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# Oscillatory motion in Bénard cell due to the Soret effect

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The period of oscillations for the Bénard problem in a two-component system taking into account thermal diffusion is given. Schmidt–Milverton plots are presented for water–methanol and water–isopropanol systems. Anomalous heating curves are observed. Thermocouple responses are given for some heating powers and show oscillations in the temperature field. A qualitative agreement exists with the predicted values of the period given by the theory.

## 1. Introduction

It is well known that the principle of exchange of stabilities applies for the usual Bénard problem (Chandrasekhar 1961, p. 24). However, this is no longer true when a second stabilizing force acts on the system, for example, the effect of rotation or a magnetic field (Chandrasekhar 1961, p. 114), or a stabilizing solute gradient (Veronis 1968; Sani 1965; Nield 1967; Shirtcliffe 1969; Baines & Gill 1969). Instability may then arise as oscillations of increasing amplitude.

Recently some importance has been attached to the Bénard problem in a two-component system in which an initially *homogeneous* mixture is subjected to a temperature gradient. Then thermal diffusion (also known as the Soret effect; see De Groot & Mazur (1962, p. 273)) takes place and as a result, a mass fraction distribution is established in the liquid layer. The sense of migration of the molecular species is determined by the sign of the Soret coefficient. The total density now contains two contributions:

$$\rho = \rho_0[1-\alpha(T-T_0)+\gamma(N_1-N_{10})]. \tag{1}$$

In (1), $N_1$ is the mass fraction of component 1. This new contribution will completely change the linear stability analysis of the Bénard problem. The rough predictions are as follows.

(*a*) When the denser component migrates towards the cold plate (positive Soret coefficient), here the upper boundary, we expect the liquid layer to be less stable than in the pure-liquid case.

(*b*) Migration of the denser component towards the hot plate (negative Soret coefficient), here the lower boundary, produces of course an opposite effect: the critical Rayleigh number increases.

The importance that thermal diffusion could have in the Bénard instability was first suggested by Prigogine and an experimental study was reported by Legros, Van Hook & Thomaes (1968*a*, *b*); the same idea was also given by Hurle & Jakeman (1969). The linear stability analysis and experiments were then carried out independently by the two groups of researchers: Hurle & Jakeman (1969, 1971) and the group at the University of Brussels directed by Professor Prigogine and coworkers at the Universities of Austin and Mons (Legros *et al.* 1968*a*, *b*; Legros, Rasse & Thomaes 1970; Schechter, Prigogine & Hamm 1972; Platten 1971; Legros, Platten & Poty 1972; Platten & Chavepeyer 1972*a*, *b*). A stabilizing effect (increase of the critical Rayleigh number) was reported in experiments by Legros *et al.* (1970). The linear stability analysis has been performed by Schechter, Prigogine & Hamm and appeared recently in the literature (Schechter *et al.* 1972). They mainly focused their attention on the case of exchange of stabilities for rigid boundaries, but noted that overstable motions were also possible for negative Soret coefficients. Moreover, in order to have a self-adjoint problem, the coefficients of $\nabla N$ and $\nabla T$ in the starting equations were kept constant. In another publication on the subject, Legros *et al.* (1972) removed the above assumptions. This new formulation leads to a non-self-adjoint problem and was solved by a variational method referred to as the 'local potential technique'. For positive Soret coefficients the principle of exchange of stabilities was found by extrapolation of the numerical results, but the conditions for overstability were not clarified in that paper. They were obtained later by Platten (1971) for free boundaries and by Platten & Chavepeyer (1972*a*) for rigid boundaries. A first experimental example of oscillations obtained in steady-state conditions (fixed temperature at the two boundaries) was given by Platten & Chavepeyer (1972*b*). These oscillations were recorded for 10 h.

Two other recent papers of relevance to the present work are those of Hurle & Jakeman (1971) and Caldwell (1970). As has already been stated, Hurle & Jakeman investigated exactly the same problem as the other group. Although some simplifying assumptions were made in their analysis [which were removed in the paper by Legros *et al.* (1972)], they came essentially to the same conclusions regarding the variation of the critical Rayleigh number. The Bénard cell that Hurle & Jakeman used was not operated in steady-state conditions, and they could only record a few cycles in the temperature field (see figure 10, plate 1, of their paper). The second paper of interest is that of Caldwell (1970), who reported Bénard experiments in sea water. He obtained heating curves with a negative-slope portion and a hysteresis phenomenon. The same features are also observed in our experiment described in this paper. The aim of this paper is to give new numerical results concerning the frequency of the oscillations after a short review of the theory and to present Schmidt–Milverton plots of water–alcohol systems and thermocouple responses showing oscillations in the temperature field.

## 2. Oscillations in the two-component Bénard problem: theory

For an incompressible fluid, the conservation equations for mass, momentum and energy are

$$\frac{\partial N_1}{\partial t} = -v_j\frac{\partial N_1}{\partial x_j} + D\frac{\partial^2 N_1}{\partial x_j^2} + D'\frac{\partial}{\partial x_j}\left(N_1 N_2 \frac{\partial T}{\partial x_j}\right), \tag{2}$$

$$\frac{\partial v_i}{\partial t} = -v_j\frac{\partial v_i}{\partial x_j} - \frac{1}{\rho_0}\frac{\partial p}{\partial x_i} + \frac{\rho}{\rho_0}F_i + \nu\frac{\partial^2 v_i}{\partial x_j^2}, \tag{3}$$

$$\frac{\partial T}{\partial t} = -v_j\frac{\partial T}{\partial x_j}+\kappa\frac{\partial^2 T}{\partial x_j^2}. \tag{4}$$

As usual, the Boussinesq approximation has been used. Moreover, in (4) we have neglected the Dufour effect: the modification of the heat flow due to the concentration gradient is indeed very small in liquids (but not in gases; see De Groot & Mazur 1962, p. 279). Equations (2)–(4) with $D' = 0$ are equivalent to the problem of a stabilizing solute gradient (with of course different boundary conditions). Owing to the sign of $D'$, one has now either a stabilizing effect ($D' < 0$) or a destabilizing effect ($D' > 0$).

When (2)–(4) are linearized in the disturbances, one gets a system of linear differential equations with variable coefficients. To avoid this difficulty the product $N_1N_2$ in the thermal diffusion term of (2) is kept constant, equal to its initial value $N_1^*N_2^*$ and not subject to fluctuations. This new assumption, *which we shall remove later in the analysis*, leads to the following eighth-order dispersion equation, after the usual normal-mode analysis and elimination of all the variables except the amplitude $W$ of the upward component of the velocity (see Platten 1971) and with a time dependence given by $\exp(\sigma t)$:

$$\begin{aligned}&(D^2+k^2-\sigma Pr)\,(D^2-k^2-\sigma Sc)\,(D^2-k^2-\sigma)\,(D^2-k^2)\,W\\&+(D^2-k^2-\sigma Pr)\,k^2R_{Th}(Sc/Pr)\,\mathscr{S}'\,W\\&+(D^2-k^2-\sigma Sc)\,k^2Ra\,W+(D^2-k^2)\,k^2R_{Th}\mathscr{S}'\,W = 0.\end{aligned} \tag{5}$$

The notation is that adopted in the papers by Legros and Platten:

$Pr$ = Prandtl number = $\nu/\kappa$,
$Sc$ = Schmidt number = $\nu/D$,
$Ra$ = Rayleigh number = $g\alpha\Delta T\, d^3/\kappa\nu$,
$R_{Th}$ = thermal diffusion Rayleigh number = $g\gamma N_1^*\, d^3/\kappa\nu$,
$\mathscr{S}'$ = the Soret number = $(D'/D)\,\Delta T\,.\,N_2^*$.

For free boundaries and at the marginal state ($\sigma = \sigma_R+i\sigma_I$; $\sigma_R = 0$) one has (see Platten 1971 for more details)

$$\sigma_I = \left[\frac{-R_{Th}\mathscr{S}'}{3\,Pr(Pr+1)}-\frac{9\pi^4}{4\,Sc^2}\right]^{\frac{1}{2}}. \tag{6}$$

It must be kept in mind that all the variables are reduced and thus $\sigma_I$ is a dimensionless frequency. From (6) we recover the conditions for overstability deduced elsewhere (Platten 1971): $\sigma_I$ being a real quantity, one has

$$\mathscr{S}' < 0,$$

$$|\mathscr{S}'| > \frac{27\pi^4}{4}\frac{Pr\,(Pr+1)}{Sc^2R_{Th}}.$$

The dimensional period (in seconds) follows from (6) as

$$T_s = 2\pi d^2/\nu\sigma_I. \tag{7}$$

|  |  |  |  | $Ra^c$ from local potential for rigid boundaries | $\sigma_I$ |  |
|---|---|---|---|---|---|---|
| $\mathscr{S}$ | $R_{Th}$ | $Sc$ | $Pr$ |  | From local potential for rigid boundaries | From (9) |
| $-2\times10^{-3}$ | $10^2$ | $10^3$ | 10 | 1759·06 | $0{\cdot}2110\times10^{-3}$ | $0{\cdot}2112\times10^{-3}$ |
| $-2\times10^{-3}$ | $10^3$ | $10^3$ | 10 | 1760·7 | $0{\cdot}2961\times10^{-2}$ | $0{\cdot}2954\times10^{-2}$ |
| $-2\times10^{-3}$ | $10^4$ | $10^3$ | 10 | 1777·1 | $0{\cdot}3045\times10^{-1}$ | $0{\cdot}3038\times10^{-1}$ |
| $-2\times10^{-3}$ | $10^5$ | $10^3$ | 10 | 1941·4 | $0{\cdot}3054\times10^{0}$ | $0{\cdot}3047\times10^{0}$ |
| $-4\times10^{-3}$ | $10^4$ | $10^4$ | 10 | 1781·2 | $0{\cdot}6130\times10^{-1}$ | $0{\cdot}6096\times10^{-1}$ |
| $-4\times10^{-3}$ | $10^4$ | $10^4$ | 100 | 1795·8 | $0{\cdot}6380\times10^{-3}$ | $0{\cdot}6629\times10^{-3}$ |
| $-4\times10^{-3}$ | $10^4$ | $10^4$ | 1000 | 1873·4 | $0{\cdot}5389\times10^{-5}$ | $0{\cdot}5763\times10^{-5}$ |
| $-2\times10^{-3}$ | $10^4$ | $10^2$ | 10 | 1858·2 | $0{\cdot}2093\times10^{-1}$ | $0{\cdot}2112\times10^{-1}$ |
| $-2\times10^{-3}$ | $10^4$ | $10^3$ | 10 | 1777·1 | $0{\cdot}3045\times10^{-1}$ | $0{\cdot}3038\times10^{-1}$ |
| $-2\times10^{-3}$ | $10^4$ | $10^4$ | 10 | 1767·6 | $0{\cdot}3071\times10^{-1}$ | $0{\cdot}3048\times10^{-1}$ |
| $-2\times10^{-3}$ | $10^4$ | $10^3$ | 10 | 1777·1 | $0{\cdot}3045\times10^{-1}$ | $0{\cdot}3038\times10^{-1}$ |
| $-4\times10^{-3}$ | $10^4$ | $10^3$ | 10 | 1794·9 | $0{\cdot}6099\times10^{-1}$ | $0{\cdot}6086\times10^{-1}$ |
| $-6\times10^{-3}$ | $10^4$ | $10^3$ | 10 | 1812·4 | $0{\cdot}9150\times10^{-1}$ | $0{\cdot}9134\times10^{-1}$ |
| $-8\times10^{-3}$ | $10^4$ | $10^3$ | 10 | 1829·5 | $0{\cdot}1220\times10^{0}$ | $0{\cdot}1218\times10^{0}$ |
| $-10^{-2}$ | $10^4$ | $10^3$ | 10 | 1846·4 | $0{\cdot}1526\times10^{0}$ | $0{\cdot}1523\times10^{0}$ |

TABLE 1. Square of the dimensionless frequency for the two-component Bénard problem.

A numerical estimation of the period of oscillations for values of the dimensionless numbers (Prandtl number, Schmidt number, etc.) compatible with experiments in liquids shows that such oscillations can be very easily detected in laboratory experiments. The order of magnitude of $T_s$ is, for example, 1 min.

Equation (7) can be considerably simplified (see appendix) and gives

$$T_s \simeq \frac{4d^2}{3\pi\kappa[-S/(1+S)]^{\frac{1}{2}}}. \tag{8}$$

The meaning of the new parameter $S$ is very simple: it is a density correction factor, i.e. the contribution of the thermal diffusion to the density gradient relative to that resulting from the temperature gradient. This parameter was first introduced by Schechter *et al.* (1972). For the pure-liquid case

$$S = 0 \quad \text{implies} \quad T_s \rightarrow \infty.$$

No oscillations are possible. From (8) oscillations are possible in the range

$$-1 < S < 0.$$

When $S = -1$, the contribution of thermal diffusion to the density gradient is equal, but in opposite direction, to the contribution of the temperature gradient. When $S < -1$, the density gradient becomes stable.

Two assumptions used previously are incompatible with experiments: (i) two free boundaries and (ii) the fact that the product $N_1 N_2$ is replaced by its initial value $N_1^* N_2^*$ and does not vary. This has been recognized for a long time, and the linear stability analysis as well as the conditions for overstability was studied without these two unrealistic assumptions (Legros *et al.* 1972; Platten &

Chavepeyer 1972*a*). In that case it was not possible to find an exact analytical solution. The problem was solved by a numerical technique (a variational method based on the notion of a local potential). In this numerical study, the attention was focused on the *sign* of the real part of the amplification factor $\sigma$, or preferably on the value of the Rayleigh number such that the real part of $\sigma$ was zero. No attempt was made to find the value of the imaginary part of $\sigma$ ($\sigma_I$) at the critical point. We rerun the problem explained in detail in the papers by Legors *et al.* (1972) and Platten & Chavepeyer (1972*a*), but we now calculate the imaginary part of $\sigma$ at the critical point. In table 1, the critical Rayleigh number *Ra* and the square of $\sigma_I$, as given by the local potential method are reproduced for a few values of the relevant parameters. These results are compared with those given by equation (9) for $\sigma_I^2$ (see below). The complete numerical study that we have performed involved about 600 determinations of $\sigma_I$ by the local potential method. These results show that $\sigma_I$ obeys the law (within a 3 % error)

$$\sigma_I^2 = C_1 \frac{-R_{Th}\mathscr{S}}{Pr\,(Pr+1)} - C_2 \frac{1}{Sc^2}, \tag{9}$$

with $C_1 = 0{\cdot}167629$ and $C_2 = 93{\cdot}5492$. It is remarkable that $\sigma_I$ obeys for rigid boundaries the same type of law as that expressed by (6) for free boundaries, the two constants $C_1$ and $C_2$ being of course different. From (9), it is possible to recover the conditions for overstability found elsewhere (Platten & Chavepeyer 1972*a*):

$$\mathscr{S} < 0,$$

$$|\mathscr{S}| > \frac{C_2}{C_1}\frac{Pr(Pr+1)}{Sc^2 R_{Th}}.$$

The ratio $C_2/C_1 \simeq 558$ must be compared with the value 554·5 obtained previously, when we studied the branch point of the overstability curve on the exchange of stabilities curve without determining $\sigma_I$. The agreement is quite acceptable.

## 3. Oscillations in the temperature field: experiments

It has been shown in § 2 that the conditions for the exchange of stabilities are violated for the Bénard problem in a two-component system. Thus instability arises as oscillations of increasing amplitude. Although a linear theory is unable to predict the new state reached by a system beyond an instability point, it seems credible that this new state will not be steady, but fully oscillatory when the principle of exchange of stabilities does not apply, and that the magnitude of the frequency will be of the same order as that given by a linear theory, provided that the difference $R_a - R_a^c$ is small enough. In § 2, the dimensionless frequency was given for this problem and the numerical estimates seem to indicate that the oscillations could be easily detected. The aim of this part of the paper is to give thermocouple records showing, indeed, oscillations in the temperature field.

The apparatus that we have used is very classical and of very simple design, but yet accurate enough for our purpose. The liquid layer is bounded by two copper plates of radius 13 cm. The depth of the layer, and thus the distance

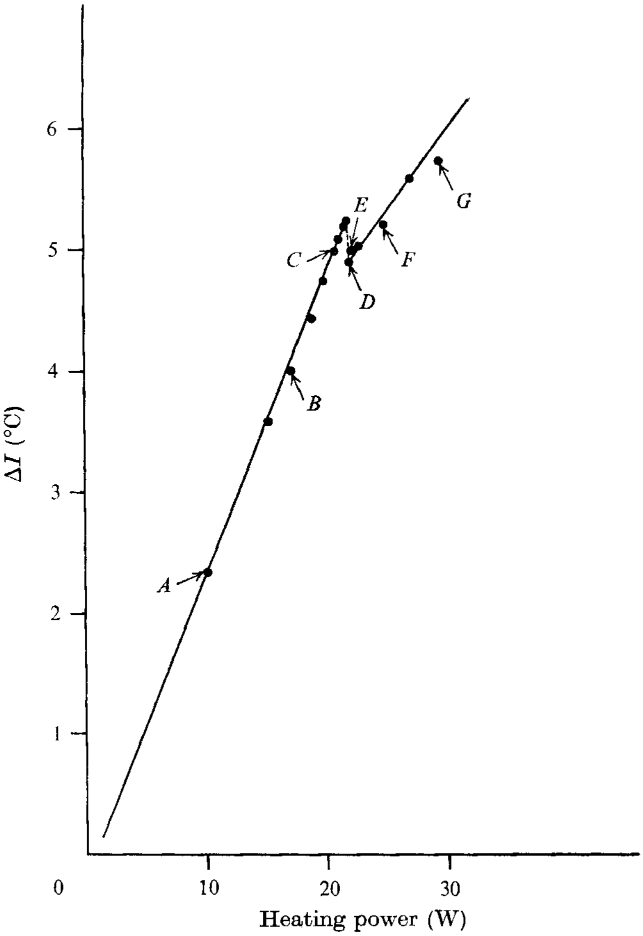

FIGURE 1. Schmidt–Milverton plot for the system with 90 % by weight water and 10 % ethanol.

between the two plates, is maintained at the desired value by a nylon joint. The upper boundary is kept at a fixed temperature by water flowing from a constant-temperature bath. The lower boundary is heated electrically by a Hewlett–Packard regulated power supply (model 895 A). This Bénard apparatus is surrounded by a constant-temperature enclosure. The temperature difference between the two plates is recorded versus the heat power. Schmidt–Milverton plots (Schmidt & Milverton 1935) are then possible. A thermocouple junction is placed inside the liquid layer more or less midway between the two plates. The cold junction lies in a thermostat at the temperature of the upper boundary.

The thermocouple response is recorded versus time, for each heat power, for several hours (from 4 to 10 h). A first experiment was performed on a water–ethanol system (10 % by weight alcohol). The depth of the layer was 3·2 mm. Schmidt–Milverton plots are already available for this system (Legros *et al.* 1970). The Soret coefficient is negative and the system is thus stabilized against infinitesimal disturbances. Transition is not observed at the usual value 1708 of the

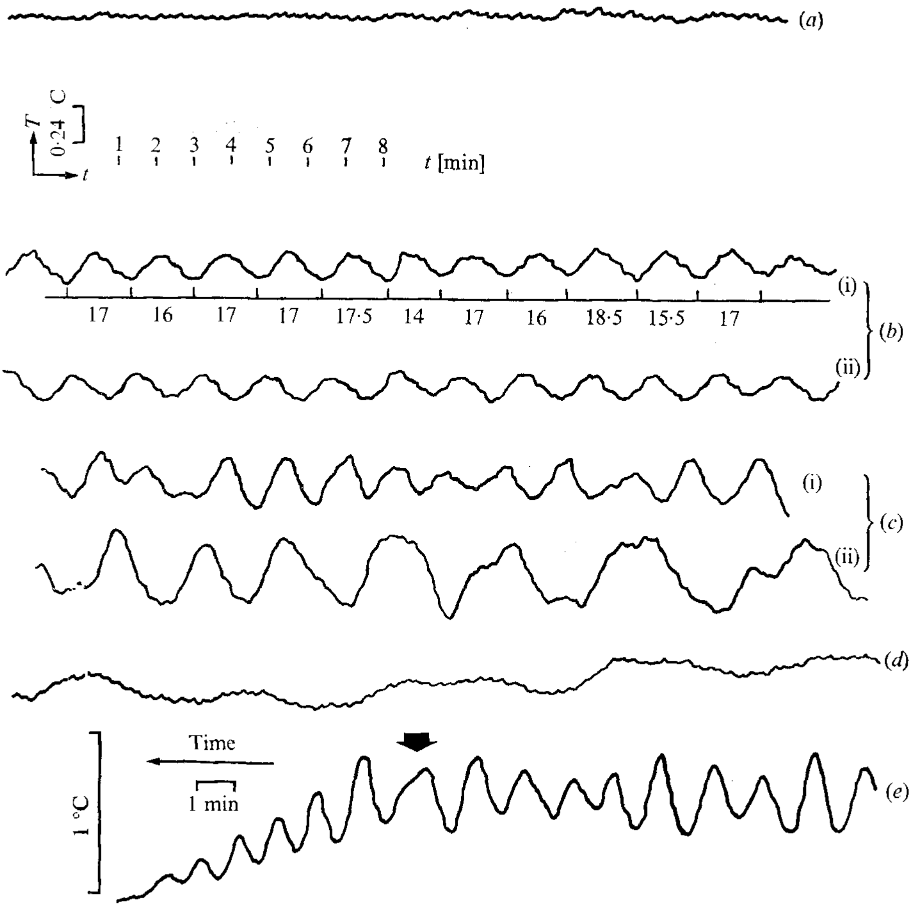

FIGURE 2. Temperature records in the water–ethanol system for different heating powers. (*a*) 20·63 W. (*b*) 21·78 W. (*c*) 24·77 W. (*d*) 29·38 W.

critical Rayleigh number but for significantly larger values. The heating curve that we have obtained (see figure 1) is quite similar to that of Legros *et al.* (1970) and that of Caldwell (1970) in sea water. The most important feature is the negative slope in this curve just beyond the critical point. Such an anomalous heating curve is well known and we shall not give more details here. This curve is reproduced in figure 1. However, we want to emphasize the thermocouple response for 7 particular heat powers of figure 1, labelled $A$–$G$. The temperature of the upper plate is always $19 \pm 0{\cdot}1$ °C. The heating powers corresponding to $A$, $B$ and $C$ are respectively 10·08, 16·93 and 20·63 W. The thermocouple outputs are quite similar and one example is given on figure 2 (*a*). Very small oscillations of short period ( ~ 14 s) are seen. This period corresponds exactly to the 'heat on–heat off' cycles of the contant-temperature bath in which the cold junction of the thermocouple lies. We shall not take into account such oscillations. Thus in figure 2 (*a*) the thermocouple output is constant in time. The time and temperature scales are given between figures 2 (*a*) and (*b*). The next heating power of interest on figure 1 is labelled $D$ (21·78 W, $\Delta T = 4{\cdot}9$ °C). Despite the fact that the

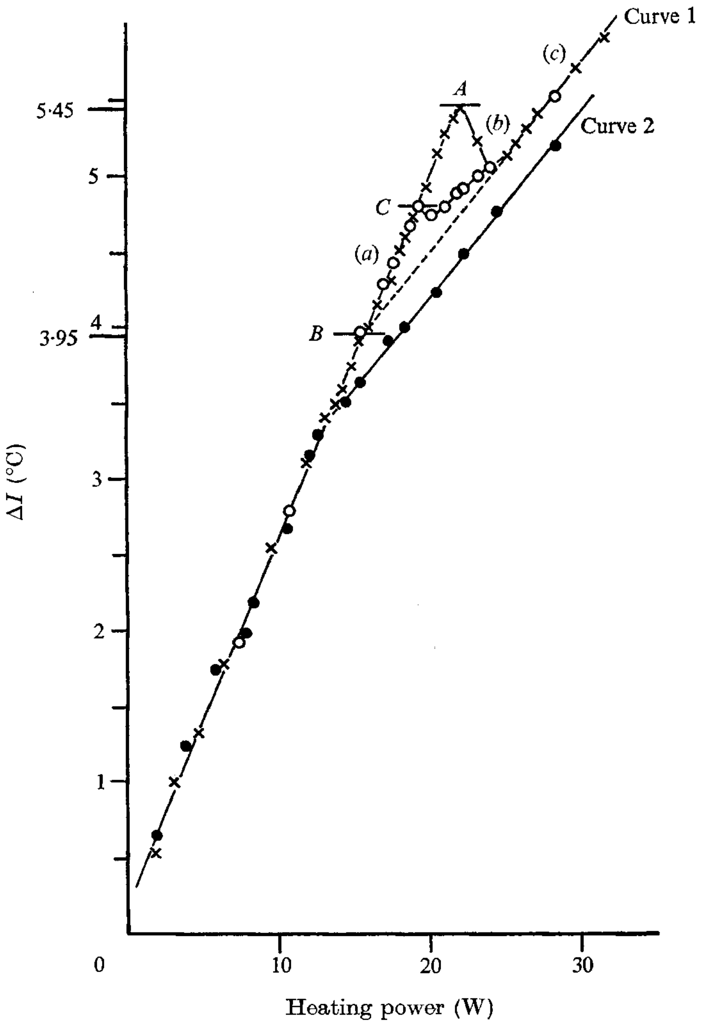

FIGURE 3. Schmidt–Milverton plots for two systems. Curve 1, 90% by weight water and 10% isopropanol: ×, heating power increased; ○, heating power decreased. Curve 2: ●, pure water.

heating power is higher, the temperature difference between the two plates is smaller than for the previous measurement (point *C*). After a transient period, oscillations in the temperature field appear and persist (at least at first sight) as long as the heating power is held at the desired value. The thermocouple response that we reproduce in figure 2 (*b*) was recorded after 15 h. These oscillations are quite regular. In graph (i) of figure 2 (*b*), the period is given in arbitrary units (10 units = 1 min). The same features are also observed for the heating power labelled *E* on figure 1. For a heating power of 24·77 W ($\Delta T$ = 5·23 °C; point *F*) we leave the negative-slope part of the heating curve and we are far from the critical point. Nevertheless oscillations are always present (figure 2 *c* (i)) but become more irregular. After several hours (more or less one night) the period changes con-

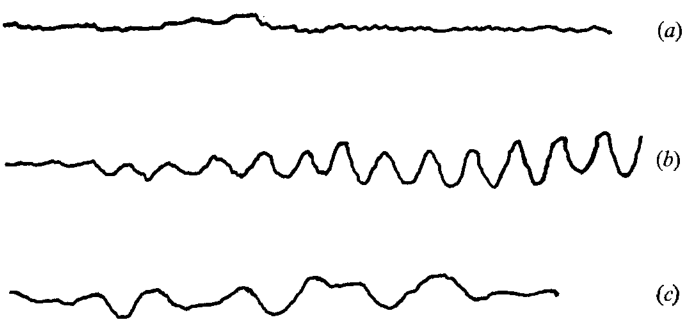

FIGURE 4. Temperature records in the water–isopropanol system for different heating powers.

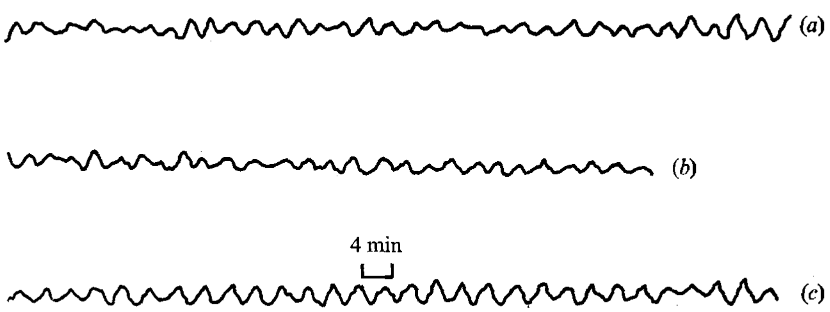

FIGURE 5. Oscillations in a water–ethanol mixture.

siderably (figure 2*c*(ii)). The reason for this change is not yet understood, the experimental situation being of course unchanged.

For larger heating powers (e.g. point *G* of figure 1, at 29·38 W, $\Delta T = 5{\cdot}72\,^{\circ}\mathrm{C}$), there are always oscillations, but of very large period and small amplitude (see figure 2*d*). Figure 2(*e*) shows oscillations in the temperature field beyond the critical value. At a time indicated by the arrow, the heat power is lowered below the critical point. The mean temperature decreases with oscillations of decreasing amplitude. After a few minutes ($\sim 7$) the system has reached a non-oscillatory steady state.

The experiments were repeated for the water–isopropanol system (90 % by weight water and 10% alcohol), for which the Soret coefficient is not available. The Schmidt–Milverton plot is reproduced in figure 3. Two main features are once more seen.

(*a*) Curve 1 is divided into a 'pure condition' regime, from the origin to *A* (part (*a*)), a part (*b*) of negative slope and the 'conduction + convection' regime (part (*c*)). When *W*, and thus $\Delta T$, is increased, we expect instability at point *B* but thermal diffusion prevents this instability. The temperature difference between *B* and *A* is a measure of the increase of the critical Rayleigh number predicted by the linear stability analysis. This increase of 40 % is not in contradiction with previous theoretical results. At *A*, instability sets in and convection destroys the mass fraction distribution, inside the liquid layer.

(*b*) When the heat power is decreased from its maximum value, the curve is not retraced. (It should be kept in mind that all measurements were taken in steady-state conditions.) This hysteresis loop in $\Delta T$ was really important.

In figure 3 curve 2 refers to pure water. Thermocouple records for the 'water–isopropanol' system are given in figure 4. No oscillations are recorded before the instability point. The thermocouple output is similar to that shown on figure 2 (*a*). Just beyond the expected instability point, but very near to it, large temperature fluctuations are recorded, but no oscillations (see figure 4*a*). This was of course unexpected but it may be that the initial fluctuation could have an influence on the state reached by the system. The heating power is raised a little above the value imposed in the previous measurement. After a short transient period, oscillations appear with approximately the same period (70–75 s) (figure 4*b*). They were recorded for several hours, but the regularity became worse. After 10 h, with the same heating power as in figure 4 (*b*), the oscillations are always present, but the period is quite different (figure 4*c*); if the heating power is lowered, the oscillations disappear immediately. The same experiment was repeated in pure water (curve 2 of figure 3). The temperature records before instability and for different heating powers in the presence of convection show no oscillations. Thus the introduction of small amounts of alcohol (ethanol or isopropanol) induces oscillations. We believe that this phenomenon is really connected with thermal diffusion.

The same experiment was repeated with a different depth in the water–ethanol system: 4·73 mm. Of course the critical point was lowered and the importance of the negative-slope part of figure 1 was reduced. But in that part of the heating curve, oscillations were reproduced (see figure 5; the time scale is different from that of the previous figure). As expected, the period of the oscillations increases with the depth of the liquid layer. The mean period seems to change slightly with time. Figure 5 (*a*) gives the time evolution of the temperature 4 h after the heat power has been set to a value such that the resulting temperature gradient exceeds the critical one. The mean period in figure 5 (*a*) is 177 s. Figure 5 (*b*) reproduces oscillations after 8 h. The mean period is now 183 s. Oscillations in figure 5 (*c*) are recorded after 12 h with a mean period of 200 s.

Since the bulk of this manuscript was prepared, we have changed the method of detecting oscillations, substituting for the thermocouples a negative temperature coefficient resistor (NTC). We have used a NTC resistor from *M.B.L.E.*, type R 634·01/6K8. The temperature dependence of the resistance is given by $R = A\,e^{B/T}$ with $A = 0{\cdot}033211\,\Omega$ and $B = 3633{\cdot}28\,^{\circ}\mathrm{K}$, and thus

$$(dR/dT)_{300\,^{\circ}\mathrm{K}} \simeq -243\ \Omega/^{\circ}\mathrm{K}.$$

This instrument is thus very sensitive. This NTC resistor placed in the liquid layer forms one of the resistances of a Wheatstone bridge. Our experimental device allows us to detect variations of the order of 0·001 °K and make absolute measurements precise to within 0·01 °K. The experiments were repeated in a water–isopropanol system. Beyond the instability point, oscillations were once more recorded (see figure 6*a*). For the same sensitivity of our recorder system as in figure 6 (*a*), the temperature before the instability point is a straight line.

Of course, at higher sensitivity, fluctuations of about 0·01 °K are recorded before instability and at the critical point these fluctuations increase in amplitude and become regular in frequency, and the fully developed oscillations are off the scale of the record paper. The sensitivity is reduced in order to record oscillations on the scale of the record paper as shown in figure 6 (*a*). Being very patient, we have tried to approach as close as possible to the critical point. Very regular oscillations are then observed (see figure 6 (*b*); the time scale is different) and recorded with the *same regularity* for more than 10 h.

## 4. Summary of the experimental results and comparison with the theory

First of all, the theory presented in §2 is only valid at the critical point. Beyond the critical point, many wavenumbers are amplified and thus many frequencies should be present in the thermocouple response. A Fourier analysis should then be made. We shall thus only compare with the theory the experimental period concerning the point the nearest the critical one, in order to have only one frequency present. For instance, this seems to be the case for figure 2 (*b*). A second difficulty arises when one tries to evaluate the different dimensionless numbers for the mixtures considered. The transport coefficients at a given composition and temperature are not always available in the literature.

We summarize in table 2 the experimental and calculated values of the period. The experimental values of the period for $d = 3{\cdot}2$ mm are taken from figures 2 (*b*) and 4 (*b*) for the water–ethanol and water–isopropanol systems respectively while the value for $d = 4{\cdot}73$ mm comes from figure 5.

The calculated period for the water–ethanol system with $d = 3{\cdot}2$ mm is found as follows. The temperature of the upper boundary was 19 °C and the critical temperature gradient 5·25 °C (see figure 1). Thus the mean temperature at which the transport coefficients are evaluated is 21·6 °C. Most of the transport coefficients are obtained by linear interpolation between the values given in *Lange's Handbook of Chemistry* (1967, revised 10th edn.). We obtain in this way for the expansion coefficients

$$\alpha \simeq -\frac{1}{\rho}\left(\frac{\Delta\rho}{\Delta T}\right)_N \simeq 2{\cdot}93\times 10^{-4}\,{}^{\circ}\mathrm{C}^{-1},$$

$$\gamma \simeq \frac{1}{\rho}\left(\frac{\Delta\rho}{\Delta N}\right)_T \simeq 1{\cdot}462\times 10^{-1},$$

for the kinematic viscosity $\nu = \eta/\rho = 1{\cdot}497$ cst and for the heat diffusivity $\kappa = \lambda/\rho c_v \simeq 1{\cdot}329\times 10^{-3}\,\mathrm{cm}^2/\mathrm{s}$. Estimation of the Soret coefficient (from Legros 1971) gives

$$D'/D \simeq -10^{-3}\,{}^{\circ}\mathrm{C}^{-1}.$$

Thus we find for the dimensionless parameters

$$Pr = \nu/\kappa \simeq 11{\cdot}26,$$

$$R_{Th}\mathscr{S}' = \frac{g\gamma N_1^* d^3}{\kappa\nu}\times\frac{D'}{D}\Delta T^c N_2^* \simeq -111{\cdot}6.$$

| System | Experimental | | Calculated | |
|---|---|---|---|---|
| | $d = 3{\cdot}2$ mm | $d = 4{\cdot}73$ mm | $d = 3{\cdot}2$ mm | $d = 4{\cdot}73$ mm |
| 90 % water and 10 % ethanol by weight | 101·5 s | 180–200 s | 117 s | 220 s |
| 90 % water and 10 % isopropanol by weight | 70 s | — | 64 s | — |

TABLE 2

We next evaluate the dimensionless frequency using (9). The last term in (9) may be dropped because of the large value of the Schmidt number ($Sc \simeq 10^{+3}$). We get

$$\sigma_I \simeq 0{\cdot}368$$

and thus

$$T_s = 2\pi d^2/\nu\sigma_I = 117\,\mathrm{s} \quad \text{for} \quad d = 3{\cdot}2\,\mathrm{mm}.$$

We want to know if the period of the oscillations is indeed proportional to $d^2$. Thus, we start with the experimental period of 101·5 s for $d = 3{\cdot}2$ mm in the water–ethanol system and multiply this experimental result by the square of the ratio of the two depths 3·2 mm and 4·73 mm. We obtain in this way 220 s for the calculated value of $T_s$ for $d = 4{\cdot}73$ mm.

The period of 64 s for the water–isopropanol system for $d = 3{\cdot}2$ mm is a very approximate value, owing to the lack of experimental data. However, it was shown by Platten (1971) that the critical Rayleigh number $Ra^c$ obeys, in the case of overstability, the law

$$Ra^c = 657{\cdot}5\,\frac{(1+Sc)(Sc+Pr)}{Sc^2} - R_{Th}\mathscr{S}'\frac{Pr}{1+Pr}.$$

If $Sc \gg Pr$, which is true for water–alcohol systems, then this equation reduces to

$$Ra^c \simeq 657{\cdot}5 - R_{Th}\mathscr{S}'[Pr/(Pr+1)].$$

This is of course only true for free boundaries, but this last equation shows that for $\mathscr{S}' < 0$ the stabilizing effect is proportional to $R_{Th}\mathscr{S}'$. Let us *suppose* that this is also true for rigid boundaries, thus

$$Ra^c - 1708 \simeq -R_{Th}\mathscr{S}'[Pr/(Pr+1)].$$

But

$$Ra^c - 1708 = [g\alpha\delta(\Delta T^c)\,d^3]/\kappa\nu,$$

where $\delta(\Delta T^c)$ is the stabilizing effect measured in units of $\Delta T$ in Schmidt–Milverton plots. Clearly for water and isopropanol (see figure 3)

$$\delta(\Delta T^c) = |T_A - T_B| = (5{\cdot}45 - 3{\cdot}95)\,^\circ\mathrm{C}.$$

Moreover, *suppose* that coefficients such as $\nu$, $\kappa$ and $\alpha$, and thus $Sc$ and $Pr$, are not really different in water–ethanol and water–isopropanol systems. Then using the subscripts $e$ and $i$ respectively for the water–ethanol and water–isopropanol systems

$$\frac{\delta(\Delta T^c)_e}{\delta(\Delta T^c)_i} = \frac{[R_{Th}\mathscr{S}']_e}{[R_{Th}\mathscr{S}']_i}$$

and consequently owing to (9) we get for the period of oscillations

$$T_i = T_e \left[\frac{\delta(\Delta T^c)_e}{\delta(\Delta T^c)_i}\right]^{\frac{1}{2}},$$

or from figures 1 and 3

$$T_i = 101{\cdot}5 \left[\frac{0{\cdot}6}{1{\cdot}5}\right]^{\frac{1}{2}} \mathrm{s} \simeq 64\,\mathrm{s}.$$

What we have shown is that the period of oscillations decreases when the stabilizing effect increases. The order of magnitude is also predicted.

## 5. Conclusions

As predicted by the linear theory, oscillations are indeed observed in the two-component Bénard problem for systems with negative Soret coefficients. The order of magnitude of the period of oscillations is predicted by the linear theory and confirmed by experiments. They show that this period increases with the depth of the liquid layer and decreases with the magnitude of the stabilizing effect. This is also in agreement with the theory. These oscillations are really induced by thermal diffusion. They never appear in pure fluids.

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## Appendix: simplifications involved in (8)

Suppose that the conditions of overstability are firmly established:

$$|\mathscr{S}'| \gg \frac{27\pi^4}{4}\frac{Pr(Pr+1)}{R_{Th}Sc^2}. \tag{A 1}$$

This is usually the case in the liquid phase. For example, with $Pr = 10$, $R_{Th} = 4\times 10^3$, $Sc = 10^3$, $D'/D = -10^{-2}$ and $N_2^* = \frac{1}{2}$, equation (A 1) requires that at the critical point

$$\Delta T \gg 0{\cdot}05\,^{\circ}\mathrm{C}.$$

Equation (7) then reduces to

$$T_s \simeq \frac{2\pi d^2}{\nu[-R_{Th}\mathscr{S}'/3\,Pr(Pr+1)]^{\frac{1}{2}}}. \tag{A 2}$$

The critical temperature gradient $\Delta T^c$, hidden in $\mathscr{S}'$, is included in the right-hand side of (A 2). We wish to express the period of oscillations at the critical point, as a function of the properties of the liquid only. It was shown by Platten (1971) that the critical Rayleigh number in the case of overstability was given by

$$Ra^c = \frac{27\pi^4}{4}\frac{(1+Sc)(Sc+Pr)}{Sc^2} - R_{Th}\mathscr{S}'\frac{Pr}{Pr+1}. \tag{A 3}$$

From (A 3) we deduce the critical temperature difference between the two plates:

$$\Delta T^{c} = \left\{\frac{27\pi^4}{4}\frac{(1+Sc)\,(Sc+Pr)}{Sc^2}\right\}\Bigg/\left\{\frac{g\alpha d^3}{\kappa\nu}+R_{Th}\frac{D'}{D}N_2^*\frac{Pr}{(Pr+1)}\right\}. \tag{A 4}$$

Equation (A 4) is substituted into (A 2) to give

$$T_s \cong \frac{2\pi d^2}{\nu}\left[\frac{-27\pi^4 N_2^*(1+Sc)\,(Sc+Pr)}{12Sc^2\,Pr(Pr+1)\left(\dfrac{\alpha}{\gamma}\dfrac{1}{N_1^*}\dfrac{D}{D'}+N_2^*\dfrac{Pr}{Pr+1}\right)}\right]^{-\frac{1}{2}}. \tag{A 5}$$

Equation (A 5) relates the period of oscillations to the properties of the liquid layer.

Further simplifications involve

$$Sc \gg 1 \quad \text{or} \quad Pr, \quad Pr \gg 1. \tag{A 6}$$

This is quite acceptable for usual organic mixtures, but inadequate for gases or liquid metals. This leads to

$$T_s \simeq \frac{4d^2}{3\pi\kappa\left(-\dfrac{S}{1+S}\right)^{\frac{1}{2}}}, \tag{A7}$$

where

$$S = \frac{\gamma}{\alpha}\frac{D'}{D}N_1^*N_2^*. \tag{A 8}$$

The physical meaning of $S$ is very clear. Indeed,

$$\frac{\partial\rho}{\partial N_1} = \rho_0\gamma, \quad \frac{\partial N_1}{\partial z} = \frac{D'}{D}N_1^*N_2^*\Delta T,$$

$$\frac{\partial\rho}{\partial T} = \rho_0\alpha, \quad \frac{\partial T}{\partial z} = \Delta T.$$

Thus $S$ can be viewed as

$$S = \frac{\dfrac{\partial\rho}{\partial N_1}\dfrac{\partial N_1}{\partial z}}{\dfrac{\partial\rho}{\partial T}\dfrac{\partial T}{\partial z}} = \frac{\left(\dfrac{\partial\rho}{\partial z}\right)_T}{\left(\dfrac{\partial\rho}{\partial z}\right)_{N_1}},$$

the contribution of the thermal diffusion to the density gradient relative to that resulting from the temperature gradient. One also has

$$\partial\rho^{\text{tot}}/\partial z = \rho_0\alpha\Delta T(1+S). \tag{A 9}$$

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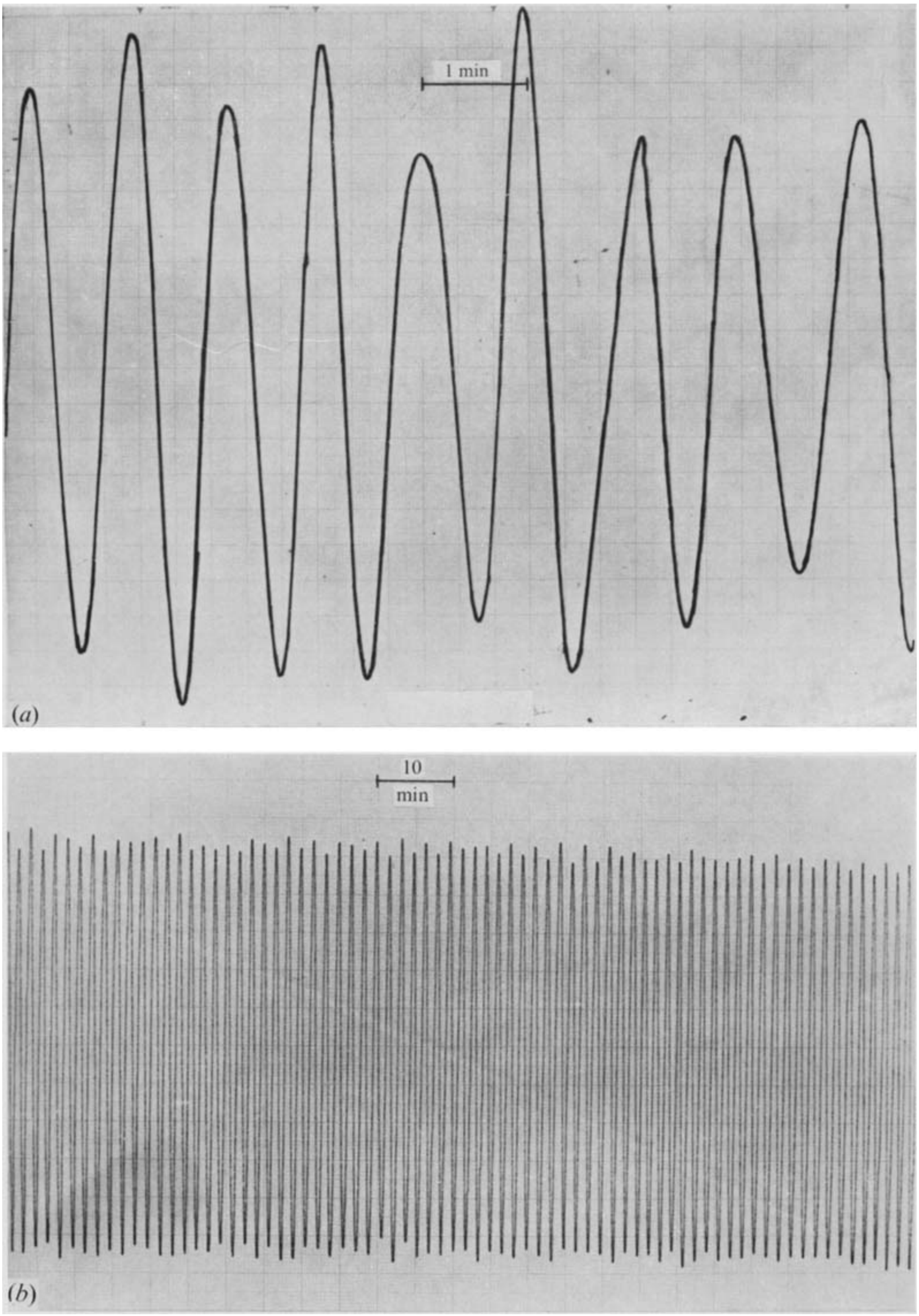

FIGURE 6. Oscillations in a water–isopropanol mixture, using a NTC resistor as a probe.