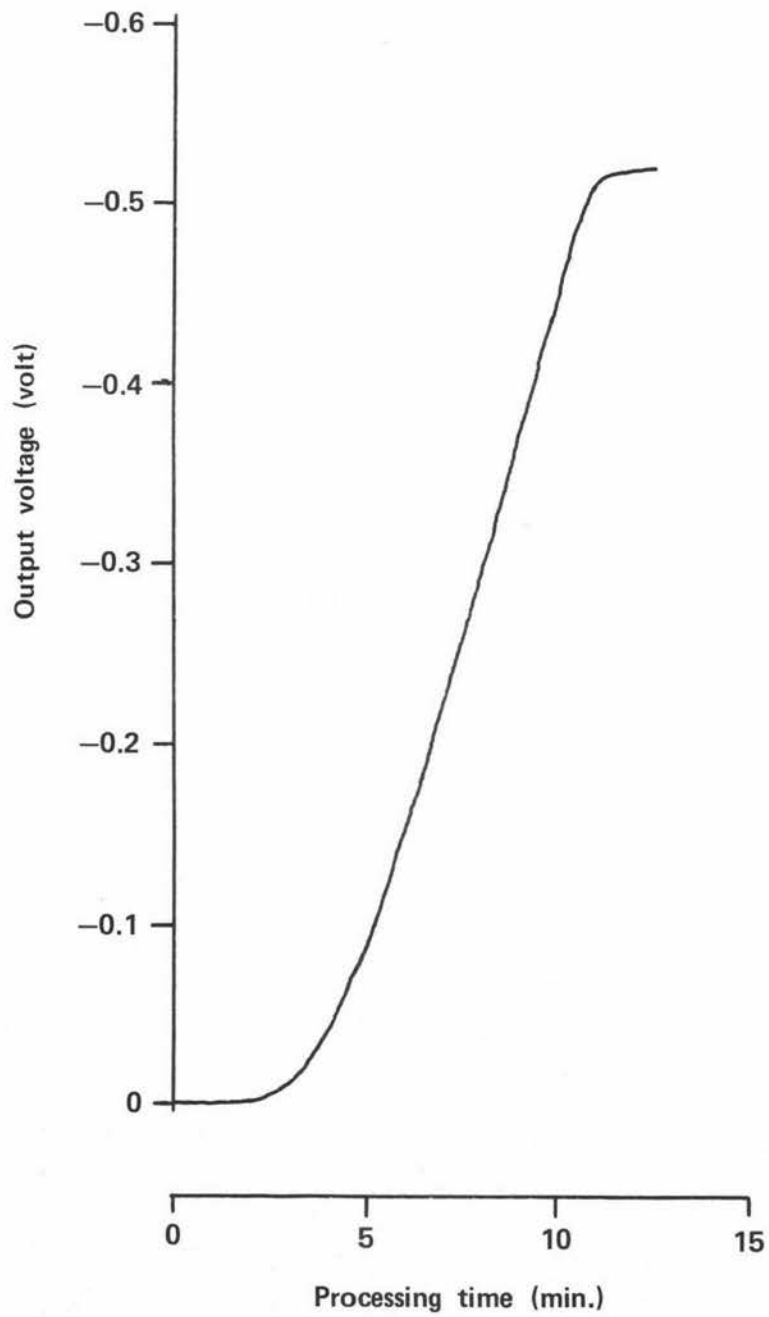


FIGURE VII.3

TEMPERATURE AND TIME PROFILE IN THE VICINITY OF THE SENSOR OF
THE ANALOGUE IN A MICROBIAL STERILIZATION

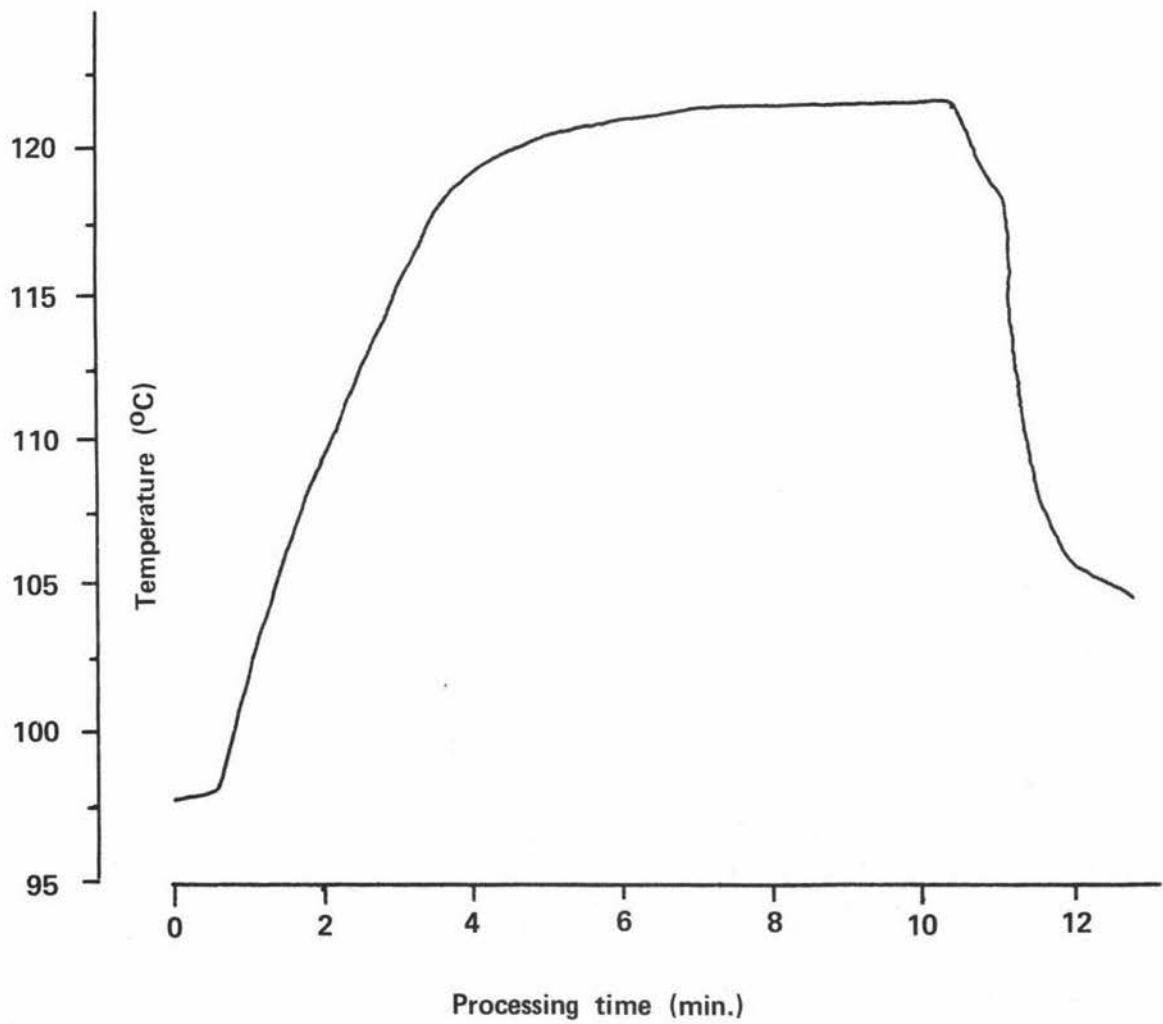


FIGURE VII.4

OUTPUT VOLTAGE FROM THE ANALOGUE SYSTEM IN FOLLOWING THE
PROGRESS OF THE DESTRUCTION OF THE CHEMICAL SPECIES

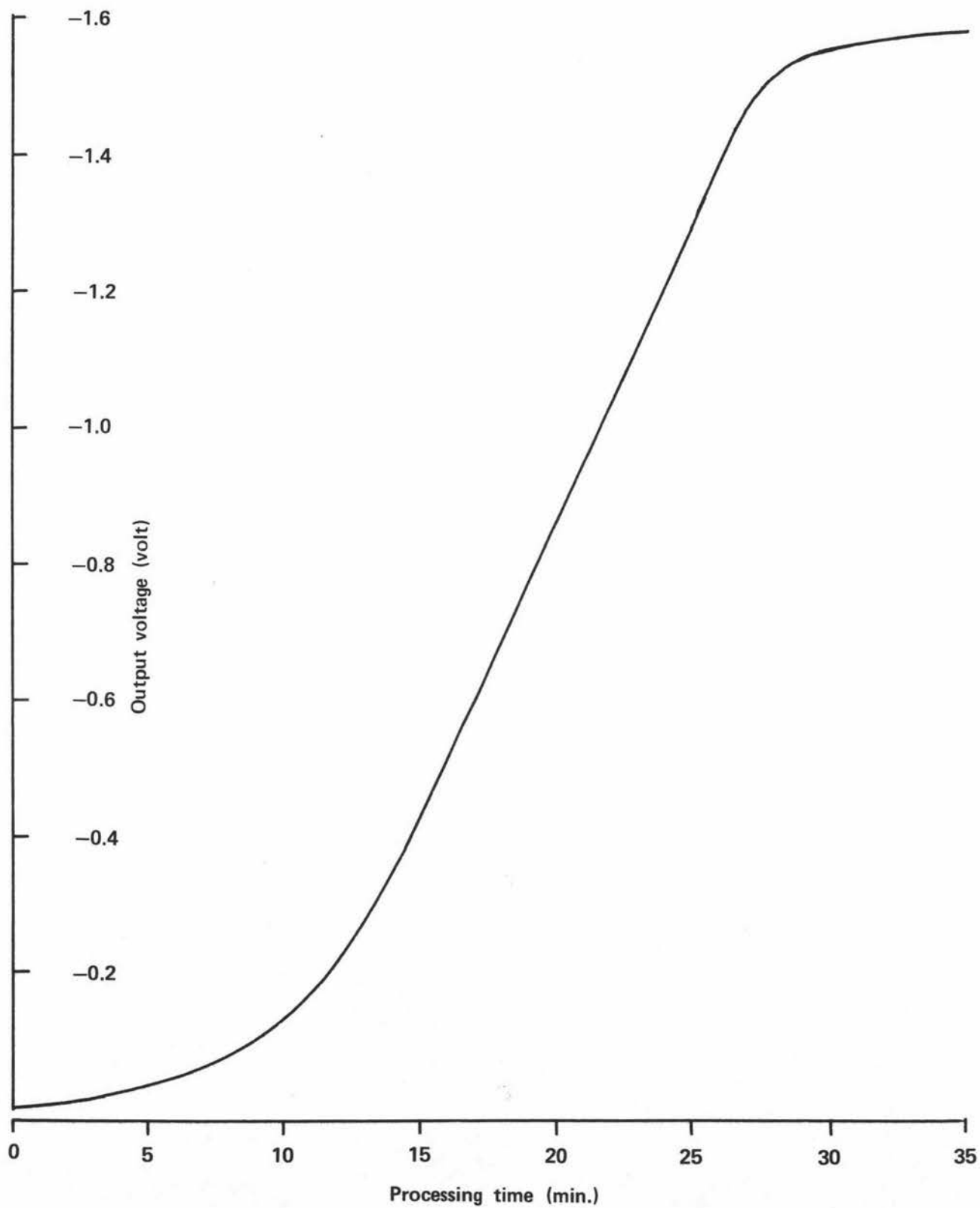
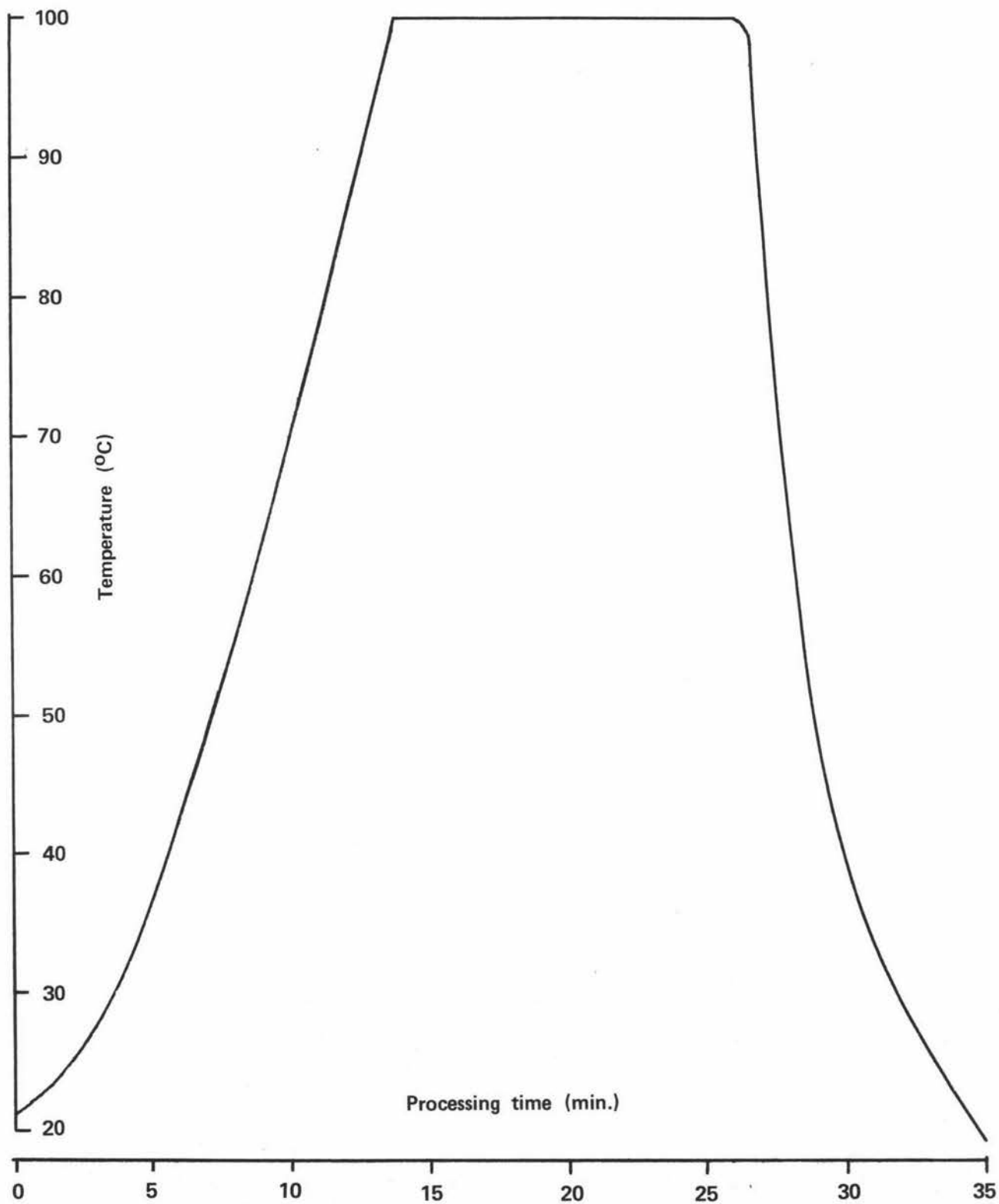


FIGURE VII.5
TEMPERATURE AND TIME PROFILE IN THE VICINITY OF THE SENSOR
OF THE ANALOGUE IN A CHEMICAL DESTRUCTION REACTION



VIII. DISCUSSION OF RESULTS

A. TESTING OF THE ANALOGUE SYSTEM

1. Generation of the Primary Reaction Rate v_1

The results obtained in Table VII.1 were analysed to verify equation IV.4, and hence the performance of the analogue in generating the primary reaction rate v_1 . A plot of $\ln v_1$ against $1/T$ according to the Arrhenius equation is shown in Figure VIII.1. A linear regression method for analysing the data is outlined in Appendix C. The correlation coefficient of the set of $\ln v_1$ and $1/T$ was found to be 0.9996. The experimental temperature coefficient B , was found to be 3657°K which was in agreement with the nominal value given by the manufacturer of the thermistors (35). The nominal value of B was $3750^\circ\text{K} \pm 5\%$ at 25°C . The pertinent values associated with the analysis of the data are summarized in Table C.1.

2. Generation of the Reaction Rate v_2 with Application of the Analogue Multiplier

The results obtained in each table from Table VII.2 to VII.8 were analysed to verify equation IV.7 and hence the performance of the analogue when analogue multipliers were applied to produce the reaction rate v_2 at various integer multiple n , of the temperature coefficient. Plots of $\ln v_2$ against $1/T$ according to the Arrhenius equation, for different values of n the multiplier of the temperature coefficient, are shown in Figures VIII.2 to VIII.8. Linear regression was used to analyse the data in a similar manner to that for the primary reaction rate generation. The results obtained are

summarized in Table VIII.1 and the values associated with the analysis of data are summarized in Table C.1. A plot of the temperature coefficient nB of the generated reaction, against the multiplier n , is shown in Figure VIII.9. The statistical method shown in Appendix D was used to estimate the errors of the temperature coefficient, in the generated reaction rate, associated with the application of the analogue multipliers. For a 99.8% confidence interval, the errors of the temperature coefficient were estimated to be $\pm 4.55\%$. The temperature coefficient of the generated reaction rate could therefore be expressed as $3657 n^{\circ}K \pm 4.55\%$. The errors arising from the application of the analogue multiplier could seriously distort the temperature dependency of the reaction rate generated by the analogue. The precision of such an analogue in following the progress of processing would thus be limited particularly when the temperature coefficient is large and the processing temperature is low.

3. The Analogue Integrator

For any voltage v , applied at the input terminal of the integrator in Figure V.4, the output voltage v_0 from the integrator would be described by the equation:

$$\begin{aligned}
 v_0 &= - \frac{1}{10^1 RC} \int_0^{t'} v dt \\
 &= - \frac{1}{K} \int_0^{t'} v dt
 \end{aligned}
 \tag{VIII.1}$$

where RC = time constant of the integrator, approximately
68 sec.

$K = 101 RC$, the constant associated with the integration, approximately 104 min.

$R =$ input resistance of the integrator, approximately 10 Mohm.

$C =$ feed back capacitance of the integrator, approximately 6.8 uF.

Differentiating equation VIII.1 would give:

$$-\frac{dv_O}{dt} = \frac{v}{K} \quad (\text{VIII.2})$$

In order to estimate the experimental value of the constant K associated with the integration, the constant rate of change of the output voltage $-dv_O/dt$ in integrating a constant input voltage v , was measured from results in Figure VII.1 and summarized in Table VIII.2. The values of the rate of change of integrating output voltage and the corresponding input voltage are plotted as shown in Figure VIII.10. The slope of the plot in Figure VIII.10 is $1/K$ according to equation VIII.2. Estimation of the constant K and the error of integration is shown in Appendix E. The value of the constant K was found to be approximately 109.9 min. The error associated with application of the integrator was estimated to be $\pm 7.25\%$ for 99% confidence interval.

The error in the analogue system was the total error taking into account the existing experimental arrangements. This total error would include experimental error, imperfection of the analogue system, and drifting of the offset of the analogue system according to the ambient temperature change.

B. THE ANALOGUE SYSTEM IN THERMAL PROCESSING

The output voltage v_0 from the analogue system shown in Figure VII.2 is related to the progress of the thermal sterilization by application of equations IV.15 and IV.34, giving:

$$-\frac{v_0}{\ln(c_{w0}/c_{wf})} = \frac{1}{K} \frac{v_{2, 394^\circ K}}{k_{394^\circ K}} \quad (\text{VIII.3})$$

where c_{w0} = initial concentration of the microorganism
 c_{wf} = final concentration of the microorganism
 K = the constant associated with the analogue integration which was found to be 109.9 min.

$v_{2, 394^\circ K}$ = generated reaction rate at $394^\circ K$ with nB approximating E/R

= 8000 mV as described in section VI.E

$k_{394^\circ K}$ = reaction rate of the thermal sterilization of microorganism at $394^\circ K$

= 11.5 min^{-1} as described in section VI.E.

After substituting the numerical value of the parameters described in equation VIII.3, the result is:

$$-\frac{v_0}{\ln(c_{w0}/c_{wf})} = 6.34 \text{ mV} \quad (\text{VIII.4})$$

The output voltages v_0 from the analogue system and the times in Figure VII.3 can thus be converted to the data of $\ln(c_{w0}/c_{wf})$ and time, using equation VIII.3. The results are shown in Table VIII.3.

The temperature and time data (Figure VII.3) in the vicinity of the sensor of the analogue were converted to the corresponding reaction rate and time data according to Appendix

B1. The results are shown in Figure VIII.11. Graphical integration of the reaction rate and time data gives the progress of the process reaction ($\ln \frac{c_{W0}}{c_{Wf}}$ vs. time according to equation V.14) as shown in Table VIII.3. Comparison of progress of the sterilization processing detected by the analogue system, with that detected by the temperature and time measurement is shown in Figure VIII.12. Throughout the period of the thermal sterilization, the integrated results from the analogue system deviated from that obtained by the temperature and time measurement by approximately 7.8%. The difference might be accounted for by factors similar to those described in the previous section on the testing of the analogue system.

The output voltage v_0 from the analogue system shown in Figure VII.4 is related to the progress of the thermal destruction of the chemical species in a similar manner to that in the example of sterilization. The relationship of the output voltage v_0 from the analogue and the composition of the chemical species under consideration can be shown to be:

$$- \frac{v_0}{\ln(c_{W0}/c_{Wf})} = 82 \text{ mV} \quad (\text{VIII.5})$$

where c_{W0} = initial concentration of the chemical species

c_{Wf} = final concentration of the chemical species

The output voltages v_0 from the analogue system and the times in Figure VII.3 can thus be converted to the data of $\ln(c_{W0}/c_{Wf})$ as a function of time, using equation VIII.5. The results are shown in Table VIII.4.

The temperature and time profile, (Figure VII.5) in the vicinity of the sensor of the analogue, were converted to the corresponding reaction rate and time profile according to Appendix B2. The results are shown in Figure VIII.13. Graphical integration of the reaction rate and time data gives the progress of the process reaction ($\ln(c_{wO}/c_{wF})$ vs. time) as shown in Table VIII.4. Comparative progresses of the thermal destruction of the chemical species detected by the analogue system and that detected by the temperature and time measurement are shown in Figure VIII.13. Throughout the period of the thermal processing (35 min.), the integrated results from the analogue system deviated from that obtained by the temperature and time measurement by approximately 3.2%.

This reduced deviation of the electrical analogue in following the progress of the thermal destruction of the chemical species in comparison to the thermal sterilization which is probably due to the lower temperature coefficient of the reaction rate in the former process with fewer multipliers in the analogue circuits.

TABLE VIII.1

SUMMARY OF RESULTS OF REACTION RATE GENERATION
BY THE ANALOGUE

n	Experimental Values of nB (°K)	Correlation Coefficient of ln v and $\frac{1}{T}$
1	3,657	.9996
2	7,597	.9993
4	14,284	.9998
6	21,572	.9996
8	29,181	.9998
10	34,873	.9997
12	42,392	.9992
16	60,988	.9906

TABLE VIII.2

MEASURED OUTPUT VOLTAGE CHANGES OF INTEGRATOR
AT VARIOUS INPUT VOLTAGES

Input Voltage v	Rate of Output Voltage Changes - (dv/dt) mV min. ⁻¹
1	8.7
2	17.4
3	27.0
4	36.6
5	45.4
6	56.1
7	64.3
8	72.5
9	83.7
10	94.8

TABLE VIII.3

COMPARISON OF PROGRESS OF THE THERMAL STERILIZATION
 DETECTED BY THE ANALOGUE AND THAT BY THE
 TEMPERATURE-TIME PROFILE

End of Processing Time (min.)	Analogue $\ln(c_{w0}/c_{wf})$	$\ln(c_{w0}/c_{wf})$ according to the Temperature- Time Data
1	0	0
2	.05	.035
3	1.6	1.8
4	6.4	7.0
5	14.7	16.0
6	24.3	26.3
7	36.0	38.0
8	47.8	50.2
9	59.7	62.6
10	71.6	75.6
11	81.0	85.7
12	82.0	88.9
13	82.0	88.9

TABLE VIII.4

COMPARISON OF PROGRESS OF THE THERMAL DESTRUCTION
 OF THE CHEMICAL SPECIES DETECTED BY THE ANALOGUE
 AND THAT BY THE TEMPERATURE-TIME PROFILE

End of Processing Time (min.)	Analogue $\ln(c_{w0}/c_{wf})$	$\ln(c_{w0}/c_{wf})$ according to the Temperature- time Data
2.5	.184	.160
5.0	.444	.389
7.5	.837	.813
10.0	1.60	1.55
12.5	3.07	3.05
15.0	5.45	5.40
20.0	10.7	10.4
25.0	16.0	15.5
27.5	18.4	17.6
30.0	19.0	18.2
32.5	19.2	18.5
35.0	19.4	18.8

FIGURE VIII.1

PLOT OF THE PRIMARY REACTION RATE GENERATED BY THE
ANALOGUE ACCORDING TO THE ARRHENIUS EQUATION

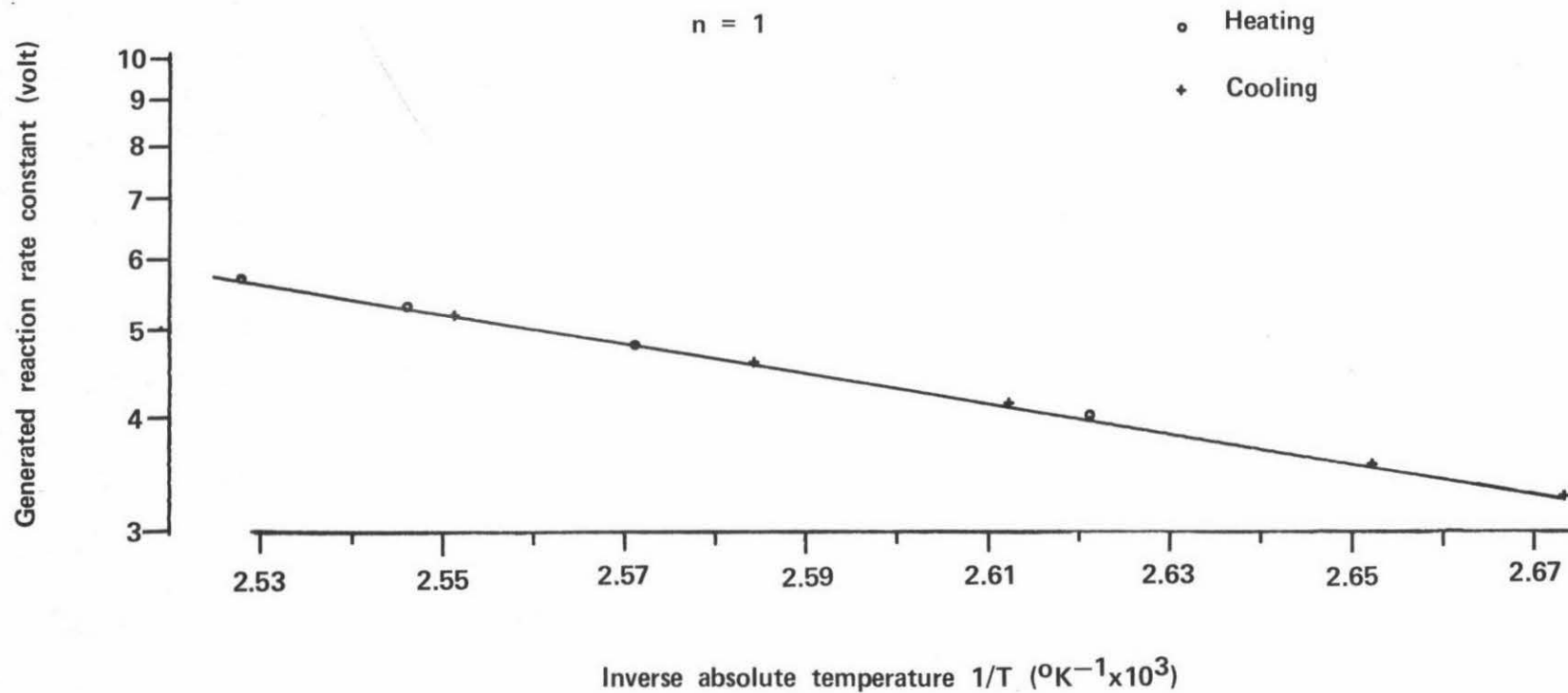


FIGURE VIII.2

PLOT OF THE REACTION RATE GENERATED BY THE ANALOGUE

ACCORDING TO THE ARRHENIUS EQUATION

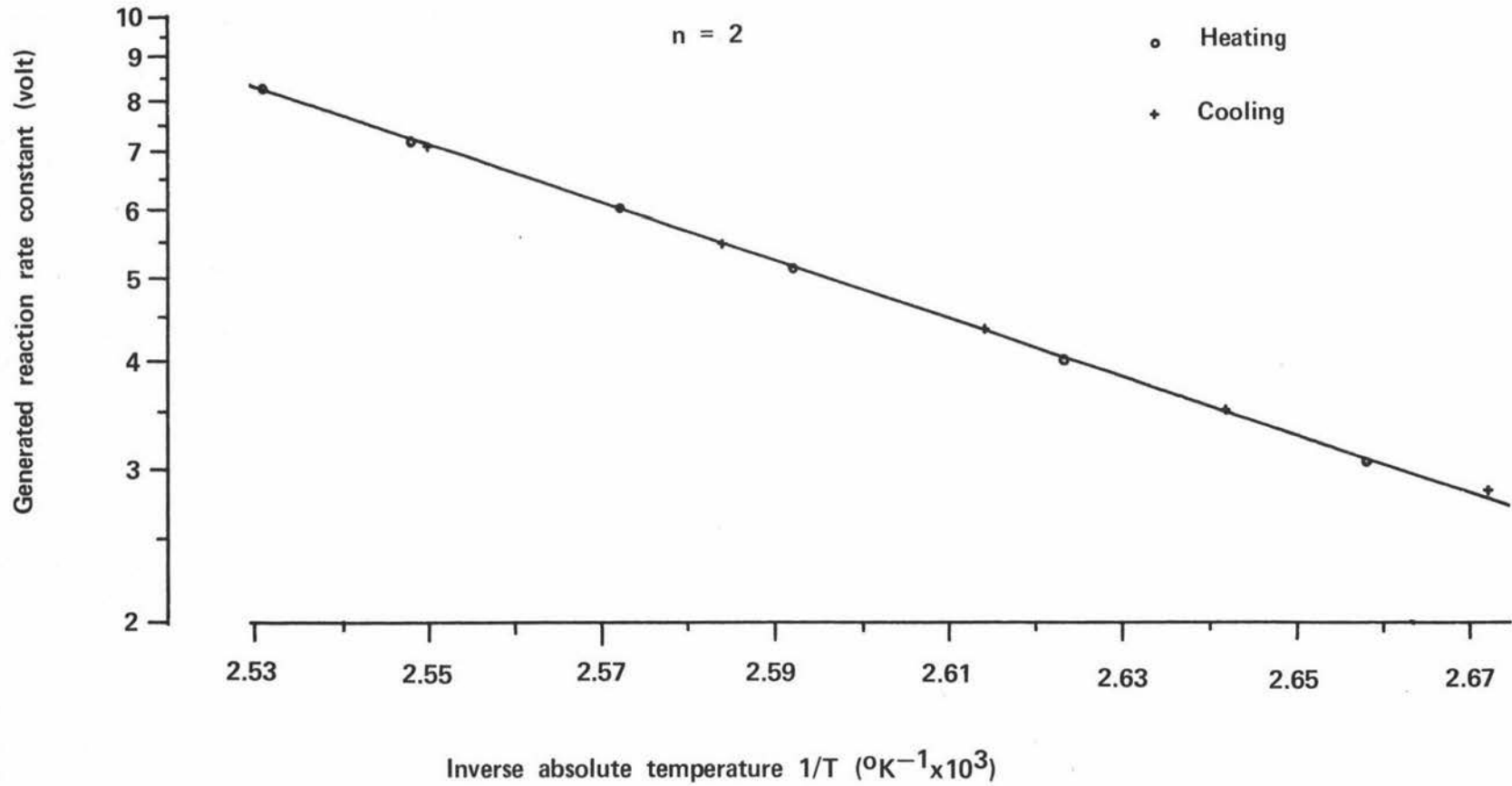


FIGURE VIII.3

PLOT OF THE REACTION RATE GENERATED BY THE ANALOGUE

ACCORDING TO THE ARRHENIUS EQUATION

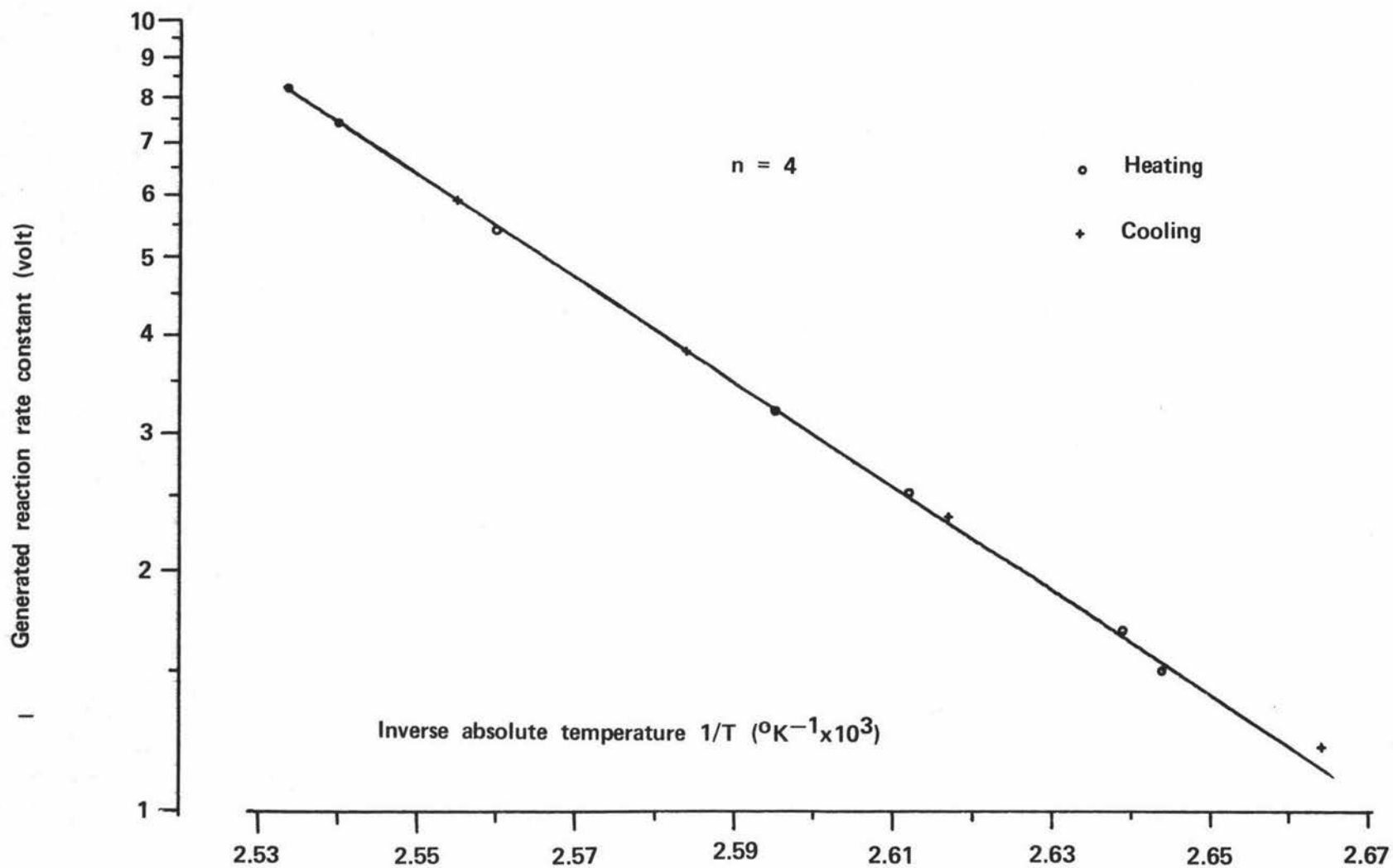


FIGURE VIII.4
PLOT OF THE REACTION RATE GENERATED BY THE ANALOGUE
ACCORDING TO THE ARRHENIUS EQUATION

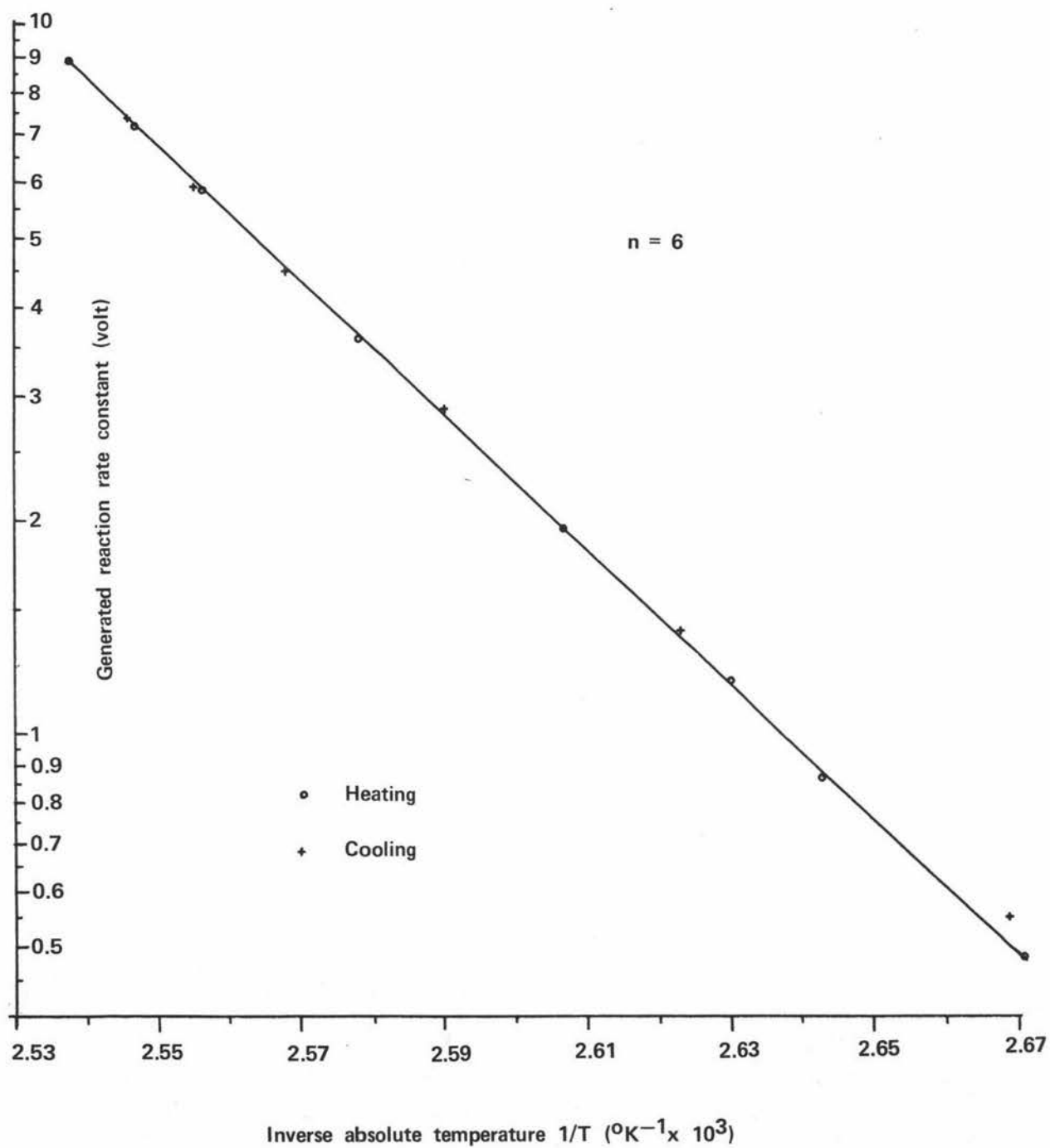


FIGURE VIII.5

PLOT OF THE REACTION RATE GENERATED BY THE ANALOGUE
ACCORDING TO THE ARRHENIUS EQUATION

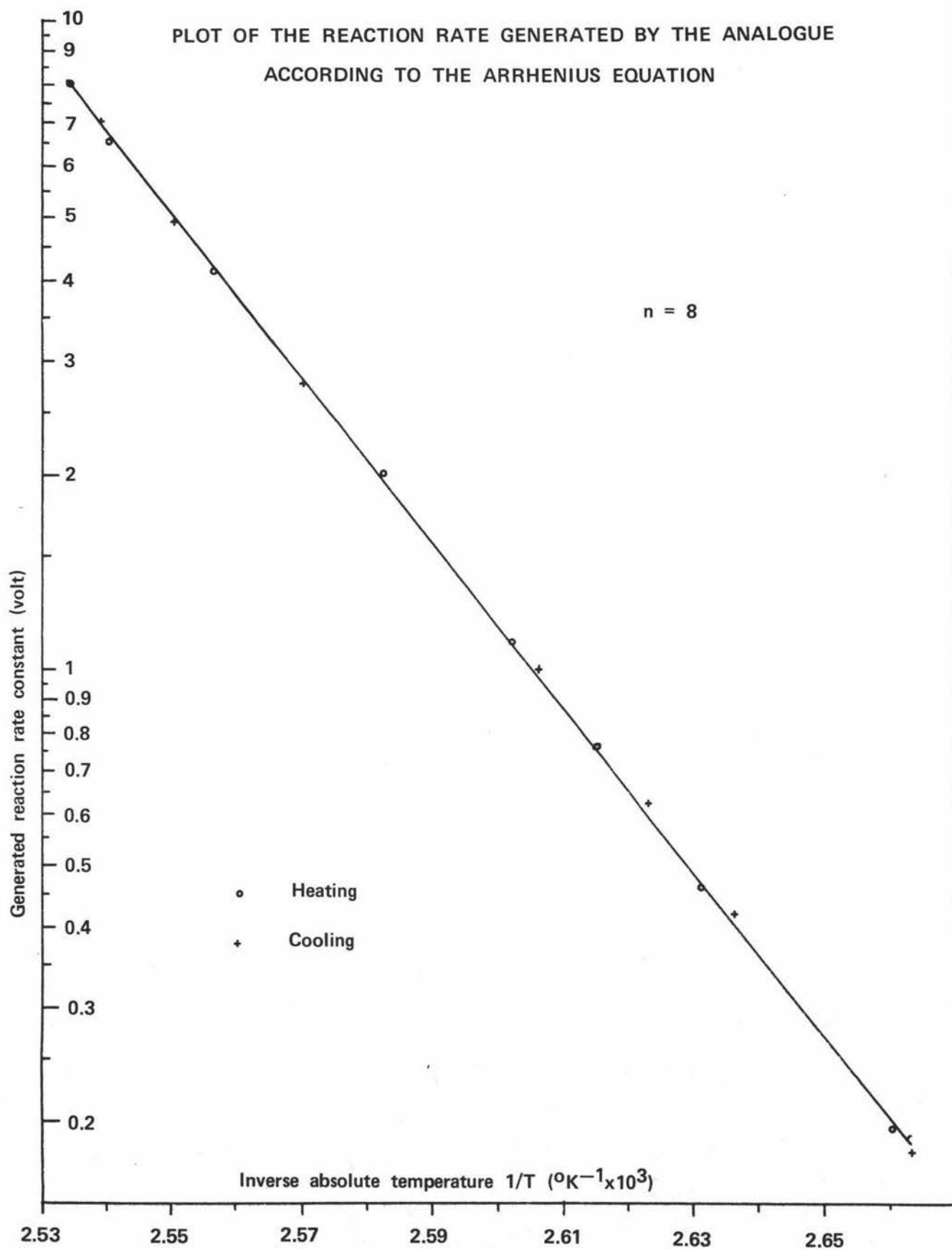
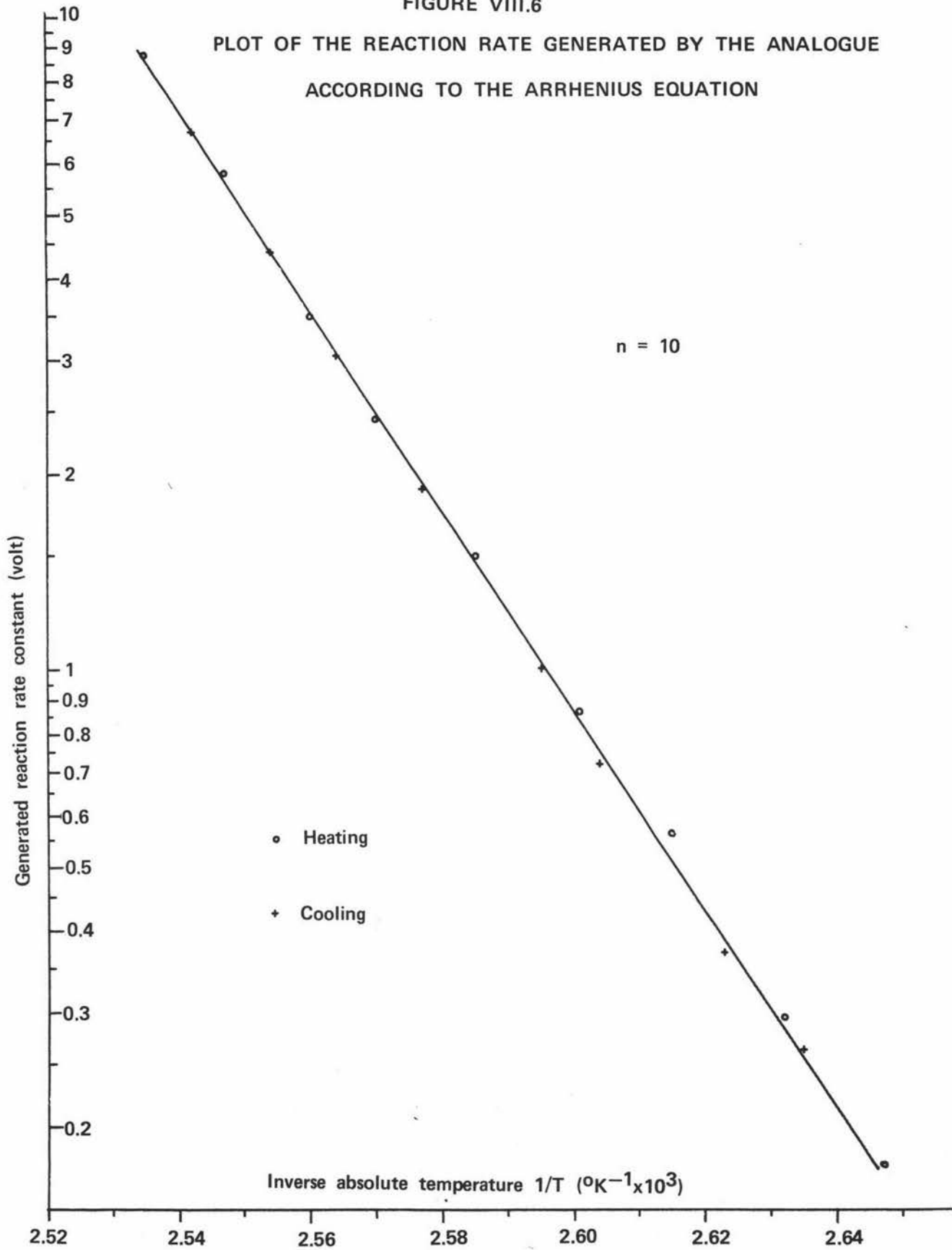


FIGURE VIII.6

PLOT OF THE REACTION RATE GENERATED BY THE ANALOGUE
ACCORDING TO THE ARRHENIUS EQUATION



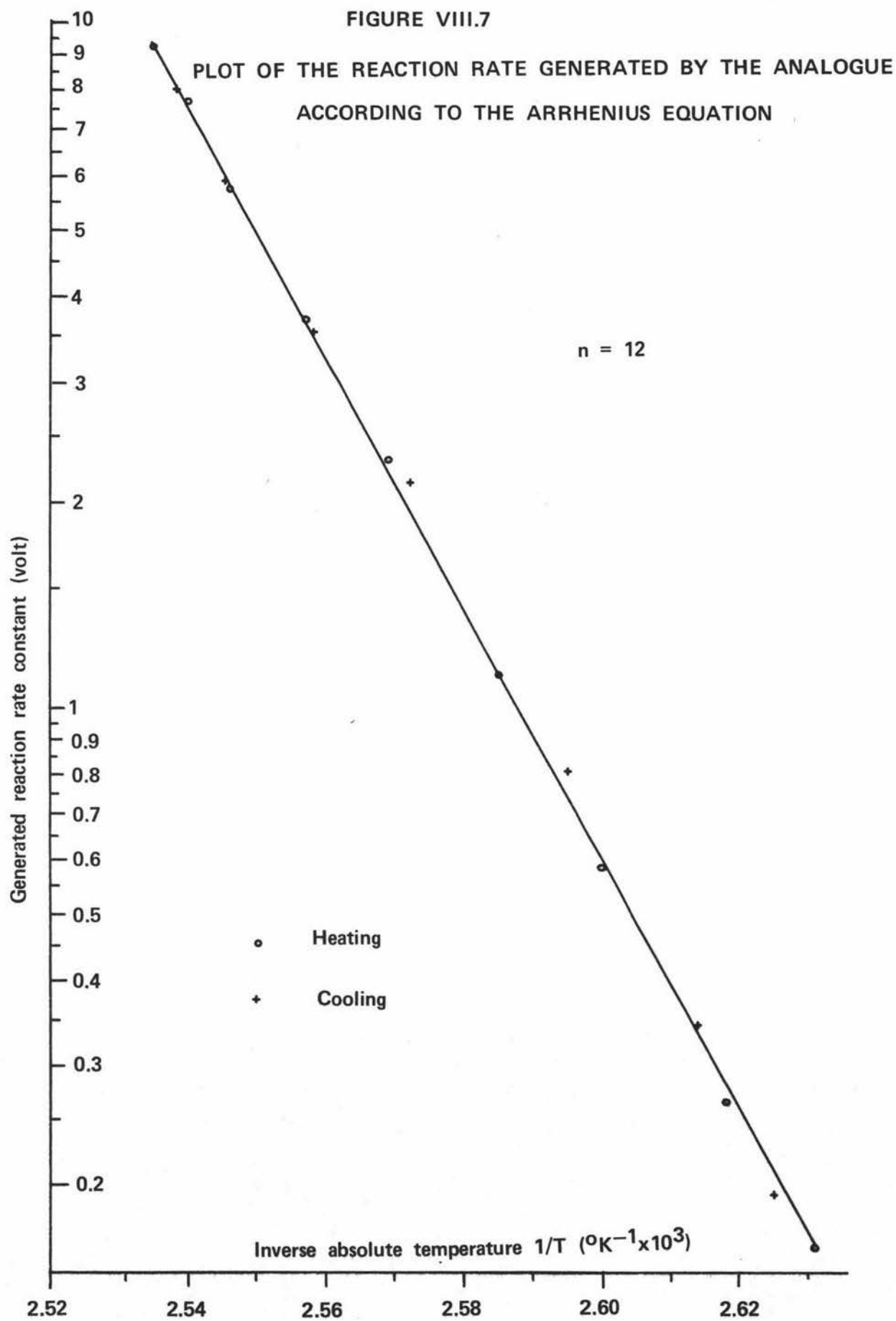


FIGURE VIII.8

PLOT OF THE REACTION RATE GENERATED BY THE ANALOGUE
ACCORDING TO THE ARRHENIUS EQUATION

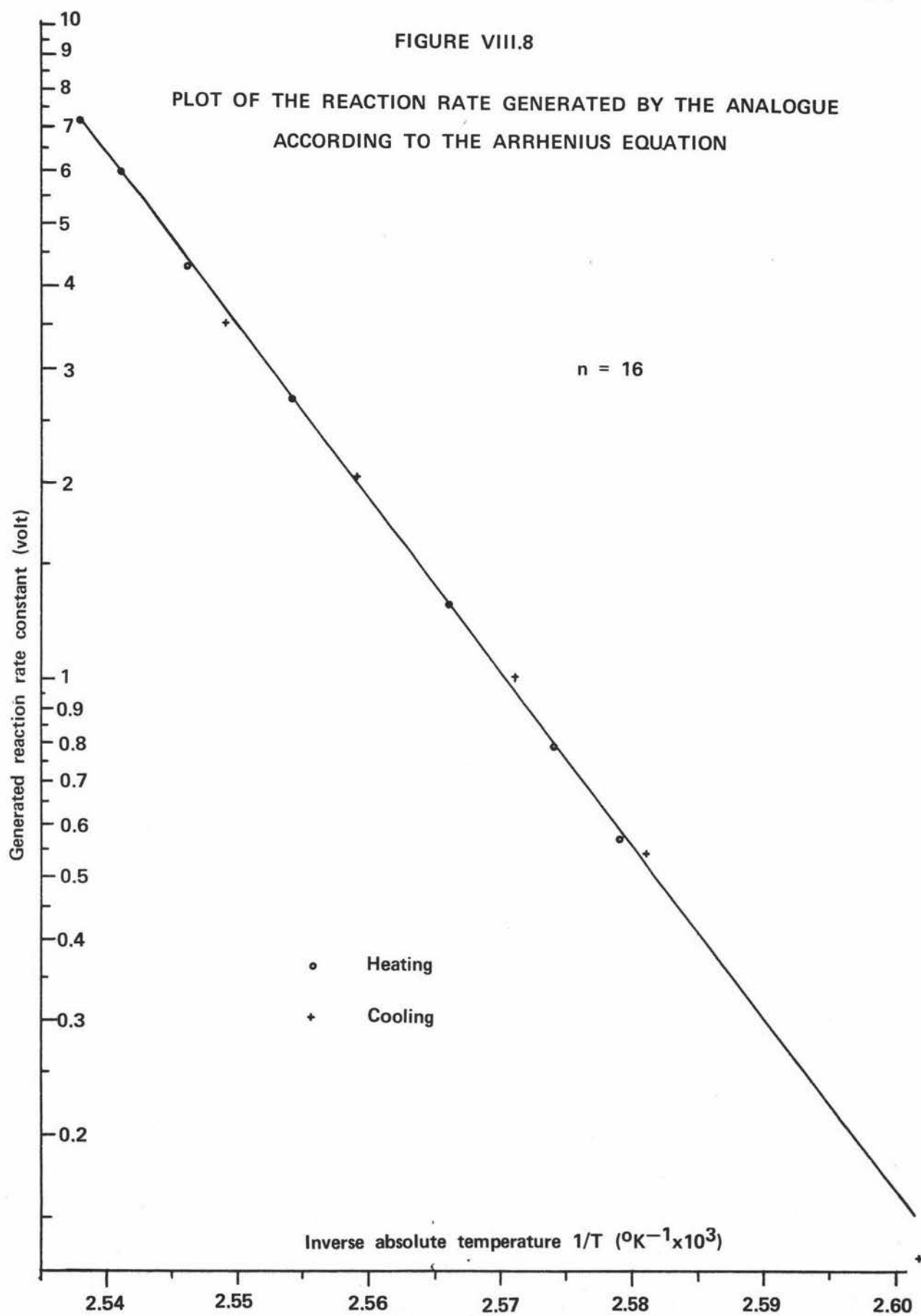


FIGURE VIII.9

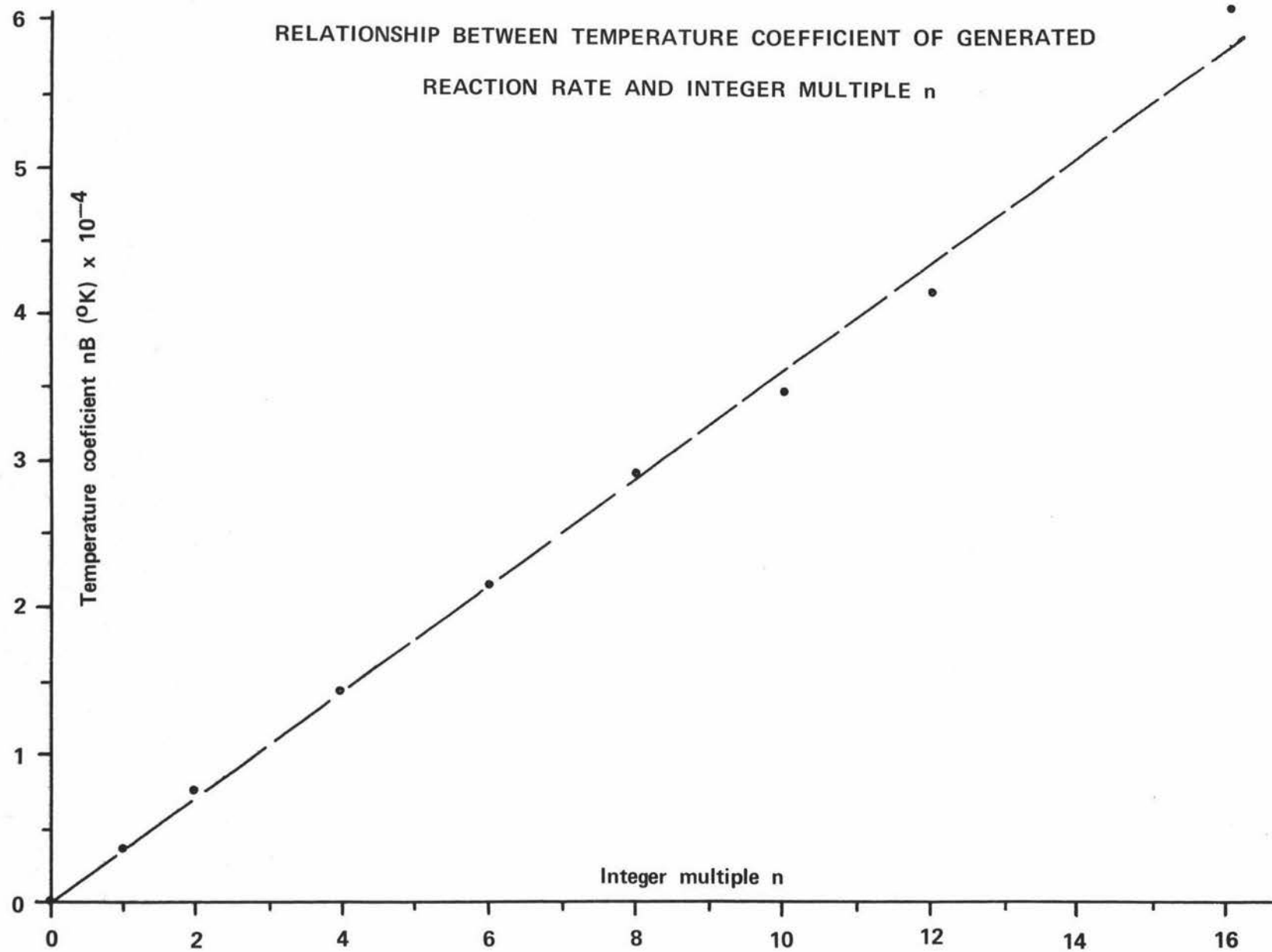


FIGURE VIII.10
MEASURED OUTPUT VOLTAGE CHANGES OF
INTEGRATOR AT VARIOUS
INPUT VOLTAGES

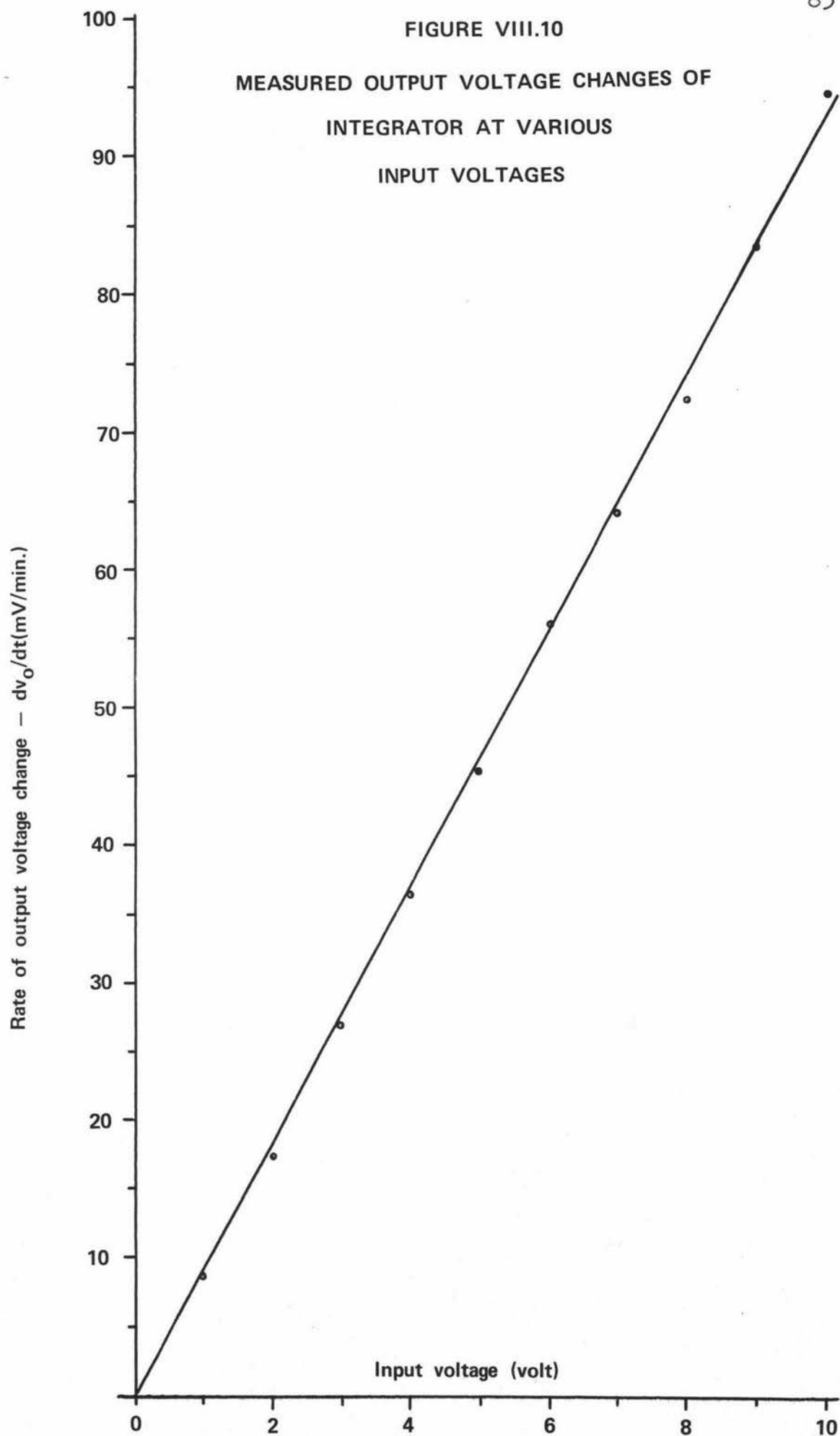


FIGURE VIII.11

REACTION RATE AND TIME PROFILE IN THE VICINITY OF THE SENSOR
OF THE ANALOGUE IN A THERMAL STERILIZATION

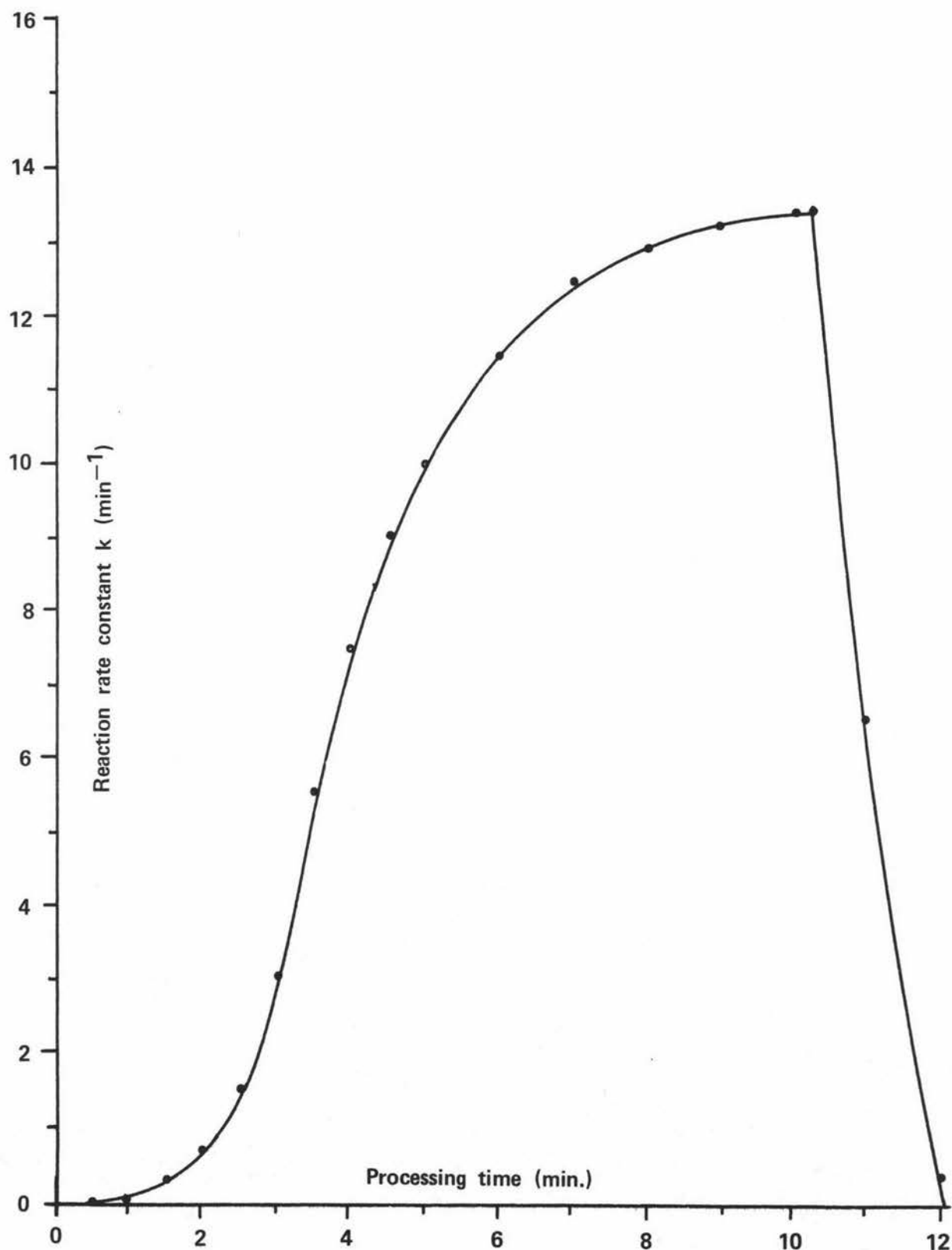


FIGURE VIII.12

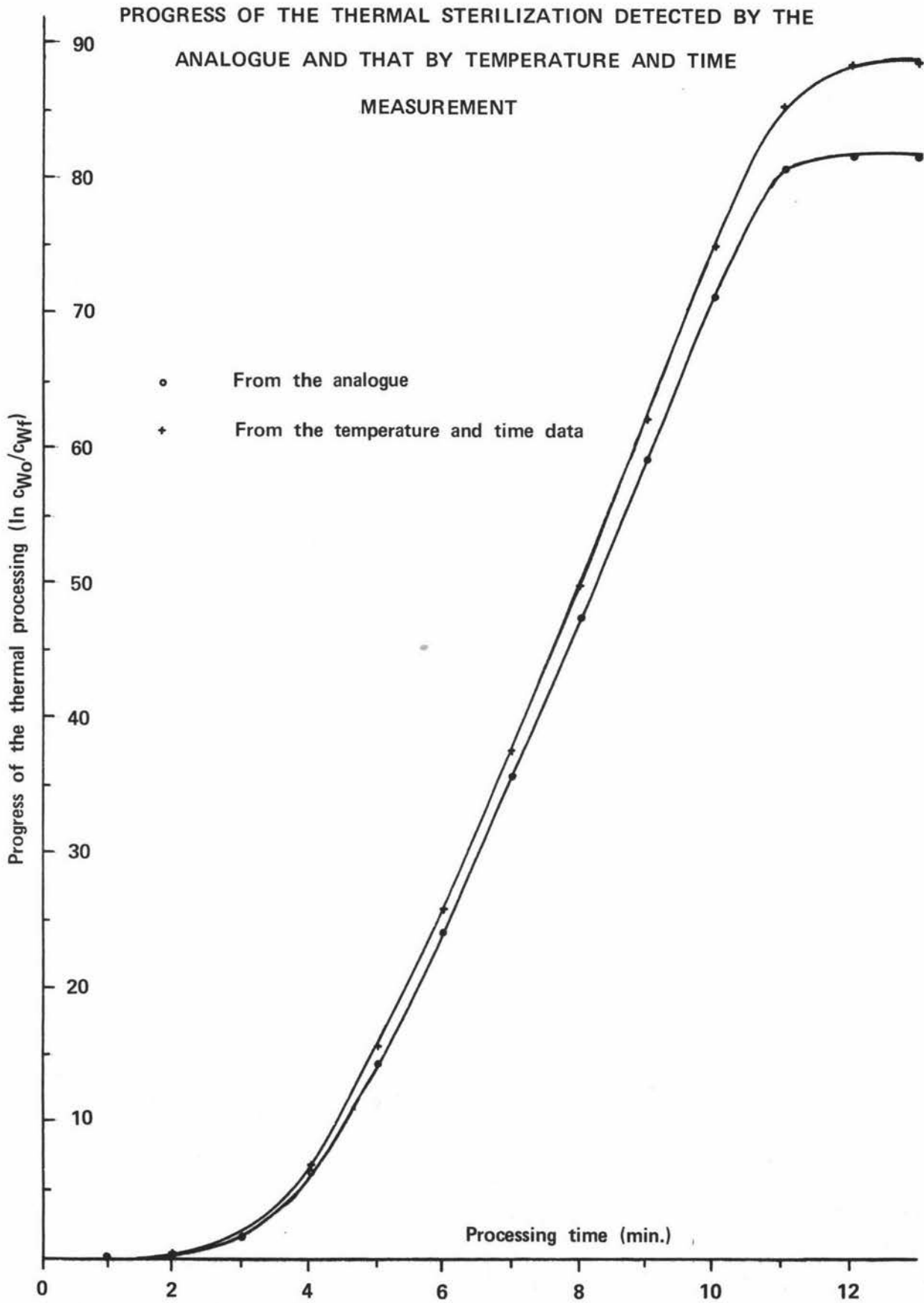


FIGURE VIII.13

REACTION RATE AND TIME PROFILE IN THE VICINITY OF THE SENSOR OF
THE ANALOGUE IN A THERMAL DESTRUCTION OF A CHEMICAL SPECIES

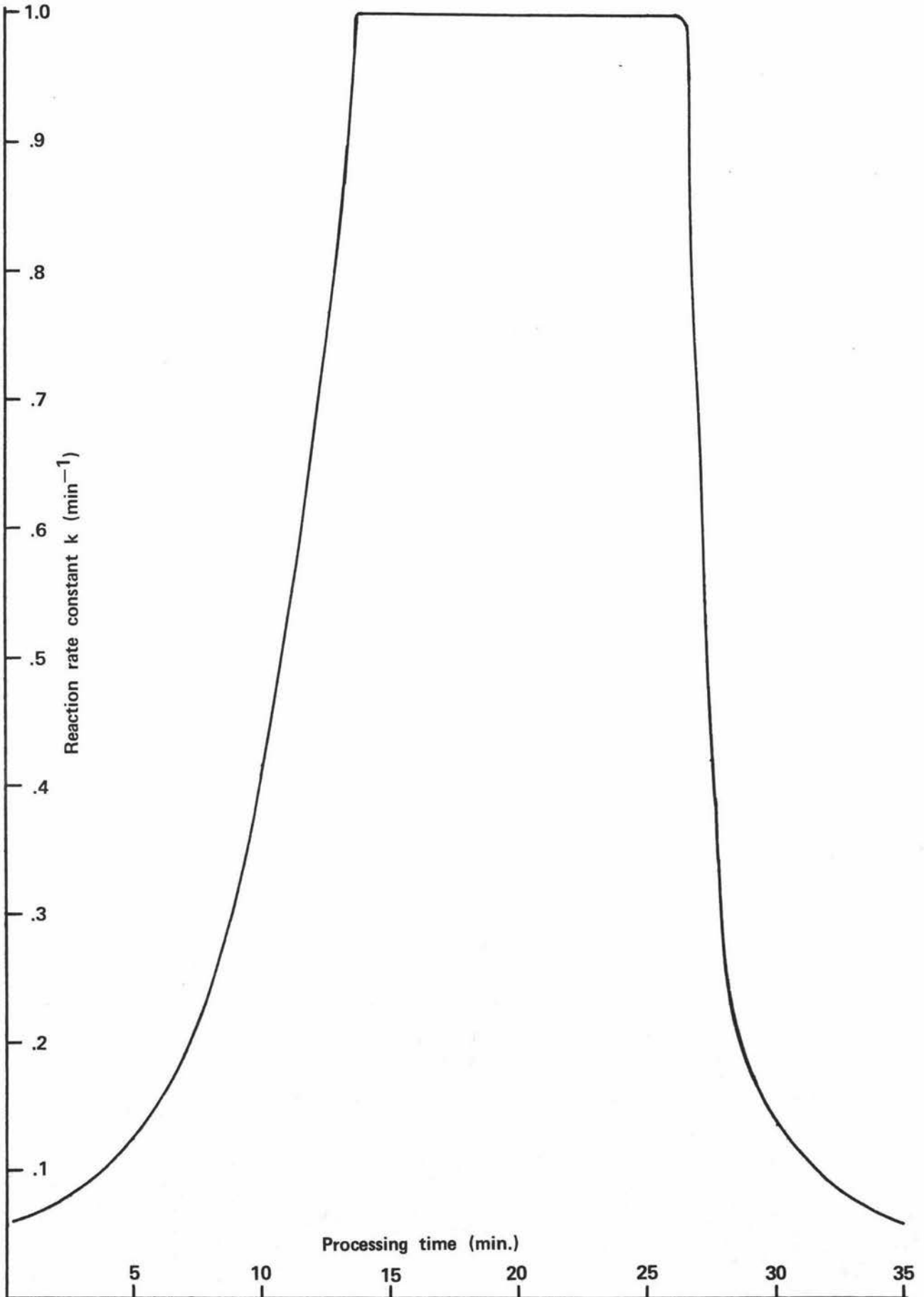
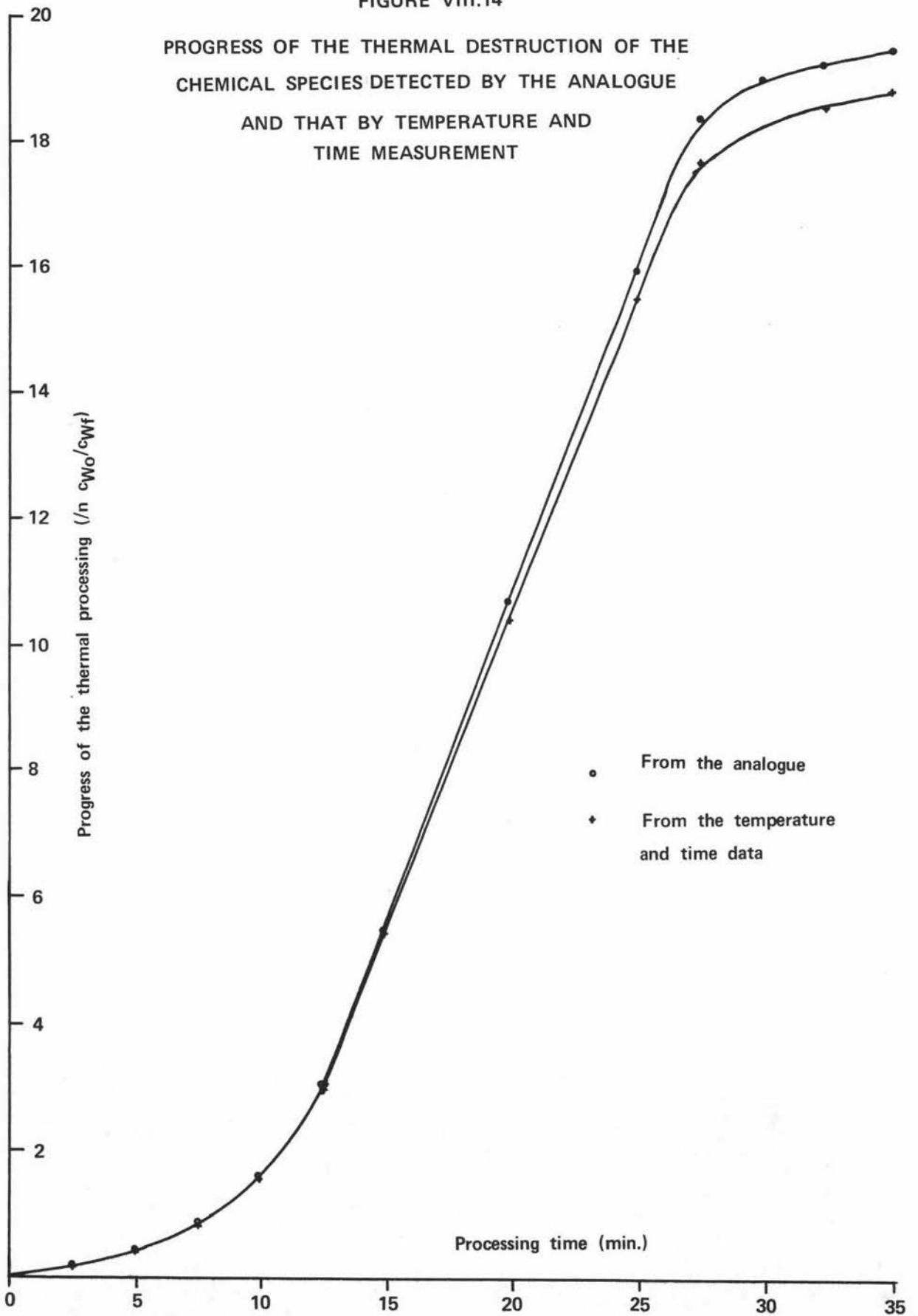


FIGURE VIII.14

PROGRESS OF THE THERMAL DESTRUCTION OF THE
CHEMICAL SPECIES DETECTED BY THE ANALOGUE
AND THAT BY TEMPERATURE AND
TIME MEASUREMENT



IX. CONCLUSIONS

1. Thermal processing of biological and biochemical materials may be described, in many cases, as a single stage irreversible process reaction. The progress of such thermal process reaction can be detected by following the integral of the process reaction rate with respect to time, provided that initial composition and reaction rate equation are known.

2. Advantages of thermal processing depend on the nature of the temperature dependency of the processing reaction rate. When the temperature dependency of a processing reaction rate is described by the Arrhenius equation, an analogue system may be employed to follow the progress of the processing reaction rate provided that the temperature coefficient of the processing reaction rate can be accurately simulated. In any analogue system when the temperature coefficient of the processing reaction rate cannot be accurately simulated, temperature dependency of the relationship between the signal from an analogue system and the progress of processing reaction cannot be eliminated.

3. A simple electrical analogue system was constructed using negative temperature coefficient thermistors as sensing elements. Analogue multipliers were used to increase the temperature coefficient of the thermistors so as to approximate the temperature coefficient of a processing reaction rate. Proper selection of NTC thermistors and the manipulation of analogue multipliers were necessary to produce the temperature coefficient corresponding to a particular processing reaction rate. An

analogue integrator was used to integrate the generated reaction rate during processing.

4. The simple electrical analogue system so constructed cannot be considered as a precision instrument. The performance of such an analogue system will be particularly prone to error when it is applied to a thermal process with a long processing cycle time or with a high temperature coefficient of the processing reaction rate. The temperature coefficient of a thermal processing reaction rate can be produced by the electrical analogue with an error of approximately $\pm 4.55\%$. The error associated with application of the analogue integrator for integrating the generated reaction rate was approximately $\pm 7.25\%$. Application of such an electrical analogue is limited to:

- a. Approximate checking of a proposed thermal processing condition.
- b. Approximate checking of a thermal processing manipulation to achieve a specified conversion in a small region in a batch reactor.
- c. Guiding a thermal processing operator to manipulate a reactor to achieve a desired conversion.

APPENDIX A

CHARACTERISTICS OF COPPER CONSTANTAN THERMOCOUPLE

AND

CONVERSION OF ITS MILLIVOLT OUTPUT TO CORRESPONDING

INVERSE ABSOLUTE TEMPERATURE

TABLE A.1

CHARACTERISTICS OF COPPER CONSTANTAN THERMOCOUPLE,
ACCORDING TO BS 1828 (8),
WITH REFERENCE JUNCTION AT 0°C

Hot Junction Temperature (°C)	Electrical Potential (mV)
100	4.239
105	4.472
110	4.704
115	4.940
120	5.176

TABLE A.2

RELATIONSHIP OF INVERSE ABSOLUTE TEMPERATURE AT HOT
 JUNCTION AND ELECTRICAL POTENTIAL OF THE COPPER-CONSTANTAN
 THERMOCOUPLE, WITH REFERENCE JUNCTION AT 0°C

Electrical Potential	Inverse Temperature at Hot Junction
(mV)	(°K) ⁻¹ x 10 ³
4.420	2.653
4.510	2.640
4.635	2.621
4.732	2.607
4.885	2.585
4.995	2.569
5.250	2.532

FIGURE A.1
CHARACTERISTICS OF COPPER-CONSTANTAN THERMOCOUPLE

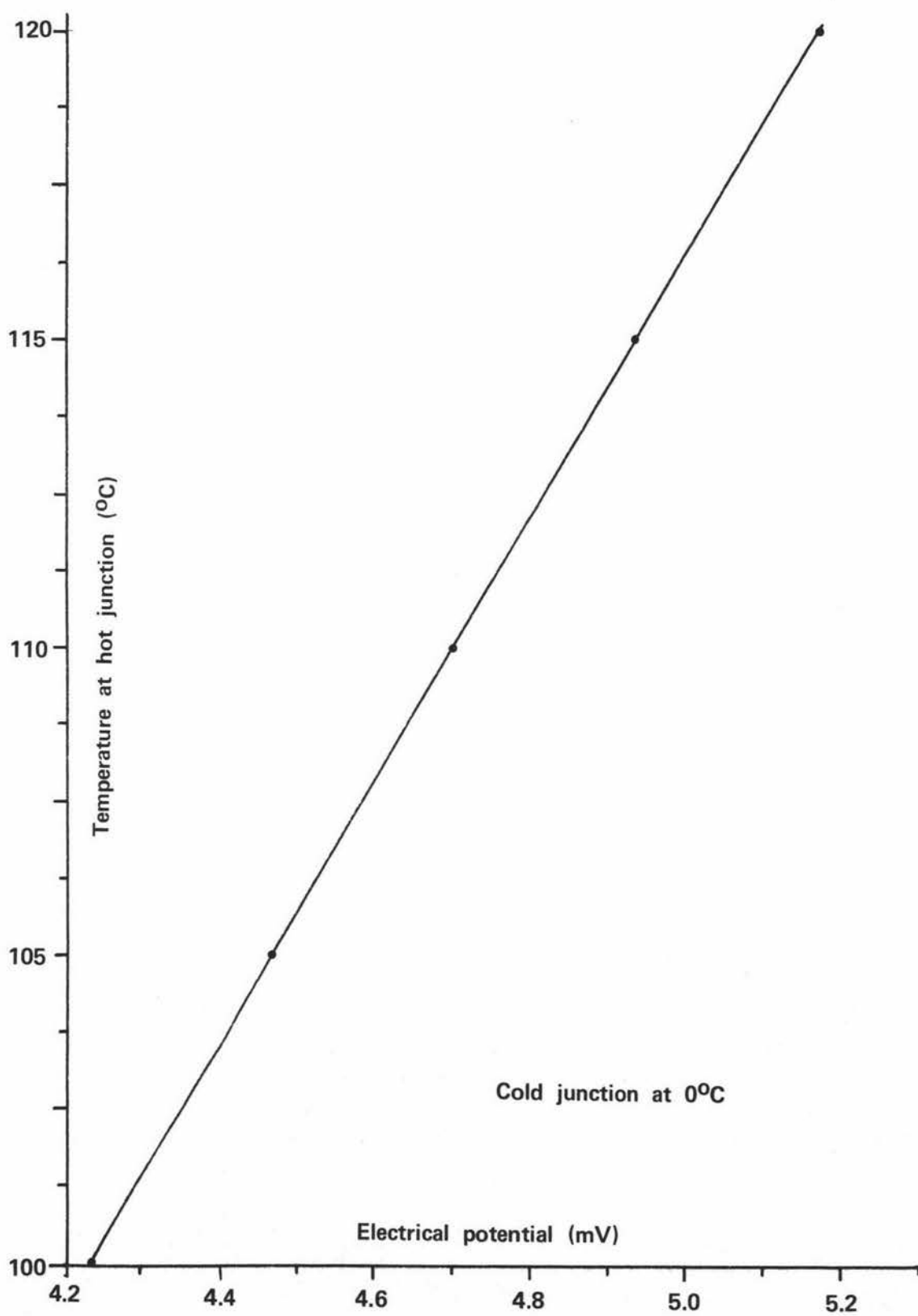
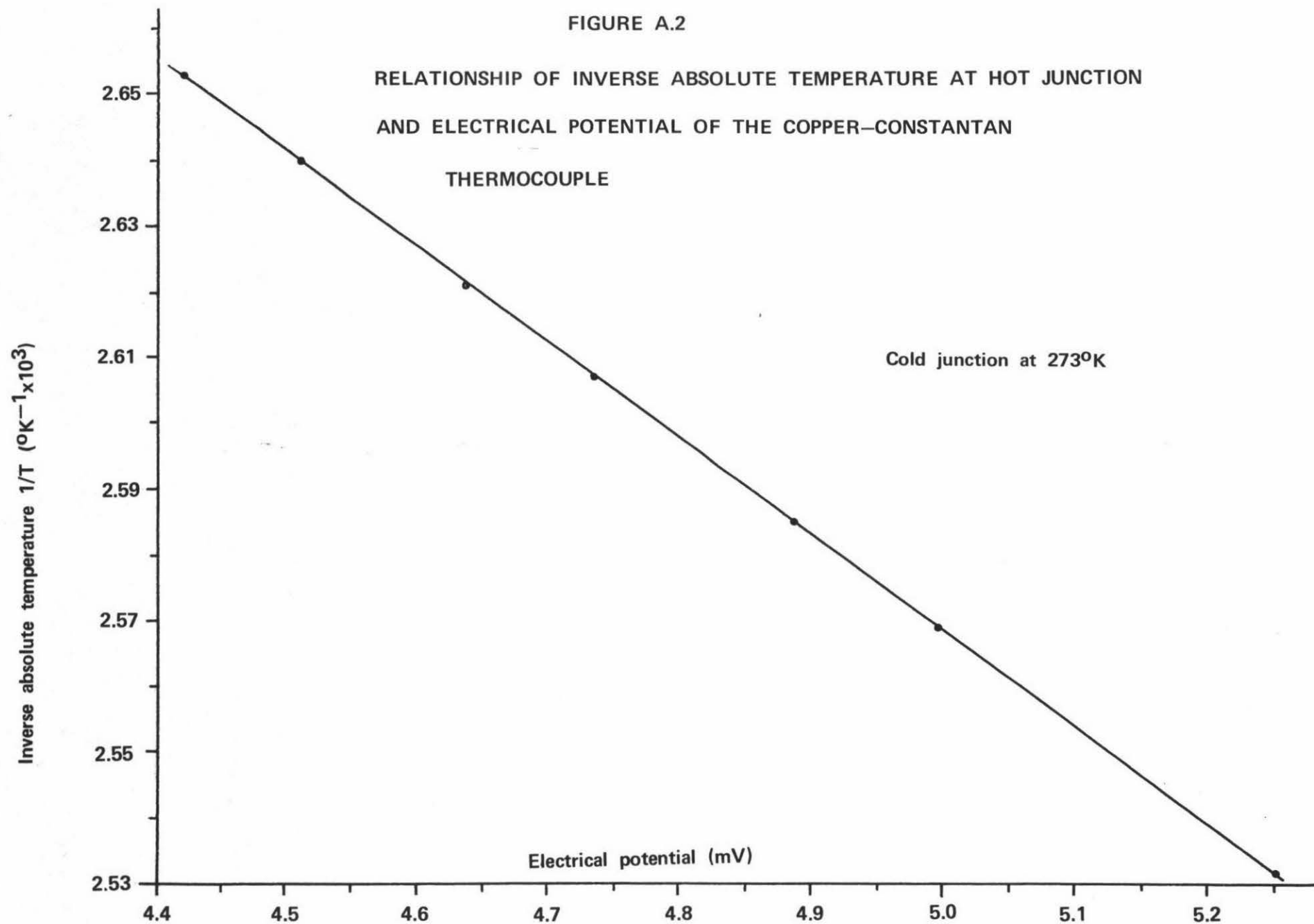


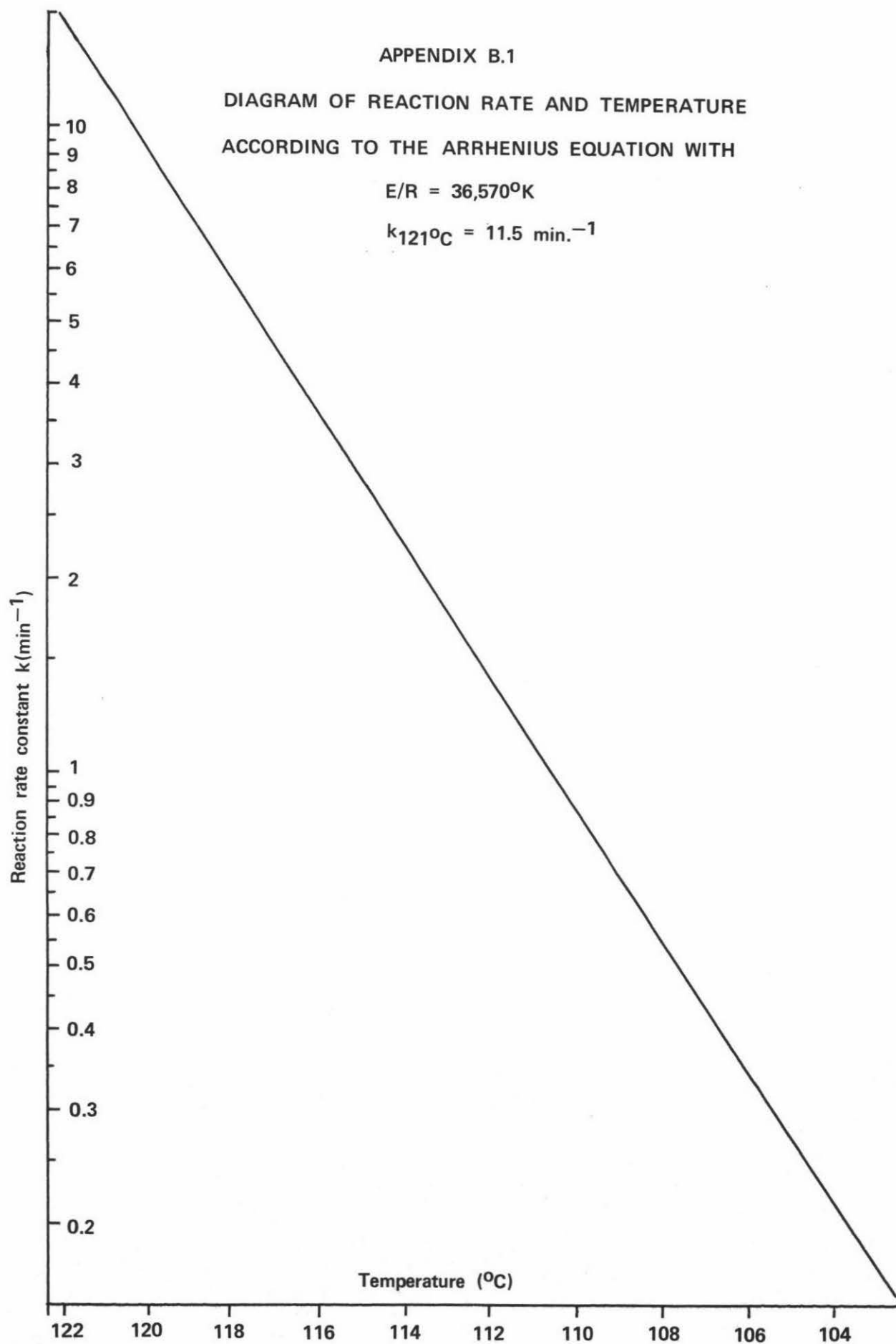
FIGURE A.2

RELATIONSHIP OF INVERSE ABSOLUTE TEMPERATURE AT HOT JUNCTION
AND ELECTRICAL POTENTIAL OF THE COPPER-CONSTANTAN

THERMOCOUPLE

Cold junction at 273°K

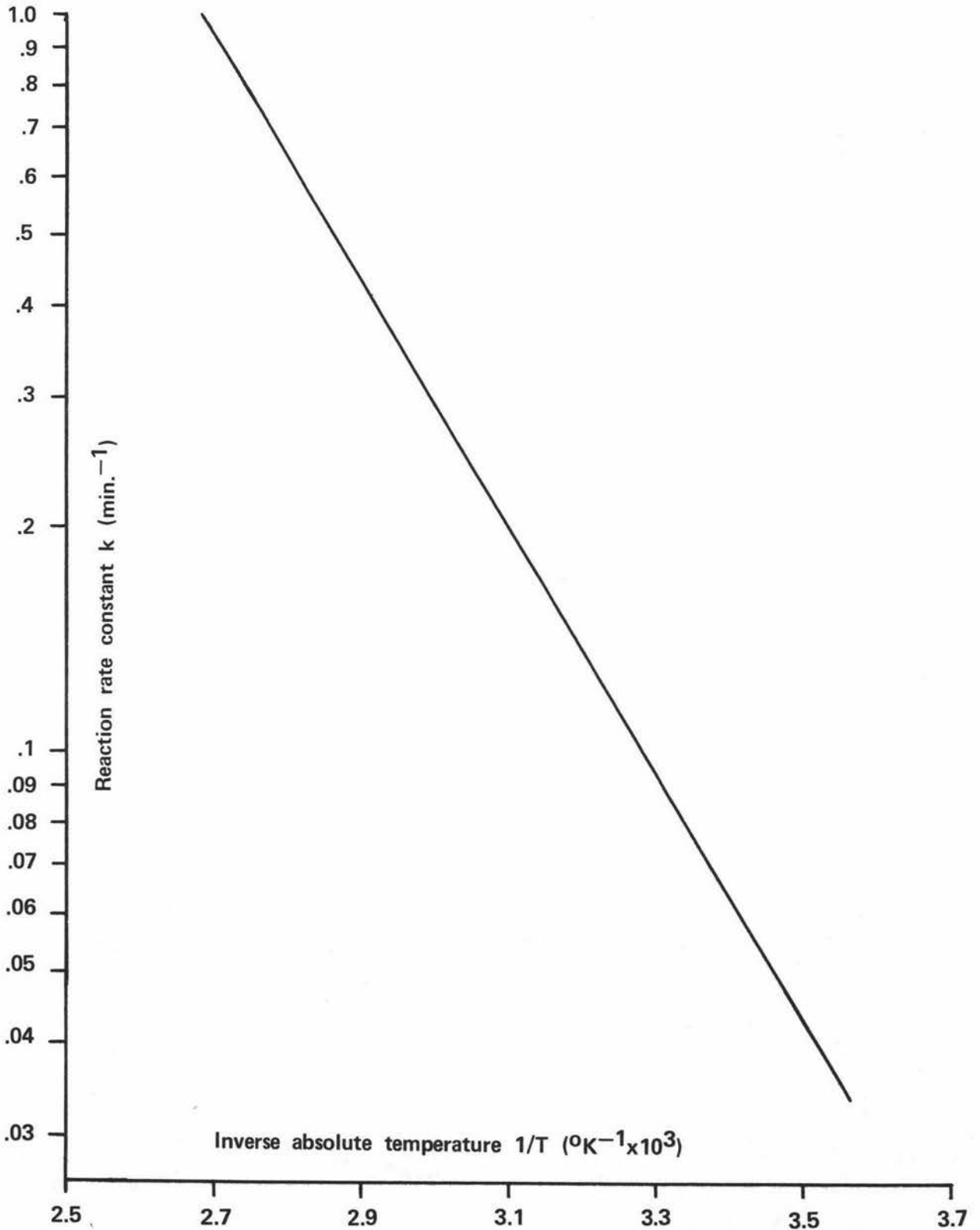




APPENDIX B.2

DIAGRAM OF REACTION RATE AND TEMPERATURE ACCORDING TO THE
ARRHENIUS EQUATION WITH $E/R = 7,314^{\circ}\text{K}$

$$k_{100^{\circ}\text{C}} = 1.0 \text{ min.}^{-1}$$



APPENDIX C

LINEAR REGRESSION OF THE EXPERIMENTAL REACTION RATE
GENERATED BY THE ANALOGUE

The Arrhenius equation was expressed as:

$$\ln k = -\frac{E}{R} \frac{1}{T} + \ln A$$

Correlation coefficient, γ , of $\ln k$ and $1/T$ can be shown to be:

$$\gamma = \frac{\sum_i \left(\frac{1}{T_i} - \bar{\frac{1}{T}} \right) (\ln k_i - \overline{\ln k})}{\sqrt{\sum_i \left(\frac{1}{T_i} - \bar{\frac{1}{T}} \right)^2 \sum_i (\ln k_i - \overline{\ln k})^2}}$$

Using linear regression to estimate the slope of the regression line, $-E/R$, it can be shown that:

$$-\frac{E}{R} = \frac{\sum_i \left(\frac{1}{T_i} - \bar{\frac{1}{T}} \right) (\ln k_i - \overline{\ln k})}{\sum_i \left(\frac{1}{T_i} - \bar{\frac{1}{T}} \right)^2}$$

where k = reaction rate

E = activation energy

R = universal gas constant

T = absolute temperature

A = frequency factor

i = the i th observation

$\bar{\frac{1}{T}}$ and $\overline{\ln k}$ = mean values of $\frac{1}{T}$ and $\ln k$ respectively

TABLE C.1

PERTINENT VALUES ASSOCIATED WITH ANALYSIS OF EXPERIMENTAL
REACTION RATES GENERATED BY THE ANALOGUE

n	$\bar{\frac{1}{T}} \times 10^3$	$\overline{\ln k}$	$\sum_i \left(\frac{1}{T_i} - \bar{\frac{1}{T}}\right) \times (\ln k_i - \ln k) \times 10^6$	$\sum_i \left(\frac{1}{T_i} - \bar{\frac{1}{T}}\right)^2 \times 10^{12}$	$\sum_i (\ln k_i - \ln k)^2$
1	2.593	8.3951	72.368	19789	0.2648
2	2.599	8.4915	167.806	22089	1.27579
4	2.598	8.0380	364.865	24441	5.4491
6	2.594	7.8532	600.188	27823	12.9573
8	2.594	7.2402	798.971	27380	23.3224
10	2.587	7.2202	684.445	19627	23.8838
12	2.577	7.3817	704.644	16622	29.9173
16	2.563	7.3251	238.400	3909	14.8159

APPENDIX D

ESTIMATION OF ERRORS ASSOCIATED WITH TEMPERATURE
COEFFICIENT IN REACTION RATE GENERATED
BY THE ANALOGUE

Assume that

$$\frac{\text{Temperature coefficient}}{n} = B + e$$

where n is an integer greater than or equal to 2

B is the primary reaction rate = 3657°K

e is the error which is normally distributed with mean 0 and standard deviation s

Then standard deviation can be estimated as:

$$s = \pm \sqrt{\frac{\sum e^2}{m}}$$

where m is number of observation

$$\begin{aligned} \sum e^2 &= \sum \left(\frac{\text{Temperature coefficient}}{n} - B \right)^2 \\ &= 20290.6 \end{aligned}$$

$$s = \pm \sqrt{\frac{\sum e^2}{7}} = 53.84$$

For 99.8% confidence interval

$$\begin{aligned} \frac{\text{Temperature coefficient}}{n} &= 3657 \pm 3.09 \times s \\ &= 3675 \pm 166.36 \\ &= 3675 \pm 4.55\% \end{aligned}$$

Hence temperature coefficient = $3657 \pm 4.55\%$

APPENDIX E

ESTIMATION OF CONSTANT, K, AND THE ERROR IN INTEGRATION

Equation VIII.2 may be written as

$$\frac{-dv_0/dt}{v} = \frac{1}{K}$$

Assuming that $(-dv_0/dt)/v$ is normally distributed with mean $1/K$ and standard deviation s . The mean can be estimated as:

$$\frac{1}{K} = \frac{\sum (-\frac{dv_0}{dt} / v)}{m}$$

where m is the number of observations.

The standard deviation can be estimated as:

$$s = \pm \sqrt{\frac{\sum (-\frac{dv_0}{v} - \frac{1}{K})^2}{m - 1}}$$

According to the results in Table VIII.2.

$$m = 10$$

$$\sum (-\frac{dv_0}{dt} / v) = 0.09101 \text{ min.}^{-1}$$

$$K = 109.9 \text{ min.}$$

$$\sum (-\frac{dv_0}{dt} / v - \frac{1}{K})^2 = 5.895 \times 10^{-7} \text{ min.}^{-2}$$

$$s = \pm 0.00256 \text{ min.}^{-1}$$

$$= \pm 2.812\%$$

For 99% confidence interval,

$$\begin{aligned} -\frac{dv_0}{dt} / v &= \frac{1}{K} + 2.58 s \text{ min.}^{-1} \\ &= 0.009109 \pm 7.2\% \text{ min.}^{-1} \end{aligned}$$

$$\text{Hence } v_0 = -\frac{1}{K} \int_0^{t'} v dt \pm 7.2\%$$

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