in our opinion, however, a radical reaction. This radical reaction does not start a chain reaction, as in the case of oxygen.

Summary.

SO$_2$ catalyses the cis-trans-isomerisation of unsaturated fatty acids, such as oleic acid. At somewhat higher temperatures it also catalyses the conjugation of linoleic and linolenic acids.

Both catalytic reactions may be explained by assuming that SO$_2$ forms an addition product, which has the character of a bi-radical. Intramolecular rearrangements and subsequent splitting off of SO$_2$ result in the isomerisations.

When the typical features of this and other isomerisation catalysts are compared, the following differences may be pointed out:

a) In the isomerisation by a heterogeneous catalyst a hydrogen atom is taken away from the molecule and when another hydrogen atom is added to the resultant radical this addition may take place at another carbon atom.

b) In the isomerisation by means of alkali, a OH-group and a H-atom may be added to a double bond, whereupon the OH-group and a hydrogen atom from another carbon atom are removed.

c) In the isomerisation by SO$_2$, a molecule of SO$_2$ is added to the double bond and performs the transfer of a hydrogen atom of one carbon atom of the molecule to another carbon atom.

Chemistry. — *Contribution to the explanation of motory and desintegration phenomena in complex coacervate drops in the electric field.* By L. DE RUITER and H. G. BUNGENBERG DE JONG.

(Communicated at the meeting of September 27, 1947.)

A. Introduction.

In a previous article [1] it was suggested that local changes in the interfacial tension (σ) coacervate-medium might play an essential part in the occurrence of the motory and desintegration phenomena, which have been observed in complex coacervate drops in the electric field and in diffusion fields of substances, which have a swelling or densifying influence on the coacervate.

It was supposed that the assumed σ-changes in the electric field would be due to variations of pH caused by polarisation of the surface of the drops. No immediate data however were available at that time concerning the influence of diverse variable factors on σ.

No more had the postulated pH changes been directly demonstrated.

Some data concerning the value of σ and the influence thereon of mixing proportion and salt concentration in gum arabic (A)-gelatine (G) systems have since been obtained [2].

In the present article some experiments will be mentioned, which were carried out on gum arabic-gelatine systems in order to demonstrate the postulated pH changes. Although we did not succeed therein (which may be due to the fact that we worked with buffered systems), we found indications for the existence of another factor, which may be responsible for the assumed changes of σ, viz. a local shift of the composition of the coacervate in the electric field.

Finally it will be undertaken to give, in the light of these recent data, a more detailed explanation of the phenomena observed in coacervate drops in electric and diffusion fields.

B. Description of phenomena in the electric field.

In our experiments we used systems prepared by mixing 2 % A- and 2 % G sols at 40° C. These stock sols had been buffered with a mixture of sodium acetate and acetic acid at pH 3.7 [3]) and were of the following composition:

> 20 gr. G, resp. A, (airdry)
> 50 cc 0,1 n. sodium acetate
> 50 cc 1 n. acetic acid
> 920 cc dest. water.

[1]) H. G. BUNGENBERG DE JONG and E. G. HOSKAM, Proc. Ned. Akad. v. Wetensch., Amsterdam, 44, 1099 (1941).

[2]) L. DE RUITER and H. G. BUNGENBERG DE JONG, Proc. Kon. Ned. Akad. v. Wetensch., Amsterdam, 50, 836 (1947).

[3]) H. G. BUNGENBERG DE JONG and E. G. HOSKAM, Proc. Ned. Akad. v. Wetensch., Amsterdam, 45, 585 (1942).

Whenever in the following pages a e.g. "70 % A system" is mentioned, a system is meant consisting for 70 % of stock sol 2 % A and for 30 % of stock sol 2 % G.

For every single observation a small quantity of equilibrium liquid in which coacervate drops were suspended was brought on a starched [3a] heated (about 40° C.) glass surface under the microscope. The electric current was applied to the preparation by means of the electrodes mounted on the objective of the microscope, which have been described before [3a]. We used fields ranging from ± 0,5—5 V/cm: the intensity of the current has hardly any effect on the phenomena. In very weak fields only they are less clearly seen, whereas in too strong fields they follow one another so rapidly that accurate observations are impossible.

The phenomena occurring in electrophoretically charged (+ or —) drops in the electric field may be shortly described as follows (in the normal sequence):

1. In alternating fields the originally circular drops become elliptical in form (short axis parallel to direction of field). This is called the BÜCHNER-effect. No other effects of alternating fields have been observed. The BÜCHNER effect occurs in direct current fields as well (see fig. 1—4), but the elliptical form may become more or less irregular, when the effect of movements within the drops is superposed on it (fig. 3).

2. In direct current fields a cloud of small vacuoles originates on one side of the drops, at some distance under their surface. This we called the "coarse vacuolisation". On which side it will occur is determined by the sign of the electrophoretic charge of the drop and the direction of the field (see fig. 1).
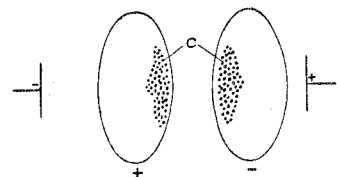

Fig. 1. c = coarse vacuolisation.

3. On the other side of the drop at the extreme periphery a single layer of very small and very closely packed vacuoles is formed, the socalled "peripheral vacuolisation". These vacuoles move as soon as they are formed in the direction of the poles of the drops (i.e. the points where the long axis cuts the surface). At the aequator however the formation of the small vacuoles is continued as long as the layer can be clearly seen (fig. 2, p).

4. In the mean time, on the side where the coarse vacuolisation is found, in the equilibrium liquid outside the drop and at a certain distance from its surface, a number of very small coacervate droplets is formed (fig. 2, a).

3a)   See note 1.

5. During these events a movement of the coarse vacuoles to the inner parts of the drop begins. This movement is fastest at the aequator. The
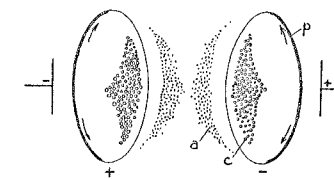

Fig. 2.   a = coacervation in the equilibrium liquid;
c = coarse vacuolisation;
p = peripheral vacuolisation.

movement of the peripheral vacuoles is continued; they pass the poles and begin to move along the opposite surface of the drop. Then however it seems as though they are arrested by the coarse vacuolisation: they turn off and near both poles a small vortex is formed. Often the drops slightly bulge out there (fig. 3). In the meantime the formation of coarse vacuoles has gone on in their original areal, and soon the drop is quite filled up with vacuoles, which makes further observation difficult. The movements slow
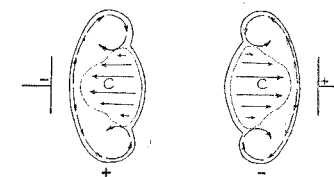

Fig. 3.   Movements of vacuoles in a coacervate drop in the electric field (schematically).
c = coarse vacuolisation.

down and become very irregular. The vacuoles increase in size and number and continually break through to the outside. The regular form of the drop is totally destroyed.

Somewhat different are the phenomena in direct current fields observed in electrophoretically neutral drops (about 48 % A). It is comparatively difficult to realize this case and it was observed only a few times. The most striking phenomenon is that the movements of the coacervate within the drop form a "four-quadrant-system" (fig. 4). Less clear are the vacuolisation processes in this case. In one preparation we initially observed coarse vacuolisation on one side, then, when after a short interruption the
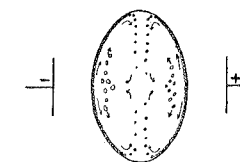

Fig. 4.   Schematical drawing of morphological phenomena in an electrophoretically neutral drop in which vacuolisation of both types was observed on both sides.

current was closed again, on both sides of the drop a peripheral and a coarse vacuolisation (fig. 4). In one case also we observed the formation of small coacervatedrops in the equilibrium liquid on both sides of the drop.

A transport of coarse vacuoles across the drop, parallel to the direction of the field was never observed in electrophoretically neutral drops. In some cases however they showed a slow movement in the direction of the poles (fig. 4).

C. *Observations in the electric field on coacervates coloured with pH indicators.*

These experiments were carried out in order to ascertain whether indeed pH changes occur in the coacervate surface in the electric field. We used the following indicators:

Indicator	pH interval	acid-alkali colour change
Bromophenol blue	3,0—4,6	yellow-blue
Congo red	3,0—5,2	blueish-red
Methyl orange	3,1—4,4	red-yellow

It was necessary to use the indicators in relatively high concentrations, (e.g. 5 cc of a 0.4 % neutralized solution of bromophenol blue in 10 cc of the stock sols) otherwise the difference in intensity of colour between coacervate and equilibrium liquid was insufficient. An inevitable consequence was that the coacervate was slightly vacuolized already at the beginning of the experiment.

The colour differences described hereafter are, in as far as observed through the microscope, although indeniable, never very striking. Favorable light therefore is an essential factor in these experiments. For observation on bromophenol blue and congo red: daylight, for Janus green: light from an ordinary electrical bulb, proved preferable. Of equal importance was the moment chosen for the observation: as soon as vacuolization becomes too intensive, it is very difficult to see the colour differences.

In the experiments with methyl orange no colour change was ever observed in the coacervate drops on closing the current.

Experiments with other indicators and with the dye Janus green (2 cc of 0.1 % solution in 10 cc) gave the following results (see next page).

In several experiments with bromophenol blue it was observed that on reversal of the direction of the field the originally still blue side turns greenish and the other one blue again.

The experiments (see table next page) do prove indeed that in the electric field colour changes occur in the drops, which are determined by the direction of the field and are independent of the electrophoretical charge of the drop. The possibility that this is due to pH changes however is excluded by the fact that bromophenol blue changes to its more acid colour on the

Indicator	Colour of coacervate	Mixing proportion	Elec. troph. charge	Change of colour in coacervate drop at the side of the	
				cathode	anode
Br. ph. Blue	blue	± 1 A : 1 G	—	stays deep blue	turns greenish
		id.	—	,, ,, ,,	,, ,,
		3 A : 7 G	+	,, ,, ,,	,, ,,
		id.	+	,, ,, ,,	,, ,,
		id.	+	,, ,, ,,	,, ,,
		1 A : 2 G	+	,, ,, ,,	,, ,,
		id.	+	,, ,, ,,	,, ,,
		id.	+	,, ,, ,,	,, ,,
		id.	+	,, ,, ,,	,, ,,
		id.	+	,, ,, ,,	,, ,,
		id.	+	,, ,, ,,	,, ,,
		2 A : 1 G	—	,, ,, ,,	,, ,,
		id.	—	,, ,, ,,	,, ,,
		id.	—	,, ,, ,,	,, ,,
		id.	—	,, ,, ,,	,, ,,
Congo red	violet	± 1 A : 1 G	—	turns red.	
		G rich	+	too weakly coloured, no changes.	
		id.	+	no evident change	
		A rich	—	no evident change	
		id.	—	turns slightly reddish purple	dirty blue green *)
Janus green	blue	2 G : 1 A	—	violet	greenish-blue
		2 A : 1 G	—		greenish

*) Very large drop of coacervate.

anodal side of the drop, whereas congo red does the same on the kathodal side of the drop! Moreover methyl orange shows no colour changes at all.

In this connection the following observations are important (see next page):

It is true that the pH of the 2 stock sols is very slightly different, as the buffer can only be used in low concentration [4]. This however cannot be the cause of the observed colour differences: the colour of stock sol G with bromophenol blue does not occur at all in the colour-interval of this indicator.

Besides it was found that addition of great quantities of buffer (i.e. neutralisation of the supposed pH shift) did not in the least reduce the colour difference between the 2 stock sols when coloured with Janus green.

The experiments mentioned above indicate that systems containing gelatine are coloured abnormally by bromophenol blue, congo red and Janus green (which in the case of indicators is generally known as "protein errors" of the indicators).

[4] H. G. BUNGENBERG DE JONG and E. G. HOSKAM, Proc. Ned. Akad. v. Wetensch., Amsterdam, loc. cit. (1942).

Mixing proportion	Indicator	Colour
100 % Stock sol A (pH 3.7)	Br. ph. blue	dirty blue green
100 % Stock sol G (pH 3.7)	id.	clear deep blue
Acetate buffer (pH 3.7)	,,	dirty blue green
1 A : 2 G eq. liquid coacervate *)	,,	clear deep blue
	,,	blue
2 A : 1 G eq. liquid coacervate	,,	greenish
	,,	bleu green
100 % Stock sol A (pH 3.7)	Congo red	blue
100 % Stock sol G (pH 3.7)	id.	clear red
Acetate buffer (pH 3.7)	,,	blue
G rich coacervate	,,	reddish violet
A rich coacervate	,,	violet
100 % Stock sol A (pH 3.7)	Janus green	green blue (electr. light!)
100 % Stock sol G (pH 3.7)	id.	violet
Acetate buffer (pH 3.7)	,,	green blue
G rich coacervate	,,	greenish blue
A rich coacervate	,,	colours **)

*) In these experiments the colour of the coacervates was observed in about 0,2 mm thick layers.

**) These colours are difficult to distinguish.

Now the explanation of the colour changes observed in coacervate drops in the electric field is obvious. It is to be expected that in the electric field a transport of the coacervate components will occur, gelatine molecules moving in the direction of the kathode and gum arabic molecules moving in the direction of the anode. Consequently the kathodal side of the drop will get relatively rich in G, the anodal side relatively rich in A. The observed colour changes are in perfect agreement with this hypothesis: the colour changes on the cathodal side always indicate an increase of the relative quantity of gelatine.

Indicator	Colour at pH 3.7	Colour in Stock sol G.	Colour change in coac. drop on	
			kathodal side	anodal side
Br. ph. blue	blue green	clear deep blue	blue	greenish
Congo red	blue	violet	red purple	greenish blue
Janus green	greenblue	violet	violet	green blue

In consequence of this transport of A and G within the drop in opposite directions, the 2 sides of each drop might become oppositely charged. We did however not yet succeed in demonstrating this directly.

D. *Explanation of the morphological phenomena in coacervate drops in the electric field.*

The experiments which were described above indicate that in a direct current field A—G coacervate drops will become relatively rich in A on the anodal side and relatively rich in G on the kathodal side. Now measurements [5]) of the interfacial tension (σ) coacervate-equilibrium liquid have proved that such changes in the composition of a coacervate will always be accompanied by a change in σ, the direction of which is determined by the fact that σ reaches a maximum value at the optimal mixing proportion (i.e. the mixing proportion at which the coacervate volume is maximal, which nearly coincides with the point at which reversal of charge occurs).

So in the first place it can be stated that the σ changes, postulated before for the explanation of the motory phenomena, will indeed occur, though in consequence of another mechanism than previously assumed. Moreover the observed shifts in colloid composition are responsible for a number of "desintegration" phenomena as will be apparent from the following paragraphs in which the explanation of these phenomena is given as far as possible at the present time.

1. The BÜCHNER effect will probably be due to the accumulation of opposite electrical charges on the surfaces of the drop facing the electrodes, in consequence of differences in conductivity or dielectrical constant between drops and equilibrium liquid [6]). This will cause the deformation. Every deformation of a spherical body increases its area and is therefore opposed by the surface tension. As in our case the deforming energy has a finite value, equilibrium will be reached as soon as these two energies are equal to each other. This agrees with our observations.

2. The origin of the coarse vacuoles may be explained as follows:

In fig. 5 a schematical phase diagram (isotherm) for $A + G + H_2O$ systems is given. The two loops, which are parts of one closed curve, represent the compositions of the coacervates (the big loop) and of the equilibrium liquids (the small loop near the origin) respectively. When we start from a positive coacervate drop (situated at $+$), the change in composition on the kathodal side of the drop will be represented by k (simultaneous increase of G and decrease of A), the change that tends to occur at the anodal side by a (simultaneous decrease of G and increase of A). This vector a is however directed towards the interior of the heterogeneous region, representing two-phase systems.

At the anodal side therefore the system will separate into a smaller quantity of equilibrium liquid and a larger quantity of coacervate, i.e. the coacervate will vacuolise (see fig. 1). No unmixing however will occur

[5]) L. DE RUITER and H. G. BUNGENBERG DE JONG, Proc. Kon. Ned. Akad. v. Wetensch., Amsterdam, 50, 836 (1947), see fig. 4 and 5.

[6]) E. H. BÜCHNER and A. H. H. VAN ROYEN, Kolloid Z. 49, 249 (1929).

on the kathodal side, vector k being directed towards the interior of the homogeneous region.

Similar argumentation for a negatively charged drop (situated at — in fig. 5) leads to the conclusion, that vacuolisation will occur on the kathodal side. This is in full agreement with the experiments (fig. 1).
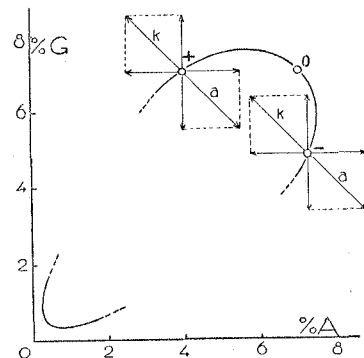

Fig. 5. Schematical representation of a phasediagram for 2 % A—2 % G mixtures. The shift which tends to occur in the composition of positive (+) and negative (—) coacervate drops on the sides facing the kathode (k) and anode (a) respectively has been indicated. The lengths, absolute as well as relative, of the vectors have been arbitrarily chosen and probably exaggerated. It will be clear however that, whatever their real length be, in positive drops vacuolisation will occur at the anodal side, in negative drops at the kathodal side, the corresponding vectors being directed towards the interior of the heterogeneous region.

Moreover fig. 6 gives some indication that in favorable circumstances it will be possible to obtain coarse vacuolisation in electrophoretically neutral drops either at the cathodal or at the anodal side. This will depend on the intensity of the transport within the drop, about which no quantitative data are available. It will be clear however that the observed case in which vacuolisation was seen on both sides at the same time must have
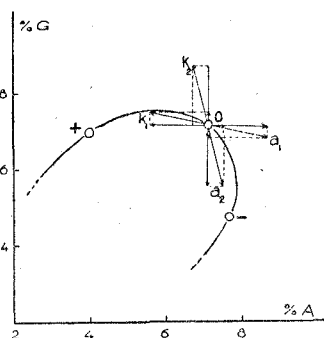

Fig. 6. Schematical representation of the coacervate part of a phasediagram for 2 % A—2 % G mixtures. It is indicated that when the relative and absolute rates of colloid transport within the drop remain within certain limits vacuolisation may occur either at the kathodal or at the anodal side (k_1 and a_2 resp.). In each of these cases however simultaneous vacuolisation on the other side of the drop is impossible, as is indicated by the vectors a_1 and k_2.

been due to the previous treatment of that preparation: on the kathodal side vacuolisation can normally occur only when the transport of A is faster than that of G (fig. 6, k). This however precludes vacuolisation on the anodal side, as therefore it is necessary that the transport of G prevails on that of A (fig. 6, a).

3. At the present time the explanation of the peripheral vacuolisation still offers difficulties, though it may be stressed that it occurs at that side of the drop where in consequence of the disturbance of the equilibrium the coacervate tends to dissolve.

4. The movements of the peripheral vacuoles however can be explained. In fig. 7—9 the relation between the interfacial tension coacervate — equilibrium liquid and the mixing proportion of the colloids (at constant pH) has been represented graphically. It should be noted that the σ values in the present experiments will have been slightly higher than those men-
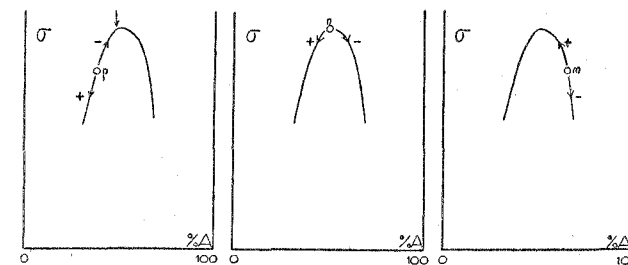

Fig. 7, 8 and 9. Illustrations of the changes in σ on anodal (—) and kathodal (+) side of electrophoretically positive (fig. 7, p.), neutral (fig. 8, n.) and negative (fig. 9, m.) coacervate drops in consequence of changes of composition. The arrow in fig. 7 indicates the point where reversal of charge occurs. (48 % A)

tioned in a previous article [7]), as we worked now with systems in which the Na· concentration of the buffer amounted to 5 maeq. p.l. only instead of 10 maeq. Qualitatively however this has no influence.

In fig. 7, p may represent the interfacial tension of a positive coacervate drop. It is evident that in the electric field σ of this drop will decrease at the cathodal side (fig. 7, +) but increase at the anodal side (fig. 7 ,—) as a consequence of the transport of A and G within the drop.

Now it is a wellknown fact that substances tend to move from places with lower to places with higher interfacial tension. It is therefore to be expected that the coacervate in the surface of a positive drop in the electric field will move from the cathodal side (i.e. the side where the peripheral vacuoles originate) to the anodal side, which is confirmed by the experiments: the peripheral vacuoles are taken along by this current, and also subperipheral layers partake in the same movement.

The movement of the surface of the drop is demonstrated too by a

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[7]) L. DE RUITER and H. G. BUNGENBERG DE JONG, loc. cit.

creeping movement of the drop over its substrate in the direction of the cathode. [8])

In the same way it can be explained that the surface of a negative coacervate drop moves from anodal to cathodal side (see fig. 9 in which m represents a negative drop and $+$ and $-$ the changes on kathodal and anodal side respectively).

5. The formation of a "4-quadrant-system" in an electrophoretically neutral drop can be explained in the same way. Its interfacial tension may be represented by n in fig. 8, as maximal σ and reversal of charge nearly coincide. In this case it is evident that on both cathodal and anodal side σ will decrease, so that on both sides the coacervate will move to the poles of the drop (where σ does not change).

6. Another factor however will influence the movements of the vacuoles. Apart from being moved passively by the currents in the coacervate drop they also move actively in the electric field (as was known already [9])), behaving as though they had an electrical charge of the same sign as the drop in which they are contained. This factor will contribute to the movement of the coarse vacuoles across the drop and to the formation of a vortex near both poles of the drops. In electrophoretically neutral drops the vacuoles will of course also be neutral, so that in this case the movements are exclusively due to changes of σ. It is perfectly clear now that this is the only case in which a movement of coarse vacuoles in the direction of the poles of the drop was to be observed: In electrophoretically charged drops σ is exactly maximal in the region where the coarse vacuoles are formed, so no movement from there to the poles could occur, nor was it ever observed although we paid special attention to it.

7. It also seems to be possible to give an explanation of the formation of small coacervate drops in the equilibrium liquid near bigger coacervate drops in the electric field.

In figure 10, the equilibrium liquids of a positive, a negative and a neutral coacervate have been represented in a phasediagram. The transport of colloids in the electric field through the equilibrium liquid itself will cause in a point near the anodal side of a positive drop a very slight decrease of A and an equally slight increase of G, as the equilibrium liquid contains only very small quantities of colloid in comparison to the coacervate. In the drop itself however a great quantity of A is accumulated on the anodal side, part of which will be solved in the equilibrium liquid. The net result will be a considerable rise of A content in the equilibrium liquid, whereas the percentage G does not or nearly not change. This result is represented

[8]) See note 1.

[9]) H. G. BUNGENBERG DE JONG and W. A. L. DEKKER, Biochem. Z. **221**, 403 (1930).

by a (in fig. 10, $+$) from which can be seen that coacervation will occur in the equilibrium liquid.

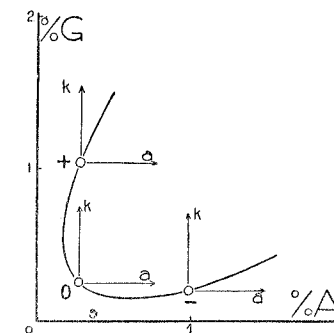For the same reasons on the cathodal side of a positive drop an increase

Fig. 10. Schematical representation of the equilibrium liquid part of a phasediagram for 2 % A—2 % G mixtures. The vectors indicate the changes of composition of the equilibrium liquid that will occur near the kathodal (k) and anodal (a) side of electrophoretically positive, neutral and negative coacervatedrops. The major part of these changes is due to the solution of colloid from the drops into the liquid. The relatively slight changes due to tranport of colloids of the equilibrium liquid have been omitted. The length of the vectors is arbitrarily chosen. It is evident however that in strongly positive and strongly negative systems coacervation can occur only near the anodal resp. kathodal side of the drop, whereas in electrophoretically neutral systems and in those that are near the equivalent mixing proportion, coacervate may be formed in the equilibrium liquid near both surfaces of the coacervate drops.

of G will occur, whereas A is practically not changed. This change may be indicated by k (in figure 10, $+$). Here no coacervation will occur.

Further it is to be expected, that in systems where A is in excess i.e. negative coacervates, coacervation in the equilibrium liquid will occur near the kathodal sides of the coacervate drops (fig. 10, $-$) and finally in neutral coacervates, coacervation in the equilibrium liquid may occur on both sides (fig. 10, 0).

All this is in perfect agreement with the results of our experiment (compare fig. 2).

E. *Phenomena in swelling or densifying media.*

The data we obtained concerning the influence of the salt concentration on the interfacial tension coacervate-medium, are sufficient to confirm in some points the previously given hypothesis, which sought the explanation of motory phenomena in coacervate drops in diffusion fields of swelling or densifying substances in local changes of σ [10]).

In normal gum arabic-gelatine complex coacervates, σ decreases with increasing salt concentration. This agrees with the picture given previously of the movements of vacuoles in coacervate drops (on which NaCl evi-

[10]) H. G. BUNGENBERG DE JONG and E. G. HOSKAM, loc. cit. (1941).

dently had a swelling influence) in a NaCl diffusion field. The assumption is made here that the addition of urea and resorcinol in these experiments did not influence the qualitative behaviour. This appears to be justified by the fact that the presence of these non electrolytes did not qualitatively alter [11]) the general characteristics of the complex coacervation, the latter depending solely on the interaction of the electric charges of both macro-molecular colloids.

Summary.

1. Drops of complex coacervates, suspended in their equilibrium liquids, show a number of morphological phenomena in the electric field. These phenomena are described in greater detail than hitherto published.

2. In a previous article it was supposed that in the explanation of the motory phenomena local changes of the interfacial tension (σ) coacervate medium might play an essential part. It was assumed that these changes of σ would be due to pH changes by polarisation of the surface of the drops. Experiments were therefore carried out in order to demonstrate these pH changes in gum arabic (A)-gelatine (G) coacervates.

3. No changes in pH could be proved, which may be due to the use of buffered stock sols. These experiments however indicated that in the electric field gum arabic is accumulated at the anodal and gelatine at the cathodal side of the drop in consequence of electrophoresis of these components within the drop. As most of the indicators we used in these experiments were found to have "protein errors", on account of which systems rich in G had another colour than those rich in A, these shifts of the mixing proportion on both sides of a drop manifested themselves in slight colour differences of the parts of the drops facing the electrodes.

4. It appears from now available data concerning σ that these changes, and not, as far as is now known, changes in pH, can be held responsible for the σ-variations postulated for the explanation of the motory phenomena.

5. Moreover it is demonstrated that the changes in mixing proportion themselves are also important factors in the explanation of a number of the socalled desintegration phenomena.

6. Starting from the results of these experiments and the data on σ explanations have been given for the greater part of the morphological phenomena that have been described.

Laboratory for Medical Chemistry of the University, Leiden.

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[11]) H. G. BUNGENBERG DE JONG and E. G. HOSKAM, loc. cit. (1942).

Mathematics. — *The Growth-Curve.* By J. W. N. LE HEUX. (Communicated by Prof. A. PANNEKOEK.)

(Communicated at the meeting of October 25, 1947.)

1. In T. BRAILSFORD ROBERTSON's "Chemical basis of Growth and Senescence" (No. 1) the growth $\frac{dN}{dt}$ of an organism N in a time t is given by an equation of the form

$$\frac{dN}{dt} = N(b - aN)$$

where a and b are constants. Introducing the maximum value of $N = \frac{b}{a} = A$, we get

$$\frac{dN}{dt} = aN(A - N) = bN\left(1 - \frac{N}{A}\right)$$

with the solution

$${}^e\log \frac{N}{A - N} = b(t - t_1)$$

or

$$N = A \frac{e^{b(t - t_1)}}{1 + e^{b(t - t_1)}}$$

t_1 is the time, corresponding to $N = 0.5\,A$.

Now, sets of values for N and t being given by experiment and admitting, that the given relation holds true, the most probable values of the constants A, b and t_1, may be calculated by the method of least squares.

In this way and using ordinary logarithms, ROBERTSON finds f.i. the equation

$${}^{10}\log \frac{N}{320 - N} = 0.127\,(t - 1.57)$$

from the following experimental data:

weight of male British infants in ounces

| 148 | 169 | 194 | 219 | 234 | 252 | 269 | 276 | 283 | 300 | 303 | 314 |

time in months

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |

If — as often occurs — only an approximate comparison of theory and observation is required, the constants may be found in a much shorter way by using a graphical method, that will be described in the following lines.