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Thermosolutal convection in a solution with large negative Soret coefficient

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The large negative Soret coefficient of 1N-LiI gives rise in a Rayleigh–Bénard experiment to a density distribution which is observed to stabilize the fluid layer for values of the Rayleigh number as large as 196 times the value of 1708 for the onset of convection in a pure fluid. The Soret transport also affects the convective heat flux. A power law relating heat flux and temperature difference is found with the same exponent as is found in pure fluids but with a lower value of the multiplicative constant. The Rayleigh number at the onset of power-law behaviour depends on the Soret coefficient. Three types of oscillation are seen: transient oscillations at onset, low frequency fluctuations at low Rayleigh number, and higher frequency oscillations similar to those observed in pure water. The intermediate state found after onset in NaCl solutions is not found in LiI.

1. Introduction

The onset of convection in solutions, and in particular the influence of the Soret effect, has received considerable attention recently (e.g. Veronis 1965, 1968; Hurle & Jakeman 1971; Legros, Platten & Poty 1972; Caldwell 1970, 1974; Velarde & Schecter 1972). The transport of solute by Soret diffusion can either induce weak convection or provide stabilization in a layer of fluid heated from below depending on the sign of S_T, the Soret coefficient. If S_T is negative and has a sufficiently large magnitude, great stabilization is provided. These effects have been studied in mixtures of organic liquids, where S_T is small (e.g. Legros, Rasse & Thomas 1970), in aqueous NaCl solutions and sea water, where S_T is larger, and to some extent in liquid metals (e.g. Harp & Hurle 1968).

Theoretical studies have been successful in predicting the onset of convection in these systems, and in predicting the periods of the small oscillations with which convective motions begin. The transition to the convective state has been shown experimentally to be accomplished by the growth of these oscillations to an amplitude so large that a finite amplitude mode of the system is triggered, as suggested by Veronis (1965). The complex phenomena seen experimentally in the convective states cannot be explained on a theoretical basis at present.

In order to investigate further the applicability of the theoretical calculations of onset and to describe more clearly the phenomena occurring during the convection, a series of experiments was undertaken with a 1 N aqueous LiI solution in the Rayleigh–Bénard apparatus used previously with NaCl and sea water

Symbol	Definition	Value or formula	Units
R	Rayleigh number	$g\alpha\Delta T d^3/\nu\kappa$	—
Nu	Nusselt number	(Heat flux)/(Conductive heat flux)	—
σ	Non-dimensional frequency	$2\pi d^2/\nu P$	—
δ	Stability ratio	$s_T C\beta/\alpha$	—
T	Mean temperature of fluid layer	—	°C
ΔT	Temperature difference across fluid layer	—	°C
g	Acceleration due to gravity	980	$\mathrm{cm/s^2}$
α	Thermal expansion coefficient of LiI	$10^{-5}(7{\cdot}25+1{\cdot}24T-0{\cdot}0106T^2)$	$^{\circ}\mathrm{C}^{-1}$
d	Depth of fluid layer	1·12	cm
ν	Kinematic viscosity	η/ρ	$\mathrm{cm^2/s}$
κ	Thermal diffusivity	$\kappa/\rho C_p$	
P	Period of oscillation	—	s
ρ	Density of LiI	$1{\cdot}098-1{\cdot}322\times10^{-4}T-10^{-6}T^2$	$\mathrm{g/cm^3}$
k	Thermal conductivity	$10^{-3}(1{\cdot}338+0{\cdot}0024T)$	cal/s cm °C
C_p	Specific heat of LiI	0·961	cal/g °C
η	Dynamic viscosity	$\{2{\cdot}148[T-8{\cdot}435+(8078+(T-8{\cdot}435)^2)^{\frac{1}{2}}]-120\}^{-1}$	Stokes
C	Concentration of solute	—	Mass fraction
S_T	Soret coefficient	$10^{-3}(-0{\cdot}391+0{\cdot}0042T)$	$^{\circ}\mathrm{C}^{-1}$
β	Saline contraction	$\rho^{-1}\,\partial\rho/\partial C = 0{\cdot}80$	C^{-1}

TABLE 1. Definitions and values of various quantities

(Caldwell 1970, 1974). In the LiI solution, very large negative Soret coefficients were found, and values of the critical Rayleigh number and the oscillation period at onset agreeing with the theoretical calculations were observed (Caldwell 1975), at values of the stabilization parameter much larger than previous observations.

To see what form the heat transfer and fluid oscillations take in such a solution, a further series of experiments was undertaken. Answers to the following questions were sought.

(i) What modes of convective motion are revealed by loci on a plot of Rayleigh number R *vs.* the product of R and the Nusselt number Nu and by the oscillations seen by a thermistor placed in the fluid layer?

(ii) Does the stirring by convective motions make the solution transfer heat like a pure fluid when the convective motions are great?

(iii) By large sudden changes in heating can the system be put into modes of motion not attainable through a succession of small changes?

One interesting aspect of this subject is its possible connexion with the layered convection observed by investigators with oceanographic applications in mind. In layering experiments, layers are induced in a convective solution either during the initial filling of the tank or by sudden heating from below, although the overall stability parameter for the system indicates stability with no convection. It would be interesting to see if a similar transition to a layered system could be induced in a Soret-stabilized solution. No sign of such a transition was seen in the

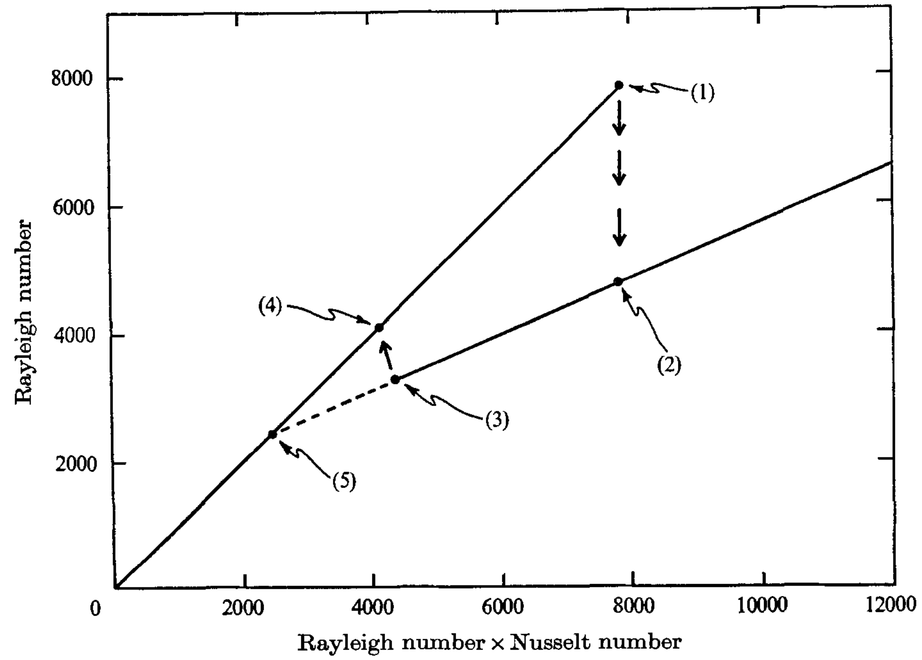


FIGURE 1. Non-dimensionalized temperature difference (Rayleigh number) *vs.* non-dimensionalized heat flux (Rayleigh number times Nusselt number). Mean temperature at onset of convection (1) is 11·71 °C. Other significant points on the plot are: (2) equilibrium attained after onset of convection by small increments in the heat flux, (3) smallest temperature difference attainable during convection at this bath setting, (4) point to which system jumps after cessation of convection brought about by small decrements in the heat flux and (5) the point at which the extrapolated convection line crosses the conduction line.

experiments described here, possibly because large Rayleigh numbers were not reached.

2. Experimental details

The apparatus used has not been altered since it was described previously (Caldwell 1974) except for the insertion of a 0·15 cm diameter thermistor bead into the fluid layer a little below the vertical midpoint, about 3 cm from the wall. Again, pains were taken to ensure that every measurement represented an equilibrium. Usually only one change in heating was made in a day.

Definitions and values of the various quantities required in computations are given in table 1. Procedures and calculations were similar to those described previously.

3. Equilibrium states

Surprisingly, the R *vs.* $R\,Nu$ plots have a somewhat different appearance from those for 0·5 N-NaCl. Instead of three states being possible near onset, there are only two (figure 1). For each value of $R\,Nu$, there is only one convective state. The intermediate state seen in NaCl (Caldwell 1974, figure 4) is missing.

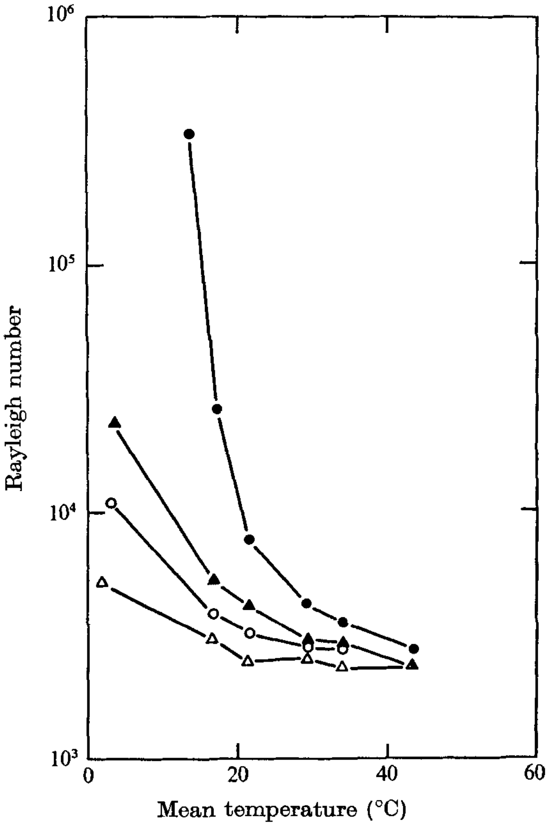


FIGURE 2. Values of the Rayleigh number at the various points indicated in figure 1 *vs.* mean temperature. ●, point 1; ○, point 3; ▲, point 4; △, point 5.

Other features of the plot are similar to those of the NaCl plots: (i) a large decrease in R at the onset of convection; (ii) persistence of convection to values of R and $R\,Nu$ below that attained at onset. However, in LiI, when $R\,Nu$ is being decreased convection does not persist until the conduction line is rejoined, but instead the system 'jumps' back to conduction, R increasing in the process.

Five specific points can be identified on this plot: (1) the highest value of R attained in the non-convective condition; (2) the value of R at which the system comes to equilibrium after onset; (3) the lowest value of R obtained in convection; (4) the value of R at which conduction is regained; and (5) the value of R at which a line drawn through the convective points intersects the conduction line.

The dependence of these quantities on the mean temperature of the fluid is extreme (figure 2), especially that of the 'critical' R for the onset of convection. The reason for this strong temperature dependence is the great variation in the thermal expansion with temperature. One significant point is that the value of R at point 5 is *not* 1708. In a similar plot for a pure fluid, the convective line would run through 1708, and in fact has been observed to do so to within 1% in this same apparatus filled with distilled water (Caldwell 1974, figure 2). Thus the

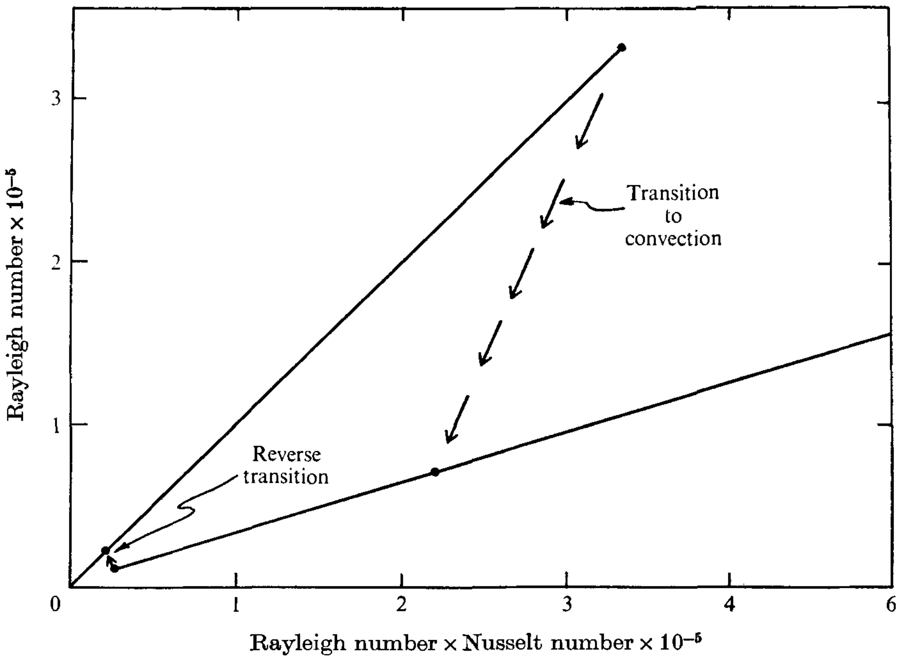


FIGURE 3. Rayleigh number *vs.* product of Rayleigh number and Nusselt number for highest stabilization seen. Bath temperature is 1·70 °C, mean temperature of fluid at onset of the convection is 16·7 °C.

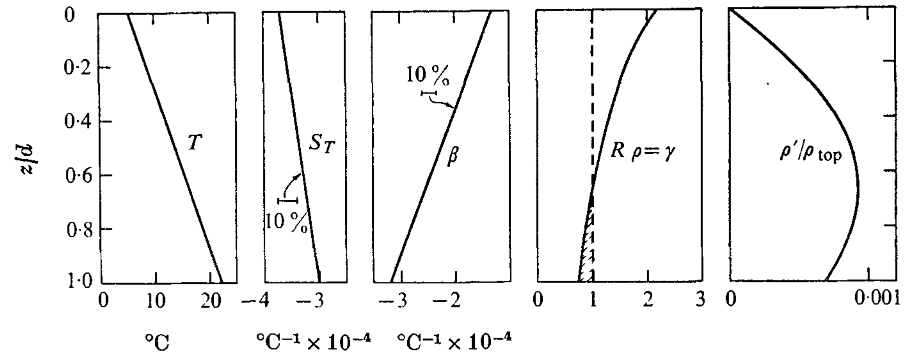


FIGURE 4. Variation of various quantities with vertical position in fluid layer. ρ'/ρ is the relative variation in ρ, defined to be zero at the upper boundary.

convective motion must be different from that observed in a pure fluid; other differences will also appear.

With the bath maintained near 0° C, very great stabilization is observed (figure 3). A Rayleigh number of 335000 is reached before convection begins. The temperature difference at onset, 16·9 °C, is so large that the properties of the solution vary a good deal across the fluid layer (figure 4). The density profile is stable in most of the layer, the density increasing with height only near the bottom. As noted previously (Caldwell 1975, figure 3), the observed critical Rayleigh number

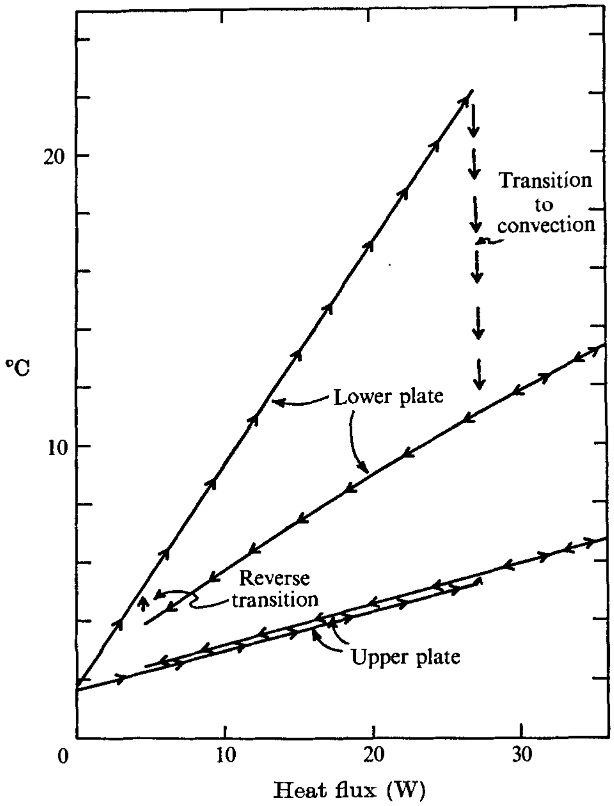


FIGURE 5. Temperatures of upper and lower plates for same data as figure 3.

does not fit in with observations at higher mean temperatures. This is probably because the property variation is so severe; it is surprising that the discrepancy is only 15% or so. It might be noted that in this case the lowest third of the layer, taken by itself, would be unstable by the Hurle–Jakeman calculation, so perhaps the instability begins in only this region. To show further how transition occurs in this case, a dimensional plot of upper and lower boundary temperature *vs.* heat flux is shown (figure 5).

4. High Rayleigh number heat flux

A plot of $\log_{10} Nu$ *vs.* $\log_{10} R$ (figure 6) for the convective state shows variations depending on the temperature of the upper plate. At the lower temperatures, when the influence of the Soret effect is greater, the Nusselt number is higher in the range $20000 \leqslant R \leqslant 130000$. Although a simple power law does seem appropriate for high enough R in all cases, the onset of this power-law behaviour is delayed to higher R for the colder temperatures (figure 7).

In a previous paper (Caldwell 1974) there is a discussion of the reasons why pure-fluid behaviour might not be found at high R.

If the relation $Nu = cR^n$ is assumed, c and n are found to be the same for all

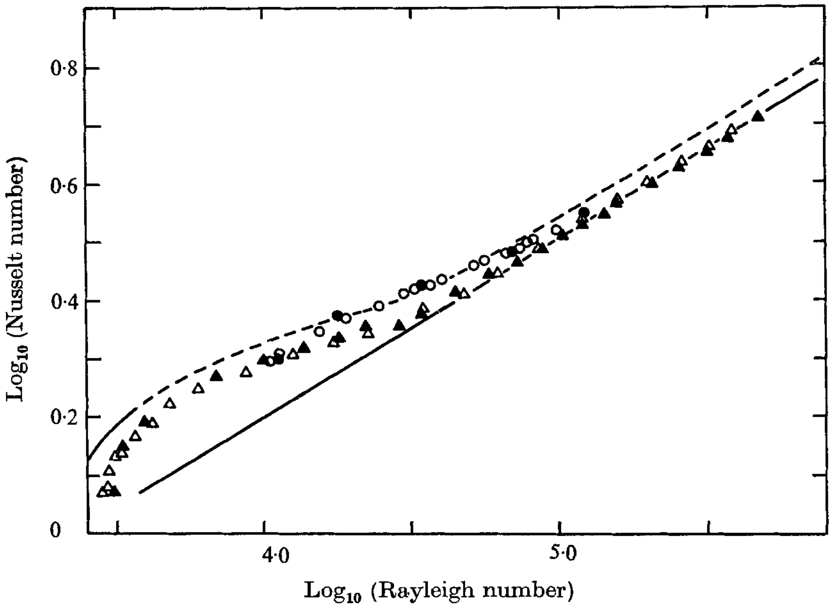


FIGURE 6. Variation of Nusselt number with Rayleigh number for pure water (dashed line) and 1N-LiI. Bath temperature for LiI: ●, 1·0 °C; ○, 1·7; ▲, 34; △, 44. The slope of the solid line is one-third.

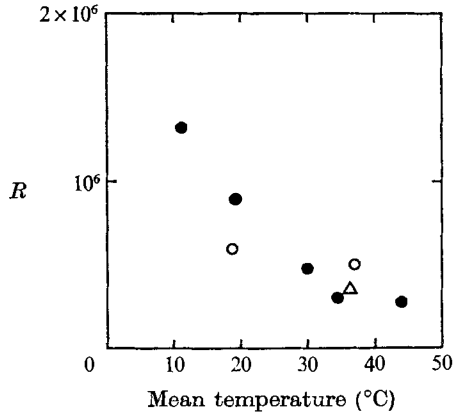


FIGURE 7. Rayleigh number at which power-law behaviour begins *vs.* mean temperatures. ●, 1N-LiI; ○, pure water; △, 0·5N-NaCl.

temperatures, when calculated using data points for which the power law is clearly appropriate. On comparison with the pure-water results in the same apparatus, n is found to be very nearly the same, but c is less, being 0·1114 in pure water but only 0·0991 in LiI solution. The exponent n is 0·301 for pure water and 0·302 for LiI solution, not a significant difference. Comparable values for c and n observed by others are (i) $c = 0{\cdot}130$ and $n = 0{\cdot}293$ (Garon & Goldstein 1973), (ii) $c = 0{\cdot}131$ and $n = 0{\cdot}300$ (Rossby 1969) and (iii) $c = 0{\cdot}111$ and $n = 0{\cdot}310$ (Silveston 1958). Garon & Goldstein's data came from measurements with

$R > 10^7$ and so might be expected to differ a bit from the others, which are for a range similar to that in my experiments, but why for pure water my values of c agree with Silveston's while my values of n agree with Rossby's, I do not know.

In any case, it seems clear that even at high R where a power law holds the solute exerts an influence on the heat flux other than just changing the values of physical properties. In this connexion we might note that the Prandtl number is not substantially different for the LiI solution and pure water.

5. Oscillations

Some controversy has arisen as to whether stable oscillations occur after the onset of Soret-influenced convection. Platten & Chavepeyer (1972) observed persistent oscillations in the temperature at a point inside the fluid layer. These oscillations had periods of the order of those predicted by the linear perturbation theory. The periods increased with layer depth and decreased with the magnitude of the stabilizing effect, in agreement with that theory. They did not observe similar oscillations in pure fluids.

Hurle & Jakeman (1973), on the other hand, found similar behaviour in early 'crude' experiments, but found only transient oscillations in more refined experiments. But when the cell was made slightly wedge-shaped, they found oscillations in both mixtures and pure fluids. They say that "both inexact leveling and obstructing thermocouples promoted" these oscillations, which were rather irregular and unreliable.

In pure fluids, similar oscillations of low frequency are seen somewhat above the critical Rayleigh number, but these are dismissed by Willis & Deardorff (1967) as being "probably associated with gradual adjustments of the large scale temperature pattern... They may also be highly dependent upon the geometry of the convection chamber, small experimental imperfections, and slow changes of Rayleigh number." At $R = 40\,000$ or so in water, higher frequency oscillations are also found. The experiments with mixtures mentioned above do not extend to this regime.

In previous experiments with 0·5N-NaCl, the present author found a more complicated heat-flux plot near onset than was found by Platten & Chavepeyer or by Hurle & Jakeman. After the small oscillations predicted by the linear theory (presumably Hurle & Jakeman's transient oscillations) had triggered a finite amplitude mode, the value of R did not drop to the value found when the heat flux was decreased from large values, but assumed an intermediate value (Caldwell 1974, figure 4). In this state, an oscillation in the temperature at points inside the fluid is found, with period of the order of the period of the transient oscillations at onset. This period varies with the heat flux, increasing by a factor of three for a 10% change in RNu (Caldwell 1974, figure 13).

When the heat flux was decreased from higher values to a value near onset, oscillations of much longer period were found which seemed to involve oscillations of the temperature of the bottom plate. These were thought to be associated with the thermal capacity of the bottom plate as discussed by Busse (1967).

In LiI, no intermediate state is found; only two lines are found on the R *vs.*

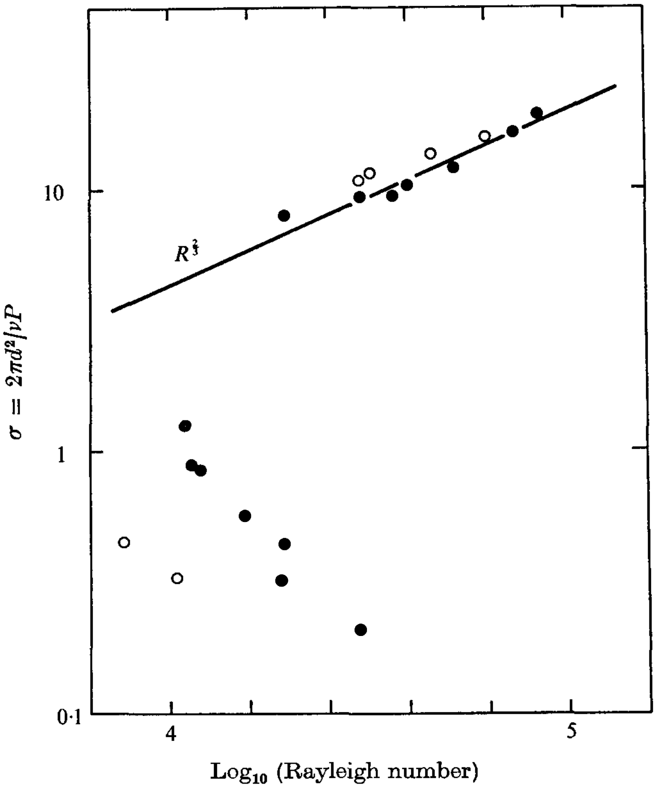


FIGURE 8. Non-dimensionalized frequency of oscillations *vs.* Rayleigh number. Bath temperature: ●, 1·7 °C; ○, 21·7 °C.

$R\,Nu$ plots, one for conduction and one for convection, and no stable oscillation with period of the order of the period of the transient oscillations is found. For example, when the bath temperature was 29·2 °C, the period of the transient oscillation was 270 s, but the stable oscillations had a period of ~1300 s. At a bath temperature of 21·5 °C, the transient period was 153 s and the period in the convective regime 2800–3600 s (figure 8). These oscillations persisted until at least $R = 20\,000$, overlapping with the higher frequency oscillations discussed below. These long period oscillations may be identified with the slow fluctuations discussed by Willis & Deardorff (1967), or perhaps the plate temperature oscillations discussed by Busse (1967), but seem unlikely to be associated with the small amplitude oscillations observed at onset because of the difference in period. A similar conclusion with respect to the oscillations seen by Platten & Chavepeyer (1972) seems logical.

In addition to the transient oscillations at the onset of convection and the low frequency fluctuations seen after onset, another type of oscillation is found as R is increased. At a value of R in the neighbourhood of 20000 high frequency oscillations are seen (figure 9). They seem to be similar to the oscillations seen in pure fluids by several authors (Willis & Deardorff 1967; Krishnamurti 1970; Busse & Whitehead 1974), whose frequency had an $R^{\frac{2}{3}}$ dependence. The frequency

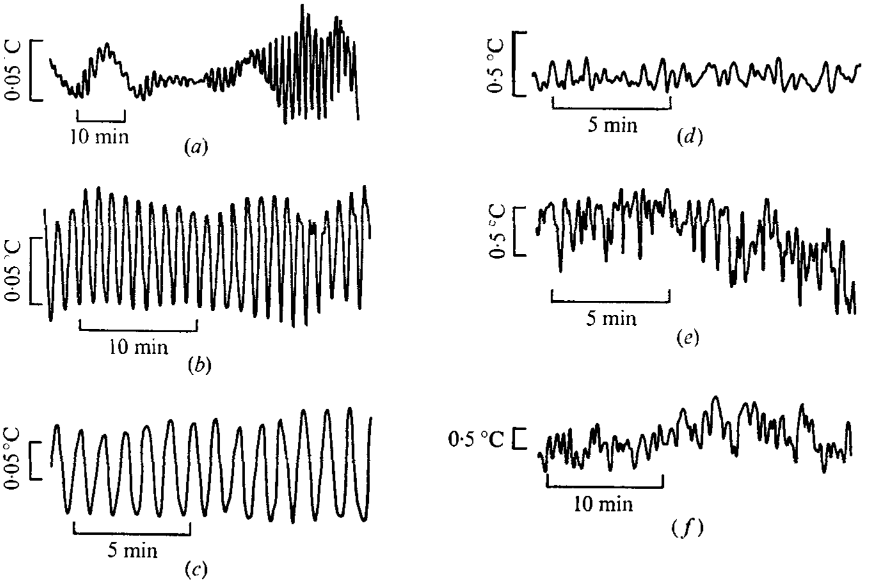


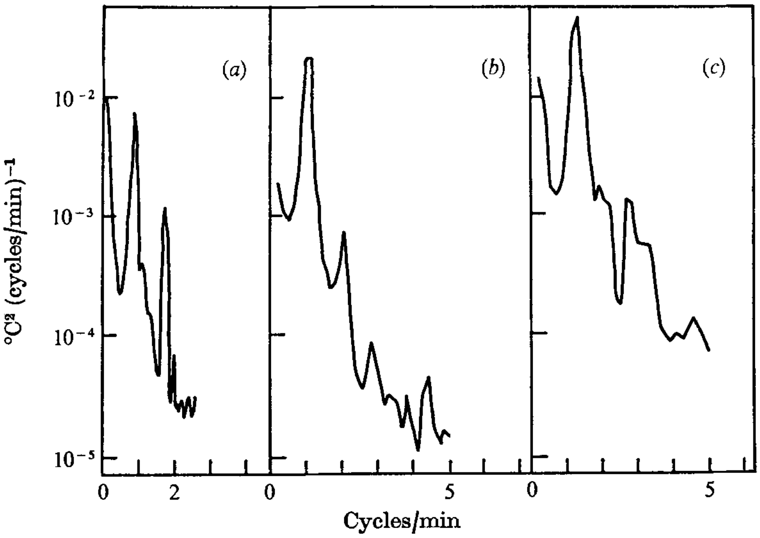
FIGURE 9. Strip-chart recordings of high frequency oscillations. (a) $R = 30700$. (b) $R = 33500$. (c) $R = 46600$. (d) $R = 63000$. (e) $R = 116000$. (f) $R = 342500$.

of the high frequency oscillations in LiI also has this sort of R dependence (figure 8), so the mechanisms are probably similar in nature. According to Busse & Whitehead (1974), if no wavelength is imposed on the convection pattern, no definite critical Rayleigh number for the onset of these oscillations should be expected.

In LiI, these oscillations are observed over a wide range of R, from 20000 to 100000. At the higher values of R the oscillations become more and more irregular (figure 9). Plots of power spectra of the signals show a distinct peak at low R which is swamped by increasing 'turbulence' as R increases (figure 10).

6. Transient characteristics

Wondering whether states other than the ones obtained by slowly increasing or decreasing the heat flux could be attained through sudden changes, we undertook a series of experiments in which the heat flux was changed abruptly. In each case, whether the heat flux was increased or decreased, the steady-state point on the R *vs.* RNu diagram was on one of the lines already found. Examples of transient paths followed in the R, RNu plane when the heat flux is suddenly increased from zero (figure 11) show that the steady convection state can be passed through, as in the curves labelled 60 and 65. The time required for the experiment to settle down depends greatly on the path followed (figure 12), the slowest response being seen when the fluid almost settles in one state, but goes on changing, finally settling in another (curve labelled 65). The results of suddenly decreasing the heat flux from high values are similar. Quantitative interpretation of these results is difficult because of the severe effect of the thermal capacities of the bounding plates.



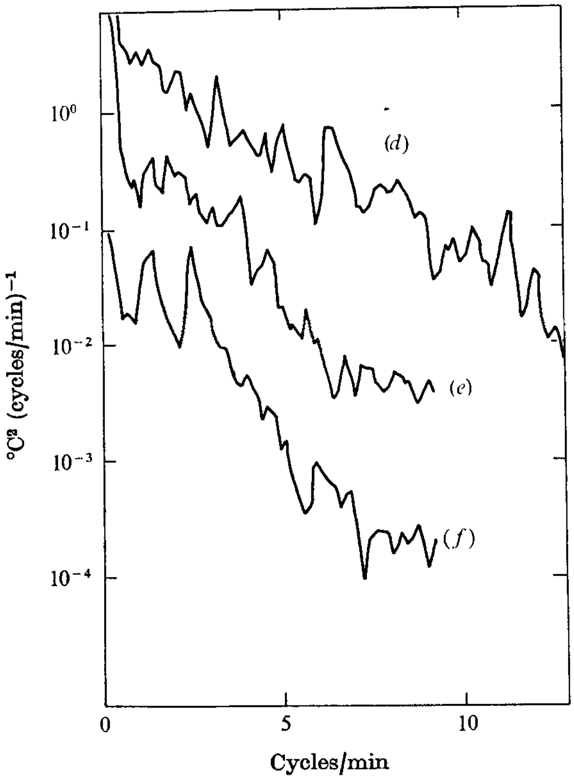


FIGURE 10. Spectra of high frequency oscillations. (*a*) $R = 30700$, $\Delta T = 1{\cdot}777$, $T = 18{\cdot}07$. (*b*) $R = 33500$, $\Delta T = 1{\cdot}277$, $T = 18{\cdot}19$. (*c*) $R = 46600$, $\Delta T = 1{\cdot}720$, $T = 18{\cdot}77$. (*d*) $R = 63000$, $\Delta T = 2{\cdot}243$, $T = 19{\cdot}46$. (*e*) $R = 116000$, $\Delta T = 3{\cdot}700$, $T = 21{\cdot}67$. (*f*) $R = 342500$, $\Delta T = 7{\cdot}85$, $T = 29{\cdot}38$.

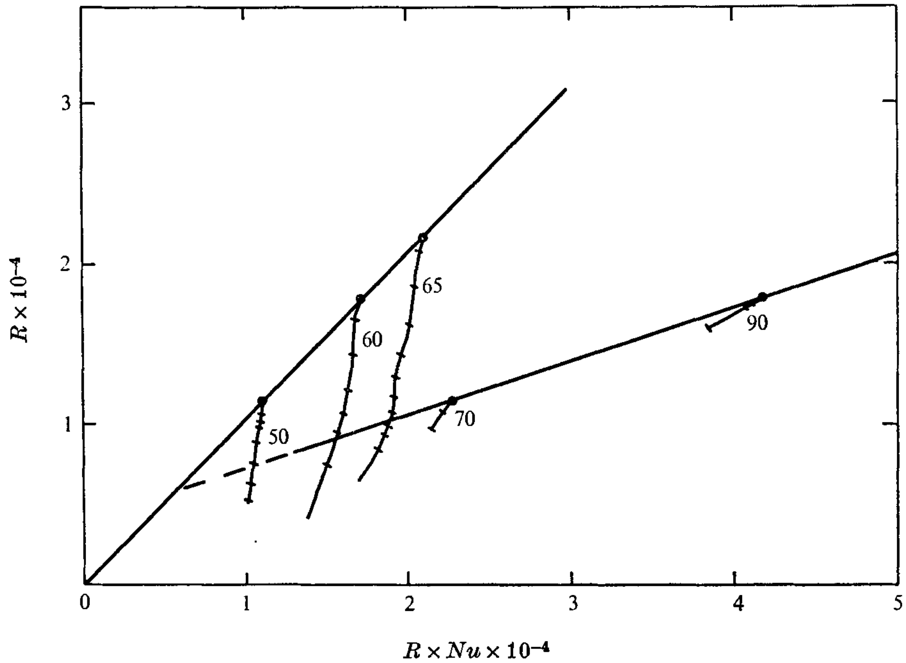


Figure 11. Paths followed when heat flux is increased from zero in one step and equilibrium is sought. Labels denote voltage across heater, and have no significance otherwise.

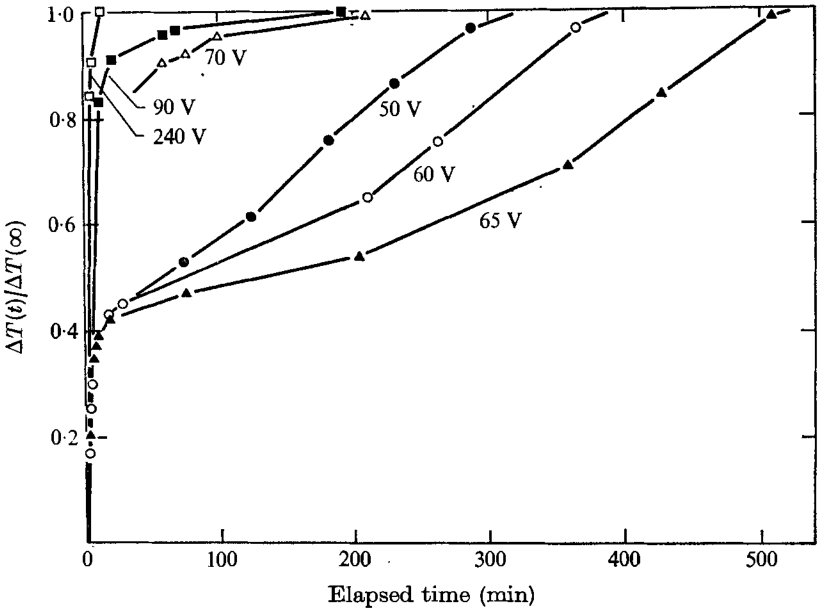


Figure 12. Ratio of temperature difference to its equilibrium value *vs.* time elapsed after a sudden increase in heat flux from zero for various values of heat flux.

7. Conclusions

(*a*) Values of the thermal Rayleigh number as large as 335 000 can be attained in an LiI solution heated from below with no onset of convection.

(*b*) In LiI solutions, no more than two values of the Rayleigh number are found for a given value of the non-dimensionalized heat flux.

(*c*) The value of the Rayleigh number at which an extrapolation of the convective measurements meets the conduction line on the R *vs.* $R\,Nu$ plot (point 5 on figure 1) is far above 1708.

(*d*) The beginning of the region where the Rayleigh number dependence of the Nusselt number can be represented by a power law increases as the mean temperature of the solution is decreased.

(*e*) The exponent in the power law is the same as for pure water, but the 'constant' factor is about 10% lower.

(*f*) The oscillations found are of three types: (i) transient oscillations at the onset of convection predicted by the linear theory; (ii) slow fluctuations at low Rayleigh number which may be either the random motions described by Willis & Deardorff (1967) or the oscillation in the temperature of the bounding plate predicted by Busse (1967); (iii) high frequency oscillations beginning at $R = 20\,000$ whose periods have an $R^{-\frac{2}{3}}$ dependence.

(*g*) Large changes in heat flux produce no states of the system not reached by small slow changes.

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