Biochemistry. — Elastic-viscous oleate systems containing KCl<sup>1</sup>). II.
a) Period and logarithmic decrement as function of the radius of the sphere for a system containing 1,2 % oleate, in 1,52 N KCl + 0,08 N KOH at 15° and 23° C; b) Shear modulus and relaxation time as function of the temperature. By H. G. BUNGENBERG DE JONG and H. J. VAN DEN BERG.

(Communicated at the meeting of December 18, 1948.)

#### 1. Introduction.

The object of the investigations described in the following communication was to obtain insight into the character of the damped oscillations of KCl containing oleate systems <sup>2</sup>). This was possible with the aid of formulae, developed by J. M. BURGERS <sup>3</sup>) on the basis of older work by LAMB, giving the period T and the logarithmic decrement  $\Lambda$  for an elastic medium completely filling a spherical space, performing one of the three types of oscillations, already mentioned in Part I. BURGERS has considered three possible causes of damping:

(a) purely viscous damping; (b) damping through relaxation of elastic tensions, characterized by a single constant relaxation time; (c) damping through slipping along the wall of the vessel.

It is found in all cases that the period is directly proportional to the radius; hence the experimental confirmation of this proportionality (already obtained in Part I for the case of the rotational oscillation) does not allow to distinguish between the three possible causes of damping. Such a distinction, however, can be made when data are available concerning the dependence of the logarithmic decrement  $\Lambda$  on the radius R, as in the case of viscous damping  $\Lambda \sim R^{-1}$ , in the case of relaxation damping  $\Lambda \sim R$ , while in the case of damping through slipping  $\Lambda$  appears to be independent of R.

# 2. Experimental method.

As has been mentioned in preliminary investigations 4) on the elastic behaviour of KCl containing oleate systems, the elastic properties are a function of the KCl concentration, and it was found that in the case of the rotational oscillation the number of visible oscillations n has a maximum for a definite value of the KCl content.

<sup>1)</sup> Part I has appeared in these Proceedings 51, 1197 (1948).

 $<sup>^2)</sup>$  In the execution of the measurements we were assisted by D. VREUGDENHIL, to whom we express our thanks also here.

<sup>&</sup>lt;sup>3</sup>) J. M. BURGERS, these Proceedings 51, 1211 (1948).

<sup>&</sup>lt;sup>4</sup>) H. G. BUNGENBERG DE JONG and G. W. H. M. VAN ALPHEN, Proc. Kon. Ned. Akad. v. Wetensch., Amsterdam, 50, 1227 (1947).

For the present work we have used a concentration, nearly corresponding to this maximum of n, so that the damping was as small as possible. In order to prevent the appearance of auto-sensibilisation as a consequence of hydrolysis, it is necessary to ensure a sufficiently high pH (above 11), for which purpose a small amount of KOH is added <sup>5</sup>).

The solution used was prepared by mixing 4,5 litres of a solution of Na-oleate (90 gr Na-oleinicum pur. pulv. "Merck" 6), dissolved in 4050 cm<sup>3</sup> aqua destillata to which is added afterwards 450 cm<sup>3</sup> KOH 2 N) with 3 litres of KCl 3,8 N. The mixture was thoroughly shaken for an extensive period in order to make it homogeneous, after which it was put into a thermostate at  $15,0^{\circ}$  C for two days, in order to obtain the desired temperature and to get rid of the air content. (In Part I we have already mentioned the disturbances that are caused by the presence of air bubbles).

The measurements were then started; the rotational, the meridional and the quadrantal oscillations were measured on three consecutive days; for details concerning the method applied we refer to Part I. We mention that the experiments with the very large reservoirs (the largest one has a capacity of 6 litres) had to be done outside the thermostate. The vessels were put on the turning table, described in Part I, and found themselves during 20 minutes in air of  $18^{\circ}$  C. The very large volume of these reservoirs and the low rate of heat exchange with the surroundings, combined with the relatively small values of the temperature coefficients of period and damping ratio for this system in the range of temperatures from  $2^{\circ}$  to  $19^{\circ}$  C (see Part I), make this permissible. It will appear that even in the less favourable case of measurements with a solution at a temperature of  $23^{\circ}$  C, the results concerning the functional relation between T and R or between  $\Lambda$  and R for a single type of oscillation still were satisfactory.

It is possible nevertheless that results obtained in this way are less satisfactory when it is desired to make comparisons between the three types of oscillation. There are indications that such comparisons can safely be made only when data are obtained with a vessel completely surrounded by thermostate water.

<sup>&</sup>lt;sup>5</sup>) H. G. BUNGENBERG DE JONG and G. W. H. M. VAN ALPHEN, Proc. Kon. Ned. Akad. v. Wetensch., Amsterdam, 50, 849 (1947).

H. G. BUNGENBERG DE JONG, H. L. BOOIJ and G. G. P. SAUBERT, Protoplasma, 29, 536 (1938).

<sup>&</sup>lt;sup>6</sup>) The concentration of Na-oleate in the final mixture is 1,2% = 0,04 N Na-oleate. Relatively to the large concentration of K-ions (1,60 N) the small concentration of the Na-ions is negligible, so that we may consider our system practically as a K-oleate system.

In principle it might be possible to dissolve oleic acid in KOH, in order to arrive at a system containing exclusively K-ions; actually, however, this procedure proved to be unsatisfactory, which probably must be ascribed to the circumstance that the liquid oleic acid is much more liable to chemical alterations than the solid Na-oleate. Nevertheless also the latter substance gradually changes, even when it is left in its original packing (paraffined bottles, not opened). Pure Na-oleate when shaken must behave as a fine dusty powder. After deterioration it takes the form, first of coarse grains, finally of a compact viscous mass. Compare the first paper mentioned in footnote  $^{5}$ ).

## 3. Period and logarithmic decrement as functions of R. Measurements at 15° C.

Owing to the difficulties inherent in the measurement of the damping ratio, it was necessary to use vessels of large radius. For this purpose it was decided to use Pyrex and Jena "round bottom" vessels, of nominal capacities of 6 litres, 3 litres, 1,5 litres and 750 cm<sup>3</sup>. The actual volumes contained in these vessels till the beginning of the tube-shaped neck were: 6000, 3309, 1738 and 754 cm<sup>3</sup> respectively. Assuming an exact spherical shape, the radii become: 11,27; 9,24; 7,46; 5,65 cm.

TABLE I.Measurements with a 1,2 % oleate system (containing 1,52 N KCl + 0,08 N KOH)<br/>at 15.0° C.

Type of oscillation	<i>R</i> (cm)	n	$10 \times \frac{T}{2}$ (sec)	<i>b</i> 1/ <i>b</i> 3	$\begin{pmatrix} A \\ \left(=2.303\log\frac{b_1}{b_3}\right) \end{pmatrix}$	$10 \times \frac{T}{2}$ corr.	$\begin{pmatrix} \lambda \text{ (sec)} \\ \left(=\frac{T}{2\Lambda}\right) \end{pmatrix}$	G (dynes/cm <sup>2</sup> )
Rotational	11.27 9.24 7.46 5.65 2.33*	$\begin{array}{c} 28.8 \pm 0.1 \\ 32.2 \pm 0.2 \\ 37.5 \pm 0.3 \\ 42.6 \pm 0.2 \\ 47.5 \pm 0.5 \end{array}$	$12.31 \pm 0.020$ $10.09 \pm 0.029$ $8.28 \pm 0.024$ $6.41 \pm 0.015$ $2.44 \pm 0.015$	$\begin{array}{c} 1.702 \pm 0.029 \\ 1.553 \pm 0.026 \\ 1.408 \pm 0.014 \\ 1.352 \pm 0.008 \\ 1.111 \pm 0.003 \end{array}$	$\begin{array}{c} 0.532 \pm 0.017 \\ 0.440 \pm 0.017 \\ 0.342 \pm 0.010 \\ 0.301 \pm 0.006 \\ 0.105 \pm 0.003 \end{array}$	12.27 10.07 8.27 6.40 2.44	2.31 2.29 2.42 2.13 2.32 mean 2.29	44.4 44.3 42.8 41.0 48.0
<b>Me</b> ridional	11.27 9.24 7.46 5.65	$\begin{array}{c} 29.5 \pm 0.3 \\ 33.5 \pm 0.2 \\ 34.0 \pm 0.3 \\ 37.3 \pm 0.3 \end{array}$	$9.39 \pm 0.019$ 7.67 ± 0.018 6.26 ± 0.015 4.74 ± 0.020	$1.440 \pm 0.014 \\ 1.385 \pm 0.023 \\ 1.267 \pm 0.006 \\ 1.207 \pm 0.004$	$\begin{array}{c} 0.365 \pm 0.009 \\ 0.326 \pm 0.016 \\ 0.237 \pm 0.004 \\ 0.188 \pm 0.003 \end{array}$	9.37 7.66 6.26 4.74	2.57 2.35 2.64 2.52 mean 2.52	46.2 46.5 45.4 45.4 45.4
Quadrantal	11.27 9.24 7.46 5.65	$\begin{array}{c} 35.1 \pm 0.3 \\ 40.0 \pm 0.3 \\ 43.3 \pm 0.3 \\ 47.2 \pm 0.3 \end{array}$	$7.87 \pm 0.024$ $6.33 \pm 0.010$ $5.13 \pm 0.016$ $3.89 \pm 0.013$	$1 369 \pm 0.009 \\1.310 \pm 0.012 \\1.231 \pm 0.006 \\1.193 \pm 0.005$	0.314±0.007 0.270±0.009 0.208±0.005 0.176+0.005	7.86 6.32 5.13 3.89	2.50 2.34 mean 2.47 2.21 2.38	44.6 46.4 45.9 45.8

\* In this case an approximately spherical reservoir of  $52,7 \text{ cm}^3$  capacity has been used, immersed in the thermostate of  $15^\circ$  C. The damping ratio could be measured in the case of the rotational oscillation only, as for the other two forms the period of the oscillation was too short.

Table I for the temperature of  $15^{\circ}$  C gives the experimental results concerning: type of oscillation, total number *n* of visible oscillations;  $10 \times T/2$  (*i.e.* the time for 10 turning points, that is 5 complete oscillations); the damping ratio  $b_1/b_3$  calculated from the position of 4 consecutive turning points, read off on the scale of the ocular micrometer 7); and the corrected value of  $10 \times T/2$ , obtained with the aid of the formula

$$T_{\rm corr} = \frac{T}{\sqrt{1 + (\Lambda/2\pi)^2}}$$

<sup>&</sup>lt;sup>7</sup>) The measurements of the period and of the damping ratio are performed with the aid of the telescope of a kathetometer, from a distance of approximately 1 m. The total

The last two columns of the table will be considered later. All data given are averages derived from 10 measurements of n, from 20 measurements of  $10 \times T/2$ , and from 20 measurements of  $b_1/b_3$ . The mean error [calculated from  $\sqrt{\sum \Delta^2/n(n-1)}$ ] has been stated in each case.



Fig. 1, 2 and 3 give the corrected values of  $10 \times T/2$  and the values of  $\Lambda$  in function of the radius R.

It is evident that the period is directly proportional to R, for each of the three types of oscillation. The points are situated so closely to a straight line passing through the origin, that we did not consider it necessary to indicate the mean errors in the diagrams. In the case of the decrement, where the spreading is larger, the errors have been represented. When due regard is given to these errors it is found that also the  $\Lambda$ -points, on the whole, are sufficiently close to a straight line through the origin. In two cases, however, the distance of the points from the line is much larger than the mean error. We must suppose that here some irregularity has occurred, the nature of which is unknown. Nevertheless the general conclusion is allowed that for the system considered both T and  $\Lambda$  are pro-

length of the scale of the ocular micrometer (50 divisions) corresponds to a length of ca. 13 mm in the vessel filled with the oleate solution. The displacements of the air bubbles at first exceed the length of this scale, and measurements of the damping ratio can be carried out only when the amplitude has decreased. According to our notes the length  $b_1$  (distance between the position of the bubbles at the first turning point and their position at the next turning point) ordinarily does not exceed 25 scale divisions, which represents an actual displacement of ca. 6 mm. The deviation from the equilibrium position thus is ca. 3 mm. For the points on which the telescope was focussed compare Part. 1.

portional to R, which proves that the damping in this case must be ascribed to relaxation with a constant relaxation time <sup>8</sup>).



4. Period and logarithmic decrement as functions of R. Measurements at  $23^{\circ}$  C.

With the same oleate system similar measurements were performed at a

<sup>&</sup>lt;sup>8</sup>) The reader must be warned against the idea that this result should apply to all elastic oleate systems. In the next communication we shall encounter a case where the relation between  $\Lambda$  and R is different.

temperature of 23° (two days later). Whereas the measurements described in the preceding section referred to a point on that branch of the  $b_1/b_3$ -temperature curve, which presents the smaller inclination, the higter temperature was chosen so as to give a point on the steep branch of this



curve (compare Part I, fig. 4). The measurements have been executed in a single day, which, however, made it necessary to restrict to the rotational and the meridional types, as measurements with the quadrantal oscillation always are more difficult, in particular at the higher temperature.

The experimental results and the data derived from them are given in Table II.

Type of oscillation	<i>R</i> (cm)	n	$10  imes rac{T}{2}$ (sec)	<i>b</i> 1/ <i>b</i> 3	$\left(=2.303\log\frac{b_1}{b_3}\right)$	$10 \times \frac{T}{2}$ corr.	$\begin{array}{c}\lambda \text{ (sec)}\\\left(=\frac{T}{2\Lambda}\right)\end{array}$	G (dynes/cm²)
Rotational	11.27 9.24 7.46 5.65	$7.1 \pm 0.1 \\ 9.3 \pm 0.3 \\ 12.7 \pm 0.2 \\ 17.0 \pm 0.1$	12.04±0.058* 10.08±0.042* 8.00±0.027 6.13±0.018	$\begin{array}{c} 3.195 \pm 0.098 \\ 2.480 \pm 0.042 \\ 2.311 \pm 0.048 \\ 1.687 \pm 0.032 \end{array}$	$\begin{array}{c} 1.162 \pm 0.031 \\ 0.909 \pm 0.017 \\ 0.838 \pm 0.021 \\ 0.523 \pm 0.019 \end{array}$	11.84 9.98 7.93 6.11	1.02 1.10 mean 0.95 1.17	47.7 45.1 mean 46.6 <b>46.1</b>
Meridional	11.27 9.24 7.46 5.65	$\begin{array}{c} 7.1 \pm 0.1 \\ 10.1 \pm 0.2 \\ 12.9 \pm 0.1 \\ 17.1 \pm 0.1 \end{array}$	9.38±0.060* 7.60±0.038* 6.21±0.017 4.65±0.016	$\begin{array}{c} 2.473 \pm 0.055 \\ 2.047 \pm 0.036 \\ 1.669 \pm 0.032 \\ 1.531 \pm 0.023 \end{array}$	$\begin{array}{c} 0.906 \pm 0.022 \\ 0.717 \pm 0.018 \\ 0.512 \pm 0.019 \\ 0.426 \pm 0.017 \end{array}$	9.28 7.55 6.19 4.64	1.02 1.05 mean 1.21 1.09	47.1 47.9 mean 46.4 <b>47.2</b> 47.4

 TABLE II.

 Measurements with the same system as that of Table I, at 23,0° C.

\* As the number of observable oscillations was too small, we have measured  $5 \times T/2$  instead of  $10 \times T/2$ . The results and the mean errors all have been multiplied by 2.

It will be seen that the mean errors have become larger at the higher temperature, in particular those for the damping.

In figures 4 and 5 the corrected values of  $10 \times T/2$  and the values of  $\Lambda$  have been represented as functions of R.

The experimental points on the whole are again situated on straight lines through the origin, although in the case of  $\Lambda$  the distances of the points from the line sometimes exceed the mean errors. We believe that it is permitted to consider these deviations as the results of unsystematic errors, and conclude that the relations  $T \sim R$ ,  $\Lambda \sim R$  are also valid at 23° C. Hence also at this temperature damping must be asscribed to relaxation with a constant relaxation time. We shall come back to this point in the last section of this paper.

### 5. Coefficients occurring in BURGERS' formulae.

BURGERS has given the following expressions for the period and the logarithmic decrement of an elastic medium, confined in a spherical space and describing oscillations damped through relaxation:

rotational oscillation ...  $T_0 = \frac{2\pi}{4.49} R \sqrt{\frac{\varrho}{G}}$  and  $\Lambda_0 = \frac{\pi}{4.49} R \frac{1}{\lambda} \sqrt{\frac{\varrho}{G}}$ meridional oscillation ...  $T_1 = \frac{2\pi}{5.76} R \sqrt{\frac{\varrho}{G}}$  and  $\Lambda_1 = \frac{\pi}{5.76} R \frac{1}{\lambda} \sqrt{\frac{\varrho}{G}}$ quadrantal oscillation ...  $T_2 = \frac{2\pi}{6.99} R \sqrt{\frac{\varrho}{G}}$  and  $\Lambda_2 = \frac{\pi}{6.99} R \frac{1}{\lambda} \sqrt{\frac{\varrho}{G}}$  in which:

T = period for a complete oscillation in sec R = radius of the spherical vessel in cm  $\varrho =$  density of the elastic medium in gr/cm<sup>3</sup> G = shear modulus in dyne/cm<sup>2</sup>  $\lambda =$  relaxation time in sec.

When these formulae are applied to our oleate system they allow the calculation of the characteristic quantities G and  $\lambda$ , so that it becomes possible to investigate the dependence of these quantities on various parameters (temperature, KCl concentration, oleate concentration etc.).

The formulae give a direct proportionality for T and  $\Lambda$  with R, which has already been confirmed experimentally.

The next point to be considered are the values of the ratios  $T_0/T_1$ ,  $\Lambda_0/\Lambda_1$ ,  $T_0/T_2$ ,  $\Lambda_0/\Lambda_2$ , for which the equations give:

$$T_0/T_1 = \Lambda_0/\Lambda_1 = 5.76/4.49 = 1.283;$$
  
 $T_0/T_2 = \Lambda_0/\Lambda_2 = 6.99/4.49 = 1.557.$ 

The values calculated from the experimental results (Table I) obtained at  $15^{\circ}$  C are given below:

R	$T_{0}/T_{1}$	$\Lambda_0/\Lambda_1$	$T_{0}/T_{2}$	$\Lambda_0/\Lambda_2$	
11.27	1.309	1.458	1.561	1.694	
9.24	1.315 (mean	1.350 mean	1.593 (mean	1.630 mean	
7.46	1.321 (1.324	1.443	1.612 (1.603	1.644 1.668	
5.65	1.350 )	1.601 1.463	1.645 )	1.704	

The mean values of the ratios found experimentally are higher than the theoretical ones: 3 % and 3 % respectively for the period, and 14 % and 7 % respectively for the decrement. It must be kept in mind, however, that, as our primary purpose was to find the relation between T and R, and between  $\Lambda$  and R for a single type of oscillation, the three types have been investigated on consecutive days, so that perhaps the circumstances are not completely identical for the three types.

This supposition is supported by the following data, referring to the experiments (Table II) performed at  $23^{\circ}$  C:

R	$T_0/T_1$		$\Lambda_0/\Lambda_1$		
11.27 9.24 7.46 5.65	1.276 1.322 1.281 1.317	mean 1.299	1.283 1.268 1.637 1.228	mean 1.372 (1.260)	

The measurements from which these numbers have been deduced were performed on a single day, and it will be seen that the difference between the experimental values of the ratios and the theoretical ones is less (1 %

for T, 14 % for  $\Lambda$ ). Amongst the experimental values of  $\Lambda$  there is one which apparently is in error (the value 1.637 for R = 7.46 cm); if this value is omitted, the mean becomes 1.260 (indicated between brackets), which deviates only 2 % from the theoretical value.

A further inspection of the data shows that the differences between the experimental and the theoretical values of the ratios generally increase with decrease of the radius of the vessel. It is possible that the deviation must partly be ascribed to the fact that the vessels, when put on the turning table, found themselves in air of a temperature differing from that inside the fluid. Whilst this circumstance was not of much importance in the investigations on the relation between T and R and that between  $\Lambda$  and R, it has apparently been more harmful in the present case, which requires a higher degree of precision.

We therefore decided to perform new determinations with a single vessel, executing all measurements in one consecutive series, in such a way that heat exchange with the surroundings was excluded. For this purpose we put on the turning table a wide glass cylinder, through which — also during the measurements — passed a constant flow of water of  $15^{\circ}$  C, taken from the thermostate. The vessels, placed on the cork-ring on the bottom of the cylinder (see Part I, fig. 2) found themselves surrounded with this thermostate water to the neck.

The results have been given in Table III.

Type of oscillation	$10  imes rac{T}{2}$ (sec)	<i>b</i> <sub>1</sub> / <i>b</i> <sub>3</sub>	Λ	$10 \times \frac{T}{2}$ corr.(sec)
Rotational Meridional Quadrantal	$\begin{array}{c} 8.10 \pm 0.024 \\ 6.31 \pm 0.014 \\ 5.12 \pm 0.021 \end{array}$	$\begin{array}{c} 1.400 \pm 0.016 \\ 1.302 \pm 0.008 \\ 1.233 \pm 0.0043 \end{array}$	$\begin{array}{c} 0.337 \pm 0.011 \\ 0.264 \pm 0.006 \\ 0.209 \pm 0.003 \end{array}$	$\begin{array}{c} 8.09 \pm 0.024 \\ 6.30 \pm 0.014 \\ 5.12 \pm 0.021 \end{array}$
	$\frac{T_0}{T_1} = \frac{T_0}{T_2} =$	1.28 <b>4</b> 1.580	$\frac{\Lambda_0}{\Lambda_1} = 1.2$ $\frac{\Lambda_0}{\Lambda_2} = 1.6$	77

TABLE III. Determination of T and  $\Lambda$  ratios at 15° C.

It will be seen that in this case, where heat exchange with the surrounding air had been prevented, there is a satisfactory agreement with the theoretical values, in particular for  $T_0/T_1$  and  $\Lambda_0/\Lambda_1$ . The other two quotients,  $T_0/T_2$ ,  $\Lambda_0/\Lambda_2$  still are slightly too high.

In this connection we think it useful to mention some measurements of the ratio  $T_0/T_2$ , performed under conditions which prevented heat exchange with the surroundings, in an earlier part of this research <sup>9</sup>). They refer to an oleate system of slightly different composition; the oscillations

<sup>&</sup>lt;sup>9</sup>) These measurements were made before we knew anything about the theoretical formulae.

were excited with the aid of the pendulum apparatus (see Part I, fig. 3). The vessels were wholly immersed in a thermostate of  $15^{\circ}$  C. The results of four series of measurements have been given in Table IV.

Nominal volume of the spherical vessel in c.c.	$10  imes rac{T_0}{2}$ (sec.)	$10 \times \frac{T_2}{2}$ (sec.)	$T_{0}/T_{2}$
1500	8.64	5.49	1.574
750	7.66	4.87	1.573
750	$7.63 \pm 0.04$	$4.90 \pm 0.02$	1.557
500	$6.48 \pm 0.02$	$4.18 \pm 0.03$	1.550

TABLE IV. Determinations of  $T_0/T_2$  at 15°.

The results for the first two cases (nominal volumes 1500 and 750 cm<sup>3</sup>) are deduced each from ten determinations of  $10 \times T/2$ ; those for the last two cases (nominal volumes 750 and 500 cm<sup>3</sup>)-bave been deduced from 50 and 60 determinations of  $10 \times T/2$  respectively and the mean errors are very small. The values of the ratio  $T_0/T_2$  obtained in these cases (1.550, 1.557) are even nearer to the theoretical value 1.557 than the value 1.580 given in Table III <sup>10</sup>).

Hence judging by the most reliable measurements we come to the conclusion that the experimental values of the ratios  $T_0/T_1$ ,  $T_0/T_2$ ,  $\Lambda_0/\Lambda_1$ ,  $\Lambda_0/\Lambda_2$  are very near to the theoretical ones.

This proves that the theoretical formulae, deduced by BURGERS, are valid for the oleate system to which the measurements refer (1.2 % oleate, with 1.52 N KCl and 0.08 N KOH), and that the elastic behaviour of this system can be described by means of two constants; the shear modulus G and the relaxation time  $\lambda$ .

6. Shear modulus and relaxation time as functions of the temperature.

The values of G and  $\lambda$ , calculated with the aid of BURGERS' formulae, assuming the value  $\varrho = 1.074$  for the density, have been inserted into the last columns of Tables I and II. The overall mean values of these quantities are found to be:

at 15° C: 
$$G = 45.2$$
 dynes/cm<sup>2</sup>;  $\lambda = 2.40$  sec.  
at 23° C:  $G = 46.7$  dynes/cm<sup>2</sup>;  $\lambda = 1.08$  sec.

<sup>&</sup>lt;sup>10</sup>) The value 1.580 has been obtained by using the turning table. It may be that this method of exciting the oscillations is the cause of the abnormal values of  $T_0/T_2$  and in particular of  $\Lambda_0/\Lambda_2$  in Table III. The exact measurement of quantities referring to the quadrantal oscillation is difficult, when it is markedly combined with the rotational oscillation, as the air bubbles describe complicated curves instead of straight lines. It is in particular the determination of  $b_1/b_3$  which is influenced in this way. The application of the pendulum apparatus for exciting the oscillation has the advantage that with a sufficiently strong impulse the rotational oscillation appears to be nearly suppressed, so that the quadrantal oscillation is much better obversable (see Part I, section 6).

Increase of temperature appears to have a small effect on the shear modulus and a much larger effect on the relaxation time.

In view of the remarkable form of the  $b_1/b_3$ -curve, described in Part I, it is of interest to re-calculate the values for the series of experiments considered there, so as to obtain the corresponding values of G and  $\lambda$ . As the values of  $10 \times T/2$  had been determined at temperatures not equal to those to which refer the values of  $b_1/b_3$ , we have drawn smooth curves through the experimental points, from which we have read off the values of the period and of the damping ratio for a series of temperatures (2.5°; 5°; 7.5°, etc.). These values have been collected in Table V and the values calculated for G and  $\lambda$  have been added.



It is again found (compare fig. 6) that there is a slight increase of G with temperature, whereas there is a marked decrease of  $\lambda$ . It is remarkable, however, that the decrease of  $\lambda$  occurs in two stages: the curve exhibits two branches, joining with a relatively sharp bend. Hence there is a definite temperature (19.5° C) at which the behaviour of  $\lambda$  changes in such a way that its temperature coefficient suddenly increases. There is no indication of a similar change in the curve for G.

It seems premature to attempt an interpretation of the course of the curves for G and  $\lambda$  as functions of the temperature. A much more extended

Temp. °C	$10 \times T/2$ (sec.)	<i>b</i> <sub>1</sub> / <i>b</i> <sub>3</sub>	Л	$10 \times T/2$ corr. (sec.)	λ (sec.)	G (dynes/cm <sup>2</sup> )
2.5	5.57	1.170	0,157	5.57	3.57	43.5
5	5.56	1.185	0.170	5.56	3.28	43.7
7.5	5.54	1.195	0.178	5.54	3.11	44.0
10	5.53	1.205	0.186	5.53	2.97	44.2
12.5	5.51	1.215	0.194	5.51	2.83	44.5
15	5.48	1.225	0.203	5.48	2.70	45.0
17.5	5.46	1.235	0.211	5.46	2.59	45.3
19	5.44	1.245	0.219	5.44	2.49	45.6
19.5	5.44	1.250	0.223	5.44	2.44	45.6
20	5.43	1.270	0.239	5.43	2.28	45.8
20.5	5.43	1.295	0.258	5.43	2.10	45.8
21	5.42	1.325	0.281	5.41	1.93	46.2
21.5	5.42	1.365	0.311	5.41	1.74	46.2
22	5.41	1.425	0.354	5.40	1.53	46.3
22.5	5.41	1.550	0.438	5.40	1.23	46.3
23	5.40	1.750	0.559	5.38	0.96	46.7

TABLE V. Shear modulus and relaxation time as functions of the temperature.

material will be necessary, allowing the discussion of the influence of a greater number of parameters.

In the next communication we shall consider the influence of the oleate concentration.

#### Summary of Part II.

1. Measurements of the period and the logarithmic decrement of the rotational, the meridional and the quandrantal oscillations have been executed with an 1.2 % oleate system (containing 1.52 N KCl + 0.08 N KOH), at temperatures of 15° and 23° C. The dependence of these quantities on the radius of the vessel has been investigated.

2. It has been found that both the period and the logarithmic decrement are proportional to the radius of the vessel, which proves that at both temperatures the damping of the elastic oscillations of this oleate system must be ascribed to relaxation of the elastic stresses, characterized by a single and constant relaxation time.

3. Theoretical formulae developed by BURGERS make it possible to calculate the shear modulus and the relaxation time. The shear modulus is only slightly dependent on the temperature:  $G = 45 \text{ dyne/cm}^2$  at  $15^\circ$  and 47 dyne/cm<sup>2</sup> at  $23^\circ$  C. There is a larger change in the relaxation time:  $\lambda = 2.4$  sec at  $15^\circ$  and 1.1 sec at  $23^\circ$  C.

4. Using subscripts 0, 1 and 2 in order to distinguish between quantities referring to the rotational, the meridional and the quadrantal oscillations respectively, it has been found that the experimental values of the ratios  $T_0/T_1$ ,  $\Lambda_0/\Lambda_1$ ,  $T_0/T_2$ ,  $\Lambda_0/\Lambda_2$  are very near to the theoretical values  $T_0/T_1 = \Lambda_0/\Lambda_1 = 1.28$  and  $T_0/T_2 = \Lambda_0/\Lambda_2 = 1.56$ , the differences being of the order 1 or 2 %.

5. Making use of results of experiments already mentioned in Part I, curves have been constructed giving the course of G and  $\lambda$  with the temperature. The shear modulus presents a slight gradual increase with temperature. The relaxation time decreases; the curve exhibits two straight, branches, joining at ca. 19° C with a not very marked bend. Above 20° the temperature coefficient of  $\lambda$  is about 5 or 6 times as large as below 19°.