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The Behaviour of Two-Valued Response Regulators Applicable to Adiabatic Calorimeters

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THE BEHAVIOUR OF TWO-VALUED RESPONSE REGULATORS APPLICABLE TO ADIABATIC CALORIMETERS

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This paper describes an approximate method of computing the 'average' behaviour of two-valued response regulators when applied to several types of adiabatic calorimeter. The method is based upon the concept of 'uniform operation' and uses an approximate description of the thermal conduction process which determines the operation of the regulator. The physical basis of this approximation is discussed in some detail and it is shown that the same formal description of the conduction process is obtained in two different physical situations, although the probable accuracy of the approximation is different in the two cases. In the case where the probable error is greater, the results when the approximation is applied to a linear response thermostat regulator are compared with those obtained by an exact treatment.

In the adiabatic calorimeters discussed, the heat change which would be observed under ideally adiabatic conditions may be computed as the sum of the heat change actually observed and a correction term which, in general, has to be calculated for each experiment. The approximate analysis indicates that with one special type of two-valued response regulator this correction term is proportional to the heat change actually observed, the constant of proportionality depending only on measurable physical characteristics of the apparatus. The correction term is, however, subject to an uncertainty, the estimation of which is discussed in appendix I. With the other two-valued response regulators discussed, the correction term can only be evaluated in terms of the detailed behaviour of the regulator during the experiment. It is shown that in these cases it is sufficient to know, in addition to the relevant physical characteristics of the apparatus, the way in which the ratio of positive and negative half-cycle periods of the regulator varies with time during the experiment. The half-cycle periods can usually be observed directly; but a numerical integration has to be carried out for each experiment.

The analysis is extended to take account of time delay in the regulator servomechanism, and the effects of time delay are discussed in terms of numerical examples. A similar discussion is developed also for the use of an auxiliary signal to improve the performance of regulators of this type. It is shown that while this device always reduces the amplitude of the temperature oscillation, the mean temperature may be less accurately controlled than in the absence of the device.

The predictions of the approximate analysis concerning the behaviour of two-valued response regulators are compared with experimental results obtained from an externally compensated adiabatic calorimeter and from various thermostats. The agreement appears to be satisfactory.

The numerical evaluation of performance data for a simple two-valued response regulator is discussed in detail in appendix II, which includes tabulated solutions to the equations describing the behaviour of the regulator. When the values of the relevant physical characteristics of a particular apparatus are known, together with the variation of the ratio of positive and negative half-cycle periods in a particular experiment, these tables may be used to compute the correction term to the observed heat change. The tables may also be used to calculate the difference between the mean temperature in a thermostat and the datum temperature for which the regulator is set in terms of the ratio of positive and negative half-cycle periods.

1. Introduction

A regulator may be defined as a device for maintaining constant over a period of time some physical property of an experimental system. It contains three essential elements: a signal source which is excited by departures of the experimental system from some datum configuration; an amplifier which interprets the signal; and a servomechanism, actuated by the amplifier, which affects the experimental system in such a way that the signal tends to zero.

Two main classes of regulators may be distinguished according to the form of the relation between the output of the amplifier and the signal. These are discrete-valued response regulators, in which only a small number of fixed values, usually two, is open to the amplifier output and continuous response regulators, in which the amplifier output, and hence the controlling action, is a continuous function of the signal. Thus a thermostat regulator working on the 'on-off' principle is a two-valued response regulator; a more elaborate thermostat regulator in which the net power disposed by the heaters is directly proportional to the signal, i.e. to the departure of the bath temperature from its datum value, is a linear response regulator.

It is in principle possible to use automatic control in three distinct methods of adiabatic calorimetry. In the externally compensated adiabatic calorimeter the calorimeter vessel is surrounded by an insulating space, usually evacuated, as shown in figure 1. Heat losses from the calorimeter vessel are minimized by altering the temperature at the outer boundary of the insulating space to follow that of the calorimeter vessel itself. In the facsimile compensated adiabatic calorimeter two similar vessels, the test calorimeter vessel and the facsimile calorimeter vessel, are situated within a common insulating space, as shown in figure 2. Measured amounts of energy are added to or abstracted from the facsimile calorimeter vessel in such a way that its surface temperature is always close to that of the test calorimeter vessel. The heat change in the test calorimeter vessel is then nearly equal to the total heat added to or abstracted from the facsimile calorimeter vessel irrespective of heat losses, since these are similar from both vessels. The physical arrangement of the internally compensated adiabatic calorimeter is similar to that of the externally compensated calorimeter, but in the former the temperature at the outer boundary of the insulating space is kept constant. The temperature at the surface of the calorimeter vessel also is kept nearly constant, by adding or abstracting measured amounts of heat from the calorimeter vessel. In each of these methods two surfaces separated by an insulating space, usually evacuated, are kept close to thermal equilibrium by controlling the temperature of one of the surfaces. These two surfaces may be distinguished as the *datum* surface and the *controlled* surface. In the externally compensated calorimeter the outer surface of the calorimeter vessel is the datum and the inner surface of the jacket vessel is controlled, while in the internally compensated calorimeter the reverse is the case; in the facsimile compensated calorimeter the surface of the test calorimeter vessel is the datum and the surface of the facsimile calorimeter vessel is controlled.

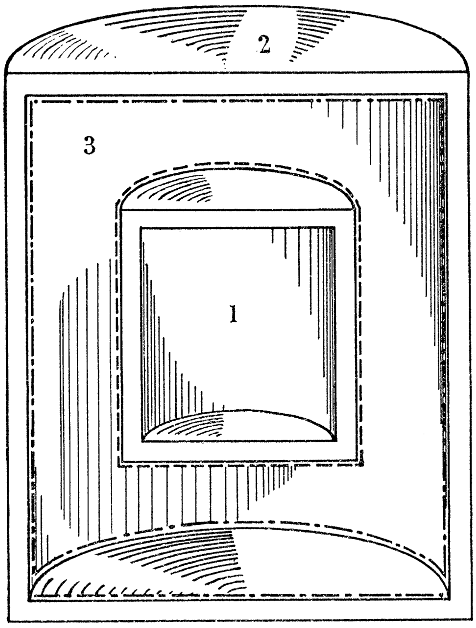

Figure 1. Schematic section of an externally compensated adiabatic calorimeter. 1, calorimeter vessel; 2, jacket vessel; 3, insulating space; ----, datum surface; -·-·-·-, controlled surface.

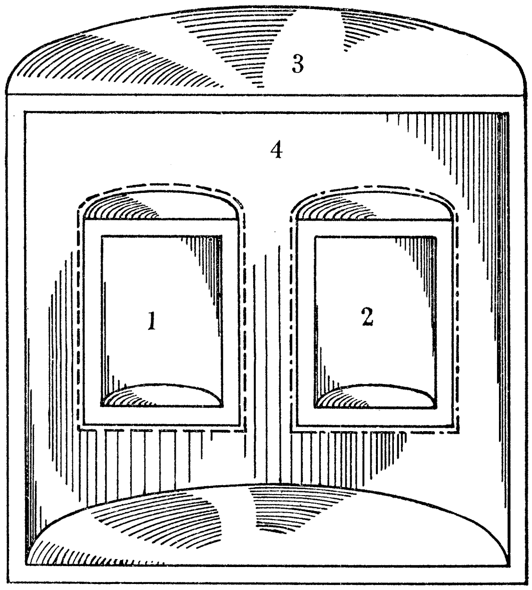

Figure 2. Schematic section of a fascimile compensated adiabatic calorimeter. 1, test calorimeter vessel; 2, facsimile calorimeter vessel; 3, jacket vessel; 4, insulating space; ----, datum surface; -·-·-·-, controlled surface.

Temperature differences between the datum and controlled surfaces during an experiment cause 'uncompensated' heat transfer between the calorimeter vessel and the jacket vessel, and this necessitates the addition of a correction term to the observed heat change in the calorimeter vessel. In a well designed calorimeter the whole extent of each of the datum and controlled surfaces may be assumed to be at uniform temperature (this is discussed on p. 410). Then the correction term to be added to the observed heat change may be computed as follows. Consider, for example, the case of the externally compensated adiabatic calorimeter (see figure 1). Let the temperatures of the datum and controlled surfaces be denoted by T_1 and T_2, respectively. Now the instantaneous rate of transfer of thermal energy between the calorimeter vessel and the jacket vessel depends only on the instantaneous values of T_1 and T_2. (In the facsimile compensated calorimeter it is of course the difference between the thermal transactions of the calorimeter vessel and the facsimile vessel with their common environment which depends only on T_1 and T_2.) Both conduction and radiation processes will contribute to the transfer of energy across the insulating space. Consequently the contribution to the time rate of change of the datum temperature T_1

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resulting from the thermal transactions with the insulating jacket (or the uncompensated part of this contribution in the case of facsimile compensation) will be given approximately by

$$(\mathrm{d}T_1/\mathrm{d}t)_{\text{jacket}} = \gamma_1(T_2 - T_1) + \gamma_2(T_2^4 - T_1^4),$$

where γ_1 is the conduction coefficient and γ_2 is the radiation coefficient, in that experiment. The coefficients γ_1 and γ_2 are equal respectively to the conduction and radiation transfer coefficients each divided by the total heat capacity of the calorimeter vessel and its contents. Provided that $(T_2 - T_1)$ is small in comparison with T_1 we may then write

$$(\mathrm{d}T_1/\mathrm{d}t)_{\text{jacket}} \doteqdot (\gamma_1 + \gamma_2 T_1^3)(T_2 - T_1).$$

The coefficient $(\gamma_1 + \gamma_2 T_1^3)$ defined in this way depends not only on the geometry of the insulating space and the absolute temperature T_1, but also varies inversely with the total heat capacity of the calorimeter vessel. Whenever T_1 changes, the effect of any accompanying departure from thermal equilibrium between the datum and controlled surfaces will reduce the final value of T_1 by an amount close to

$$\delta T = -\int_{t_0}^{t_f} (\gamma_1 + \gamma_2 T_1^3)(T_2 - T_1)\,\mathrm{d}t,$$

where t_0 represents some time before T_1 commences to change and t_f is any time after the completion of the change. If the change in T_1 is relatively small then δT will be adequately approximated by

$$\delta T \doteqdot -(\gamma_1 + \gamma_2 T_m^3) \int_{t_0}^{t_f} (T_2 - T_1)\,\mathrm{d}t, \tag{1·1}$$

where T_m is the mean value of T_1 between t_0 and t_f. Then the change $\Delta T^{\text{id.}}$ in T_1 which would be observed in an externally compensated calorimeter under ideally adiabatic conditions is related to the observed change ΔT in T_1 by

$$\Delta T^{\text{id.}} = \Delta T + \delta T \doteqdot \Delta T - (\gamma_1 + \gamma_2 T_m^3) \int_{t_0}^{t_f} (T_2 - T_1)\,\mathrm{d}t.$$

Exactly analogous relations expressed in terms of thermal energy instead of temperature may be deduced for the internally compensated and facsimile compensated adiabatic calorimeters. Thus in all three cases, in order to evaluate the correction term to the observed heat change it is necessary only to be able to evaluate the time integral of the difference between the temperatures of the controlled and datum surfaces. Moreover, since equation (1·1) refers to the whole outer surface of the calorimeter vessel, it follows that the equation remains sufficiently accurate for practical purposes even when there are transient *small* temperature variations over the surface of the calorimeter vessel, provided that T_1 is taken as the *mean* surface temperature of the calorimeter vessel, as measured, for example, by a multi-junction thermocouple of suitable geometry.

When a regulator is applied to an adiabatic calorimeter it is obviously desirable that the signal source should measure the difference between the controlled and datum temperatures. It is then convenient to express the signal in terms of temperature, as

$$S = T_2 - T_1.$$

The problem is then simply to evaluate the time integral of the signal over the complete experiment.

The temperature in any element of volume can be altered only by the transport of entropy into or out of the element, or by the creation of entropy within the element. While it is in principle possible to heat the surface of an electrical conductor directly and uniformly, it is extremely difficult to apply this principle either to the outer surface of a calorimeter vessel or to the inner surface of a jacket vessel; and it is not generally possible to cool any surface uniformly and directly except by radiation or convection, neither of which are applicable within the calorimeter insulating space. Consequently in adiabatic calorimetry we have to assume that alteration of the temperature of the controlled surface will be effected indirectly, by thermal conduction processes. Thus the investigation of the behaviour of automatic regulators applied to adiabatic calorimeters involves at the outset the problem of how to incorporate an adequate description of thermal conduction processes into the equations describing the operation of the regulator.

The form of the thermal conduction processes to be considered is determined by the geometry of the calorimeter. Thus it is obvious that in the three methods of adiabatic calorimetry discussed above the surface at which the controlling action takes place—the *controlling* surface—must lie to that side of the controlled surface away from the insulating space. In practice the controlling action takes place adjacent to either the inner or outer surface of a cylindrical vessel, the controlling action being determined by the variation of the temperature at the other, controlled, surface relative to that of the datum surface, which is separated from the controlled surface by the insulating space, as shown in figure 1. If the wall thickness of this cylindrical vessel is small in comparison with its length and diameter, the conduction processes across the wall may be treated as a case of linear conduction across a parallel-sided slab of finite thickness but infinite extent.

Consider an element of such a slab, the element having unit surface area. It is characteristic of such an element that temperature, heat flux, etc., are uniform over any geometric surface drawn parallel to the outer surfaces of the slab. Consequently any point within the element is adequately characterized by its distance x from the outer surface adjacent to which the controlling action takes place. The controlling surface is then defined as $x = 0$ and the controlled surface by $x = l$, where l is the thickness of the slab in centimetres. The general conduction equation then has the form

$$\frac{\partial T}{\partial t} = D\frac{\partial^2 T}{\partial x^2}, \tag{1·2}$$

where T is the temperature at x, t represents time and D is the diffusivity of the material, given by $\lambda/\rho c$, the thermal conductivity divided by the density times the specific heat. Equation (1·2) is subject to two boundary conditions, one for each surface. Since in practice the rate of heat transport to or from the controlled surface due to radiation across the insulating space is very much smaller than the rate of heat transport due to conduction across the slab, we may, for simplicity, assume the controlled surface to be completely insulated. The boundary condition for this surface is then

$$(\partial T/\partial x)_{x=l} = 0. \tag{1·3}$$

The situation at the controlling surface, $x = 0$, depends on whether the total heat capacity of the servomechanism is large or small in comparison with that of the region between the controlling and controlled surfaces. In fact many designs of adiabatic calorimeter may be assigned to one or other of two classes which may be discussed in terms of the two limiting cases as the effective heat capacity of the servomechanism is either decreased or increased.

The first case, in which the heat capacity of the servomechanism may be assumed to be much smaller than that of the region between the controlling and controlled surfaces, is exemplified by the externally compensated adiabatic calorimeter shown in figure 3. The regulator operates upon the inner of the two concentric jackets, the servomechanism consisting of heaters and refrigerating coils wound onto the outer surface of the inner jacket.

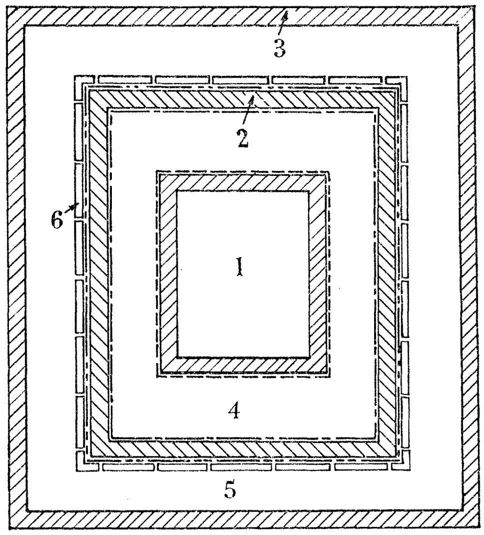

FIGURE 3. Section of an externally compensated adiabatic calorimeter with low heat capacity servomechanism. 1, calorimeter vessel; 2, inner jacket vessel; 3, outer jacket vessel; 4, 5, insulating spaces; 6, servomechanism (heating and cooling); - - - - -, datum surface (T_1); -·-·-·-·-, controlled surface (T_2); -··-··-··-, controlling surface (T_3).

If we ignore radiation across the outer insulating space, the servomechanism is in thermal contact only with the controlling surface. If the heat capacity of the servomechanism is very small, then, whenever the thermal power changes, the servomechanism will rapidly attain an equilibrium temperature which just suffices to make the heat flux across the controlling surface equal to the new thermal power. The boundary condition at the controlling surface then takes the form

$$-\lambda(\partial T/\partial x)_{x=0} = Q, \tag{1·4}$$

where Q bears a simple relation to the output of the regulator amplifier. In a two-valued response regulator, for example, Q has successively the values $+Q'$, $-Q''$, $+Q'$, etc., while in a linear response regulator Q is given by

$$Q = -q(T_2 - T_1) = -qS,$$

where q is the *sensitivity* of the regulator in cal cm^{-2} s^{-1} deg^{-1}.

The second limiting case is exemplified by the arrangement of figure 4. The controlling surface is in contact with a volume of well-stirred fluid and the servomechanism consists

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of heaters and refrigerating coils immersed in the fluid, which may consequently be assumed always to be at a uniform temperature T_3 (see p. 415). In dealing with practical calorimeters of this type we cannot ignore the effects of imperfect thermal contact between the fluid and the outer (controlling) surface of the jacket vessel. Instead, we must ascribe to the 'boundary layer' between the bulk of the fluid and the controlling surface a transfer coefficient κ (cal cm^{-2} s^{-1} deg^{-1}), and the heat flux across the controlling surface is given then by

$$Q = \kappa(T_3 - T_4),$$

where T_4 is the temperature at the controlling surface, $x = 0$. The boundary condition at this surface then takes the form

$$-\lambda(\partial T/\partial x)_{x=0} = \kappa(T_3 - T_4), \qquad (1\cdot 5)$$

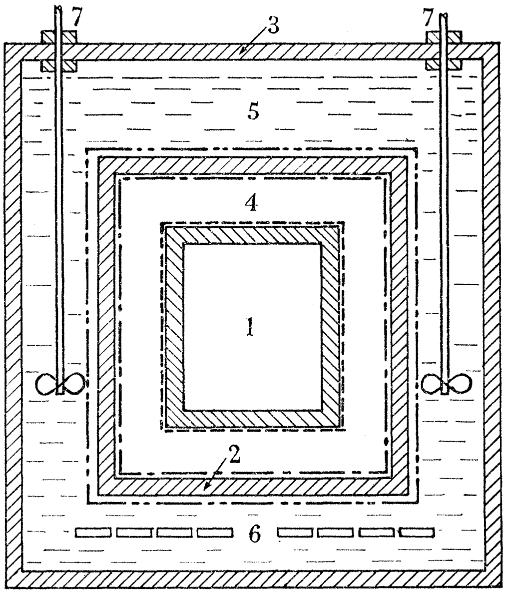

FIGURE 4. Section of an externally compensated adiabatic calorimeter with high heat capacity servomechanism. 1, calorimeter vessel; 2, jacket vessel; 3, environment vessel; 4, insulating space; 5, liquid environment (T_3); 6, heating and cooling coils; 7, stirrers; - - - - -, datum surface (T_1); -·-·-·-·-, controlled surface (T_2); -··-··-··-, controlling surface (T_4).

together with the subsidiary relation specifying ($\mathrm{d}T_3/\mathrm{d}t$). Thus, with a two-valued response regulator,

$$\mathrm{d}T_3/\mathrm{d}t = +a', \quad \mathrm{d}T_3/\mathrm{d}t = -a'',$$

while with a linear response regulator

$$\mathrm{d}T_3/\mathrm{d}t = -r(T_2 - T_1) = -rS,$$

where r is the sensitivity of the regulator expressed in reciprocal seconds.

The general solutions to the conduction equation (1·1) with the boundary conditions (1·3) and either (1·4) or (1·5) are well known (see Carslaw & Jaeger 1947, § 43), but it does not appear to be possible to deduce general relations describing the average behaviour of the signal of a two-valued response regulator operating in either of these situations. The nature of the difficulty is well illustrated by the case of a two-valued response regulator operating in the situation described by equations (1·2), (1·3) and (1·4), the heating and cooling rates being $+Q'$ and $-Q''$. By using the Laplace transformation (see Carslaw & Jaeger 1947, § 120), we can obtain the steady periodic part of the function $S = S(t)$ in terms of arbitrary values for the half-cycle periods during which the controlling action is $+Q'$ and $-Q''$, respectively. Then, making use of the appropriate terminal values of S (see § 3 below) we can, in principle, solve for the half-cycle periods corresponding to steady periodic behaviour. It seems, however, that in practice the relevant equations can only be solved numerically, and an elaborate computation is necessary for each particular case. Since our primary objective in setting out to obtain the average behaviour of the signal during a calorimetric experiment is to compute a relatively small correction term to the observed heat change, there is a strong case in favour of using approximate descriptions of the thermal conduction processes in order to simplify the computation of the average behaviour of the signal. Moreover, the approximations used in this paper enable some general statements to be made about the effects of changing the relevant physical properties of the apparatus upon the average behaviour of the signal.

2. Nature of the approximation

(a) *The case of conduction across a liquid to solid interface*

The cases in which the thermal conduction process upon which the operation of the regulator depends is described by equations (1·2), (1·3) and (1·5) are exemplified by the externally compensated adiabatic calorimeter arranged as in figure 4. We may, for convenience, assume that the bath of stirred liquid in which the jacket vessel is immersed (the calorimeter environment) has a total heat capacity large in comparison with that of the jacket vessel. This implies that the time rate of change of the temperature in the calorimeter environment is effectively independent of the conduction processes across the wall of the jacket vessel and depends only on the net thermal power disposed by the regulator servo-mechanism.

The outer surface of the jacket vessel is inevitably separated from the bulk of the stirred liquid forming the calorimeter environment by a 'boundary layer' of stationary or nearly stationary liquid. It is characteristic of such boundary layers that they have relatively low thermal conductivity, although the detailed structure, and hence the apparent thermal conductance, of the layer varies widely according to the nature of the solid surface, the viscosity and rate of stirring, etc., of the liquid. If the thermal conductivity of the material of the jacket is relatively large then, whenever the mean temperature of the calorimeter environment is changing, the magnitude of the apparent temperature gradient (measured normal to the surface of the jacket vessel) in the boundary layer will be much greater than the magnitude of the steepest temperature gradient within the wall of the jacket vessel. Consequently, if the wall of the jacket vessel is not more than a few millimetres thick, then the temperature difference across the boundary layer will be much greater than the temperature difference across the wall of the jacket vessel. The relevant properties of aluminium, for example, are

$$\lambda = 0{\cdot}296\,\text{cal}\,\text{s}^{-1}\,\text{cm}^{-1}\,\text{deg}^{-1}, \qquad \rho = 2{\cdot}85\,\text{g}\,\text{cm}^{-3},$$
$$c = 0{\cdot}203\,\text{cal}\,\text{deg}^{-1}\,\text{g}^{-1}, \qquad D = 0{\cdot}512\,\text{cm}^2\,\text{s}^{-1}$$

(see Turner 1936), while the thermal transfer coefficient, κ, for water to metal contacts usually lies within the range $0{\cdot}01$ to $0{\cdot}1\,\text{cal}\,\text{cm}^{-2}\,\text{s}^{-1}\,\text{deg}^{-1}$ (Kay 1957). Then if a slab of aluminium 0·5 cm thick has one surface completely insulated and the other in contact with a body of stirred water whose temperature is increasing uniformly, it is easily established using equation (2·5) below, that the temperature difference across the boundary layer is between 10 and 100 times as great as the temperature difference across the metal slab itself. Similar results are found with other metals whose thermal conductivity is relatively high.

In a practical calorimeter of the type illustrated in figure 4 the wall of the jacket vessel will almost certainly be less than 0·5 cm thick so it seems reasonable to neglect the temperature difference across the wall itself in comparison with the temperature difference across the boundary layer. This is equivalent to assuming that the boundary layer has finite thermal conductance but zero heat capacity while the wall of the jacket vessel has finite heat capacity but infinitely large thermal conductivity, so that the whole of its extent, including the inner (controlled) surface is at a uniform temperature which may be denoted by T_2.

The situation in the calorimeter environment is essentially similar to that in the jacket vessel wall. That is to say, provided that the stirring system is carefully designed to effect both rapid circulation and good mixing throughout the whole of the environmental liquid, the temperature gradients in the bulk of the liquid during a change of mean temperature are negligible in comparison with the temperature difference across the boundary layer. It is then convenient to define the controlling surface as the outer limit of the boundary layer, so that the temperature T_3 at the controlling surface is identical with that in the body of the calorimeter environment. The rate of heat transfer across unit area of the boundary layer is then given by

$$Q = \kappa(T_3 - T_2) \quad (\text{cal cm}^{-2}\,\text{s}^{-1}), \tag{2·1}$$

and the corresponding rate of change of T_2 is

$$\frac{dT_2}{dt} = \frac{Q}{\rho c l}, \tag{2·2}$$

where l is the thickness of the jacket vessel wall, so that $\rho c l$ is the heat capacity per unit surface area of the jacket vessel wall. Equations (2·1) and (2·2) may be combined as

$$\frac{dT_2}{dt} = \frac{\kappa}{\rho c l}(T_3 - T_2) = b(T_3 - T_2). \tag{2·3}$$

The coefficient b then has the dimensions of second^{-1} and is analogous to a Newton cooling coefficient. The effects of any small variation in κ over the surface of the jacket vessel of course disappear in this approximation, and measured values of the coefficient b represent the behaviour of the whole surface of the jacket vessel.

(b) *The special case of the liquid-bath thermostat*

The arrangement of a liquid-bath thermostat is essentially similar to that just discussed. Thus the servomechanism normally acts upon the bulk of the bath liquid, while all the common types of signal source measure the temperature of a 'controlled' surface or region separated from the bath liquid by a solid wall which gives rise to at least one boundary effect. All signal sources of the liquid thermometer type obviously fall into this class and it is found in practice that the behaviour of both mercury in glass and toluene in copper signal sources, for example, conforms closely to that predicted using equation (2·3). This is true also of those types of resistance thermometer in which the heat capacity of the resistance element and its support is large in comparison with that of the outer sheath. In dealing with thermostats of this type we are of course primarily interested in the behaviour of the temperature T_3 in the bulk of the bath liquid rather than in that of the temperature T_2 registered by the signal source; but it is a simple matter to obtain the variation of T_3 from the analysis of the corresponding calorimeter regulators (see § 7 below).

(c) *The case where the controlling surface is heated directly*

When, as in an externally compensated adiabatic calorimeter arranged according to figure 3, the thermal conduction process determining the operation of the regulator is described by equations (1·2), (1·3) and (1·4), an approximation may be derived in terms of the limiting case of 'steady-state' conduction across the uniform slab $0 < x < l$. It is easily established that if the temperature at the controlling surface, $x = 0$, of the slab is increased at constant rate over a sufficiently long time, the temperature profile across the slab will, with increasing time, tend towards a parabolic form defined by

$$\partial^2 T/\partial x^2 = \text{constant} \quad (0 < x < l).$$

This of course implies that $(\partial T/\partial t)$ is constant and has the same value at all points in the slab, and under these conditions equation (1·2) may be integrated directly to give

$$T_3 - T_2 = \frac{l^2}{2D}\frac{dT_3}{dt} = \frac{l^2}{2D}\frac{dT_2}{dt}, \tag{2·4}$$

where T_3 is the temperature at the surface $x = 0$ and T_2 is the temperature at the surface $x = l$. The approximation then consists in assuming that (dT_2/dt), the time rate of change of the temperature at the controlled surface, is given by

$$\frac{dT_2}{dt} = \frac{2D}{l^2}(T_3 - T_2), \tag{2·5}$$

whatever the variation with time of the temperature T_3 at the controlling surface. The quantity $2D/l^2$ is then analogous to the coefficient b in equation (2·3), and the equations (2·3) and (2·5) are therefore formally identical.

Comparison of cases (a) and (c)

The physical situations upon which equations (2·3) and (2·5) are based differ in important respects and, correspondingly, the nature of the approximation is different in the two cases. The accuracy of equation (2·3) is determined mainly by the physical properties of the material of the jacket vessel and those of the boundary layer at the outer surface of the vessel, and is only slightly dependent on the form of the function $T_3 = T_3(t)$. Equation (2·5), on the other hand, approaches exactitude with increasing time whenever (d^2T_3/dt^2) remains zero, but becomes formally incorrect whenever (d^2T_3/dt^2) differs from zero. Comparison with an exact analysis of the case of the uniform slab with no heat flow at the surface $x = l$ when the temperature T_3 at the surface $x = 0$ is constrained to a simple function of time (see Carslaw & Jaeger 1947, §§ 37, 38) indicates that when, as with a two-valued response calorimeter regulator, $T_3 = T_3(t)$ is a periodic function of the 'saw-tooth' type, equation (2·5) predicts incorrectly the phases of $T_3 = T_3(t)$ at which stationary values of T_2 (assuming the mean value of T_3 is constant) occur; but provided that the period of $T_3 = T_3(t)$ is relatively large equation (2·5) predicts fairly accurately the behaviour of T_2 near the phases of $T_3 = T_3(t)$ at which $(\mathrm{d}T_2/\mathrm{d}t)$ has its greatest magnitudes. Now the greatest magnitudes of $(\mathrm{d}T_2/\mathrm{d}t)$ obviously occur immediately prior to the reversal points of $T_3 = T_3(t)$. In a two-valued response regulator only these reversal points are directly determined by the variation of the signal, $S = T_2 - T_1$, where T_1 is the datum temperature, so that the period of $T_3 = T_3(t)$ should be predicted with fair accuracy. This analysis takes no account of the fact that in practice the conduction processes across the wall of the jacket vessel are modified by the finite curvature of the jacket vessel wall, and by the 'end effects' at the top and bottom. The first effect is unlikely to be important in the case of a relatively thin-walled vessel, and since the end effects operate only upon a small fraction of the total surface area of the jacket vessel they are almost certainly negligible, at least in the context of the proposed approximation.

Application of the 'steady-state' approximation

There remains the difficulty that equation (2·5) treats T_3 as the primary variable, whereas in the situation to which equations (1·2), (1·3) and (1·4) refer, the primary variable is the heat flux Q per unit area at the controlling surface, $x = 0$. With a two-valued response regulator $Q = Q(t)$ is a 'square-wave' function defined by $+Q'$ and $-Q''$. Provided that the periods of constant response are relatively long in comparison with the decay time of the exponential terms in the general solution to equations (1·2), (1·3) and (1·4) the temperature profile $T = T(x)$ between $x = 0$ and $x = l$ at the reversal times of the controlling action (the times at which $Q = +Q'$ is replaced by $Q = -Q''$ and vice versa) differs only insignificantly from the parabolic form. Now the increase in the mean temperature in the region $0 < x < l$ during a positive half cycle $(Q = +Q')$ is necessarily

$$\Delta \overline{T} = +Q' t_1/\rho c l,$$

where t_1 is the duration of the half cycle. If T_3 differs from the datum temperature T_1 by $-\theta_1$ at the commencement of a positive half cycle and by $+\theta_2$ at the termination of that positive half cycle, then, in the case where T_1 remains constant the increase in T_3 is

$$\Delta T_3 = (\theta_1 + \theta_2).$$

If the terminal values of $S = T_2 - T_1$ are respectively $-\phi$ and $+\phi$ (see § 3), then the terminal values of $(T_3 - T_2)$ are $-(\theta_1 - \phi)$ and $+(\theta_2 - \phi)$. Assuming $T = T(x)$ to be parabolic, it follows that the total increase in T_3 is related to Q' by

$$\Delta T_3 = Q' t_1/\rho c l + \tfrac{2}{3}(\theta_2 - \phi + \theta_1 - \phi),$$

so that the average heating rate during a positive half cycle is close to

$$a' \doteqdot \frac{3Q'}{\rho c l} - \frac{4\phi}{t_1}. \tag{2·6}$$

Correspondingly, the mean cooling rate during a negative half cycle is close to

$$a'' \doteqdot \frac{3Q''}{\rho c l} - \frac{4\phi}{t_2}, \tag{2·7}$$

where t_2 is the duration of the negative half cycle. The use of these relations involves only a comparatively simple successive approximations technique, using the tables of appendix II to obtain values of t_1 and t_2 which are then inserted in equations (2·6) and (2·7) to obtain better values of a' and a'' and so on.

Usefulness of the 'steady-state' approximation

An indication of the range of usefulness of the approximation is obtained by applying equation (2·5), together with the defining relations, to a linear response thermostat regulator. Turner (1936) has used a partial solution of equations (1·2), (1·3) and (1·4) to calculate the amplitude and period of $T_3 = T_3(t)$ in such a regulator when the sensitivity has that value above which the operation of the regulator is unstable.

In order to apply equation (2·5) to a linear response regulator it is convenient to define, in addition to the signal, the thermal head H, the difference between the controlling and datum temperatures

$$S = T_2 - T_1, \quad H = T_3 - T_1, \tag{2·8}$$

where, as before, T_1 is the datum temperature, T_2 is the temperature at the controlled surface and T_3 is the temperature at the controlling surface. The defining relations for the regulator when T_1 remains constant are then

$$\mathrm{d}S/\mathrm{d}t = b(H-S), \tag{2·9}$$

corresponding to equation (2·5), and

$$\mathrm{d}H/\mathrm{d}t = -rS, \tag{2·10}$$

where r is the apparent sensitivity of the regulator expressed in reciprocal seconds, analogous to the apparent heating and cooling rates of a two-valued response regulator defined by equations (2·6) and (2·7). The 'law of control' may be formulated by linear combination of equations (2·9) and (2·10) as

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(S - \frac{\nu}{r}H\right) - (\nu - b)\left(S - \frac{\nu}{r}H\right) = 0, \tag{2·11}$$

where ν is defined by

$$\nu^2 - \nu b + rb = 0. \tag{2·12}$$

Integration of equation (2·11) leads to

$$S = S^0\left[\frac{\beta\,\mathrm{e}^{\beta t} - \alpha\,\mathrm{e}^{\alpha t}}{\beta - \alpha}\right] + bH^0\left[\frac{\mathrm{e}^{\beta t} - \mathrm{e}^{\alpha t}}{\beta - \alpha}\right], \tag{2·13}$$

where S^0 and H^0 are the values of S and H when $t = 0$ and α and β are the roots of equation (2·12). Whenever r is greater than $\frac{1}{4}b$, S, and hence H also, is a periodic function of time, the period being

$$t = \frac{2\pi}{[b(r - \frac{1}{4}b)]^{\frac{1}{2}}}. \tag{2·14}$$

The amplitude of S always decreases with increasing time in proportion to e^{-bt}; that is to say, the use of equation (2·5) predicts that the operation of the regulator is stable for all values of the apparent sensitivity r. Now according to equations (2·9) and (2·10) the magnitude of $(H-S)$ has maxima whenever S is zero, and again the temperature profile $T = T(x)$ may be assumed to depart only insignificantly from the parabolic form at these stationary points of $H = H(t)$. Since S is zero at the stationary points of $H = H(t)$ in any linear response regulator, it follows that for a particular cycle the amplitude of H will be close to that which would be expected if the apparent sensitivity r were given by

$$r = 3q/\rho cl, \tag{2·15}$$

where q is the actual sensitivity of the regulator according to the relation

$$Q = -qS,$$

Q being the instantaneous heat flux per unit area at the controlling surface. Substituting for r in equation (2·14) gives

$$\boldsymbol{t} = 2\pi\Big/\left[b\left(\frac{3q}{\rho cl}-\tfrac{1}{4}b\right)\right]^{\frac{1}{2}}. \tag{2·16}$$

According to Turner's (1936) analysis, there exists a critical value of q for which the periodic function $H = H(t)$ maintains a constant amplitude; with higher values of q the amplitude of $H = H(t)$ increases with increasing time; that is to say, the operation of the regulator is unstable. The critical value of q thus represents the complete breakdown of the assumptions underlying equations (2·5) and (2·15).

When the material separating the controlling and controlled surfaces is aluminium, with the properties quoted on p. 414, the critical value of q, according to Turner's calculations, is close to

$$q_{\text{crit.}} \doteqdot 17·6\lambda/l, \tag{2·17}$$

and the corresponding value of the period is

$$\boldsymbol{t}_{\text{crit.}} = 1·118l^2 = 1·144/b. \tag{2·18}$$

Introducing the value of q given by equation (2·17), together with the appropriate values of λ, ρ and c, into equation (2·16) and putting b equal to $2D/l^2$ leads to

$$\boldsymbol{t}_{\text{crit.}} = 1·200l^2 = 1·228/b. \tag{2·19}$$

In both cases $\boldsymbol{t}_{\text{crit.}}$ is close to $1·2/b$, while the critical value of r is close to $27·0b$, corresponding to q close to $9·0b\rho cl$. It must be noted that according to equation (2·14) a relatively large alteration in r produces only a small change in $\boldsymbol{t}$. Nevertheless, the agreement between equations (2·18) and (2·19) is such as to suggest that the approximation represented by equations (2·5) and (2·15) will predict at least the period of $H = H(t)$ in a linear response thermostat regulator with fair accuracy whenever the sensitivity q is small in comparison with the value given by equation (2·17). It may then be inferred that equations (2·5), (2·6) and (2·7), in the case of a two-valued response regulator, also predict with fair accuracy the half-cycle periods of $H = H(t)$, provided that each half-cycle period exceeds, say, $1/b$. This implies that, as stated above, the behaviour of the signal close to the reversal points of $H = H(t)$ is also described with fair accuracy by this approximation.

The average behaviour of S over many cycles is obviously closely connected with the behaviour of S close to the reversal points of $H = H(t)$. It then seems reasonable to expect that both the approximations described above will predict the average behaviour of S accurately enough for practical purposes, such as the evaluation of correction terms to calorimetric experiments by means of equation (1·1).

Since the numerical results corresponding to the second approximation, equations (2·5), (2·6) and (2·7), can easily be obtained from those corresponding to the first approximation, equation (2·3), only the latter case will be discussed here.

3. Uniform operation of two-valued response regulators

The principle of a two-valued response regulator is that as soon as the signal exceeds a characteristic small positive magnitude $+\phi$, there results a response in the negative sense, that is to say in the sense that will eventually decrease the signal to less than zero. This negative-going response persists with constant magnitude until the signal attains the value $-\phi$, when a positive-going response is initiated. This persists with constant magnitude until the signal again attains the value $+\phi$. The magnitude of the response may or may not be the same in both senses. In an externally compensated adiabatic calorimeter arranged as in figure 4 the two responses are, respectively, heating and cooling of the calorimeter environment.

The method employed here to analyze the behaviour of such a regulator depends on establishing the existence, in each of two situations, of a *condition of uniform operation* towards which the behaviour of the regulator always tends so long as that situation persists, irrespective of the initial conditions. These two situations are that in which the datum temperature T_1 remains constant, and that in which T_1 varies linearly with time. While the analysis requires only straightforward algebra, a rigorous examination of the general case in which the positive-going and negative-going responses are unequal inevitably involves a great many logical steps. Therefore, in order to simplify the discussion as far as possible we shall first examine in detail the case in which the two responses are of equal magnitude. The conclusions pertaining to this case are extended to the general case in the following section.

With a two-valued response regulator applied to an externally compensated adiabatic calorimeter of the type illustrated in figure 4 the regulator response may conveniently be measured by $(\mathrm{d}T_3/\mathrm{d}t)$, the time rate of change of the temperature in the calorimeter environment, the signal being a measure of the difference between the controlled and datum temperatures. When the heating and cooling rates of the calorimeter environment are equal the defining relations are, for a positive half cycle,

$$\mathrm{d}T_3/\mathrm{d}t = +a,$$

commencing when the signal $S = T_2 - T_1$ decreases through $-\phi$, and for a negative half cycle

$$\mathrm{d}T_3/\mathrm{d}t = -a,$$

commencing when S increases through $+\phi$. The rate $a(\deg\,\mathrm{s}^{-1})$ is characteristic of the particular apparatus. Each half cycle may be taken as commencing when the magnitude of the signal S is ϕ and increasing, and terminating when the signal next attains the value equal in magnitude and opposite in sign to the initial value. Taking as positive and negative half cycles the periods during which T_3 is increasing and decreasing respectively, the time variation of T_3 is given by

$$\left.\begin{aligned} T_3 &= T_3' + at \quad \text{(positive half cycle)},\\ T_3 &= T_3'' - at \quad \text{(negative half cycle)}, \end{aligned}\right\} \tag{3·1}$$

where the prime and double prime indicate the value of the variable at the commencement of the half cycle. In these equations the variable t is given the value zero at the commencement of each half cycle, so that it is properly described as the duration of the half cycle.

Although this usage differs from that in the preceding sections, equation (2·3), being a differential form, remains valid, while the difficulties which would arise from the discontinuous variation of the time derivatives of T_3 are avoided.

Introducing the thermal head $H = T_3 - T_1$ into the equations (3·1) leads to

$$H = H_n \pm at - \int_0^t \left(\frac{dT_1}{dt}\right) dt, \tag{3·2}$$

where H_n is the value of H at the commencement of the nth half cycle and the sign of the second term is determined by whether the nth cycle half is positive or negative. Then, introducing into equation (2·3) the thermal head $H = T_3 - T_1$ and the signal $S = T_2 - T_1$, and substituting for H according to equation (3·2), we have

$$S + \frac{1}{b}\frac{dS}{dt} = H_n \pm at - \int_0^t \frac{dT_1}{dt} dt - \frac{1}{b}\frac{dT_1}{dt}. \tag{3·3}$$

Uniform operation when T_1 remains constant

For the first positive half cycle the initial value of S is $-\phi$, and the solution to equation (3·3) is

$$S = H_1 - a/b + at + (a/b - \phi - H_1)\, e^{-bt}. \tag{3·4}$$

This positive half cycle terminates after a period t_1 when S attains the value $+\phi$. The corresponding value of H is

$$H_2 = H_1 + at_1 \tag{3·5}$$

and this is then the initial value of H at the commencement of the succeeding negative half cycle. This negative half cycle is described by

$$S = H_2 + a/b - at - (a/b - \phi + H_2)\, e^{-bt}. \tag{3·6}$$

The negative half cycle terminates after a period t_2 when S attains the value $-\phi$. The initial value of H for the next (positive) half cycle is then

$$H_3 = H_2 - at_2. \tag{3·7}$$

The detailed behaviour of H may be deduced by replacing S, on the left-hand side of equations (3·4) and (3·6), by its appropriate terminal values. Thus at the termination of the first positive half cycle,

$$(a/b - \phi - H_1)\, e^{-bt_1} - (a/b + \phi - H_1) + at_1 = 0. \tag{3·8}$$

Equation (3·8) has a real positive solution in t_1 for all values of H_1. Further, the behaviour of the regulator subsequent to the first complete cycle is always subject to certain regularities. Thus it follows from equation (2·3) that if S is increasing while T_1 remains constant, then S must be less than H, so that H_2 always exceeds $+\phi$. Consequently, the coefficient of the exponential term in equation (3·6) is always less than $-a/b$, and during the negative half cycle

$$S < H_2 + a/b - at,$$

so that at the termination of the negative half cycle

$$H_3 > -a/b - \phi.$$

It is easily established in terms of equation (2·3) that H_3 is always less than $-\phi$, so that irrespective of H_1,

$$-\phi > H_3 > -\phi - a/b, \tag{3·9}$$

and correspondingly

$$+\phi < H_4 < +\phi + a/b. \tag{3·10}$$

The restrictions (3·9) and (3·10) necessarily apply to all subsequent cycles. Equation (3·8) may be written

$$(a/b - \phi - H_1)\, \mathrm{e}^{-b(H_2 - H_1)/a} - (a/b + \phi - H_2) = 0, \tag{3·11}$$

while for the succeeding negative half cycle

$$(a/b - \phi + H_2)\, \mathrm{e}^{-b(H_2 - H_3)/a} - (a/b + \phi + H_3) = 0. \tag{3·12}$$

Equations (3·11) and (3·12) have a symmetrical solution θ,

$$\phi < \theta < \phi + a/b, \tag{3·13}$$

defined by

$$\ln \frac{a - b(\theta - \phi)}{a + b(\theta - \phi)} = -\frac{2b\theta}{a} = -bt_n, \tag{3·14}$$

such that if $H_1 = -\theta$, then $H_2 = +\theta$, $H_3 = -\theta$ and so on. This is the condition of uniform operation. Then, given the values of a, b and ϕ, equation (3·14) defines the amplitude 2θ of the periodic variation of the thermal head H, and hence the half cycle period t_n, when the condition of uniform operation obtains. Since equation (3·14) can be regarded as a special case of the general treatment presented in § 4 below, the technique for solving it need not be discussed here.

It remains to show that the behaviour of the regulator always tends towards this condition of uniform operation when T_1 remains constant. If H_1 is denoted by $-(\theta + h)$ and H_2 by $+(\theta + j)$, then equation (3·11) may be written

$$j - h = (a/b + \phi - \theta - h) - (a/b - \phi + \theta + h)\, \mathrm{e}^{-b(2\theta + h + j)/a}, \tag{3·15}$$

whence, by virtue of equation (3·14),

$$\mathrm{e}^{-b(h+j)/a} = \frac{[a + b(\theta - \phi)]\,[a - b(\theta - \phi + j)]}{[a - b(\theta - \phi)]\,[a + b(\theta - \phi + h)]}. \tag{3·16}$$

The condition (3·13) ensures that

$$a + b(\theta - \phi) > a - b(\theta - \phi)$$

and that both these quantities are positive. Now if ξ is any magnitude between zero and unity, $\mathrm{e}^{-\alpha}$ and $(1+\xi)/(1+\xi+\alpha)$ converge towards zero as α increases towards infinity, and are equal when α has some value between $-1{\cdot}59\xi$ and -2ξ, depending on ξ, while all functions

$$\frac{(1+\xi)\,(1-\xi-\alpha+\epsilon\alpha)}{(1-\xi)\,(1+\xi+\epsilon\alpha)} \quad (0 < \epsilon < 1)$$

become equal when α has the value -2ξ. Then, for positive α,

$$\frac{1+\xi}{1+\xi+\alpha} > \mathrm{e}^{-\alpha} > \frac{1-\xi-\alpha}{1-\xi}. \tag{3·17}$$

By analogy, for every positive h, equation (3·16) defines a unique j, also positive but less than $(a/b - \theta + \phi)$. Similarly when h lies between zero and $-1{\cdot}59(b/a)\,(\theta - \phi)$, equation

(3·16) defines a unique j, lying between zero and $-(b/a)(\theta-\phi)$, according to the conditions (3·9) and (3·10). Since the situation

$$h < -(\theta-\phi)$$

cannot occur after the first complete cycle, the situation

$$h < -1{\cdot}59(\theta-\phi),$$

which may lead to j greater than zero, may be ignored. Then, after one complete cycle,

$$a/b-\theta+\phi > h, \quad j > -\theta+\phi, \tag{3·18}$$

and h and j always have the same sign. When both h and j are positive the right-hand side of equation (3·16) is less than unity but greater than zero. Conversely, when h and j are negative, the right-hand side of equation (3·16) is greater than unity. For the first case, expanding both sides of equation (3·16) leads to

$$\frac{j}{h} \leqslant \frac{a-b(\theta-\phi)}{a+b(\theta-\phi)}. \tag{3·19}$$

Thus the ratio j/h is always less than unity. As h is made progressively smaller the inequality (3·19) approaches the corresponding equality. When h and j are negative, the same result is achieved by first inverting equation (3·16). Thus, irrespective of H_1, the condition (3·18) holds good after the completion of one cycle and the departures of succeeding $|H_n|$ from θ decrease and approach conformity to a geometric progression of the ratio (3·19).

General aspects of behaviour when T_1 varies

When T_1 varies, the situation at the termination of a positive half cycle is, as before,

$$(a/b-\phi-H_1)\,e^{-bt_1}-(a/b+\phi-H_2) = 0, \tag{3·20}$$

but H_2 is now given by
$$H_2 = H_1+at_1-\int_u^{u+t_1}\left(\frac{dT_1}{dt}\right)dt, \tag{3·21}$$

where u is the time of commencement, on an arbitrary scale, of the half cycle. At the termination of the succeeding negative half cycle

$$(a/b-\phi+H_2)\,e^{-bt_2}-(a/b+\phi-H_3) = 0, \tag{3·22}$$

with
$$H_3 = H_2-at_2-\int_{u+t_1}^{u+t_1+t_2}\left(\frac{dT_1}{dt}\right)dt. \tag{3·23}$$

The limits of integration take account of the fact that the variation of T_1 is not determined by the duration t_n of successive regulator half cycles. To ensure that the half-cycle periods t_1 and t_2 are finite positive quantities it is sufficient that

$$a > \left|\left(\frac{dT_1}{dt}\right)\right|_{\text{max.}}. \tag{3·24}$$

The successive terminal values H_n of H are subject to restrictions similar to those applying when T_1 remains constant; thus after the first complete cycle,

$$-\phi+\frac{1}{b}\left(\frac{dT_1}{dt}\right)_{t_{2n}} > H_{2n+1} > -(a/b+\phi), \tag{3·25}$$

$$+\phi+\frac{1}{b}\left(\frac{dT_1}{dt}\right)_{t_{2n+1}} < H_{2n+2} < +(a/b+\phi). \tag{3·26}$$

The extreme limits are unchanged by variations of T_1 (see the restrictions (3·9) and (3·10)) but when T_1 is increasing the upper limit of H_{2n+1} increases and may be positive, while the lower limit of H_{2n+2} is also increased. This suggests that uniform operation when T_1 varies corresponds to H_{2n+1} and H_{2n+2} having unequal magnitudes, i.e. this condition of uniform operation is defined by

$$H_1 = H_3 = H_5 = \ldots = \theta_1, \quad H_2 = H_4 = H_6 = \ldots = \theta_2. \tag{3·27}$$

The terminations of the first two positive half cycles are then described by

$$(a/b-\phi-H_1)\,\mathrm{e}^{-bt_1}-(a/b+\phi-H_2) = 0,$$
$$(a/b-\phi-H_3)\,\mathrm{e}^{-bt_3}-(a/b+\phi-H_4) = 0.$$

If $H_1 = H_3$, then $H_2 = H_4$ only if $t_1 = t_3$; H_2 and H_4 are related to H_1 by equations (3·21), (3·23) and by

$$H_4 = H_1+at_3+\int_{u+t_1+t_2}^{u+t_1+t_2+t_3}\left(\frac{\mathrm{d}T_1}{\mathrm{d}t}\right)\mathrm{d}t. \tag{3·28}$$

The condition (3·27) thus requires that the integrals in equations (3·21) and (3·28) are equal, and the condition (3·27) can only be satisfied if T_1 is constant or varies linearly with time.

Uniform operation when T_1 varies linearly with time

When T_1 varies according to

$$T_1 = T_1^0+pt, \tag{3·29}$$

the relation between the first two terminal values of H is given by equation (3·20) together with

$$H_2 = H_1+(a-p)\,t_1, \tag{3·30}$$

while the second and third terminal values of H, defining the first negative half cycle, are related by equation (3·22), together with

$$H_3 = H_2-(a+p)\,t_2. \tag{3·31}$$

The condition of uniform operation is then defined by substituting in equations (3·20) and (3·22) according to the conditions (3·27). Taking account of equations (3·30) and (3·31) leads to the simultaneous equations

$$\ln\frac{a-b(\theta_2-\phi)}{a+b(\theta_1-\phi)} = -\frac{b}{a-p}(\theta_1+\theta_2) = -bt_1, \tag{3·32}$$

$$\ln\frac{a-b(\theta_1-\phi)}{a+b(\theta_2-\phi)} = -\frac{b}{a+p}(\theta_1+\theta_2) = -bt_2. \tag{3·33}$$

These equations have a unique real solution $\theta_1 \neq \theta_2$ conforming to the conditions (3·25) and (3·26), provided that the magnitude of p is less than a, and is not zero. The method for obtaining this solution, as in the case of equation (3·14), follows that used in the general case discussed in § 4. When p is zero, both equations (3·32) and (3·33) reduce to equation (3·14).

That the operation of the regulator when T_1 varies linearly with time always tends towards the conditions (3·27) may be established by the method used to derive the relation (3·19). Thus if, in equation (3·20), H_1 is denoted by $-(\theta_1+h)$ and H_2 by $+(\theta_2+j)$, then substituting for t_1 as

$$t_1 = \frac{\theta_1+\theta_2+h+j}{a-p} \tag{3·34}$$

leads to
$$e^{-b(h+j)/(a-p)} = \frac{[a-b(\theta_2-\phi+j)]\,[a+b(\theta_1-\phi)]}{[a+b(\theta_1-\phi+h)]\,[a-b(\theta_2-\phi)]}. \tag{3·35}$$

The corresponding relation obtained from equation (3·22) with
$$H_3 = -(\theta_1+k), \quad t_2 = \frac{\theta_1+\theta_2+j+k}{a+p},$$
is then
$$e^{-b(j+k)/(a+p)} = \frac{[a-b(\theta_1-\phi+k)]\,[a+b(\theta_2-\phi)]}{[a+b(\theta_2-\phi+j)]\,[a-b(\theta_1-\phi)]}. \tag{3·36}$$

An argument similar to that used to establish the relation (3·18) may be used to show that, provided one full cycle of the regulator operations has already been completed, the quantities h, j and k in equations (3·35) and (3·36) have always the same sign. Combining these equations after expanding the exponential terms in series leads to
$$\frac{k}{h} \leqslant \frac{[a-b(\theta_1-\phi)]\,[a-b(\theta_2-\phi)]}{[a+b(\theta_1-\phi)]\,[a+b(\theta_2-\phi)]}. \tag{3·37}$$

Since the form of equations (3·32) and (3·33) requires that when p is between zero and $+a$, θ_1 lies within the limits $\pm\theta_2$, while the condition (3·26) ensures that
$$a/b > \theta_2 - \phi > 0,$$
it follows that under these conditions the ratio k/h is always less than unity. Conversely when p is between zero and $-a$, θ_2 lies within the limits $\pm\theta_1$, while
$$a/b > \theta_1 - \phi > 0,$$
and again the ratio k/h is less than unity, so that the operation of the regulator is always stable. While this might have been inferred directly from the analogues of equations (3·4) and (3·6), the relation (3·37) gives a measure of the fractional diminution over a complete cycle of the initial departure from the condition of uniform operation.

Behaviour of the signal during uniform operation

When uniform operation obtains during an increase in the datum temperature T_1 linear with respect to time, the behaviour of the signal S during a positive half cycle is described by
$$S = (a/b+\theta_1-\phi)\,e^{-bt} - (a/b+\theta_1) + (a-p)\,t. \tag{3·38}$$

The minimum value of S is then given by
$$S_{\text{min.}} = -\theta_1 - \frac{p}{b} + \frac{a-p}{b}\ln\left\{\frac{b}{a-p}\left(\frac{a}{b}+\theta_1-\phi\right)\right\}. \tag{3·39}$$

During the succeeding negative half cycle,
$$S = -(a/b+\theta_2-\phi)\,e^{-bt} + (a/b+\theta_2) - (a+p)\,t, \tag{3·40}$$
and the maximum value of S is
$$S_{\text{max.}} = +\theta_2 - \frac{p}{b} - \frac{a+p}{b}\ln\left\{\frac{b}{a+p}\left(\frac{a}{b}+\theta_2-\phi\right)\right\}. \tag{3·41}$$

It is evident that as the ratio p/a increased towards unity, both the maximum and minimum values of S decrease, whereas it is easily established in terms of equations (3·32) and (3·33) that both θ_2 and $-\theta_1$ increase.

Integrating equation (3·38) between $t = 0$ and $t = t_1$, and taking account of equation (3·30) leads to

$$\int_0^{t_1} S\,\mathrm{d}t = +\frac{1}{b}(\theta_1+\theta_2-2\phi) - \frac{\theta_1+\theta_2}{a-p}\left[\frac{a}{b}-\tfrac{1}{2}(\theta_2-\theta_1)\right], \tag{3·42}$$

while the corresponding integral obtained from equation (3·40) is

$$\int_0^{t_2} S\,\mathrm{d}t = -\frac{1}{b}(\theta_1+\theta_2-2\phi) + \frac{\theta_1+\theta_2}{a+p}\left[\frac{a}{b}+\tfrac{1}{2}(\theta_2-\theta_1)\right]. \tag{3·43}$$

Thus the time integral of S over a complete cycle is

$$\bar{S}(t_1+t_2) = \frac{a}{b}(\theta_1+\theta_2)\left(\frac{1}{a+p}-\frac{1}{a-p}\right) + \tfrac{1}{2}(\theta_2^2-\theta_1^2)\left(\frac{1}{a+p}+\frac{1}{a-p}\right), \tag{3·44}$$

where $\bar{S}$ is the average value of S over the complete cycle. Now the period of the complete cycle is

$$t_1+t_2 = (\theta_1+\theta_2)\left(\frac{1}{a+p}+\frac{1}{a-p}\right),$$

so that

$$\bar{S} = -p/b+\tfrac{1}{2}(\theta_2-\theta_1). \tag{3·45}$$

It is implicit in the form of equations (3·32) and (3·33) that the magnitude of the first term on the right-hand side of equation (3·45) must always exceed that of the second term, so that when the datum temperature T_1 is increasing, i.e. when p is positive, the mean signal $\bar{S}$ is negative, and vice versa. Equation (3·45) also indicates that the mean signal $\bar{S}$ is less than the mean value of the thermal head H by the amount p/b, which is the value of (T_3-T_2) which would just suffice to keep T_2 increasing at the rate p.

The behaviour of the signal when T_1 remains constant is easily deduced from equations (3·42) to (3·45). In particular, the maximum and minimum values of S, during negative and positive half cycles respectively, are

$$S_{\text{max.}} = +\theta-\frac{a}{b}\ln\left\{1+\frac{b}{a}(\theta-\phi)\right\},\quad S_{\text{min.}} = -\theta+\frac{a}{b}\ln\left\{1+\frac{b}{a}(\theta-\phi)\right\}, \tag{3·46}$$

while the time integrals of S over positive and negative half cycles respectively are

$$\int_0^{t_1} S\,\mathrm{d}t = -2\phi/b,\quad \int_0^{t_2} S\,\mathrm{d}t = +2\phi/b. \tag{3·47}$$

A point of practical interest concerning the two-valued response regulator with equal heating and cooling rates is that, as may be established from the numerical data presented in appendix II, the variation of θ_1 and θ_2 is very nearly linear with respect to p for magnitudes of p/a less than about 0·5. When this condition is fulfilled, equation (3·45) may be written in the form

$$\bar{S} \doteqdot -(p/b)(1-K), \tag{3·48}$$

where K is defined by

$$\tfrac{1}{2}b(\theta_2-\theta_1) \doteqdot Kp.$$

K depends only on $b\phi/a$ and approaches unity as $b\phi/a$ approaches zero. Equation (3·48) does not, however, suffice to evaluate by means of equation (1·1) the correction δT to an observed change ΔT in the temperature T_1 of the calorimeter vessel, since it refers only to uniform operation (with p constant). In a real experiment $(\mathrm{d}T_1/\mathrm{d}t)$ necessarily changes, giving rise to periods of non-uniform operation the detailed configurations of which depend on the form of the variation of $(\mathrm{d}T_1/\mathrm{d}t)$, on the phase of the regulator cycle at which any extreme values of $(\mathrm{d}^2T_1/\mathrm{d}t^2)$ occur, and of course on the rapidity with which uniform operation is re-attained. Consequently the total time integral of S over a complete experiment is subject to a definite uncertainty and

$$\int_0^\infty S\,\mathrm{d}t \doteqdot -\frac{1-K}{b}\int_0^\infty\left(\frac{\mathrm{d}T_1}{\mathrm{d}t}\right)\mathrm{d}t \pm \zeta = -\frac{1-K}{b}\Delta T \pm \zeta, \tag{3·49}$$

where ζ is the uncertainty in the time integral of S arising from departures from uniform operation. The evaluation of ζ in one simple case is discussed in appendix I.

4. Two-valued response regulators with unequal heating and cooling rates

Let the heating rate $(\mathrm{d}T_3/\mathrm{d}t)$ of the calorimeter environment during a positive half cycle be $+a'$ and the cooling rate during a negative half cycle be $-a''$. Then at the terminations of the positive and negative half cycles respectively, when T_1 remains constant,

$$(a'/b-\phi-H_1)\,\mathrm{e}^{-bt_1}-(a'/b+\phi-H_2) = 0, \tag{4·1}$$

$$(a''/b-\phi+H_2)\,\mathrm{e}^{-bt_2}-(a''/b+\phi+H_3) = 0, \tag{4·2}$$

where

$$H_2 = H_1+a't_1, \quad H_3 = H_2-a''t_2. \tag{4·3}$$

It is easily established in terms of equations (4·1) and (4·2) that while uniform operation is established under these conditions it does not correspond to $H_1 = -H_2$. Putting

$$H_1 = H_3 = -\theta_1, \quad H_2 = +\theta_2 \tag{4·4}$$

in equations (4·1) and (4·2) leads to

$$\ln\frac{a'-b(\theta_2-\phi)}{a'+b(\theta_1-\phi)} = -\frac{b}{a'}(\theta_1+\theta_2) = -bt_1, \tag{4·5}$$

$$\ln\frac{a''-b(\theta_1-\phi)}{a''+b(\theta_2-\phi)} = -\frac{b}{a''}(\theta_1-\theta_2) = -bt_2. \tag{4·6}$$

The symmetry of these equations requires that if $a' > a''$, then $\theta_2 > \theta_1$, and vice versa, while $\theta_1 = \theta_2$ only if $a' = a''$. The detailed behaviour of θ_1 and θ_2 as a' and a'' change may be discovered from the tables in appendix II. The approach to the condition of uniform operation defined by equations (4·5) and (4·6) is given by

$$\frac{k}{h} \leqslant \frac{[a''-b(\theta_1-\phi)]\,[a'-b(\theta_2-\phi)]}{[a''+b(\theta_2-\phi)]\,[a'+b(\theta_1-\phi)]}, \tag{4·7}$$

where h and k have the same significance as in equation (3·37).

When the condition of uniform operation obtains the time integral of the signal over a positive half cycle is

$$\int_0^{t_1} S\,\mathrm{d}t = \frac{1}{2a'}(\theta_2^2-\theta_1^2)-\frac{2\phi}{b}, \tag{4·8}$$

while for the succeeding negative half cycle

$$\int_0^{t_2} S\,\mathrm{d}t = \frac{1}{2a''}(\theta_2^2-\theta_1^2)+\frac{2\phi}{b}, \tag{4·9}$$

so that for the complete cycle

$$\overline{S} = \tfrac{1}{2}(\theta_2-\theta_1). \tag{4·10}$$

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Thus when T_1 remains constant, if the magnitude of the heating rate exceeds that of the cooling rate, the mean value of the signal is positive, and vice versa.

When T_1 varies linearly with time according to equation (3·29), if $a' \neq a''$, then the condition of uniform operation is defined by

$$\ln\frac{a'-b(\theta_2-\phi)}{a'+b(\theta_1-\phi)} = -\frac{b(\theta_1+\theta_2)}{a'-p} = -bt_1, \tag{4·11}$$

$$\ln\frac{a''-b(\theta_1-\phi)}{a''+b(\theta_2-\phi)} = -\frac{b(\theta_1+\theta_2)}{a''+p} = -bt_2. \tag{4·12}$$

Provided only that $a' > p > -a''$, equations (4·11) and (4·12) give an unambiguous definition of θ_1 and θ_2. The approach to uniform operation is given by

$$\frac{k}{h} \leqslant \frac{[a''-b(\theta_1-\phi)]\,[a'-b(\theta_2-\phi)]}{[a''+b(\theta_2-\phi)]\,[a'+b(\theta_1-\phi)]} \tag{4·7}$$

in this case also. The time integrals of S over the positive and negative half cycles during uniform operation are, respectively,

$$\int_0^{t_1} S\,\mathrm{d}t = +\frac{1}{b}(\theta_1+\theta_2-2\phi) - \frac{\theta_1+\theta_2}{a'-p}\left[\frac{a'}{b}-\tfrac{1}{2}(\theta_2-\theta_1)\right], \tag{4·13}$$

$$\int_0^{t_2} S\,\mathrm{d}t = -\frac{1}{b}(\theta_1+\theta_2-2\phi) + \frac{\theta_1+\theta_2}{a''+p}\left[\frac{a''}{b}+\tfrac{1}{2}(\theta_2-\theta_1)\right]. \tag{4·14}$$

Equations (4·13) and (4·14) have the same form as equations (3·42) and (3·43) and in the present case also, $\bar{S}$ is given by

$$\bar{S} = -p/b + \tfrac{1}{2}(\theta_2-\theta_1). \tag{3·45}$$

Equations (4·13) and (4·14) differ, however, from equations (3·42) and (3·43) in that while the latter can never sum to zero for $p \neq 0$, equations (4·13) and (4·14) sum to zero if

$$a'-p = a''+p. \tag{4·15}$$

When this condition is satisfied, adding equations (4·13) and (4·14) gives

$$\oint S\,\mathrm{d}t = -\frac{\theta_1+\theta_2}{a'-p}\left[\frac{a'-a''}{b}-(\theta_2-\theta_1)\right] \tag{4·16}$$

while combining the condition (4·15) with equations (4·11) and (4·12) leads to

$$\theta_2-\theta_1 = (a'-a'')/b \tag{4·17}$$

which ensures that the right-hand side of equation (4·16) is zero.

In order to evaluate $\bar{S}$ when the condition (4·15) is not satisfied, it is necessary to solve equations (4·11) and (4·12). It is convenient to introduce the parameters

$$\mu = b(\theta_1+\theta_2)/(a'-p) = bt_1, \tag{4·18}$$

$$\eta = (a'-p)/(a''+p) = t_2/t_1, \tag{4·19}$$

when equations (4·11) and (4·12) may be written respectively,

$$1-\frac{b\theta_2}{a'}+\frac{b\phi}{a'} = \mathrm{e}^{-\mu}\left(1+\frac{b\theta_1}{a'}-\frac{b\phi}{a'}\right), \tag{4·20}$$

$$1-\frac{b\theta_1}{a''}+\frac{b\phi}{a''} = \mathrm{e}^{-\eta\mu}\left(1+\frac{b\theta_2}{a''}-\frac{b\phi}{a''}\right). \tag{4·21}$$

Multiplying these equations by the factors $(1-e^{-\eta\mu})/a''$ and $(1-e^{-\mu})/a'$ and adding leads to

$$\frac{\eta\mu}{\eta+1}-\Omega=\frac{(1-e^{-\mu})(1-e^{-\eta\mu})}{1-e^{-\mu(\eta+1)}}, \tag{4·22}$$

where
$$\Omega=2b\phi/(a'+a''). \tag{4·23}$$

Equation (4·22) has a finite positive solution μ for all positive η and Ω. It is interesting to note that if η is replaced by $1/\eta$ and μ is replaced by $\eta\mu$, which is equivalent to interchanging the values of a' and a'' and changing the sign of p, equation (4·22) transforms into itself. This means that the value of $(\theta_1+\theta_2)$ corresponding to $\eta=X$ also occurs when $\eta=1/X$. By expanding the right-hand side of equation (4·22), neglecting powers higher than the third, it may be shown that

$$\frac{(1-e^{-\mu})(1-e^{-\eta\mu})}{1-e^{-\mu(\eta+1)}}\doteqdot\frac{\eta\mu}{\eta+1}\left(1-\frac{\eta\mu^2}{12}\right),$$

whence
$$\mu^3\doteqdot 12\Omega(\eta+1)/\eta^2. \tag{4·24}$$

Now equation (4·22) may be written

$$\mu^3=\frac{12(\eta+1)}{\eta^2}\left[\Omega+\frac{(1-e^{-\mu})(1-e^{-\eta\mu})}{1-e^{-\mu(\eta+1)}}-\frac{\eta\mu}{\eta+1}\left(1-\frac{\eta\mu^2}{12}\right)\right]. \tag{4·25}$$

It follows from equation (4·24) that the second and third terms inside the brackets in equation (4·25) differ in magnitude by an amount small in comparison with Ω, and equation (4·25) may thus be solved numerically by successive approximations. Equation (4·25) remains useful until Ω exceeds about 0·2. For larger values of Ω, the right-hand side of equation (4·22) is close to unity. Under these conditions a successive approximations technique may be based on equation (4·22) itself, in the form

$$\mu=\frac{\eta+1}{\eta}\left[\Omega+\frac{(1-e^{-\mu})(1-e^{-\eta\mu})}{1-e^{-\mu(\eta+1)}}\right]. \tag{4·26}$$

The relation between $\bar{S}$ and μ may be established as follows. Rearranging equation (4·22) in the form

$$\theta_1+\theta_2-2\phi=\frac{a'+a''}{b}\left[\frac{(1-e^{-\mu})(1-e^{-\eta\mu})}{1-e^{-\mu(\eta+1)}}\right],$$

and then substituting for $\theta_1-\phi$ according to equation (4·21) and for $\theta_2-\phi$ according to equation (4·20) gives the two relations

$$\theta_2-\phi=\frac{a'+a''}{b}\left[\frac{1-e^{-\mu}}{1-e^{-\mu(\eta+1)}}\right]-\frac{a''}{b},$$

$$\theta_1-\phi=\frac{a'+a''}{b}\left[\frac{1-e^{-\eta\mu}}{1-e^{-\mu(\eta+1)}}\right]-\frac{a'}{b}.$$

The difference between these equations is

$$\theta_2-\theta_1=\frac{a'+a''}{b}\left[\frac{e^{-\eta\mu}-e^{-\mu}}{1-e^{-\mu(\eta+1)}}\right]+\frac{a'-a''}{b}. \tag{4·27}$$

Combining equations (4·27) and (3·45) gives the required relation

$$\bar{S}=\frac{\phi}{\Omega}\left[\frac{\eta-1}{\eta+1}-\frac{e^{-\mu}-e^{-\eta\mu}}{1-e^{-\mu(\eta+1)}}\right]. \tag{4·28}$$

Equation (4·28) indicates that for a given value of Ω, $\bar{S}$ depends only on the ratio η of the periods of negative and positive half cycles, and is independent of the detailed relations between a', a'' and p. In particular, equation (4·28) gives the explicit solution to equation (4·10) for the case where p is zero. This implies that for a particular apparatus, if η is the same in two cases characterized by $p = 0$ and $p \neq 0$, respectively, then the mean signal $\bar{S}$ is the same in both cases, but in the case $p \neq 0$ both θ_2 and $-\theta_1$ are greater than in the case $p = 0$ by an amount p/b, which is that value of the difference $(T_3 - T_2)$ which just suffices to keep the mean value of T_2 increasing at the rate p. Further, equation (4·28) indicates that $\bar{S}$ is zero when η is unity, and since replacing η by $1/\eta$ does not affect the value of the amplitude $(\theta_1 + \theta_2)$ of the thermal head H, it follows from equations (4·11) and (4·12) that the values of θ_1 and θ_2 are interchanged by this operation and, according to equation (3·45), $\bar{S}$ changes sign. Consequently a single set of solutions in $\bar{S}/\phi$ to equation (4·28) can be used to evaluate $\bar{S}$ in the entire class of two-valued response thermoregulators with negligible time delay. This point is discussed further in appendix II.

It is obvious that when a' and a'' are unequal there can be no general relation corresponding to equation (3·48) in the case where a' and a'' are equal since $\bar{S}$ is not zero when T_1 remains constant except when a' and a'' are equal.

5. Effect of time delay in the servomechanism

The foregoing discussion assumes implicitly that the negative-going controlling action is superseded by the positive-going controlling action simultaneously with the signal attaining the value $-\phi$. With the arrangement of figure 4, however, and in many other cases, it is impossible to avoid some delay between the signal attaining the value $-\phi$ and the initiation of the positive-going controlling action. The same considerations of course apply at the initiation of the negative-going controlling action. It is therefore of some practical importance to discover the effect on the behaviour of the regulator of this time delay in the servomechanism.

When such a time delay exists, instead of a positive half cycle terminating when the signal attains the value $+\phi$, it continues until S attains some value $+\psi_2$, depending on ϕ, on the magnitude τ of the time delay and on the behaviour of $(\mathrm{d}S/\mathrm{d}t)$ during the half cycle. Similarly the succeeding negative half cycle terminates with $S = -\psi_1$. The equations describing the behaviour of the signal S as a function of time can be rewritten in terms of ψ_1 and ψ_2 without formal alteration. Supplementary relations are of course necessary to determine ψ_1 and ψ_2; but since, according to equation (2·3), the magnitude of $(\mathrm{d}S/\mathrm{d}t)$ can never exceed that of $(\mathrm{d}H/\mathrm{d}t)$, it follows that

$$\phi < \psi_1 < \phi + (a'' + p)\,\tau, \quad \phi < \psi_2 < \phi + (a' - p)\,\tau,$$

where τ is the time delay in seconds, assumed equal at both reversals of $(\mathrm{d}H/\mathrm{d}t)$.

In the simplest case, when the calorimeter vessel temperature T_1 is constant and the heating and cooling rates are equal in magnitude, the condition of uniform operation is defined by

$$\left.\begin{aligned} H_{2n+1} &= -\theta, \quad & H_{2n+2} &= +\theta, \\ S_{2n+1} &= -\psi, \quad & S_{2n+2} &= +\psi. \end{aligned}\right\} \tag{5·1}$$

The analogue of equation (3·14) is then

$$\ln\frac{a-b(\theta-\psi)}{a+b(\theta-\psi)} = -\frac{2b\theta}{a} = -bt_n, \tag{5·2}$$

and ψ is related to the time delay by the fact that at τ seconds prior to half-cycle termination $|S| = \phi$. Then from equations (3·4) and (3·6) it follows that

$$\phi = -\theta+a(t_n-\tau)-a/b+(a/b+\theta-\psi)\,\mathrm{e}^{-b(t_n-\tau)}, \tag{5·3}$$

whence, in virtue of equation (5·2)

$$\mathrm{e}^{b\tau} = \frac{a+b(\phi-\theta+a\tau)}{a+b(\psi-\theta)}. \tag{5·4}$$

Eliminating ψ between equations (5·2) and (5·4) leads to

$$\theta = \phi+a\tau+\frac{a}{b}\left[1-\frac{2\mathrm{e}^{b\tau}}{1+\mathrm{e}^{2b\theta/a}}\right]. \tag{5·5}$$

If τ is put equal to zero in equation (5·5) and η is put equal to unity in equation (4·22), the two equations become identical. This suggests that this analysis might be capable of immediate extension to the case $a' \neq a''$, $p \neq 0$, $\tau \neq 0$, and this is in fact so.

Under these conditions the general condition of uniform operation is defined by

$$\ln\frac{a'-b(\theta_2-\psi_2)}{a'+b(\theta_1-\psi_1)} = -\frac{b(\theta_1+\theta_2)}{a'-p} = -bt_1, \tag{5·6}$$

$$\ln\frac{a''-b(\theta_1-\psi_1)}{a''+b(\theta_2-\psi_2)} = -\frac{b(\theta_1+\theta_2)}{a''+p} = -bt_2, \tag{5·7}$$

and ψ_1 and ψ_2 are defined by the fact that at τ seconds before half-cycle termination $|S| = \phi$. Then, during the positive half cycle

$$\phi = -\theta_1-a'/b+(a'-p)\,(t_1-\tau)+(a'/b-\psi_1+\theta_1)\,\mathrm{e}^{-b(t_1-\tau)},$$

so that substituting for e^{-bt_1} according to equation (5·6) gives

$$b\psi_2 = b\theta_2-a'+[a'+b\phi-b\theta_2+b(a'-p)\,\tau]\,\mathrm{e}^{-b\tau}. \tag{5·8}$$

Similarly, for the negative half cycle

$$b\psi_1 = b\theta_1-a''+[a''+b\phi-b\theta_1+b(a''+p)\,\tau]\,\mathrm{e}^{-b\tau}. \tag{5·9}$$

Equations (5·6) to (5·9) may be solved by a simple extension of the method developed in § 4. It is convenient to introduce the parameters μ and η according to the definitions (4·18) and (4·19). Then, multiplying equation (5·6) by $(1-\mathrm{e}^{-\eta\mu})$ and equation (5·7) by $(1-\mathrm{e}^{-\mu})$ and adding leads to

$$\frac{\eta\mu}{\eta+1}-\frac{b}{a'+a''}(\psi_1+\psi_2) = \frac{(1-\mathrm{e}^{-\mu})\,(1-\mathrm{e}^{-\eta\mu})}{1-\mathrm{e}^{-\mu(\eta+1)}}. \tag{5·10}$$

In order to obtain the relation determining μ in terms of b, ϕ $(a'+a'')$, τ and η, an expression for $(\psi_1+\psi_2)$ must be obtained from equations (5·8) and (5·9). Adding equations (5·8) and (5·9) and rearranging leads to

$$\frac{b}{a'+a''}(\psi_1+\psi_2) = (\Omega+b\tau)\,\mathrm{e}^{-b\tau}+(1-\mathrm{e}^{-b\tau})\left(\frac{\eta\mu}{\eta+1}-1\right). \tag{5·11}$$

Combining equations (5·10) and (5·11) then gives the required relation in the form

$$\frac{\eta\mu}{\eta+1}-\Omega-b\tau = 1+e^{b\tau}\left[\frac{(1-e^{-\mu})(1-e^{-\eta\mu})}{1-e^{-\mu(\eta+1)}}-1\right]. \tag{5·12}$$

In order to solve for μ it is convenient to write equation (5·12) in the form

$$\mu = \frac{\eta+1}{\eta}\left[1+\Omega+b\tau-\frac{(e^{\eta\mu}+e^{\mu}-2)\,e^{b\tau}}{e^{\mu(\eta+1)}-1}\right]. \tag{5·13}$$

Expanding the exponential terms of equation (5·12) and neglecting powers higher than the second gives an approximation similar to the relation (4·24)

$$\frac{\mu^3\eta^2}{12(\eta+1)} \doteqdot \Omega+b\tau. \tag{5·14}$$

Thus if equation (5·13) is written as

$$\mu^3 = \frac{12(\eta+1)}{\eta^2}\left[1+\Omega+b\tau-\frac{(e^{\mu}+e^{\eta\mu}-2)\,e^{b\tau}}{e^{\mu(\eta+1)}-1}-\frac{\eta\mu}{\eta+1}\left(1-\frac{\eta\mu^2}{12}\right)\right], \tag{5·15}$$

it follows from the relation (5·14) that the last two terms inside the bracket on the right-hand side of equation (5·15) differ from unity by an amount small in comparison with $(\Omega+b\tau)$, and equation (5·15) enables solution for μ by successive approximation. When either or both of μ and $b\tau$ are relatively large a successive approximation technique may be based upon equation (5·13). It is interesting to note that with $\tau = 0$, equation (5·13) reduces to equation (4·22), while with $p = 0$, $\eta = 1$, equation (5·13) reduces to equation (5·5).

The time integrals of S are, for the positive and negative half cycles, respectively,

$$\int_0^{t_1} S\,dt = +\frac{1}{b}(\theta_1+\theta_2-\psi_1-\psi_2)-\frac{\theta_1+\theta_2}{a'-p}\left[\frac{a'}{b}-\tfrac{1}{2}(\theta_2-\theta_1)\right], \tag{5·16}$$

$$\int_0^{t_2} S\,dt = -\frac{1}{b}(\theta_1+\theta_2-\psi_1-\psi_2)+\frac{\theta_1+\theta_2}{a''+p}\left[\frac{a''}{b}+\tfrac{1}{2}(\theta_2-\theta_1)\right]. \tag{5·17}$$

so that in this case also $\bar{S}$ is given by equation (3·45). The problem is then to evaluate $\bar{S}$ in terms of the parameters Ω, μ, η and τ. Equation (5·10) may be written in the form

$$(\theta_1+\theta_2)-(\psi_1+\psi_2) = \frac{a'+a''}{b}\left[\frac{(1-e^{-\mu})(1-e^{-\eta\mu})}{(1-e^{-\mu(\eta+1)})}\right]. \tag{5·18}$$

Substituting for $(\theta_2-\psi_2)$ according to equation (5·6) and for $(\theta_1-\psi_1)$ according to equation (5·7) leads to

$$\theta_1-\psi_1 = -\frac{a'}{b}+\frac{a'+a''}{b}\left[\frac{1-e^{-\eta\mu}}{1-e^{-\mu(\eta+1)}}\right], \tag{5·19}$$

$$\theta_2-\psi_2 = -\frac{a''}{b}+\frac{a'+a''}{b}\left[\frac{1-e^{-\mu}}{1-e^{-\mu(\eta+1)}}\right]. \tag{5·20}$$

The difference between equations (5·19) and (5·20) is

$$\theta_2-\theta_1 = \psi_2-\psi_1+\frac{a'+a''}{b}\left[\frac{e^{-\eta\mu}-e^{-\mu}}{1-e^{-\mu(\eta+1)}}\right]+\frac{a'-a''}{b},$$

and substituting for $(\theta_2-\theta_1)$ in equation (3·45) enables $\bar{S}$ to be expressed as

$$\bar{S} = \frac{\phi}{\Omega}\left[\frac{\eta-1}{\eta+1}-\frac{e^{-\mu}-e^{-\eta\mu}}{1-e^{-\mu(\eta+1)}}\right]+\tfrac{1}{2}(\psi_2-\psi_1). \tag{5·21}$$

In order to eliminate $(\psi_2-\psi_1)$ it is necessary to make use of equations (5·8) and (5·9). The difference between these equations can be written in the form

$$\tfrac{1}{2}(\psi_2-\psi_1) = (1-e^{-b\tau})\left[\tfrac{1}{2}(\theta_2-\theta_1)-\frac{\phi(\eta-1)}{\Omega(\eta+1)}-\frac{p}{b}\right]+\frac{\phi(\eta-1)}{\Omega(\eta+1)}\,b\tau\, e^{-b\tau}. \tag{5·22}$$

Combining equations (5·22) and (3·45) leads to

$$\bar{S}(1-e^{-b\tau}) = \tfrac{1}{2}(\psi_2-\psi_1)+\frac{\phi(\eta-1)}{\Omega(\eta+1)}\left[1-e^{-b\tau}(1+b\tau)\right]. \tag{5·23}$$

Eliminating $\frac{1}{2}(\psi_2-\psi_1)$ between equations (5·21) and (5·23) then gives the required relation as

$$\bar{S} = \frac{\phi}{\Omega}\left\{\frac{\eta-1}{\eta+1}(1+b\tau)-e^{b\tau}\left[\frac{e^{-\mu}-e^{-\eta\mu}}{1-e^{-\mu(\eta+1)}}\right]\right\}. \tag{5·24}$$

It is immediately obvious that when $\tau = 0$, equation (5·24) reduces to equation (4·28). Further, equation (5·24) confirms that in this case also, $\bar{S}$ is independent of the detailed relationship between a', a'' and p. This means that for a particular apparatus which has well defined values of Ω, b, ϕ and τ it is possible to solve equation (5·13), and thence compute $\bar{S}$ from equation (5·24) for a range of values of η.

Equation (5·21) indicates the main difference between the behaviour of a two-valued response regulator with time delay and that of an otherwise similar regulator having zero time delay, but an appropriately larger ϕ so that the half-cycle periods are the same in both cases. Consider two regulators, **A** having finite time delay $(\tau > 0)$ and **B** having zero time delay $(\tau = 0)$, both having the same $(a'+a'')$ and b. Comparison of equations (5·6) and (5·7) with equations (4·11) and (4·12) shows that for a given η, μ_A will be equal to μ_B provided

$$\phi_B = \tfrac{1}{2}(\psi_1+\psi_2)_A. \tag{5·25}$$

But comparison of equation (5·21) with equation (4·28) shows that under these conditions

$$\bar{S}_A = \bar{S}_B+\tfrac{1}{2}(\psi_2-\psi_1)_A. \tag{5·26}$$

That is to say the behaviour of regulator **A** differs from that of regulator **B** in that the temperature datum of regulator **A** is shifted from zero in the same sense as $\bar{S}$. This shift increases in magnitude with increasing η when η is greater than unity and with increasing $1/\eta$ when η is less than unity. Thus the magnitude of the mean signal $\bar{S}$ in a regulator with finite time delay is always greater than that in an otherwise similar regulator with zero time delay having the same $(a'+a'')$ and b and exhibiting the same half-cycle periods t_1 and t_2.

Two representative cases are examined in tables 1 and 2. Table 1 refers to a two-valued response regulator having

$$b = 0{\cdot}05\,\mathrm{s}^{-1}, \quad (a'+a'') = 0{\cdot}004\,\mathrm{deg\,s}^{-1}, \quad \phi = 0{\cdot}0004\,\mathrm{deg},$$

and table 2 refers to the case

$$b = 0{\cdot}10\,\mathrm{s}^{-1}, \quad (a'+a'') = 0{\cdot}005\,\mathrm{deg\,s}^{-1}, \quad \phi = 0{\cdot}005\,\mathrm{deg}.$$

For values of the ratio η of negative and positive half-cycle periods between 1 and about 3 the mean signal is roughly proportional to $(\eta-1)/(\eta+1)$, but this proportionality breaks down for larger η, while the effects of time delay become more obvious with increasing η. Consequently η is taken as 3 in both tables 1 and 2. The signal source of the regulator

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referred to in table 2 has the faster response, but correspondingly larger backlash, ϕ. The values of $(a'+a'')$ have been adjusted to facilitate numerical computation. In both tables the four left-hand columns describe the behaviour of the regulator with the quoted time delay when uniform operation obtains. Only the negative half-cycle period, t_2, is given since, as $\eta = 3$, t_1 is simply one-third of t_2. The two right-hand columns refer to the corresponding regulator with zero time delay but having the same values of b and $(a'+a'')$ and exhibiting the same t_1 and t_2. The quantity Ω^* is then defined by

$$\Omega^* = b(\psi_1+\psi_2)/(a'+a''), \tag{5·27}$$

where $(\psi_1+\psi_2)$ is related to μ by

$$\psi_1+\psi_2 = \frac{2\phi}{\Omega}\left[\frac{\eta\mu}{\eta+1} - \frac{(1-e^{-\mu})(1-e^{-\eta\mu})}{1-e^{-\mu(\eta+1)}}\right], \tag{5·28}$$

which is obtained by rearranging equation (5·10). The mean signal $\bar{S}^*$ in the corresponding regulator with zero time delay has been calculated by ignoring the last term in equation (5·21).

Table 1. Effect of time delay when b and ϕ are small

τ (s)	μ	t_2 (s)	$10^3\bar{S}$ (deg)	Ω^*	$10^3\bar{S}^*$ (deg)
0	0·3830	22·98	1·38	0·0100	1·38
1	0·5530	33·18	2·83	0·0285	2·71
2	0·6975	41·85	4·36	0·0546	4·04
3	0·8252	49·51	5·90	0·0846	5·30
4	0·9410	56·46	7·46	0·1186	6·46

The figures quoted in tables 1 and 2 illustrate the general conclusion that the proportionate increase in the magnitude of the mean signal for a given small time delay is less when b is large than when b is small, and greater when ϕ is small than when ϕ is large; but as the time delay is increased the magnitude of ϕ becomes less important, and the mean signal is determined primarily by b, $(a'+a'')$ and the time delay τ. In fact when the time delay is 3 s or greater the positive and negative half-cycle periods are similar in the two cases studied and the difference in the values of $\bar{S}$ may be attributed mainly to the difference in the values of $(a'+a'')$ and the difference in p which is therefore implied by the condition $\eta = 3$.

Table 2. Effect of time delay when b and ϕ are large

τ (s)	μ	t_2 (s)	$10^3\bar{S}$ (deg)	Ω^*	$10^3\bar{S}^*$ (deg)
0	1·1646	34·94	5·04	0·200	5·04
1	1·3280	39·84	6·91	0·271	6·31
2	1·4873	44·62	8·44	0·348	7·13
3	1·6437	49·31	9·96	0·431	7·84
4	1·7973	53·92	11·48	0·517	8·47

6. Effect of an auxiliary signal

It has been stated by Dole, Hettinger, Larson, Wethington & Worthington (1951) that when the backlash in a two-valued response regulator is large a significant improvement in performance may be achieved by incorporating in the regulator an auxiliary signal source which, effectively, increases the total signal during the latter part of a positive half cycle and decreases the total signal during the latter part of a negative half cycle. A control system essentially similar to that described by Dole *et al.* (1951) is shown schematically in figure 5. In this arrangement the auxiliary signal source is a multi-junction thermocouple (**A, B**) connected in series with the main signal source, shown in the figure as also a multi-junction thermocouple. Each of the two sets of like junctions in the auxiliary signal source is in contact with a small electrical heater and is provided with light thermal insulation; the common environment of the two sets of junctions and their heaters may be assumed to be kept at constant temperature. The heaters are energized by the regulator servomechanism so that during a positive half cycle, when the temperature T_3 at the controlling surface is increasing, only the junctions **B** of the auxiliary signal source are heated and during a negative half cycle, when T_3 is decreasing, only the junctions **A** are heated. Thus the auxiliary signal is positive during the latter part of a positive half cycle and negative during the latter part of a negative half cycle.

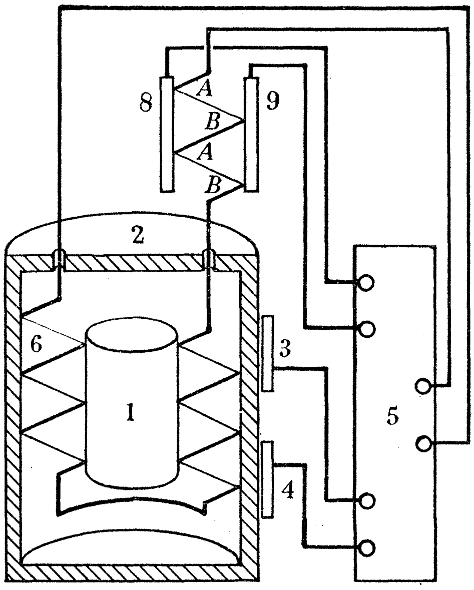

FIGURE 5. Scheme of circuit connexions for a two-valued response regulator with auxiliary signal source applied to an externally compensated adiabatic calorimeter. 1, calorimeter vessel; 2, jacket vessel; 3, 4, main servomechanism (heating and cooling); 5, amplifier and relays; 6, main thermocouple signal source; 7, auxiliary thermocouple signal source; 8, 9, heaters for auxiliary signal source.

When either the junctions **A** or the junctions **B** are heated it may be assumed that the temperature difference between **A** and **B**, and hence the auxiliary signal, will approach an ultimate value such that the thermal power input is just balanced by the radiation and conduction losses from the heated junctions, the unheated junctions having effectively attained the temperature of the common environment. The e.m.f. produced by the auxiliary signal source when thermal equilibrium has been attained is conveniently represented by the magnitude Φ (deg) of the main signal $S = T_2 - T_1$ (deg) which would give rise to the same e.m.f.

During a positive half cycle the variation of the auxiliary signal will be close to

$$s = \Phi - (\Phi - s_1)\, e^{-\nu t}, \tag{6·1}$$

where s_1 is the value of the auxiliary signal s at the commencement of the half cycle and v depends on the geometry of the auxiliary signal source. If the positive half cycle terminates at $t = t_1$, when s is equal to s_2, then during the succeeding negative half cycle,

$$s = -\Phi + (\Phi + s_2)\,\mathrm{e}^{-vt}. \tag{6·2}$$

The terminations of successive half cycles are determined by the conditions $(S+s) = \pm\phi$. It is easily shown that since the limiting values of s are finite, the operation of the regulator is stable for all positive values of Φ and v. That is to say, provided that the datum temperature T_1 is constant or varies linearly with time, there exists a condition of uniform operation for which

$$\left.\begin{aligned} H_{2n+1} &= -\theta_1, \quad & H_{2n+2} &= +\theta_2,\\ S_{2n+1} &= -\psi_1, \quad & S_{2n+2} &= +\psi_2. \end{aligned}\right\} \tag{6·3}$$

Then the analogues of equations (5·6) and (5·7) are, respectively,

$$\ln\frac{a' - b(\theta_2 - \psi_2)}{a' + b(\theta_1 - \psi_1)} = -\frac{b(\theta_1 + \theta_2)}{a' - p} = -\mu, \tag{6·4}$$

$$\ln\frac{a'' - b(\theta_1 - \psi_1)}{a'' + b(\theta_2 - \psi_2)} = -\frac{b(\theta_1 + \theta_2)}{a'' + p} = -\eta\mu, \tag{6·5}$$

where the parameters μ and η have the same significance as in §§ 4, 5. The terminal magnitudes ψ_1 and ψ_2 of the main signal are determined by the conditions for half-cycle termination, and by equations (6·1) and (6·2), the terminal values of the auxiliary signal s being $(\phi - \psi_2)$ and $-(\phi - \psi_1)$, respectively. Making these substitutions in equations (6·1) and (6·2) gives the required relations

$$(\Phi + \phi - \psi_1)\,\mathrm{e}^{-\alpha\mu} = \Phi - \phi + \psi_2, \tag{6·6}$$

$$(\Phi + \phi - \psi_2)\,\mathrm{e}^{-\alpha\eta\mu} = \Phi - \phi + \psi_1, \tag{6·7}$$

where $\alpha = v/b$. The analogue of equation (4·22) is obtained by multiplying equation (6·4) by $(1 - \mathrm{e}^{-\eta\mu})$ and equation (6·5) by $(1 - \mathrm{e}^{-\mu})$ and adding

$$\frac{\eta\mu}{\eta + 1} - \frac{b}{a' + a''}(\psi_1 + \psi_2) = \frac{(1 - \mathrm{e}^{-\mu})(1 - \mathrm{e}^{-\eta\mu})}{1 - \mathrm{e}^{-\mu(\eta+1)}}. \tag{6·8}$$

Similarly, equations (6·6) and (6·7) may be combined in the form

$$\tfrac{1}{2}(\psi_1 + \psi_2) - \phi = -\Phi\,\frac{(1 - \mathrm{e}^{-\alpha\mu})(1 - \mathrm{e}^{-\alpha\eta\mu})}{1 - \mathrm{e}^{-\alpha\mu(\eta+1)}}. \tag{6·9}$$

Combining equations (6·8) and (6·9) then gives the explicit equation determining μ as

$$\frac{\eta\mu}{\eta + 1} - \Omega = \frac{(1 - \mathrm{e}^{-\mu})(1 - \mathrm{e}^{-\eta\mu})}{1 - \mathrm{e}^{-\mu(\eta+1)}} - \frac{2b\Phi}{a' + a''}\left[\frac{(1 - \mathrm{e}^{-\alpha\mu})(1 - \mathrm{e}^{-\alpha\eta\mu})}{1 - \mathrm{e}^{-\alpha\mu(\eta+1)}}\right]. \tag{6·10}$$

Equation (6·10) has a finite positive solution in μ for all positive Ω, α, η and Φ. Equation (6·9) then ensures that $\frac{1}{2}(\psi_1 + \psi_2)$ is less than ϕ, so that this type of auxiliary signal source always reduces the effective backlash and can never cause instability.

When Φ is large, so that $2b\Phi/(a' + a'')$ is significantly greater than 1,

$$\mu \doteqdot \frac{(\eta + 1)\,\phi}{\eta\alpha\Phi}. \tag{6·11}$$

When $\eta\mu/(\eta+1)$ is smaller than Ω equation (6·10) is not susceptible to successive approximations, but equation (6·11) can be used, rewriting equation (6·10) in the form

$$\mu = \frac{(a'+a'')(\eta+1)}{2\eta\alpha\Phi b}\left\{\Omega + \frac{(1-e^{-\mu})(1-e^{-\eta\mu})}{1-e^{-\mu(\eta+1)}} - \frac{\eta\mu}{\eta+1}\left[1-\frac{2\alpha b\Phi}{a'+a''}\right] - \frac{2b\Phi}{a'+a''}\left[\frac{(1-e^{-\alpha\mu})(1-e^{-\alpha\eta\mu})}{1-e^{-\alpha\mu(\eta+1)}}\right]\right\}. \tag{6·12}$$

In other cases either equation (6·10) or the appropriate analogue of equation (4·25) may be used.

The time integrals of S are, for positive and negative half cycles, respectively,

$$\int_0^{t_1} S\,dt = +\frac{1}{b}(\theta_1+\theta_2-\psi_1-\psi_2) - \frac{\theta_1+\theta_2}{a'-p}\left[\frac{a'}{b}-\tfrac{1}{2}(\theta_2-\theta_1)\right], \tag{6·13}$$

$$\int_0^{t_2} S\,dt = -\frac{1}{b}(\theta_1+\theta_2-\psi_1-\psi_2) + \frac{\theta_1+\theta_2}{a''+p}\left[\frac{a''}{b}+\tfrac{1}{2}(\theta_2-\theta_1)\right], \tag{6·14}$$

and, as before, $\bar{S}$ is given by equation (3·45).

Now equations (6·4) and (6·5) are formally identical with equations (5·6) and (5·7) and consequently the derivation of equation (5·21) is applicable to the present case also. The term $\frac{1}{2}(\psi_2-\psi_1)$ is defined by equations (6·6) and (6·7). Substituting in equation (6·9) for $(\phi-\psi_2)$ according to equation (6·6) and then for $(\phi-\psi_1)$ according to equation (6·7) and subtracting gives the required relation as

$$\tfrac{1}{2}(\psi_2-\psi_1) = \Phi\left[\frac{e^{-\alpha\mu}-e^{-\alpha\eta\mu}}{1-e^{-\alpha\mu(\eta+1)}}\right]. \tag{6·15}$$

Combining equation (6·15) with equation (5·21) then gives the explicit relation for $\bar{S}$ as

$$\bar{S} = \frac{\phi}{\Omega}\left[\frac{\eta-1}{\eta+1} - \frac{e^{-\mu}-e^{-\eta\mu}}{1-e^{-\mu(\eta+1)}}\right] + \Phi\left[\frac{e^{-\alpha\mu}-e^{-\alpha\eta\mu}}{1-e^{-\alpha\mu(\eta+1)}}\right]. \tag{6·16}$$

The second term on the right-hand side of equation (6·16) is obviously positive when η is greater than unity and negative when η is less than unity. It then follows that the magnitude of the mean signal in a two-valued response regulator with an auxiliary signal source is always greater than that in the corresponding regulator with no auxiliary signal source having the same values of $(a'+a'')$ and b and exhibiting the same half-cycle periods t_1 and t_2.

The effects of various auxiliary signal sources with various values of α and Φ on a particular two-valued response regulator are examined in tables 3, 4 and 5. The case examined has the following values for the defining parameters

$$b = 0\cdot05\,\text{s}^{-1}, \quad (a'+a'') = 0\cdot004\,\text{deg}\,\text{s}^{-1}, \quad \phi = 0\cdot004\,\text{deg}, \quad \eta = 3.$$

The effects corresponding to smaller values of η are of course qualitatively similar to those illustrated by the tables. As in tables 1 and 2, Ω^* is the value of Ω in the corresponding regulator without auxiliary signal source, and as before it is defined by equation (5·27), the quantity $(\psi_1+\psi_2)$ being related to μ by equation (6·8). The mean signal $\bar{S}^*$ in the corresponding regulator without auxiliary signal source is calculated from equation (6·16) ignoring the last term (see equation (4·28)). Table 3 illustrates the general conclusion that when v is smaller than b, although the marked decrease in the periodic time of the regulator might seem to imply an overall improvement in performance, there is always a marked increase in the magnitude of the mean signal. This arises directly from the operation of the auxiliary signal source itself. When v is equal to b, the case illustrated in table 4, the increase in the magnitude of the mean signal is small for small Φ, and there may be some slight reduction in the magnitude of $\bar{S}$ over a small range of values of Φ. When v is greater than b, table 5 illustrates the general conclusion that there is an optimum value of Φ which gives a significant reduction in the magnitude of the mean signal $\bar{S}$ whenever η differs from unity. Thus it appears that the criteria for satisfactory design of auxiliary signal sources are first that the 'response coefficient' v of the auxiliary signal source must be greater than the 'response coefficient' b of the regulator itself, and second that the limiting magnitude Φ of the auxiliary signal must not be much greater than the backlash ϕ of the regulator itself.

Table 3. Effect of an auxiliary signal source having $v = 0{\cdot}5b$

Φ (deg)	μ	t_2 (s)	$10^3\bar{S}$ (deg)	Ω^*	$10^3\bar{S}^*$ (deg)
0	0·8800	52·80	5·85	0·1000	5·85
0·005	0·7510	45·06	6·90	0·0659	4·56
0·010	0·6351	38·11	8·21	0·0419	3·45
0·050	0·2102	12·61	25·30	0·0017	0·43

Table 4. Effect of an auxiliary signal source having $v = b$

Φ (deg)	μ	t_2 (s)	$10^3\bar{S}$ (deg)	Ω^*	$10^3\bar{S}^*$ (deg)
0	0·8800	52·80	5·85	0·1000	5·85
0·005	0·6500	39·00	5·64	0·0446	3·59
0·010	0·4639	27·84	6·48	0·0173	1·98
0·050	0·1067	6·40	24·97	0·0002	0·11

Table 5. Effect of an auxiliary signal source having $v = 2b$

Φ (deg)	μ	t_2 (s)	$10^3\bar{S}$ (deg)	Ω^*	$10^3\bar{S}^*$ (deg)
0	0·8800	52·80	5·85	0·1000	5·85
0·003	0·6568	39·41	4·41	0·0459	3·65
0·005	0·5091	30·55	3·95	0·0226	2·35
0·010	0·2753	16·52	5·06	0·0038	0·73

7. Application to other modes of compensation and to thermostats

The application of automatic regulation to facsimile compensated or internally compensated adiabatic calorimeters presents one problem which does not arise with externally compensated adiabatic calorimeters. In the first two cases it is necessary to measure precisely the total energy added to or abstracted from the facsimile calorimeter vessel, or the test calorimeter vessel as the case may be, by the regulator. One method of achieving this is to arrange continuous cooling of the calorimeter vessel, by circulating refrigerant in pipes within the vessel, and to superimpose upon this a variable heat input from the regulator servomechanism. The flow rate and the inlet and outlet temperatures of the refrigerant can then be observed continuously, while it is relatively simple to attach an integrating device to the output stage of any continuous response regulator (see Buzzell & Sturtevant 1951). With a two-valued response regulator, provided the heating and cooling rates remain constant, it is necessary only to evaluate the sum of a selected number of positive half-cycle periods and the sum of the same number of negative half-cycle periods, extending over the complete experiment. Alternatively, a set of thermocouple junctions within the calorimeter vessel may be used to effect cooling by the Peltier effect (see Calvet 1938). It is also possible, by reversing the current as required, to use a single multi-junction thermocouple to effect both heating and cooling. When a two-valued response regulator is used it is comparatively simple to make equal the magnitudes of the rates of heat transport into and out of the calorimeter vessel. If a continuous response regulator were used to alter both the magnitude and direction of the current through the controlling thermocouple, it would be easy to integrate the current passed, but to obtain directly the time integral of the heat transported might present difficulties. It is of course extremely difficult to compute the net thermal energy disposed by a two-valued response regulator whose heating and cooling rates vary, but this type of regulator is only suited to controlling the temperature in relatively large volumes, such as the environment of an externally compensated adiabatic calorimeter arranged as in figure 4, and it would not normally be used with internally or facsimile compensated calorimeters.

Many types of fluid-bath thermostat may be regarded as special cases of the externally compensated adiabatic calorimeter illustrated in figure 4 in which the datum temperature T_1 remains constant at a preselected value. It is easily established, moreover, that the variation of the temperature registered by most common sorts of thermostat signal source, or sensing element (mercury thermometer, mercury-toluene bulb, sheathed resistance thermometer, thermistor, etc.) is adequately described by equation (2·3).

Facsimile compensation

The arrangement of a facsimile compensated adiabatic calorimeter is shown schematically in figure 2. Both the test calorimeter vessel and the facsimile calorimeter vessel have thermal transactions with their common environment, but at any instant the rates of heat transfer between each vessel and the environment will differ only by a small amount depending on the difference between the surface temperature of the two vessels and the mean temperature of the whole assembly (see § 1). Thus during a complete experiment the heat loss from the test calorimeter vessel exceeds that from the facsimile calorimeter vessel by an amount

$$\delta Q \doteqdot -C(\gamma_1+\gamma_2 T_m^3)\int S\,\mathrm{d}t, \tag{7·1}$$

where C is the mean heat capacity of the test calorimeter vessel during the experiment, T_m is the mean temperature of the complete assembly and the integration extends over the entire experiment.

In practice the several satisfactory ways of arranging the regulator servomechanism in a facsimile compensated adiabatic calorimeter differ in important respects, and it is necessary to consider each arrangement individually. Thus the servomechanism will normally consist either of thermocouple junctions which effect both heating and cooling of the facsimile calorimeter vessel, or of electrical resistance heaters operating upon both the facsimile and the test calorimeter vessels. (The liberation of additional heat, over and above that evolved by the test transformation, in the test calorimeter vessel alters the temperature difference between the two calorimeter vessels in the same direction as does cooling the facsimile calorimeter vessel, while the difficulties associated with the refrigeration of a small vessel are avoided.) Both types of servomechanism may operate either inside the calorimeter vessels or directly upon the vessel walls.

The facsimile compensated calorimeter is usually used with the calorimeter vessels filled, or nearly filled, with liquid. Thus in dealing with the two cases in which the servomechanism operates inside the calorimeter vessels the temperatures at the outer surfaces of the vessels may be assumed to be related to the internal temperatures by equation (2·3). The method of analyzing the operation of two-valued response regulators used in §§ 3 to 6, however, requires one further assumption. Thus we have assumed that in an externally compensated adiabatic calorimeter the time rate of change p of the (datum) temperature at the outer surface of the calorimeter vessel, changes only slowly in comparison with the period of a two-valued response regulator. This implies that the thermal head, $H = T_3 - T_1$, can be considered as undergoing only changes linear with respect to time

$$\frac{\mathrm{d}H}{\mathrm{d}t} = a' - p, \quad \frac{\mathrm{d}H}{\mathrm{d}t} = -(a'' + p). \tag{7·2}$$

Now when the servomechanism in a facsimile compensated calorimeter operates only upon the facsimile calorimeter vessel, the assumption underlying the relations (7·2) holds good, and the analyses developed in §§ 3 to 6 apply directly. But when the servomechanism supplies heat first to the facsimile calorimeter vessel and then to the test calorimeter vessel the variation with time of the temperature in the body of the latter includes a stepwise component, and consequently the datum temperature T_1 follows a series of consecutive exponential curves, just as does the controlled temperature T_2. This difficulty is overcome if, in place of the thermal head $H = T_3 - T_1$, a new quantity, J, is defined as

$$J = T_3 - T_4, \tag{7·3}$$

where T_4 is the temperature in the interior of the test calorimeter vessel. Now during a positive half cycle

$$\frac{\mathrm{d}T_3}{\mathrm{d}t} = +a', \quad \frac{\mathrm{d}T_4}{\mathrm{d}t} = +p,$$

and during a negative half cycle

$$\frac{\mathrm{d}T_3}{\mathrm{d}t} = 0, \quad \frac{\mathrm{d}T_4}{\mathrm{d}t} = a'' + p,$$

so that during positive and negative half cycles, respectively,

$$\frac{\mathrm{d}J}{\mathrm{d}t} = a' - p, \quad \frac{\mathrm{d}J}{\mathrm{d}t} = -(a'' + p). \tag{7·4}$$

The equations (7·4) have the same form as the equations (7·2). Since the variation of both T_2 and T_1 is assumed to follow equation (2·3), and since the two calorimeter vessels are closely similar, both may be assumed to exhibit the same value of the coefficient b; thus

$$\frac{\mathrm{d}T_2}{\mathrm{d}t} = b(T_3 - T_2), \quad \frac{\mathrm{d}T_1}{\mathrm{d}t} = b(T_4 - T_1). \tag{7·5}$$

Putting $S = T_2 - T_1$ gives, for a positive half cycle,

$$S + \frac{1}{b}\frac{\mathrm{d}S}{\mathrm{d}t} = J_1 + (a' - p)\,t, \tag{7·6}$$

and for the succeeding negative half cycle

$$S+\frac{1}{b}\frac{dS}{dt} = J_2-(a''+p)\,t, \tag{7·7}$$

where J_1 and J_2 are the successive terminal values of J.

Introducing the appropriate terminal values $\pm\phi$ for S and assuming a condition of uniform operation

$$J_1 = J_3 = \ldots = -\Theta_1, \quad J_2 = J_4 = \ldots = +\Theta_2, \tag{7·8}$$

and then integrating equations (7·6) and (7·7) leads to the two equations defining the condition of uniform operation

$$\ln\frac{a'-p-b(\Theta_2-\phi)}{a'-p+b(\Theta_1-\phi)} = -\frac{b(\Theta_1+\Theta_2)}{a'-p} = -bt_1, \tag{7·9}$$

$$\ln\frac{a''+p-b(\Theta_1-\phi)}{a''+p+b(\Theta_2-\phi)} = -\frac{b(\Theta_1+\Theta_2)}{a''+p} = -bt_2. \tag{7·10}$$

It is easily shown by integrating the explicit forms of $S = S(t)$ over the positive and negative half cycles respectively that

$$\bar{S} = \tfrac{1}{2}(\Theta_2-\Theta_1). \tag{7·11}$$

It is not necessary to solve equations (7·9), (7·10) and (7·11) directly for $\bar{S}$, since introducing two arbitrary quantities θ_1 and θ_2 defined by

$$\theta_1 = \Theta_1-p/b, \quad \theta_2 = \Theta_2+p/b \tag{7·12}$$

transforms the equations into equations (4·11), (4·12) and (3·45), respectively. It then follows that in a facsimile compensated calorimeter whose servomechanism heats either the interior of the test calorimeter vessel or the interior of the facsimile calorimeter vessel $\bar{S}$ has the same value, for given b, ϕ, $(a'+a'')$ and η, as in a facsimile compensated calorimeter whose servomechanism either heats or cools the interior of the facsimile calorimeter vessel. The same value of $\bar{S}$ also occurs, of course, in an externally compensated calorimeter of the type illustrated in figure 4; it is given explicitly by equation (4·28). These two arrangements of the facsimile compensated calorimeter with two-valued response regulator differ, however, in the physical significance which can be attributed to the quantities θ_1 and θ_2. Thus when the servomechanism operates only upon the interior of the facsimile calorimeter vessel, the test calorimeter vessel is assumed to be always heating (or cooling) under steady-state conditions with

$$\frac{dT_1}{dt} = \frac{dT_4}{dt} = p,$$

so that

$$T_4 = T_1+p/b, \quad J = H+p/b.$$

The terminal values of H are then $-\theta_1$ and $+\theta_2$, and these are related to the terminal values $-\Theta_1$ and $+\Theta_2$ of J by the relations (7·12). When the servomechanism either heats the interior of the test calorimeter vessel, or the interior of the facsimile calorimeter vessel on the other hand, the quantities θ_1 and θ_2 defined by equation (7·12) do not correspond to the terminal values of $H = T_3-T_1$. It may be noted that Θ_1 and Θ_2 may be calculated, by means of equation (7·11) from $\bar{S}$ and $(\theta_1+\theta_2)$, since $(\theta_1+\theta_2)$ and $(\Theta_1+\Theta_2)$ are equal, but θ_1 and θ_2 can only be calculated by means of the relations (7·12) when p is known.

Internal compensation

In an internally compensated calorimeter the servomechanism operates upon the test calorimeter vessel itself. Provided that the calorimeter vessel is liquid filled, the temperature T_1 at the outer surface of the calorimeter vessel may be assumed to be related to the temperature T_3 in the interior of the calorimeter vessel by an equation of the form (2·3). Since the temperature T_2 at the inner surface of the insulating jacket is maintained constant, it is convenient to take it as datum. To preserve the same sign convention as in the preceding sections the signal S and the thermal head H may in this case be defined as

$$S = T_2 - T_1, \quad H = T_2 - T_3. \tag{7·13}$$

There are two contributions to $(\mathrm{d}T_3/\mathrm{d}t)$, one from the test transformation, denoted by p, and one from the servomechanism. The defining relations for a two-valued response regulator are then

$$\mathrm{d}H/\mathrm{d}t = a' - p \quad \text{(positive half cycle)}, \tag{7·14}$$

$$\mathrm{d}H/\mathrm{d}t = -(a'' + p) \quad \text{(negative half cycle)}, \tag{7·15}$$

together with

$$\mathrm{d}S/\mathrm{d}t = b(H - S). \tag{7·16}$$

Note that a' is here the cooling rate of the calorimeter vessel due to the servomechanism and a'' is the heating rate. From equations (7·14), (7·15) and (7·16) it follows that

$$S + \frac{1}{b}\frac{\mathrm{d}S}{\mathrm{d}t} = H_{2n+1} + (a' - p)\,t \quad \text{(positive)}, \tag{7·17}$$

$$S + \frac{1}{b}\frac{\mathrm{d}S}{\mathrm{d}t} = H_{2n+2} - (a'' + p)\,t \quad \text{(negative)}. \tag{7·18}$$

These equations have the same form as equations (7·6) and (7·7), and it is easily shown that in this case also the mean signal is given by equation (4·28). The amplitude $(\theta_1 + \theta_2)$ of H is given by equation (II 2, p. 455), but the difference $(\theta_2 - \theta_1)$ is given by equation (4·10) instead of equation (3·45). Thus in the internally compensated calorimeter θ_1 and θ_2 are, like the mean signal, independent of the detailed relations between a', a'' and p, being uniquely determined by the ratio η of the periods of positive and negative half cycles when uniform operation obtains. As with the externally compensated calorimeter, the mean signal is positive when η is greater than unity and vice versa, so that the tables in appendix II can be used for this type of internally compensated calorimeter. Further, if a' and a'' are equal the conclusions of § 3 apply to this case also.

The effects of time delay in the servomechanism and of an auxiliary signal source are also similar to those arising in the case of an externally compensated calorimeter.

Thermostats

The analyses developed in §§ 3 to 6 can be applied to a liquid-bath thermostat by considering it as a special case of an externally compensated adiabatic calorimeter in which the calorimeter vessel and the insulating jacket are replaced by a signal source, or sensing element, having an effective conduction coefficient b (s^{-1}) (see § 2 (b)). The liquid bath then corresponds to the calorimeter environment. The signal source gives rise to a signal whose magnitude is proportional to the difference between the temperature actually registered by the signal source and the preselected datum temperature at which the liquid bath is to be controlled. The datum temperature of the signal source then corresponds to the calorimeter vessel temperature T_1.

When a two-valued response regulator is used to operate a liquid-bath thermostat, an increase in the rate of heat loss from the liquid bath decreases the heating rate a' and increases the cooling rate a'' by the same amount; the sum $(a'+a'')$ remains constant. This sum is equal to the total thermal power disposed by the servomechanism divided by the heat capacity of the controlled system (bath liquid, container and heaters). Whenever a' exceeds a'' there is a positive mean signal and vice versa. Since

$$\bar{S} = \tfrac{1}{2}(\theta_2 - \theta_1), \tag{4·10}$$

where θ_2 and θ_1 are the magnitudes of the positive and negative terminal values of the thermal head, it follows that the mean temperature in the liquid bath differs from the datum temperature by $\bar{S}$ which, for a particular apparatus, depends only on the ratio η of the negative and positive half-cycle periods when uniform operation obtains. As with the internally compensated calorimeter, $\bar{S}$ is given explicitly by equation (4·28).

The conclusions of §§ 5 and 6 concerning the effects of time delay in the servomechanism and of the use of an auxiliary signal source apply also in the case of a two-valued response thermostat regulator.

It is interesting to note that when a linear response regulator is applied to a liquid-bath thermostat the equilibrium situation corresponds to zero signal only when the heat loss from the bath is zero (or is exactly balanced by a constant heat input independent of the regulator). Otherwise the unbalance between heat loss and invariant heat input must be offset by the action of the regulator, and this requires a non-zero signal. In fact the signal and the thermal head (the difference between the temperature of the liquid bath and the datum temperature) will both tend towards the same steady value, just sufficient to maintain equilibrium. This implies that the behaviour of linear response thermostat regulators is broadly similar to the behaviour of two-valued response regulators.

8. Experimental verification

For the operation of a particular two-valued response calorimeter regulator to accord with the predictions of §§ 3 to 6 it is necessary only that the thermal conduction processes between the controlling and controlled surfaces follow closely equation (2·3). The additional assumption in § 6 that the auxiliary signal approaches its limiting values exponentially is, in the physical circumstances, unexceptionable; and in any case it is less important in the analysis than is the assumption of the applicability of equation (2·3).

The figures quoted in § 2 show that equation (2·3) is followed closely by some conduction processes between a stirred liquid and the inner surface of a vessel immersed in the liquid when the vessel is of metal with relatively thin walls. These figures, however, give no indication as to the accuracy of equation (2·3), even in the situation just described, except when nearly steady conditions obtain. It is difficult to estimate the effects of small deviations from equation (2·3) when a major component of the variation with time of the temperature in the liquid environment is a 'saw-tooth' oscillation, as is the case with a two-valued response regulator. Further, only a relatively elaborate experimental technique would reveal directly the nature (or, indeed, the existence) of small deviations from equation (2·3). An alternative approach to the experimental verification of the present treatment is to compare, as far as is possible, the actual and predicted behaviour of calorimeters and thermostats controlled by two-valued response regulators.

Now provided that the conduction coefficient b, the sum $(a'+a'')$ of the heating and cooling rates, the backlash ϕ and the time delay τ are known for a particular apparatus the theory enables the behaviour of the apparatus to be related to the ratio η of negative to positive half-cycle periods. Thus for every value ascribed to η as primary variable the theory defines the amplitude $(\theta_1+\theta_2)$ of the oscillation of the controlling temperature T_3 about its mean value, the half-cycle periods t_1 and t_2 and the mean signal $\overline{S}$. In a calorimeter $\overline{S}$ measures the effective departure from the adiabatic condition, and in a thermostat $\overline{S}$ measures the departure of the mean bath temperature from its datum value. In practice only in the case of the half-cycle periods is direct comparison between prediction and observation possible.

The analysis developed in §§4 and 5 establishes that for given values of $(a'+a'')$, ϕ and τ the period (t_1+t_2) of a two-valued response regulator is strongly dependent upon the coefficient b. Thus comparison of the predicted and observed half-cycle periods in a particular apparatus, both when the coefficient b is made small (say, less than $0{\cdot}1\,\mathrm{s}^{-1}$) and when it is made large (say, greater than $0{\cdot}3\,\mathrm{s}^{-1}$) should give some indication of the applicability of equation (2·3) to that apparatus. The discussion of the linear response regulator in §2, on the other hand, suggests that when the controlling temperature T_3 is a periodic function of time the period is not very sensitive to the nature of the conduction process, and the same is probably true of two-valued response regulators. Thus it is necessary also to compare predicted and observed values of the mean signal $\overline{S}$, but this can only be done indirectly, in terms of the time integral of the signal during a particular experiment.

At the time of writing it has not been possible to study an apparatus to which the steady-state approximation (see §2 (*c*)) might be expected to apply. Some information is available, however, concerning the behaviour of an externally compensated adiabatic calorimeter whose design follows the scheme of figure 4. A general study has been made also of a simple water-bath thermostat, using signal sources having different values for the coefficient b.

(*a*) *The externally compensated adiabatic calorimeter*

Two sets of observations made with this apparatus are relevant to this discussion. The first is a series of measurements of the half-cycle periods occurring with various values of the conduction coefficient b, the backlash ϕ and the total time delay τ. The second is a single measurement of the total heat capacity of a water-filled calorimeter vessel, in which the magnitude of the total time integral of the mean signal was made about ten times greater than is usual. In order to relate these observations to the predictions of the theory it is necessary to describe briefly the mode of operation of the apparatus.

The calorimeter environment (see figure 4) is filled with water and its temperature is altered by adding either hotter or colder water to it. The signal source is a multi-junction thermocouple having one set of junctions cemented to the inner surface of the jacket vessel and the other set in contact with the outer surface of the calorimeter vessel. The thermocouple e.m.f. is amplified by a galvanometer and photocell arrangement using two photocells in a bridge network. The output e.m.f. of the photocell bridge is characterized as positive or negative according to whether the galvanometer image falls on the one or the other of the photocells. The photocell bridge e.m.f., after further amplification, operates a mechanical selector valve which admits to the calorimeter environment a uniform flow of water from either of two sources. The temperatures of these sources are, respectively, higher and lower than the mean temperature of the calorimeter environment so that the latter is, at a particular time, either being heated or being cooled, according to the position of the selector valve. The temperature difference between the 'hot' and 'cold' water sources, and the flow rate from either, are fixed so that the sum $(a'+a'')$ of the heating and cooling rates of the calorimeter environment remains constant at $0{\cdot}0057 \pm 0{\cdot}0002\,\mathrm{deg\,s^{-1}}$. The conduction coefficient b of the wall of the jacket vessel used in these experiments varied between $0{\cdot}058 \pm 0{\cdot}001$ and $0{\cdot}061 \pm 0{\cdot}001\,\mathrm{s^{-1}}$, according to the rate of stirring in the calorimeter environment. The backlash ϕ of the regulator depends upon the nature of the thermocouple used as signal source, but for a particular thermocouple ϕ may be varied by altering either or both of the resistance in series with the galvanometer and the controlling magnetic field in the galvanometer itself. The operation of the selector valve is subject to a total time delay τ made up of two contributions, one arising in the galvanometer and the other arising in the valve itself. This second contribution is always about 1·5 s, but the galvanometer time delay, like the backlash ϕ, depends on the galvanometer sensitivity and the thermocouple series resistance. Consequently the total time delay τ is related to the backlash ϕ; in general τ is large when ϕ is small and vice versa (see table 6).

The measurements of half-cycle periods were carried out with the calorimeter operating at about 35 °C. As soon as uniform operation was established (with the temperature of the calorimeter vessel remaining constant) the periods of selected sequences of 10 or 12 half cycles were observed. This was repeated with each of the three settings of the thermocouple series resistance, both at maximum and at minimum galvanometer sensitivity. Maximum stirring of the calorimeter environment was used during the observations at minimum sensitivity and minimum stirring was used during the observations at maximum sensitivity. The average values of the positive and negative half-cycle periods corresponding to each setting are listed in table 6 under t_1 (obs.) and t_2 (obs.), respectively. None of the recorded individual half-cycle periods differs from the average value quoted in table 6 by more than 0·5 s and the experimental uncertainty is probably less than 0·2 s. The three left-hand columns in table 6 give the values of b, ϕ and τ corresponding to the various settings of the thermocouple series resistance and the galvanometer sensitivity. The fourth column gives values of η calculated from the ratio $t_2\,(\mathrm{obs.})/t_1\,(\mathrm{obs.})$, and rounded off to the nearest 0·01. The quoted values of η have been used, together with the quoted values of b, ϕ and τ (taking $a'+a''$ as $0{\cdot}0057\,\mathrm{deg\,s^{-1}}$) to solve equation (5·15) for μ. The values of μ thus obtained have been used to calculated the values of the half-cycle periods, according to the relations

$$t_1 = \mu/b, \quad t_2 = \eta\mu/b,$$

which may be derived from the definitions (4·18) and (4·19). These calculated values of the half-cycle periods are listed in table 6 under the headings t_1 (calc.) and t_2 (calc.), respectively. The uncertainty in the quoted values of t_1 (calc.) and t_2 (calc.) is about 0·3 s, arising mainly from the uncertainty in the quoted values of τ. The errors in t_1 (calc.) and t_2 (calc.) should of course be the same for all results pertaining to a particular galvanometer setting.

Also included in table 6 (bottom line) is a set of observations corresponding to a much larger value of b. In this case the galvanometer circuit was connected to a special thermocouple having one set of junctions immersed in the calorimeter environment and the other set in the thermostat bath in which the whole calorimeter assembly is immersed. Since the thermocouple junctions have a high ratio of surface area to mass, the apparent conduction coefficient b is relatively large. The situation when the temperature of the calorimeter environment is controlled by this thermocouple is then similar to that which would obtain if the walls of the jacket vessel were very thin and the apparatus was operated in the normal way.

TABLE 6. COMPARISON OF PREDICTED AND OBSERVED HALF-CYCLE PERIODS

b (s^{-1})	2ϕ (deg)	τ (s)	η	t_1 (calc.) (s)	t_2 (calc.) (s)	t_1 (obs.) (s)	t_2 (obs.) (s)
0·061	0·00130	4·9	1·02	31·8	32·4	31·7	32·3
0·061	0·00494	2·4	1·075	26·2	28·2	26·4	28·4
0·061	0·00494	2·4	1·20	25·2	30·2	25·3	30·3
0·061	0·0117	1·9	1·00	31·1	31·1	31·0	31·0
0·058	0·00047	21·5	1·00	(77)	(77)	(75)	(75)
0·058	0·00179	6·7	1·50	31·9	47·8	32·0	47·5
0·058	0·00424	4·1	1·00	33·0	33·0	32·9	33·0
0·058	0·00424	4·1	1·20	30·1	36·1	30·0	36·0
0·058	0·00424	4·1	1·80	24·8	44·7	25·0	44·5
0·058	0·00424	4·1	4·00	17·6	70·4	18·0	70·0
0·31	0·0044	2·4	1·50	10·2	15·3	10·2	15·2

The situation described by the fifth line in table 6 is another special case, because of the very large value of τ. In fact the movement of the galvanometer image is describable by a relation formally similar to equation (2·3). When the response coefficient of the galvanometer is much greater than the coefficient b, the galvanometer may be assumed to introduce a time delay equal to the reciprocal of the response coefficient; but in the case cited the galvanometer response coefficient is 0·05 s^{-1}, rather less than b, so the assumption fails. It is easily established in terms of equation (5·13), however, that when μ is larger than about 3

$$\mu \doteqdot \frac{\eta+1}{\eta}(1+\Omega+b\tau).$$

With $\eta = 1$ this relation gives t_1 (calc.) as 77 s. The half-cycle period observed under these conditions is slightly smaller, as might be expected.

Apart from this case, the correspondence between the predicted and observed half-cycle periods set out in table 6 shows that the amplitude $(\theta_1+\theta_2)$ of the controlling temperature is correctly predicted by the theory when applied to this type of calorimeter.

A particular calorimetric measurement of the total heat capacity of a calorimeter vessel and its contents may be used in the following way to determine the accuracy with which the theory enables the time integral of the mean signal to be calculated. When the heat capacity of the calorimeter vessel and its contents is already known it is possible to use the heat input and the temperature change observed in the particular experiment to calculate the heat lost or gained by the calorimeter vessel in the course of that experiment. Dividing this heat loss or gain by the thermal transfer coefficient of the calorimeter vessel under the conditions of the experiment then gives the actual value of the time integral of the signal during the experiment. This may then be compared with the calculated value of the time integral of the mean signal. In order to compare the value of the time integral of the mean signal calculated from the observed values of the ratio η of negative to positive half-cycle periods with the actual value of the time integral of the signal it is obviously necessary to be able to estimate the actual value with reasonable accuracy. This can only be done when the magnitude of the time integral of the signal is large, so that the corresponding correction term to the observed heat change is much greater than the experimental uncertainty arising in measurements of temperature and energy input.

Results are available for only one experiment which meets the foregoing requirement. Testing the theory was not, however, the original objective of this experiment and it is for the present purpose unfortunate that a large part of the total time integral of the signal arose during a period of manual control of the temperature of the calorimeter environment subsequent to the completion of the heating process but prior to the final temperature measurement. The experiment does, nonetheless, allow definite conclusions to be arrived at concerning the applicability of the theory of this apparatus.

The experiment consisted in measuring the total heat capacity of a calorimeter vessel completely filled with water (36·218 g) under about 2 atm pressure over the temperature range 29·9 to 30·3 °C. The regulator was operated with the galvanometer at maximum sensitivity but with a large thermocouple series resistance ($2\phi = 0{\cdot}00424$ deg, $\tau = 4{\cdot}1$ s, see table 6). While the regulator was operating the periods of four successive half cycles were recorded every 5 min; these figures were later used to calculate average values of η. The calorimeter vessel was heated very slowly over a period of 2756·1 s. During the first part of this period η decreased from about 0·5 just after heating commenced to about 0·25 after 20 min and thereafter increased slowly to just over 1·0 at the end of the heating period, remaining near this value until the regulator was stopped $1\frac{1}{2}$ h after heating commenced. (The theoretical values of $\bar{S}$ corresponding to $\eta = 0{\cdot}5$ and to $\eta = 0{\cdot}25$ are $-0{\cdot}0079$ deg and $-0{\cdot}0143$ deg respectively). Graphical integration of a plot of $\bar{S}$, calculated from the successive observed values of η, against time gives the time integral of the mean signal over the period subsequent to the initial temperature measurement during which the regulator was operating as $-18{\cdot}3 \pm 0{\cdot}1$ deg s, the quoted uncertainty being that which arises in the graphical integration. After the regulator was stopped the temperature of the calorimeter environment was controlled manually for about 10 min before the final temperature measurement was made. The time integral of the signal during this period is estimated from a plot of galvanometer deflexion against time as -28 ± 2 deg s. The total energy input to the calorimeter vessel was 97·34 J and the observed increase in the temperature of the calorimeter vessel was $0{\cdot}4259 \pm 0{\cdot}0002$ deg. The thermal transfer coefficient for exchanges between the calorimeter vessel and the jacket vessel may be taken as $0{\cdot}062 \pm 0{\cdot}003\,\mathrm{J\,s^{-1}\,deg^{-1}}$ during the automatic control period and as $0{\cdot}088 \pm 0{\cdot}004\,\mathrm{J\,s^{-1}\,deg^{-1}}$ during the manual control period. (The difference arises because during the manual control period the thermocouple series resistance was reduced, thereby increasing the heat transported by the thermocouple current.) Multiplying the two time integrals of the signal each by the appropriate transfer coefficient gives the two contributions to the total heat loss from the calorimeter vessel (heat is lost from the calorimeter vessel when the signal is negative; see § 1) as 1·13 J and 2·4$_6$ J, the combined uncertainty being about 0·25 J. The measured total heat capacity of the calorimeter vessel and its contents is then given by

$$\frac{97\cdot34-3\cdot60}{0\cdot4259} = 220\cdot1\pm0\cdot6\,\mathrm{J\,deg^{-1}}.$$

The accepted heat capacity of 36·218 g of water at 30 °C is 151·3 J deg^{-1} (see Kaye & Laby 1952), while the measured heat capacity of the empty calorimeter vessel in this temperature range is 68·8 ± 0·2 J deg^{-1}, so that the actual value of the total heat capacity of the calorimeter vessel and the water is 220·1 ± 0·2 J deg^{-1}. The agreement between this and the measured value is probably fortuitous in view of the large uncertainties. Nevertheless, it seems reasonable to argue that since the measured and actual heat capacities are the same the calculated time integral of the signal during the automatic control period is unlikely to be in error by an amount significantly greater than the quoted uncertainty in the observed time integral of the signal during the manual control period. The corresponding systematic error in the calculated values of $\bar{S}$ would be about 10 %. It is therefore to be concluded from this experiment that it is improbable that the values of the mean signal calculated according to the present theory differ from the actual values by more than 10 %.

(*b*) *The water-bath thermostat*

In this thermostat the signal source is essentially a toluene thermometer. The toluene container is connected to one arm of a glass U-tube, the open end of which terminates in a section of 1 mm bore capillary. The U-tube is filled with mercury so that expansion or contraction of the toluene moves the mercury surface up or down in the capillary. A metal probe projecting into the capillary is connected to the grid control circuit of a heavy duty pentode in such a way that no current flows in the anode circuit of the pentode when the probe is in contact with the mercury. The anode circuit of the pentode includes a relay which energizes the thermostat regulating heaters whenever the pentode is conducting. Thus the regulating heaters are switched on whenever the mercury surface in the capillary arm of the toluene thermometer breaks away from the probe, and switched off whenever the mercury surface makes contact with the probe. The backlash in this regulator arises mainly in the signal source itself, and depends on the shape of the probe end and on the surface tension of the mercury. Two different relays have been used, an electromagnetic relay having negligible time delay, and a hot-wire relay which was adjusted to operate with a time delay close to 2 s. In order to study the behaviour of the regulator with different values of the conduction coefficient b of the signal source two different toluene containers were made. The first is a glass cylinder about 1 in. external diameter, containing about 150 ml. of toluene, while the second is a coil of $\frac{1}{4}$ in. copper tubing containing about 60 ml. of toluene. The second container has a much higher ratio of surface area to total heat capacity than the first, and thus a larger conduction coefficient. With the first toluene container the properties of the signal source are $b = 0\cdot031\,\mathrm{s^{-1}}$, $2\phi = 0\cdot0004$ deg, and with the second toluene container, $b = 0\cdot10\,\mathrm{s^{-1}}$ and $2\phi = 0\cdot001$ deg. The sum $(a'+a'')$ of the heating and cooling rates of the thermostat bath may be taken as 0·00133 deg s^{-1}.

The half-cycle periods of the regulator when uniform operation obtains have been observed at various values of η between 1 and 4 with each of the four possible combinations of signal source and relay. In every case the discrepancy between the predicted and observed values of the half-cycle periods is less than the uncertainty in the predicted values, and is, for each combination, independent of η. The two extreme cases, the copper coil toluene container with the electromagnetic relay, and the glass tube toluene container with the hot-wire relay, are of special interest, since the second arrangement has been commonly used in laboratory thermostats, while the first arrangement shows the extent to which performance may be improved by simple modification. In the first case the value of $\Omega = 2b\phi/(a'+a'')$ is 0·0752 and interpolation from table 7 gives $\mu = 1{\cdot}28$ when $\eta = 1$, whence the half-cycle period is 12·8 s (the observed mean value is $12{\cdot}6 \pm 0{\cdot}2$ s). Interpolation from table 8 gives the mean signal when $\eta = 1{\cdot}5$ as $+3{\cdot}0 \times 10^{-4}$ deg; that is to say, when the duration of the heating period is two-thirds that of the cooling period the mean temperature of the bath is 0·0003 deg above the datum temperature for which the signal source probe is set. In the second case $\Omega = 0{\cdot}0093$, $b\tau = 0{\cdot}062$ and the value of the half-cycle period when $\eta = 1$ calculated according to equation (5·13) is 31·8 s (the observed mean value is $32 \pm 0{\cdot}5$ s). The mean signal when $\eta = 1{\cdot}5$, calculated according to equation (5·24), is $6{\cdot}6 \times 10^{-4}$ deg.

Thus, replacing the glass toluene container by the copper coil and eliminating the time delay reduces the amplitude and period of the oscillation of the bath temperature about its mean by a factor about 2·7. This implies, according to this theory, a significant reduction in the time taken to re-establish uniform operation after a disturbance such as evolution or absorption of heat by an agency immersed in the bath, and a reduction also in the departure of the mean bath temperature from the datum value when $\eta \neq 1$ by a factor about 2. It may be noted that a similar reduction in the magnitude of the mean signal is achieved simply by eliminating the time delay when the glass container is used, but then the half-cycle period when $\eta = 1$ is nearly 20 s, and the time taken to re-establish uniform operation after a disturbance is longer than when the copper coil toluene container is used.

9. Conclusions

The conclusions reached by this investigation fall into two categories. One of these relates to the general question of the adequacy of the approximate description of the thermal conduction processes between the controlling and controlled surfaces. The other category comprises the detailed conclusions concerning the behaviour of two-valued response thermoregulators to which the initial approximation is applicable. Since some of the detailed conclusions are pertinent to the general question we shall begin by summarizing the former.

Stability

The least surprising conclusion of the detailed analyses is that the operation of these two-valued response thermoregulators is always stable, irrespective of the existence of time delay in the servomechanism or the use of an auxiliary signal source. In fact this statement remains true even when the thermal conduction processes between the controlling and controlled surfaces do not follow equation (2·3). Thus, since the heating and cooling rates at the controlling surface remain constant throughout each half cycle, if the duration of any half cycle is extended far enough the temperature profile between the controlling surface and the controlled surface must approach a well defined steady-state form depending on the magnitude of the heating or cooling rate, and the geometry of the region between the two surfaces. Under these conditions the controlling and controlled temperatures are necessarily related by an equation of the form (2·4). It follows that as the half-cycle period is increased there is a finite limit to the lag of the controlled temperature, so that the difference between the controlling and controlled temperatures during the later part of any half cycle is constrained between limits similar to the limits (3·9) and (3·10). Thus the operation of the regulator can never be unstable.

Uniform operation

Next, it has been shown that whenever the second time derivative of the datum temperature T_1 remains zero there exists a condition of uniform operation such that succeeding cycles of the operation of the regulator are congruent. Every particular condition of uniform operation is characterized by the parameters $-\theta_1$ and $+\theta_2$, which are the values at the terminations of the negative and positive half cycles, respectively, of the thermal head H (the difference between the controlling temperature and the datum temperature). These terminal values $-\theta_1$ and $+\theta_2$ are determined uniquely by the properties of the regulator, including the positive-going and negative-going time rates of change a' and a'' of the controlling temperature T_3, together with the constant value p of the first time derivative of the datum temperature T_1. The analyses show also that the behaviour of a particular regulator when a', a'' and p remain constant approaches the condition of uniform operation at a rate which depends on the properties of the regulator and on the rates a', a'' and p. In every such case the magnitudes of the departures of successive terminal values of H from $-\theta_1$ and $+\theta_2$ decrease with increasing time and approach conformity to a geometric progression of ratio less than unity. Numerical solution of the appropriate equations in selected cases shows that the time taken to diminish by half a departure from uniform operation is determined mainly by the conduction coefficient b. The larger is the coefficient b the more rapidly is the condition of uniform operation established.

Amplitude of the thermal head

A further conclusion concerning the terminal magnitudes of H when uniform operation obtains is that their sum $(\theta_1+\theta_2)$ depends only on the net time rates of change of H, which are $(a'-p)$ during a positive half cycle and $-(a''+p)$ during a negative half cycle. That is to say all sets of a', a'' and p corresponding to specified $(a'-p)$ and $(a''+p)$ give rise to the same $(\theta_1+\theta_2)$, although the separate values of θ_1 and θ_2 differ from set to set. Since the periods of positive and negative half cycles are given, respectively, by

$$t_1 = \frac{\theta_1+\theta_2}{a'-p}, \quad t_2 = \frac{\theta_1+\theta_2}{a''+p},$$

it follows that t_1 and t_2 are also determined unambiguously by $(a'-p)$ and $(a''+p)$. Alternatively, the amplitude $(\theta_1+\theta_2)$ may be regarded as being determined by the sum $(a'+a'')$ and the ratio η of negative to positive half-cycle periods, so that when $(a'+a'')$ is known the theory enables unique values of the amplitude $(\theta_1+\theta_2)$ and the half-cycle periods t_1 and t_2

to be calculated for every selected value of η. This is of course the basis of the method used to compute t_1 (calc.) and t_2 (calc.) in table 6.

Minimizing the amplitude of the thermal head

Numerical studies show that in any particular apparatus $(\theta_1+\theta_2)$ may be reduced by increasing the conduction coefficient b, and by decreasing either or both of $(a'+a'')$ and the servomechanism time delay τ. (In order to maximize b in the case of the calorimeter shown in figure 4, the walls of the jacket vessel must be made as thin as possible and the outer surface polished; rapid stirring in the calorimeter environment also helps.) When τ is small or zero, decreasing the backlash ϕ also decreases $(\theta_1+\theta_2)$ significantly. Alternatively the same result may be achieved by using a properly designed auxiliary signal source. These studies show also that $(\theta_1+\theta_2)$ always decreases as the ratio η departs from unity, so that the whole-cycle period (t_1+t_2) increases only slowly as η diverges from unity. Consequently when η is much greater than unity the positive half-cycle period t_1 is much smaller than when η is unity (see table 6).

The mean signal

The two most important conclusions concerning the mean signal $\bar{S}$, which measures the difference between the mean value of the controlled temperature and the datum temperature, may be stated in the following way. First, the mean signal is always given by

$$\bar{S} = \tfrac{1}{2}(\theta_2-\theta_1)-p/b,$$

irrespective of time delay in the servomechanism or the use of an auxiliary signal source. That is to say, whenever the datum temperature T_1 increases at rate p the mean value of the controlled temperature T_2 differs from the mean value of the controlling temperature T_3 by $-p/b$. This is just the amount which, if T_3 were increasing uniformly at rate p, would be required to keep T_2 also increasing uniformly at rate p. Secondly, as with the amplitude $(\theta_1+\theta_2)$, all sets of a', a'' and p corresponding to specified $(a'+a'')$ and η give rise to the same mean signal $\bar{S}$. Thus a selected difference between the controlled and datum temperatures may be achieved either by increasing the positive-going rate a' and decreasing the negative-going rate a'', or by decreasing the rate p by the same amount. In other words, if the sum $(a'+a'')$ remains constant the theory determines a unique mean signal $\bar{S}$ for every selected value of the ratio η of negative to positive half-cycle periods. Since the half-cycle periods can in practice be observed directly the mean signal can be evaluated as a function of time throughout a calorimetric experiment irrespective of the detailed variation of a', a'' and p during that experiment, provided only that the sum $(a'+a'')$ remains constant. This is the basis of the method used to evaluate the time integral of the signal in the calorimetric experiment discussed in § 8. Only in the case where a' and a'' are equal can the total time integral of the signal during a calorimetric experiment be related directly to the observed change in the datum temperature. In all cases the total time integral of the signal is subject to an uncertainty arising from periods of non-uniform operation. Provided that $(\mathrm{d}T_1/\mathrm{d}t)$ is always greater than about $-\tfrac{1}{2}a''$ and less than about $+\tfrac{1}{2}a'$, however, this uncertainty is unlikely to exceed 4 or 5 times the magnitude of the time integral of the signal during a single half cycle when η is unity; the uncertainty is less than this if a', a'' and p change only slowly during an experiment, so that departures from uniform operation are small.

Computation of the mean signal

In order to be able to compute the total time integral of the signal it is necessary to calculate the mean signal as a function of some observable aspect of the regulator behaviour. Now if in a particular apparatus the sum $(a'+a'')$ remains constant the mean signal depends only on the ratio η of negative to positive half-cycle periods. The condition that $(a'+a'')$ remains constant is obviously fulfilled when both a' and a'' remain constant; it is met also in at least two other cases of practical interest. Thus, in one method of realizing the externally compensated adiabatic calorimeter shown schematically in figure 4 the servomechanism adds either hot or cold liquid to the calorimeter environment. The heating and cooling rates are then determined by the temperatures in the hot and cold sources and the relation of these to the datum temperature; but if the temperature difference between the hot and cold sources, and the flow rates of the hot and cold liquid, all remain constant then the sum $(a'+a'')$ will also remain constant irrespective of small changes in the datum temperature (see § 8). A similar argument applies to a liquid-bath thermostat, since the sum $(a'+a'')$ is determined only by the thermal power of the controlling heaters and the total heat capacity of the bath and is independent of variations in the rate of heat loss to the surroundings. The time delay, if any, the backlash and the conduction coefficient will normally have well defined values, so that the dimensionless parameters Ω and $b\tau$ will have fixed values characteristic of the apparatus.

Given Ω and $b\tau$ equation (4·28), or (5·24) or (6·16), if appropriate, defines the mean signal as a function of the ratio of negative and positive half-cycle periods when uniform operations obtains. Consequently the mean signal may be tabulated for the range of η to be expected in normal operation. The class of two-valued response regulators with zero time delay and no auxiliary signal source is of considerable practical importance, and in this case the mean signal is determined by Ω and η, together with the backlash ϕ.

Minimizing the magnitude of the mean signal

The most effective ways of minimizing the magnitude of the mean signal corresponding to each value of η are making the coefficient b as large as possible and the time delay τ as small as possible. Increasing the sum $(a'+a'')$ reduces the magnitude of the mean signal corresponding to a given p, but at the cost of increasing the amplitude of the thermal head. The use of a properly designed auxiliary signal source also reduces the magnitude of the mean signal.

Time delay

The occurrence of time delay in the operation of the servomechanism always affects adversely the performance of a two-valued response regulator.

Auxiliary signal source

The use of an auxiliary signal source always decreases the amplitude of the thermal head. In order that the magnitude of the mean signal is also reduced it is necessary (i) that the response coefficient of the auxiliary signal source is much greater than the conduction coefficient of the regulator, and (ii) that the limiting magnitude of the auxiliary signal is not much greater than the regulator backlash. Further, it may be inferred that the use of an auxiliary signal source does not effect any significant reduction in the time taken to establish uniform operation after a disturbance.

Adequacy of the approximation

It is argued in § 2 that since the conduction process approaches the steady-state condition towards the end of each half cycle it is to be expected that the theory should predict the half-cycle periods with reasonable accuracy. In fact the data tabulated in appendix II, together with the calculations summarized in table 6, show that this argument fails in some cases. Thus when the conduction coefficient and the backlash are both small and the time delay is zero the magnitude of the difference between the controlling and controlled temperatures at half-cycle termination with $\eta = 1$ may easily be less than half the magnitude corresponding to steady-state conduction. This is true, for example, of the thermostat regulator discussed in § 8 when the slow response signal source is used with the electromagnetic relay. Secondly, even in cases which do not fulfil these conditions the situation at the end of the shorter half cycle when η differs greatly from unity departs significantly from the steady state. This is because when η is very different from unity the period of the shorter half cycle is much smaller than when η is near unity. When the calorimeter regulator discussed in § 8 is operated with 4·1 s time delay (see table 6), for example, the predicted difference between the controlling and controlled temperatures at the end of a positive half cycle when η is 4 ($p = 0$) is less than 55 % of the difference corresponding to steady-state conduction. For the thermostat regulator used with the low response signal source the analogous figure is 21 %.

The fact that the theory predicts correctly the half-cycle periods in these cases, together with the inference from the calorimetric experiment that the mean signal is predicted at least 90 % correctly, strongly suggests that equation (2·3) gives an adequate description of the thermal conduction processes in these two regulators.

It is therefore to be concluded that whenever the main thermal impedance between the controlling and controlled surfaces is due to one or more liquid to solid boundaries, the theory will give a description of the behaviour of a two-valued response regulator sufficiently accurate for practical purposes. In particular this applies to the difference between the mean value of the controlled temperature and the datum temperature which, especially in a thermostat, is difficult to determine by direct measurement.

Because of the lack of suitable experimental data it is not possible to draw definite conclusions concerning cases where the region between the controlling and controlled surfaces is homogeneous as in the externally compensated adiabatic calorimeter shown schematically in figure 3. Nevertheless, it seems that when this region is narrow and the material has high thermal diffusivity, so that $2D/l^2$ is larger than, say, $0{\cdot}1\,s^{-1}$, the theory is unlikely to be seriously inaccurate except, perhaps, when η is very different from unity.

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General discussion

The foregoing conclusions suggest that the behaviour of simple two-valued response regulators can be interpreted with sufficient accuracy to render advantageous the use of this form of automatic regulation with a wide range of adiabatic calorimeters. Two-valued response regulators are applicable in all cases where the time rate of change of the temperature at the outer surface of the calorimeter vessel is small (not exceeding, say, $0{\cdot}01\,\mathrm{deg}\,s^{-1}$). This includes the measurement of heat capacities, especially of solids and liquids, the measurement of heats of reaction of relatively slow reactions and of solution and mixing processes, provided that these can be made to occur slowly (one might take

10 and 200 min as rough limits for the duration of the test process). This type of regulation may also be applied, for example, to bomb calorimetry, but this requires special measures to slow down the rate of temperature change at the outer surface of the bomb and to ensure a reasonable degree of temperature uniformity.

The main design requirements for a calorimeter with which a two-valued response regulator is to be used are:

(i) the apparent conduction coefficient between the controlling and controlled surfaces should be made as large as possible;

(ii) the backlash of the regulator should be minimized by using the greatest sensitivity of the signal source consistent with

(iii) minimizing the heat transfer between the datum and controlled surfaces;

(iv) time delay in the operation of the servomechanism should be kept as small as possible;

(v) if an auxiliary signal source is used to offset the effects of large backlash, it should conform to the design specifications set out at the end of § 6 above;

(vi) the sum of the heating and cooling rates at the controlling surface should be about three times as great as the greatest expected heating or cooling rate at the surface of the test calorimeter vessel.

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Appendix I. The uncertainty in the total time integral of the signal

We shall consider only the simplest case: that of a two-valued response regulator with equal heating and cooling rates applied to an externally compensated adiabatic calorimeter. The analysis developed in § 3 can be applied only when the first time derivative of the temperature T_1 at the surface of the calorimeter vessel is constant. Consequently, it is necessary to approximate the actual time variation of T_1 by a series of linear relations, $(\mathrm{d}T_1/\mathrm{d}t)$ being assumed to change from one constant value to the next in a period short in comparison with the half-cycle period of the regulator. In practice the largest change in $(\mathrm{d}T_1/\mathrm{d}t)$ is probably that associated with the initiation of a change in T_1, i.e. the change of $(\mathrm{d}T_1/\mathrm{d}t)$ from zero to p.

If $(\mathrm{d}T_1/\mathrm{d}t)$ is initially zero, increases rapidly to p and then remains constant, a time $t = t_1$ during the half cycle in which $(\mathrm{d}T_1/\mathrm{d}t)$ changes may be defined, by extrapolation from the linearly increasing part of $T_1 = T_1(t)$ back to the initial constant value, such that if $(\mathrm{d}T_1/\mathrm{d}t)$ changed instantaneously from zero to p at $t = t_1$ the subsequent behaviour of the regulator would be the same as that when $(\mathrm{d}T_1/\mathrm{d}t)$ changes smoothly from zero to p. A detailed study of the situation necessarily involves solving either equation (3·4) or equation (3·6) for an incomplete half cycle and then solving the corresponding equation for the situation $(\mathrm{d}T_1/\mathrm{d}t) = p$. Consequently a general treatment of even this special mode of variation of T_1 is not possible; but it is obvious that if the time at which T_1 effectively starts to increase coincides with the end of a negative half cycle, then the corresponding terminal value of H is $-\theta$. This is necessarily less than $-\theta_1$, the value when uniform operation obtains, and it follows also that the next terminal value of H is greater than $+\theta_2$. If T_1 starts to increase at the end of a positive half cycle the first terminal value of H is $+\theta$, which is less than $+\theta_2$, the value corresponding to uniform operation. These are the extreme cases, and there is one point during each half cycle such that if the effective start of the increase in T_1 coincides with this point the condition of uniform operation will obtain immediately. Now when the initial value of H is less than $-\theta_1$, the minimum value of S during the first (positive) half cycle after $(\mathrm{d}T_1/\mathrm{d}t)$ attains the value p is less than the value according to equation (3·39) and the maximum value of S during the following (negative) half cycle is greater than the value given by equation (3·41), but the relation (3·37) ensures that the time integral of S over the complete cycle shows a negative departure from the corresponding integral of equation (3·48). The converse applies when the initial value of H is less than $+\theta_2$ and the time integral of S over the first complete cycle shows a positive deviation from the corresponding integral of equation (3·48).

These departures may be evaluated approximately in the extreme cases, giving a measure of the uncertainty in the total time integral of S when the phase of the regulator cycle at which T_1 effectively starts to change is randomly selected. When Ω is greater than about 0·02 the departure from uniform operation, due to the change in $(\mathrm{d}T_1/\mathrm{d}t)$, is diminished by a factor greater than 2 during the first complete cycle subsequent to the change, and numerical investigation of representative cases shows that when T_1 starts to increase at the beginning of a positive half cycle, the difference between the time integral of S, over the first positive half cycle and the value of the integral (3·42), is close to the difference ζ between the actual time integral of S over the first five cycles after T_1 starts to increase and the corresponding time integral of equation (3·48). In fact the difference between the integral of equation (3·38) between $H_1 = -\theta$, $S = -\phi$ and $H_2 = +\theta_2$ and the integral (3·42) gives a satisfactory approximation to ζ (min.). This integral of equation (3·38) is

$$\int_{H_1=-\theta}^{H_2=+\theta_2} S\,\mathrm{d}t = \frac{1}{b}\left[\frac{a}{b}+\theta-\phi\right]\left[1-\mathrm{e}^{-b(\theta+\theta_2)/(a-p)}\right]-\frac{\theta+\theta_2}{a-p}\left[\frac{a}{b}-\tfrac{1}{2}(\theta_2-\theta)\right]. \qquad \text{(I 1)}$$

The other extreme case, when T_1 starts to increase at the beginning of a negative half cycle, is not susceptible to this approximation since the greater part of ζ (max.) is inevitably associated with the second (positive) half cycle. The magnitude of ζ (max.), however, is always much smaller than that of ζ (min.). The departure of the time integral of S from zero during the period after T_1 again becomes constant has a maximum value, ζ' (max.), when T_1 becomes constant at the end of a positive half cycle and a minimum which may be negative when T_1 becomes constant at the end of a negative half cycle. This departure ζ' (max.) is well approximated by the difference between the time integral of equation (3·4) between $H_2 = +\theta_2$, $S = +\phi$ and $H_3 = -\theta$, and the integral (3·47). This time integral of equation (3·4) is

$$\int_{H_2=+\theta_2}^{H_3=-\theta} S\,\mathrm{d}t = -\frac{1}{b}\left[\frac{a}{b}+\theta_2-\phi\right]\left[1-\mathrm{e}^{-b(\theta+\theta_2)/a}\right]+\frac{\theta+\theta_2}{a}\left[\frac{a}{b}+\tfrac{1}{2}(\theta_2-\theta)\right]. \qquad \text{(I 2)}$$

Comparison of equations (I 1) and (I 2) shows that in general the magnitude of ζ' (max.) is smaller than that of ζ (min.). As with ζ (max.), ζ' (min.) can only be found by numerical calculation in particular cases, but its magnitude appears to be smaller than that of ζ' (max.).

Then, for a given increase in T_1 for which the initiation and termination can be described as above, the time integral of S over the complete process, computed according to equation (3·48), is subject to an uncertainty extending over the range

$$[\zeta\,(\text{max.})+\zeta'\,(\text{max.})] \quad \text{to} \quad [\zeta\,(\text{min.})+\zeta'\,(\text{min.})].$$

Numerical calculations in selected cases indicate that while ζ' (min.) can be neglected, ζ' (max.) is usually significant; but ζ' (max.) + ζ (max.) appears always to be smaller than $-\zeta$ (min.), so that the total uncertainty is within the range $\pm\zeta$ (min.) as computed from equations (3·48) and (I 1).

It is apparent from equations (I 1) and (I 2) that although the total time integral of S over the complete change in T_1 is nearly independent of the rate p of the change in T_1 (see equation (3·48)), the uncertainty $\pm\zeta$ (min.) decreases as p approaches zero. When Ω is less than about 0·02 a significant departure from uniform operation extends over several cycles after a change in $(\mathrm{d}T_1/\mathrm{d}t)$ and the approximations just described become less accurate; but it seems unlikely that the total uncertainty in the time integral of S over the complete change in T_1 ever exceeds significantly the magnitude $\pm\zeta$ (min.) as computed above.

Appendix II. Numerical solutions for the case of zero time delay

When there is no significant time delay in the action of the servomechanism the mean signal is uniquely determined by the three parameters Ω, ϕ and η. It is consequently convenient to tabulate $\bar{S}/\phi$ as a function of Ω and η.

In order to compare the predicted half-cycle periods with those observed, over a range of η, use may be made of the relations

$$t_1 = \mu/b, \quad t_2 = \eta\mu/b, \tag{II 1}$$

where μ is determined by equation (4·22). The variation of μ with Ω and η is summarized in table 7. It is in practice unlikely that Ω will be outside the range 0·005 to 1·00, and the range 0·25 to 4·0 of η should be adequate for most cases arising in the normal operation of regulators of this type. When η lies between zero and unity the half-cycle periods are related to the value of μ corresponding to $1/\eta$ by

$$t_1 = \mu/\eta b, \quad t_2 = \mu/b,$$

and consequently only values of η greater than unity are included in table 7. The variation of the mean signal function $\bar{S}/\phi$ over the same ranges of Ω and η is summarized in table 8. In addition it is often useful, especially in dealing with thermostats, to know the amplitude $(\theta_1+\theta_2)$ of the controlling temperature, which is related to the parameter μ by

$$\frac{\theta_1+\theta_2}{\phi} = \frac{2\eta\mu}{\Omega(\eta+1)}. \tag{II 2}$$

The variation of the amplitude function $(\theta_1+\theta_2)/\phi$ is summarized in table 9. Since the rate of change of the datum temperature in a thermostat is zero, the values of $\bar{S}$ and $(\theta_1+\theta_2)$ suffice to determine θ_1 and θ_2 so that the rate of approach to the condition of uniform operation may be calculated for each value of η.

TABLE 7. VARIATION OF μ WITH Ω AND η

Ω \ η	1·00	1·25	1·33	1·50	1·75	2·00	3·00	4·00
0·005	0·4972	0·4457	0·4322	0·4088	0·3810	0·3590	0·3020	0·2692
0·010	0·6296	0·5643	0·5472	0·5178	0·4824	0·4547	0·3830	0·3417
0·015	0·7236	0·6487	0·6290	0·5952	0·5549	0·5228	0·4408	0·3936
0·020	0·7993	0·7164	0·6949	0·6576	0·6131	0·5779	0·4876	0·4357
0·03	0·9209	0·8260	0·8007	0·7580	0·7068	0·6664	0·5630	0·5039
0·05	1·1041	0·9900	0·9602	0·9097	0·8481	0·8000	0·6775	0·6080
0·10	1·4236	1·2772	1·2387	1·1732	1·0955	1·0343	0·8800	0·7940
0·20	1·8618	1·6709	1·6214	1·5368	1·4375	1·3590	1·1646	1·0592
0·30	2·2074	1·9762	1·9180	1·8192	1·7023	1·6122	1·3893	1·2699
0·40	2·4950	2·2405	2·1750	2·0640	1·9335	1·8329	1·5866	1·4566
0·50	2·7624	2·4810	2·4090	2·2870	2·1442	2·0345	1·7678	1·6284
0·60	3·0126	2·7065	2·6282	2·4960	2·3418	2·2237	1·9385	1·7907
0·70	3·2510	2·9210	2·8371	2·6954	2·5304	2·4045	2·1018	1·9460
0·80	3·4803	3·1282	3·0385	2·8876	2·7123	2·5790	2·2597	2·0961
0·90	3·7040	3·3295	3·2344	3·0746	2·8893	2·7485	2·4132	2·2420
1·00	3·9924	3·5265	2·4260	3·2577	3·0625	2·9147	2·5634	2·3847

TABLE 8. VARIATION OF $\bar{S}/\phi$ WITH Ω AND η

Ω \ η	1·00	1·25	1·33	1·50	1·75	2·00	3·00	4·00
0·005	0	0·896	1·152	1·624	2·240	2·776	4·395	5·556
0·010	0	0·704	0·910	1·280	1·768	2·184	3·457	4·357
0·015	0	0·610	0·788	1·112	1·529	1·895	2·997	3·773
0·020	0	0·555	0·712	1·003	1·382	1·711	2·702	3·400
0·03	0	0·476	0·615	0·867	1·195	1·479	2·333	2·929
0·05	0	0·396	0·577	0·719	0·990	1·224	1·925	2·410
0·10	0	0·3025	0·3904	0·5503	0·7547	0·9340	1·4620	1·8177
0·20	0	0·2272	0·2923	0·4111	0·5633	0·6957	1·0780	1·3273
0·30	0	0·1882	0·2422	0·3403	0·4675	0·5745	0·8845	1·0829
0·40	0	0·1630	0·2098	0·2945	0·4037	0·4960	0·7591	0·9243
0·50	0	0·1448	0·1860	0·2612	0·3576	0·4388	0·6683	0·8104
0·60	0	0·1303	0·1678	0·2353	0·3217	0·3945	0·5984	0·7232
0·70	0	0·1189	0·1528	0·2142	0·2929	0·3586	0·5423	0·6536
0·80	0	0·1091	0·1404	0·1967	0·2688	0·3289	0·4958	0·5967
0·90	0	0·1009	0·1299	0·1819	0·2483	0·3038	0·4568	0·5488
1·00	0	0·0938	0·1208	0·1690	0·2308	0·2820	0·4235	0·5080

TABLE 9. VARIATION OF $(\theta_1+\theta_2)/\phi$ WITH Ω AND η

Ω \ η	1·00	1·25	1·33	1·50	1·75	2·00	3·00	4·00
0·005	99·44	99·04	98·79	98·11	96·98	95·73	90·62	86·16
0·010	62·96	62·70	62·54	62·14	61·40	60·63	57·45	54·67
0·015	48·24	48·05	47·93	47·62	47·08	46·47	44·08	41·99
0·020	39·97	39·80	39·71	39·46	39·02	38·53	36·57	34·85
0·030	30·70	30·59	30·50	30·32	29·99	29·62	28·15	26·88
0·05	22·08	22·00	21·95	21·82	21·59	21·33	20·33	19·46
0·10	14·24	14·19	14·16	14·08	13·93	13·79	13·20	12·70
0·20	9·309	9·283	9·265	9·221	9·148	9·060	8·736	8·474
0·30	7·338	7·319	7·306	7·277	7·222	7·166	6·946	6·773
0·40	6·238	6·224	6·214	6·192	6·152	6·110	5·950	5·826
0·50	5·525	5·513	5·506	5·489	5·458	5·425	5·303	5·211
0·60	5·0210	5·0120	5·0061	4·9920	4·9675	4·9416	4·8463	4·7753
0·70	4·6440	4·6365	4·6320	4·6207	4·6007	4·5800	4·5039	4·4480
0·80	4·3504	4·3444	4·3408	4·3314	4·3150	4·2983	4·2369	4·1922
0·90	4·1156	4·1105	4·1073	4·0995	4·0859	4·0719	4·0220	3·9858
1·00	3·9224	3·9183	3·9154	3·9092	3·8977	3·8863	3·8451	3·8156

When the heating and cooling rates of an adiabatic calorimeter remain equal throughout an experiment the correction term to be added to the observed temperature change may be computed by equation (3·49) and it is then necessary to evaluate the constant K in equation (3·48). This may be done by plotting $\bar{S}$ against p/a. When a' and a'' are equal the definition (4·19) of η leads directly to

$$\frac{\eta-1}{\eta+1} = -\frac{p}{a}. \tag{II 3}$$

Table 8 may then be used to relate $\bar{S}$ to η for the appropriate Ω, and equation (II 3) enables $\bar{S}$ to be related directly to p/a.

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