

SELECTIVE ADSORPTION AND DIFFERENTIAL DIFFUSION.

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Owing to the enormous surface they present, colloidal gels exhibit a powerful adsorptive action. In fact, even when percolated through such a relatively coarse grained septum as sand, most solutions issue with a materially reduced content of solute, and benzopurpurin solutions may be thus decolorized. Further, if a solute hydrolyzes into ions having different degrees of adsorbability or different rates of diffusibility, they may be actually separated by diffusion through a colloid gel.

This phenomenon is nicely exhibited by what I term my "patriotic test tube," prepared by filling a tube about two-thirds full with a slightly alkaline solution of agar containing a little potassium ferrocyanide and enough phenolphthalein to turn it pink. After the agar has set to a firm gel, a solution of ferric chloride is carefully poured on top, and even as you watch, the separation becomes evident. The iron forms with the ferrocyanide a slowly advancing band of blue, before which the more rapidly diffusing hydrochloric acid spreads a white band as it discharges the pink of the indicator. After the lapse of a few days the tube is about equally banded in red, white and blue.

Even then the tubes do not cease to be of interest, for if they are allowed to stand several weeks, the pink color is all discharged, and there develop peculiar bands or striations of blue, apparently due to the fact that the iron ferrocyanide temporarily blocks the diffusion passages, which are gradually opened again after a layer of the blue salt has diffused on from the lower surface.

Not only may ions be thus separated, but if two solutes in the same solvent possess different rates of diffusion or different degrees of adsorbability, they also may be separated from each other by diffusion through a colloidal gel or septum.

To illustrate this vividly, I have prepared diffusion drop tests¹ made by dropping mixtures of dyes on blotting paper. The colors possessing the greater diffusibility through the paper, naturally form an outer ring. The degree of diffusibility is of course influenced by the purity of the dyes, their selective adsorption by the paper, and by the precipitative or coagulative action of the dyes on each other. Thus, with mixtures of auramin and eosin, the outer ring may be pink or yellow depending upon the proportions used. Further the results given below apply to the particular paper used; they may vary with other kinds of paper, and would undoubtedly be entirely different with sheets composed of wool, silk, or other adsorptive

¹ These experiments are simply illustrative. The strip diffusion method as described by Goppelsroeder, must of course be used for accurate work. See F. Goppelsroeder, *Kolloid-Z.*, 4, 23 (1909).

material. For comparison I also give the results obtained with the un-mixed dyes. One per cent. solutions were used, and these were mixed in the proportions indicated. The measurements give the diameters of the rings as closely as possible, for sometimes the rings blend into each other

UNMIXED COLORS.			
Color.	Inner ring.	Outer ring.	Water ring.
1 Soluble Prussian blue.....	8.0 mm. lighter	10.5 mm. darker	17.0 mm.
2 Methylene blue.....	9.0 mm.	slightly larger	15.0 mm.
3 Auramin O.....	10.0 mm.	same	15.5 mm.
4 Rhodamin 5 G.....	7.0 mm. lighter	10.0 mm. darker	16.5 mm.
5 Eosin B B Extra.....	8.0 mm. darker	15.0 lighter	17.5 mm.
6 Uranin.....	9.0 mm.	16.0 mm.	17.0 mm.
7 Benzopurpurin.....	7.0 mm.	9.0 mm.	15.0 mm.
8 Congo Red.....	10.0 mm.	same	16.0 mm.

MIXTURES OF TWO COLORS (SHOWING 2 COLOR RINGS).			
Mixture.	Inner ring.	Outer ring.	Water ring.
50% ⁰ -2 } 50% ⁰ -3 }	10.0 mm. dark green	11.0 mm. slightly larger yellow	17.0 mm.
80% ⁰ -2 } 20% ⁰ -3 }	10.5 mm. blue	12.0 mm. slightly larger green	17.5 mm.
20% ⁰ -2 } 80% ⁰ -3 }	9.5 mm. light green	12.0 mm. slightly larger yellow	16.0 mm.
50% ⁰ -3 } 50% ⁰ -5 }	7.0 mm. mottled red	11.0 mm. pink	16.5 mm.
80% ⁰ -3 } 20% ⁰ -5 }	8.0 mm. yellow mottled with red	12.0 mm. yellow	17.0 mm.
20% ⁰ -3 } 80% ⁰ -5 }	8.0 slightly mottled red	14.5 mm. deep pink	17.0 mm.
50% ⁰ -3 } 50% ⁰ -8 }	6.5 mm. deep red	8.0 mm. faint yellow	16.0 mm.
80% ⁰ -3 } 20% ⁰ -8 }	6.5 mm. mottled red	10.0 mm. bright yellow	14.0 mm.
20% ⁰ -3 } 80% ⁰ -8 }	7.0 mm. dark red	9.5 mm. lighter red	15.5 mm.
50% ⁰ -2 } 50% ⁰ -6 }	11.0 mm. bluish green	14.5 mm. yellow	18.0 mm.
80% ⁰ -2 } 20% ⁰ -6 }	11.0 mm. blue	14.5 mm. light yellow	18.0 mm.
20% ⁰ -2 } 80% ⁰ -6 }	11.0 mm. pale green	15.0 mm. dark yellow	17.5 mm.
50% ⁰ -6 } 50% ⁰ -7 }	8.0 mm. red	15.5 mm. yellow	17.0 mm.
80% ⁰ -6 } 20% ⁰ -7 }	9.0 mm. light red	15.0 mm. yellow	17.0 mm.
20% ⁰ -6 } 80% ⁰ -7 }	9.0 mm. dark red	13.5 mm. light yellow	17.5 mm.

MIXTURES OF TWO COLORS¹ (SHOWING 3 COLOR RINGS).

Mixture.	Inner ring.	Middle ring.	Outer ring.	Water ring.
50% _c -5 50% _c -6	9.0 mm. bluish red	13.0 mm. reddish	15.0 mm. yellow	17.0 mm.
80% _c -5 20% _c -6	9.0 mm. blue pink	14.5 mm. pink	15.5 mm. faint yellow	17.0 mm.
20% _c -5 80% _c -6	9.0 mm. brownish pink	12.5 mm. pinkish yellow	16.0 mm. yellow	18.0 mm.
50% _c -1 50% _c -5	9.0 mm. bluish pink	11.0 mm. blue	13.0 mm. pink	16.0 mm.
80% _c -1 20% _c -5	7.5 mm. pinkish blue	9.0 mm. blue	12.0 mm. faint pink	16.0 mm.
90% _c -1 10% _c -5	8.0 mm. pinkish blue	10.0 mm. blue	12.0 mm. faint pink	16.0 mm.

MIXTURES OF THREE COLORS.

Mixture.	Inner ring	Middle ring	Outer ring	Water ring
1/3-2	7.0 mm. black	9.0 mm. green	10.5 mm. yellow	16.0 mm.
1/3-3	8.0 mm. mottled black	10.5 mm. dirty green	12.5 mm. faint yellow	18.0 mm.
1/3-5	8.0 mm. dark violet	12.0 mm. light violet	14.0 mm. pinkish orange	17.0 mm. yellow
1/3-6	19.0 mm.			

almost imperceptibly, and there are often secondary rings, some of which have been measured.²

The action of selective adsorption and differential diffusion in effecting secretion and excretion must be at once manifest. Easily hydrolyzable compounds may be thus split up in the body, and yield secretions of acid nature like the gastric juice, or of alkaline nature like the pancreatic juice, depending upon the structure of the organ, the location of its cavity and of its afferent and efferent vessels. Individual compounds in the blood stream or other body juices, may also be selectively diffused out, concentrated, or separated from other accompanying substances. By selective adsorption, circulating substances may be fixed and taken from the circulation; in fact poisons are usually taken up selectively by certain organs or tissues. An antitoxin introduced into the blood stream may act by adsorbing or coagulating the toxin. Thus, some years ago I ob-

¹ Possibly some of these colors were mixtures.

² The reverse side of the blotting paper shows pictures which sometimes vary materially from those above described.

served in the ultramicroscope the mutual coagulation of tetanus toxin by tetanus antitoxin, and of diphtheria toxin by diphtheria antitoxin. All four substances showed fields with actively moving ultramicros, and the coagulations were instantaneous and striking. However, tetanus toxin was not precipitated by diphtheria antitoxin, nor was diphtheria toxin precipitated by tetanus antitoxin. It seems to me that the presence of antibodies in a person's serum might be thus tested ultramicroscopically, just as the presence of typhoid antibodies may be demonstrated microscopically in the Widal test. This can be readily proven by those in position to make the experiments.

In plants differential diffusion and selective adsorption seem to be intimately bound up with growth and the circulation of the sap. The plant tissues are mainly colloidal gels or finely integrated structures, and as the sap circulates or diffuses through them, each tissue selectively adsorbs and elaborates certain particular constituents. Thus with the potato and tapioca plants the starch-forming substances are fixed in the roots; with the sago palm, they are fixed in the stem pith; and with cereal grains, in the seeds. As long as the adsorptive tissues are unsaturated or are multiplied, so long can growth continue, the stem and branches taking up the substances required for the upward growth, and the root taking up those required for the downward growth. As Jacques Loeb has recently shown, in the case of *Bryophyllum calycinum*,¹ each leaf seems to send into the sap, substances (or hormones) which are "root-forming" and substances (or hormones) which are "shoot-forming;" the former have a tendency to collect at the lower side of a horizontally suspended stem, and seem to be associated or identical with the substances causing the growth of the cortex on the lower side of the stem, to which geotropic curvature is due. Apical leaves favor geotropic curvature and root formation, while basal leaves have a much less or even a negative influence. Apparently then other forces than gravity are at work, and there seems to be a selective adsorption of "root-forming" substances by the more basal tissues. A piece of stem of *Bryophyllum*, containing four to seven nodes (but minus the two top nodes) will form roots at the two most basal nodes (and sometimes also at the basal surface) and new shoots at the two most apical nodes, the process being facilitated greatly by the presence of leaves on the stem. The upper parts of the plant seem, therefore, to absorb "shoot-forming" substances selectively.

Adsorption and diffusion are phenomena that lie in the colloidal zone which imperceptibly blends into the physical on the one hand and into the chemical on the other. The dimensions involved approximate the so-called radius of molecular attraction ($\rho = 50 \mu\mu$) so that the force of surface tension, capillarity, electric charge, colloidal protection and the

¹ *Science*, N. S., 44, p. 210.

like, are all influenced by chemical forces. Indeed, before substances can unite chemically, their particles must be brought first into proper subdivision and proximity, by solution, fusion, ionization, or even by mere pressure as has been demonstrated by W. Spring, who caused fine dry powders to combine by high pressure.

If the degree of subdivision is not profound enough to permit of the combination of isolated atoms or ions with each other, chemical combination in the strict sense may not occur, but there may be produced "adsorption compounds" resulting from the union of atomic or ionic mobs in indefinite or non-stoichiometric proportions, under the influence of more or less modified chemical forces.

On the other hand, if the degree of subdivision proceeds far enough, real chemical reactions may occur and be rendered irreversible by the diffusion or adsorption of one or more of the products into a surrounding colloidal sol or gel. When we consider the great variety of bio-colloids and their susceptibility to changes of structure and diffusive or adsorptive capacity, we can easily understand the almost infinite number of reactions that may go on within their recesses, as they swing the balance of the law of mass action over particles reduced to a reactive degree of subdivision. And we must not be surprised to see technical processes develop upon the basis of these principles.

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THE NITRATION PRODUCTS OF TETRACHLOROFLUORAN AND SOME OF THEIR DERIVATIVES.

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Tetrachlorofluoran.—This compound, first made by Orndorff and Black,¹ is analogous in every respect to fluoran and is formed as a by-product in the preparation of phenoltetrachlorophthalein. The tetrachlorophthalic acid residue enters the two phenol molecules in the *o*-positions to the hydroxyl groups, and at the same time, the hydroxyl groups lose a molecule of water. Tetrachlorofluoran is formed in the condensation of phenol and tetrachlorophthalic acid with sulfuric acid to the extent of about ten per cent. of the calculated amount.²

The tetrachlorofluoran was purified by boiling it several times with a 5% aqueous solution of sodium hydroxide, filtering and washing thoroughly with hot water until the wash water passed through colorless. This process was repeated until on boiling with the sodium hydroxide solution, only a faint purple color resulted; that is, until practically all

¹ *Am. Chem. J.*, 41, 366 (1909).

² THIS JOURNAL, 38, 2487 (1916).