There is, of course, a slight possibility that even a minute trace of impurity might catalyze the reduction of the phthalate. Even if this is the case, it is clear that the most careful methods of purification fail to remove this catalyst and the use of phthalates for hydrogen electrode measurements would be justified only after carefully testing them for freedom from change under continued use.

The authors are indebted to Dr. F. D. Dodge for his kindness in testing the purity of our potassium hydrogen phthalate. Dr. Dodge reported that after carefully examining the products we had purified for both the initial and check experiments, he could detect no impurities and the two samples were identical in being pure potassium hydrogen phthalate.

Summary

1. The most carefully purified phthalate solutions gave a progressive decrease in hydrogen-ion concentration when in continued contact with the hydrogen electrode.

2. This decrease in hydrogen-ion concentration is due to changes in the phthalate itself, probably a reduction reaction.

3. If impurities are responsible for the changes noted, their action must be that of catalysts in the reduction of the phthalate, as they could not possibly be present in sufficient quantity to account for the entire change by themselves.

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[Contribution from the Nela Research Laboratories]

RHYTHMIC DEPOSITION OF PRECIPITATED VAPORS

By Enoch Karrer

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The phenomenon of rhythmic or periodic precipitation and allied phenomena has received considerable attention since Liesegang[1] recorded his observations of it, now referred to frequently as Liesegang's rings or phenomenon. A common illustration of this is the rhythmic precipitation of silver chromate in concentric rings, when a crystal of silver nitrate is placed upon a gelatin film containing some dichromate. The phenomenon may be of importance in geology and is of great importance in biology,[2] where striae so frequently encountered, may be recalled. For example the structure causing iridescence in mother-of-pearl[3] may be referable to this phenomenon as well as that in various insects and beetles

[1] Liesegang, "Chemischer Vorgänge in Gallerten," Leipzig, **1898.**

[2] Liesegang, *Naturw. Wochenschr.*, **41** (1910). Bechhold, "Die Kolloide in Biologie und Medizin," Steinkopff, Leipzig, **1920.**

[3] Pfund [*J. Franklin Inst.*, **183,** 453 (1917)] has recently made a study of the color and structure of mother-of-pearl, concluding that no simple periodic condition of environment can account for it. For further illustration see Bechhold, Ref. 2.

and elsewhere. In the first case calcium carbonate has been periodically precipitated in *Conchliolin.* The structure of the retinal cones has been thus explained and it may also be suggested that the structure of the lens of the eye may be due to this process.

It appears that no adequate theory for this rhythmic precipitation has been presented.

Allied to rhythmic precipitation is the rhythmic stratification of sediment. This has received some attention from several authors, but most recently from Mendenhall and Mason.[4] These authors have shown that in the formation of layers of sediment suspended in water a temperature gradient laterally is essential. The distance between layers depends upon this gradient. They have shown that any two consecutive layers are on the confines of a system of convection currents in the liquid caused by the temperature gradient.

One might expect that the phenomenon would also take place in any two intermixing fluids, or solids, or liquid and fluid, just as in the present instance. Attempts by the author to produce such effects in water-vapor or steam and air in 1916 failed. It was thought that this case might be of interest in the formation of rhythmic or waves of clouds.[5] Experiments were then also made by using vapor such as of ammonia and hydrochloric acid which would enable one to see clearly the process of diffusion.

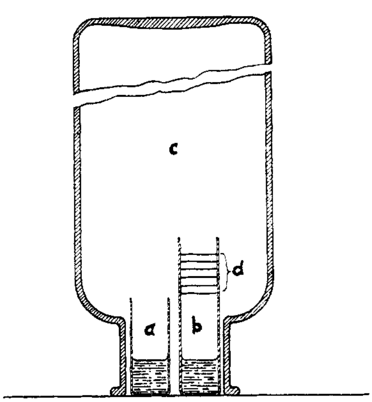

Fig. 1.

I wish now to describe the results of a few experiments which show that under suitable conditions a similar periodic formation will take place quite readily in vapors. The vapors whose behavior in this respect were first accidently noticed are those of hydrochloric acid and ammonia.[6] If small vials (a,b) containing ammonia water and hydrochloric acid respectively are placed in an enclosure C as shown in Fig. 1 there will ensue diffusion of the vapors throughout the enclosure. During the diffusion of the vapor of one vial into the other vial the resulting precipitate will be deposited in a rhythmic manner upon the inner walls of

[4] Mendenhall and Mason, paper read before the annual meeting of the American Academy of Arts and Sciences, **1921.**

[5] The common explanation of these is that due to Helmholtz stating that the precipitation is caused by low temperature of an adjacent region into which the water vapor is carried by ripples in the air.

[6] These vapors, among the best to make the course of convection currents apparent, were used to bring out the dark space around a hot wire. [See *J. Franklin Inst.*, **192,** 737 (**1921**).]

one of the vials as is also indicated in Fig. 1, d. The deposition invariably takes place on the walls of the vial containing the hydrochloric acid. In all cases where I have observed this formation there has been a lateral temperature gradient of rather marked degree, and it appears that this is essential to the process just as Mendenhall and Mason have observed in case of solids suspended in liquids.

The distance between the rings of precipitate depends upon the temperature gradient, and seemingly upon the time interval between the beginning of the diffusion of the vapors into each other and the setting in of the temperature gradient. When the vials are left undisturbed and the external thermal conditions are changed the deposits also change. The rings of the precipitated salt are sharply defined and lie parallel to the surface of the liquid. Under the conditions where the rings were

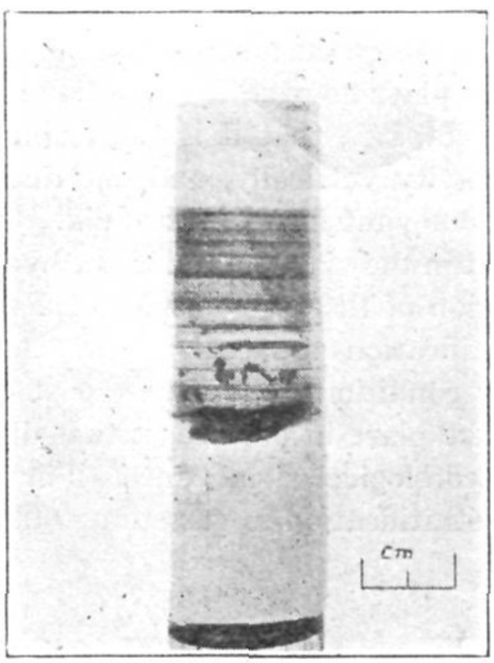

Fig. 2.

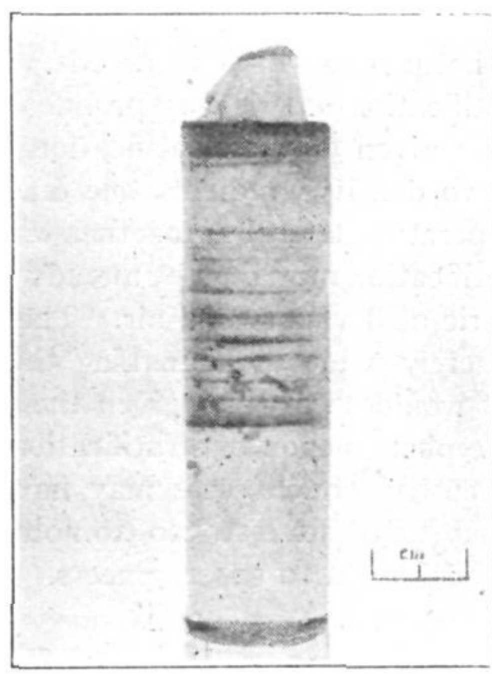

Fig. 3.

first observed, namely, after an intense beam of light had been passing through the enclosure, there were 6 or 8 rings to the centimeter. On other occasions there were more or less than this, the interval ranging from more than a centimeter to a fraction of a millimeter. In one instance the rings were so numerous that they could only with difficulty be distinguished by the unaided eye. In the latter case they formed overnight in vials which had been standing in the window exposed to intense heat of the sun.

The distance between the successive rings is seldom constant (Fig. 1), but increases or decreases gradually from the lowest upward; or, several such systems may appear. Reference has been made to the deposit only as rings upon the inner walls of the vial. These rings have, however, more or less extension radially, and in fact may be complete disks, seen edgewise. In the latter case the rings mark, as it were, cellular partitions in the tube. The uppermost ring in one experiment (Fig. 3) shows such a partitioning film, which instead of remaining horizontal, had become conical after extending beyond the edge of the vial. The convection currents near the mouth of the vial were not horizontal. Within the vial each cell marks the boundaries of a system of vertical and horizontal convection currents, the necessary elements for the formation of which are a lateral temperature gradient and a vertical density gradient.

When these conditions are changed, even after a definite system of rings has formed, the rings will be readjusted, disappearing from the original location to reappear elsewhere; and, after several hours, a new system may have succeeded the old. It required from 6 to 8 hours for a complete system to form, but it is at times noticeable very much sooner than this.

The question may be asked: What part does the ammonia play in the stratification? It is very probable that it plays no part, if the explanation above given of the stratification is correct, *viz.*, that it is the resultant of two density gradients one due to gravity vertically, and one due to temperature laterally, together with the buoyant forces in the fluid. The stratification may then be already present in the vial containing the hydrochloric acid vapors and air. The diffusion of the ammonia into the vial is merely a means of making this stratification apparent.[7]

It would seem that, given the proper conditions, one may expect this same phenomenon of stratification to take place in pure gases that differ in density. Such cases may have meteorological significance. Finally, it may be of interest, too, to note that stratification in gas storage tanks is well known to gas engineers.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF ODESSA UNIVERSITY]

NEGATIVE VISCOSITY

BY ADOLPH I. RABINOVICH

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The phenomenon which has received the wrong name of "negative viscosity" consists in the tendency of certain salts to lessen the viscosity of water, when dissolved in it. If we take the viscosity of water as unity, the viscosity of these solutions will be less than unity, in some cases by 24%, but of course not truly negative.

In non-aqueous solutions the phenomenon of negative viscosity oc-

[7] (Note added March 1, 1922.) It appears that Dr. W. H. Chapin of Oberlin College, in using ammonium chloride and hydrochloric acid vapors to illustrate the laws of diffusion, had also observed and, I am told, exhibited this phenomenon in 1917.