

Rockefeller University

Digital Commons @ RU

Collection of Reprints by Jacques Loeb

Special Collections

7-20-1920

Ionic Radius and Ionic Efficiency

Jacques Loeb

Follow this and additional works at: <https://digitalcommons.rockefeller.edu/collection-of-reprints-loeb>

IONIC RADIUS AND IONIC EFFICIENCY.

By JACQUES LOEB.

(From the Laboratories of The Rockefeller Institute for Medical Research.)

(Received for publication, May 4, 1920.)

I. INTRODUCTION.

When pure water is separated from solutions of electrolytes of not too high a concentration (generally below $m/4$) by a collodion membrane, the initial rate of diffusion of water through the membrane from the side of pure water to that of the solution is influenced in a characteristic way by ions and the following rules have been found to govern this influence.

1. Ions possessing the same sign of electrical charge as the membrane increase and ions with the opposite sign of charge diminish the initial rate of diffusion of water.

2. The relative influence of the oppositely charged ions is not the same for all concentrations. In the lowest concentrations of electrolytes the influence of the ions with the same sign of charge prevails, increasing at first with increasing concentration of the electrolyte until a maximum is reached; a further increase in concentration diminishes the rate of diffusion of water into the solution and the more so the higher the concentration of electrolyte. The turning point varies for different electrolytes but seems to lie for a number of neutral solutions at about $m/256$ or above.

3. The influence of ions on the initial rate of diffusion of water from the side of pure water through the membrane into the solution increases with their valency and with a second constitutional quantity which in the earlier papers I designated arbitrarily as the radius of the ions.

It will be shown in this paper that the second constitutional quantity seems indeed to be, for monatomic and monovalent ions, the radius of the ion and that the rule connecting the efficiency of ions with

their radius is as follows: *The efficiency of anions increases directly and that of cations inversely with the radius of the ion.* By radius of the ion we mean the distance between the positive nucleus of an ion and its outermost ring or shell of electrons. This term has a definite meaning in the case of monatomic ions.

The method of experimentation is the same as in the preceding publications. The solution of the electrolyte was put into collodion flasks of about 50 cc. content, which had previously been filled over night with a 1 per cent gelatin solution. The gelatin solution was then carefully washed out with warm water. The membrane retained on its inside a very thin film (probably of only one molecule in thickness) of gelatin. This was done to enable us to reverse the sign of charge of the membrane with dilute acid; when the hydrogen ion concentration is below $2 \times 10^{-5} N$ the membrane is negatively (and the watery phase positively) charged; while when the hydrogen ion concentration is above this value the membrane assumes a positive and the water a negative charge. The membranes used in the experiments to be described had therefore all been treated with gelatin.

The collodion flask was closed with a rubber stopper, through which a glass tube with a bore of about 2 mm. in diameter was pushed inside the flask. The latter was filled with the solution of electrolyte and suspended in a beaker with distilled water having the same hydrogen ion concentration as the solution of electrolyte. The glass tube served as a manometer to indicate the rate at which water diffused from pure water into the solution through the collodion membrane. The temperature was kept constant at 24°C. We shall treat the influence of ions on negatively and positively charged membranes separately.

II. Negatively Charged Membranes.

When an electrical double layer is formed at the boundary of a collodion membrane (previously treated with gelatin as described) the membrane assumes a negative and the watery phase a positive charge as long as the hydrogen ion concentration is below $2 \times 10^{-5} N$ and no trivalent or tetravalent cations are present. If the hydrogen ion concentration exceeds $2 \times 10^{-5} N$ and becomes $10^{-4} N$ the sign of charge on the two layers is reversed. This was proved by experi-

ments on electrical endosmose.¹ We will first describe experiments in which the membrane is negatively and the watery phase positively charged.

We have shown in a previous paper that anions accelerate and cations depress the rate of diffusion of water through negatively charged membranes.² Fig. 1 shows the relative influence of the anions of three potassium salts, KCl, KBr, and KI on the rate of diffusion of water through collodion membranes. The ordinates

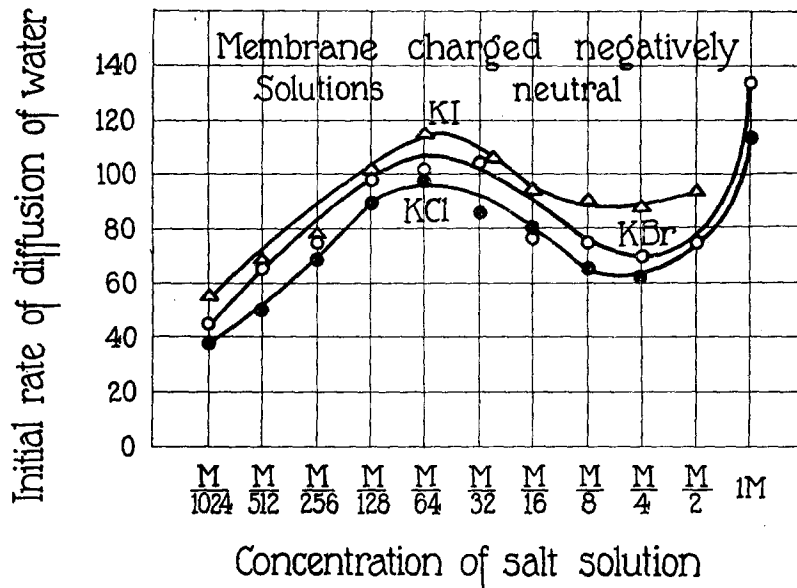


FIG. 1. The rate of diffusion of water through a negatively charged membrane (from the side of pure water to solution) and the density of the charge of the latter are increased by monovalent, monatomic anions in the order $I > Br > Cl$. Solutions almost neutral (pH about 6.0).

indicate the rise of liquid in the manometer in 20 minutes; the abscissæ indicate the concentration of the solution. The salt solutions as well as the pure water separated from the solution by the collodion membrane were almost neutral, having a hydrogen ion concentration of about 10^{-6} N. It is obvious that the accelerating influence of

¹ Loeb, J., *J. Gen. Physiol.*, 1919-20, ii, 577.

² Loeb, J., *J. Gen. Physiol.*, 1919-20, ii, 173.

anions on the rate of diffusion of water from pure water into the solution through a negatively charged membrane increases in the order $I > Br > Cl$, the accelerating influence of the I ion being the greatest.

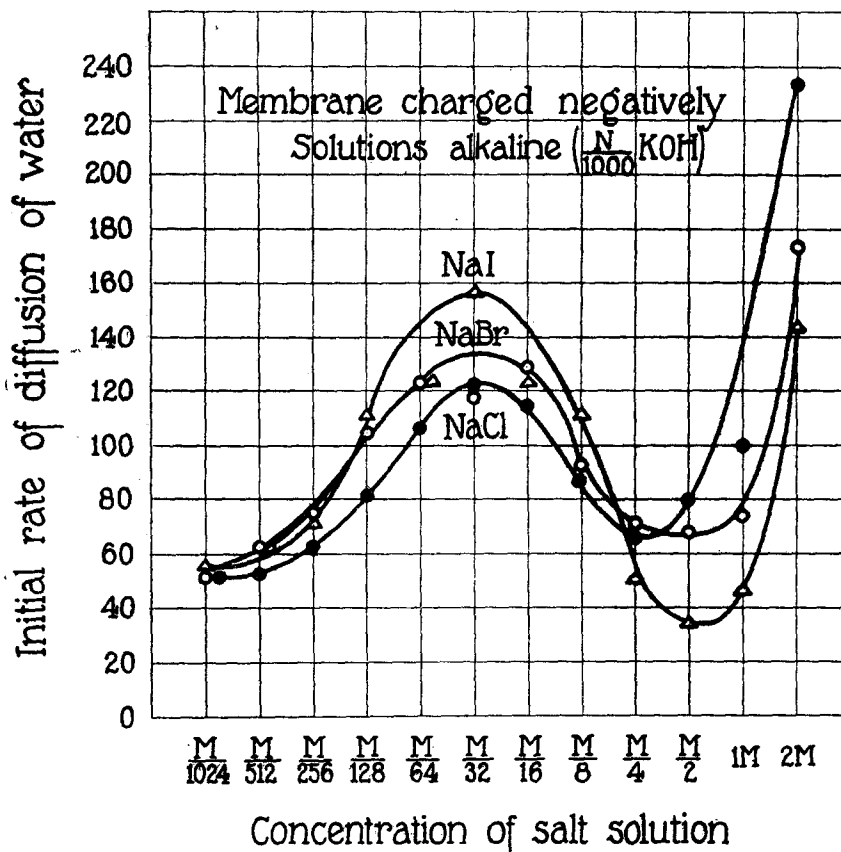


FIG. 2. The same as Fig. 1 except that the solutions and water are alkaline (pH about 11.0).

The same is true when the solution is more alkaline. Thus in Fig. 2 NaCl, NaBr, and NaI were dissolved in a $n/1,000$ solution of KOH instead of in pure water and the outside solution was $n/1,000$ KOH. The sign of charge of the membrane remained negative, however, and therefore the relative efficiency of the three anions

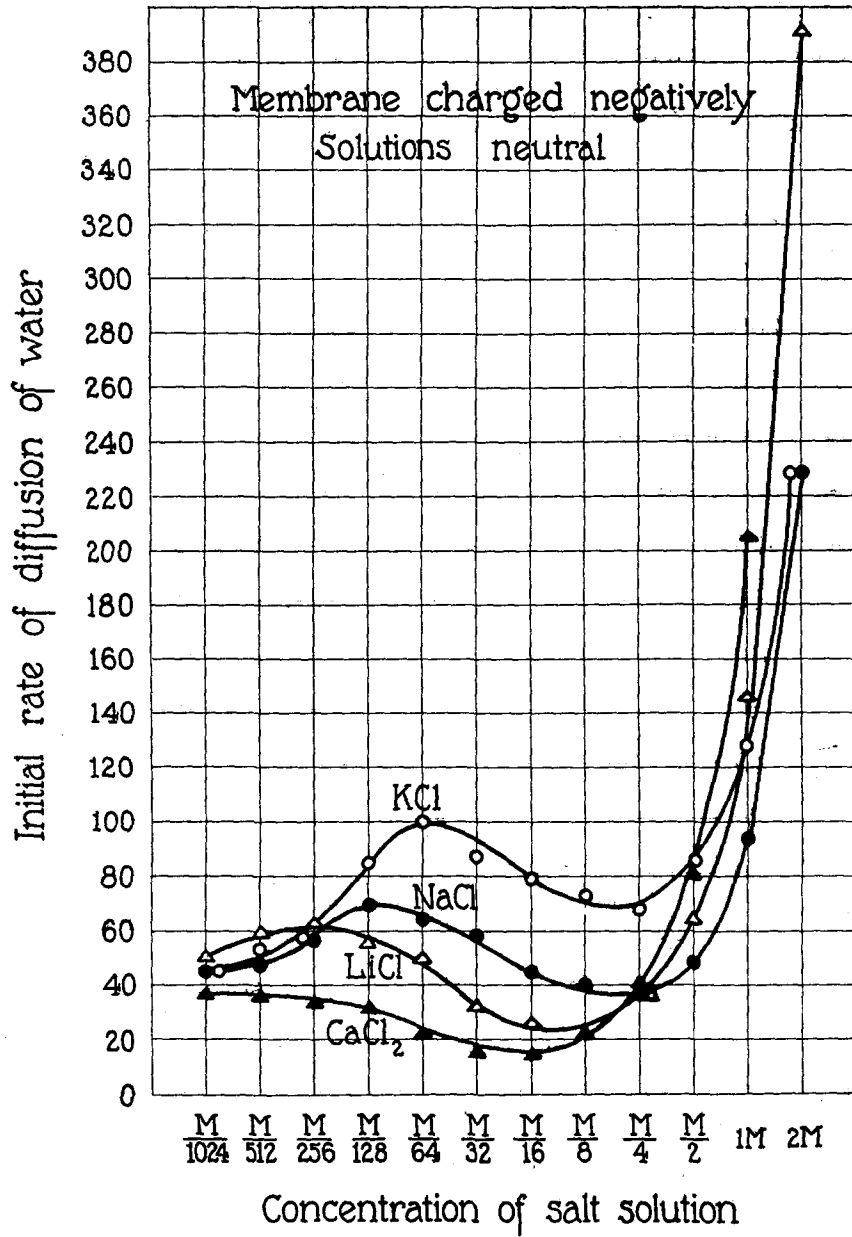


FIG. 3. The rate of diffusion of water through a negatively charged membrane and the density of charge of the latter are depressed by monovalent, monatomic cations in the order Li > Na > K. Solutions neutral (pH about 6.0).

remained the same. The rate of diffusion of water was greater in the case of solutions of NaI than in the case of NaBr, and greater in NaBr than in NaCl. Hence the statement is confirmed that when a membrane is negatively charged the rate of diffusion of water

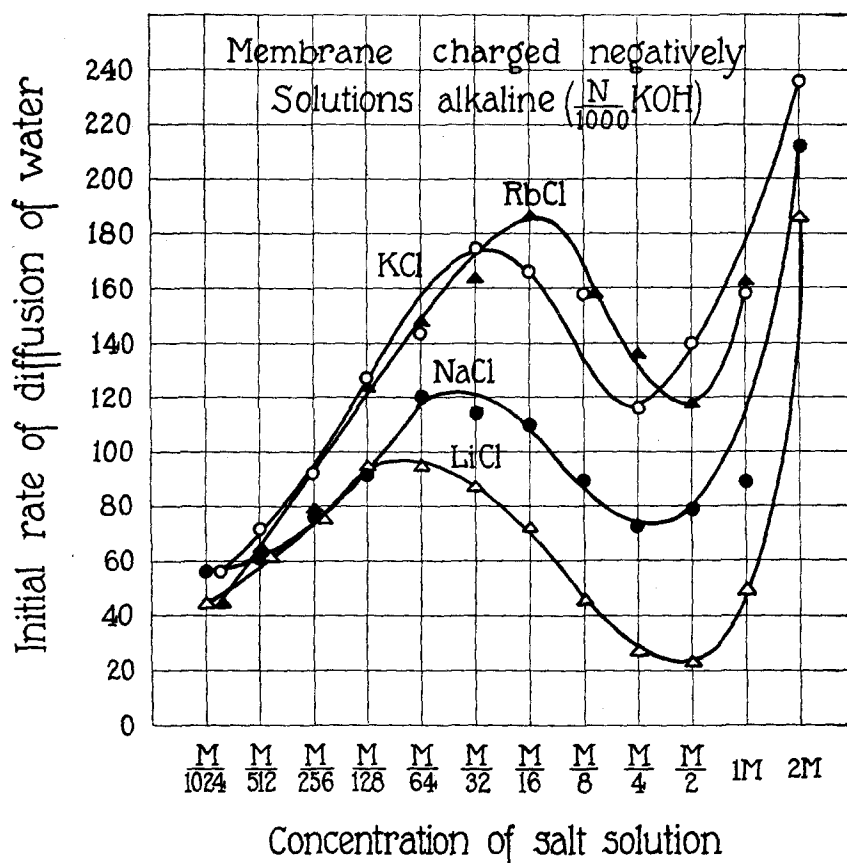


FIG. 4. The same as in Fig. 3 when solutions are alkaline (pH about 11.0). Order of depressing action of cations on negatively charged membrane $\text{Li} > \text{Na} > \text{K} > \text{Rb}$.

through the membrane from pure water into solution increases for the anions I, Br, and Cl in the order $\text{I} > \text{Br} > \text{Cl}$.

Since this is also the order of the magnitude of the ionic radius of the three anions, I having the greatest radius, we can say that the

accelerating effect of monatomic, monovalent anions upon the rate of diffusion of positively charged water through negatively charged membranes from the side of pure water to the side of the salt solution increases directly with the order of magnitude of the radius of the anion.

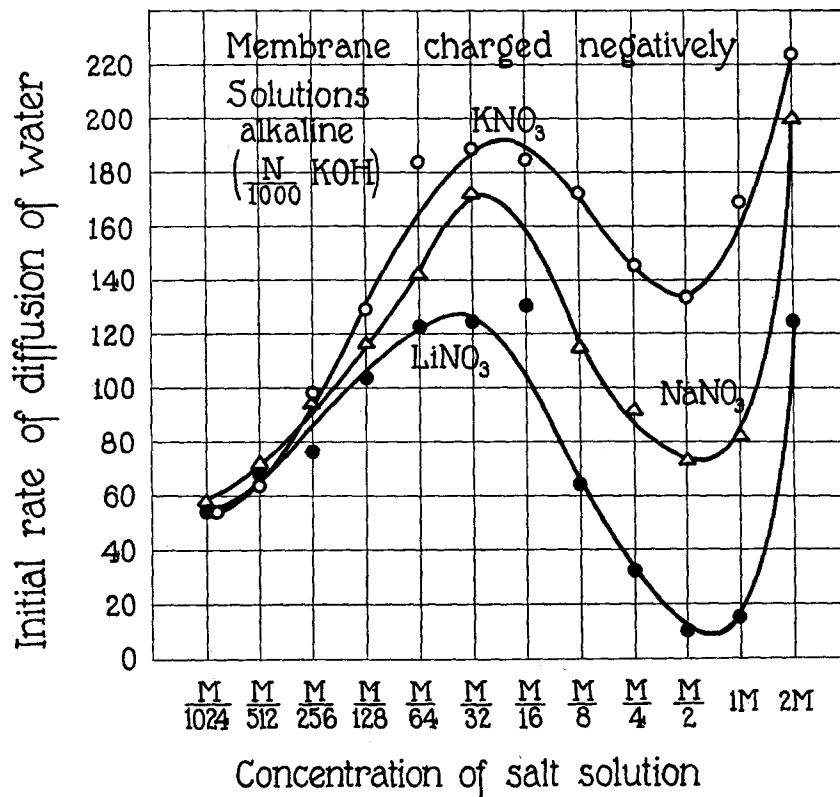


FIG. 5. The depressing order of cations upon negatively charged membranes is the same for NO₃ as for Cl (Fig. 4). Solutions alkaline, order of depressing effect Li > Na > K.

The same relative order of efficiency for the three anions was found also when they were in combination with Li.

While the anions increase the rate of diffusion of positively charged water through a negatively charged membrane cations diminish it and the question arises in what order the depressing effect of the

monovalent cations increases. Fig. 3 shows that in the case of monovalent cations the depressing effect is least in the case of K, and increases in the following order, $K < Na < Li$.

In these experiments the solutions were almost neutral (hydrogen ion concentration about $10^{-6} N$). The order of efficiency of the cations remains the same when the solutions of these salts are made up in $N/1,000$ KOH and when the distilled water in the outside solution is replaced by $N/1,000$ KOH; since in this case the membrane is also negatively and the water positively charged. Fig. 4 shows that the depressing effect of the monovalent, monatomic cations increases in the order $Rb < K < Na < Li$, where the depressing effect is least in the case of Rb, and greatest in the case of Li. This order of the depressing influence of cations is independent of the anion used as long as the anion is always the same for the different cations used. Thus Fig. 5 shows the same order of the depressing action of cations for nitrates as in Fig. 4 in the case of the chlorides.

Since this is also the order in which the ionic radius of the four ions diminishes (Rb having the greatest ionic radius) we can make the following statement.

The depressing effect of monatomic, monovalent cations on the rate of diffusion of positively charged water through a negatively charged collodion membrane from the side of pure water to the side of the salt solution increases inversely with the order of magnitude of the radius of the cation.

III. Positively Charged Membranes.

It has been shown in preceding publications that when the membrane is positively and the water negatively charged the cations increase and the anions diminish the rate of diffusion of water from the side of pure water through the membrane into the solution. In order to make a membrane, previously treated with gelatin, positively and the watery phase of the double layer negatively charged it is necessary to give the water and the solutions a hydrogen ion concentration of about $10^{-4} N$ or above. We made the solution acid by dissolving the salts in $10^{-3} N$ HNO_3 and the distilled water outside the collodion bag was also replaced by $10^{-3} N$ HNO_3 . The hydrogen

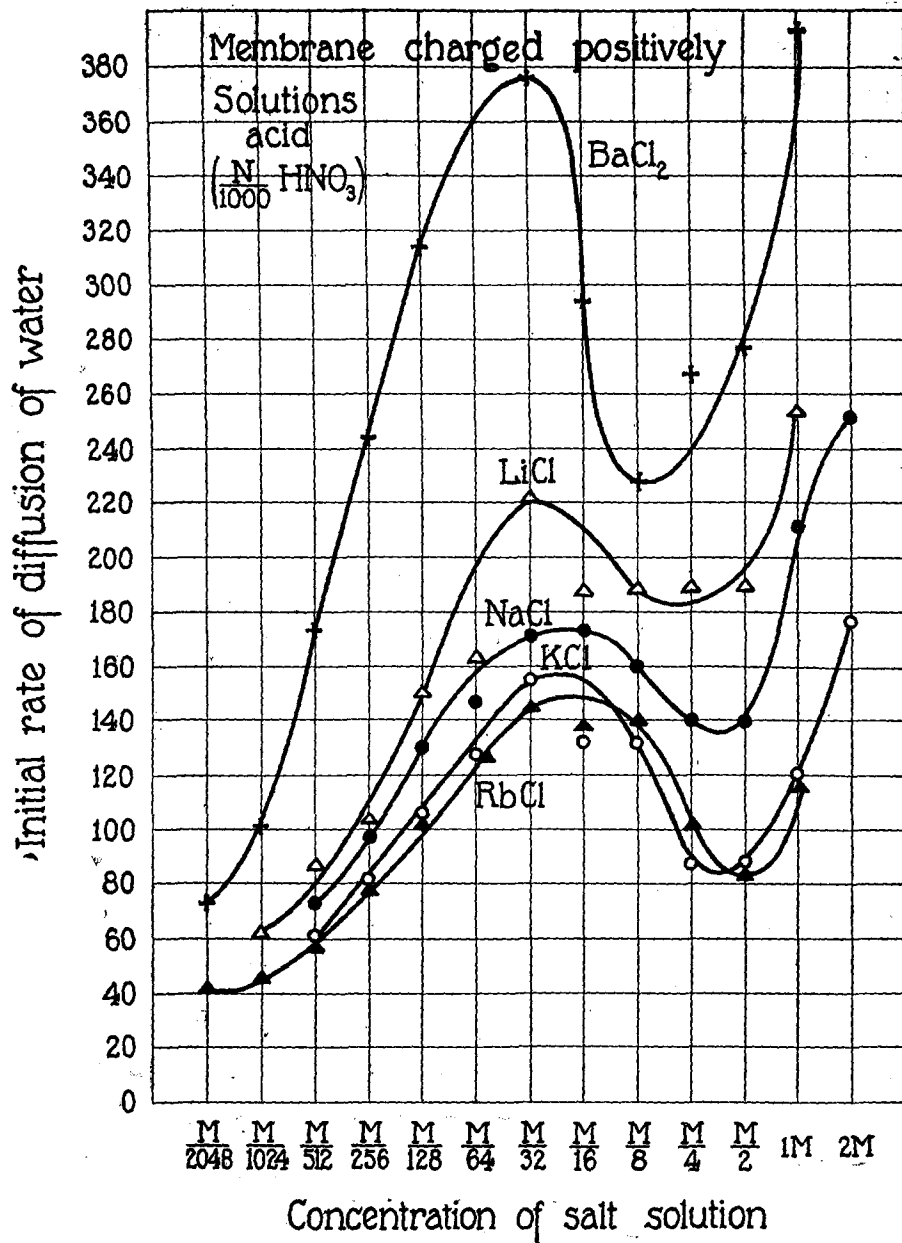


FIG. 6. The rate of diffusion of water through a positively charged membrane and the density of charge of the membrane are increased by the monovalent, monatomic cations in the order $\text{Li} > \text{Na} > \text{K} > \text{Rb}$. Solutions acid (pH about 3.0).

ion concentration of the solution inside the collodion flask and the water surrounding the collodion flask had therefore the same hydrogen ion concentration of about 10^{-3} N. Fig. 6 shows the order of influence of different cations upon the rate of diffusion of water through the membrane into the solution. The anion is always the same; namely, Cl. The order of efficiency of the cation series increases in the order

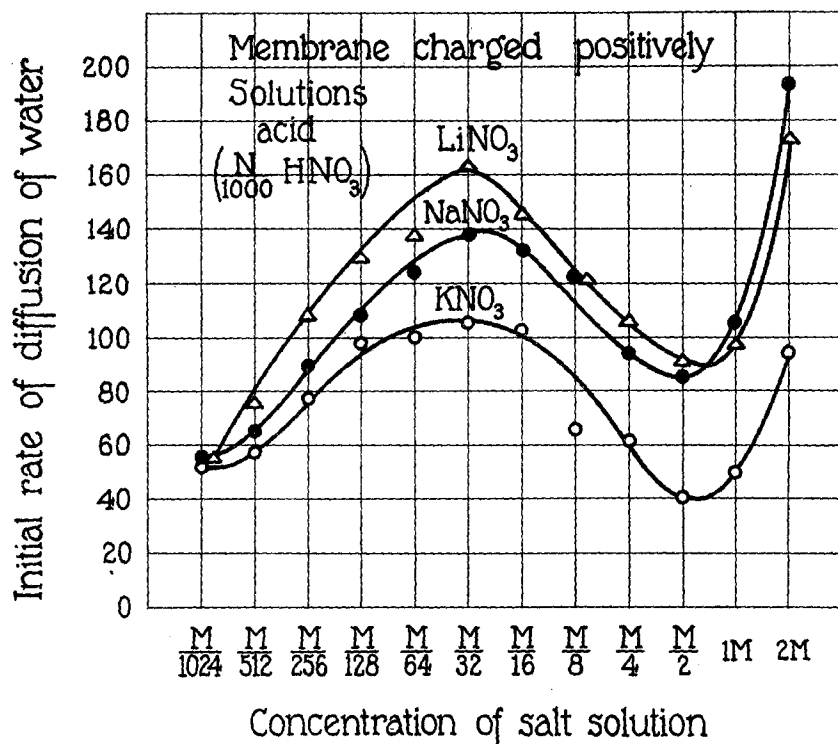


FIG. 7. The same order of efficiency of cations if the anion is NO₃.

Rb < K < Na < Li; *i.e.*, the efficiency of monovalent, monatomic cations increases inversely with the magnitude of their radius. This order is the same regardless of the anion. Thus Fig. 7 shows that the order is the same when Cl is replaced by NO₃.

The anion depresses the rate of diffusion of negatively charged water through the membrane into the solution when the membrane is positively charged. Fig. 8 shows that this depressing effect of

different potassium salts increases in the order $I > Br > Cl$, where the depressing effect of I is greatest.

This order is the same regardless of the nature of the cation. Thus Fig. 9 shows the same order of depressing effect of the anion on the rate of diffusion of water through positively charged membranes in the case of barium salts.

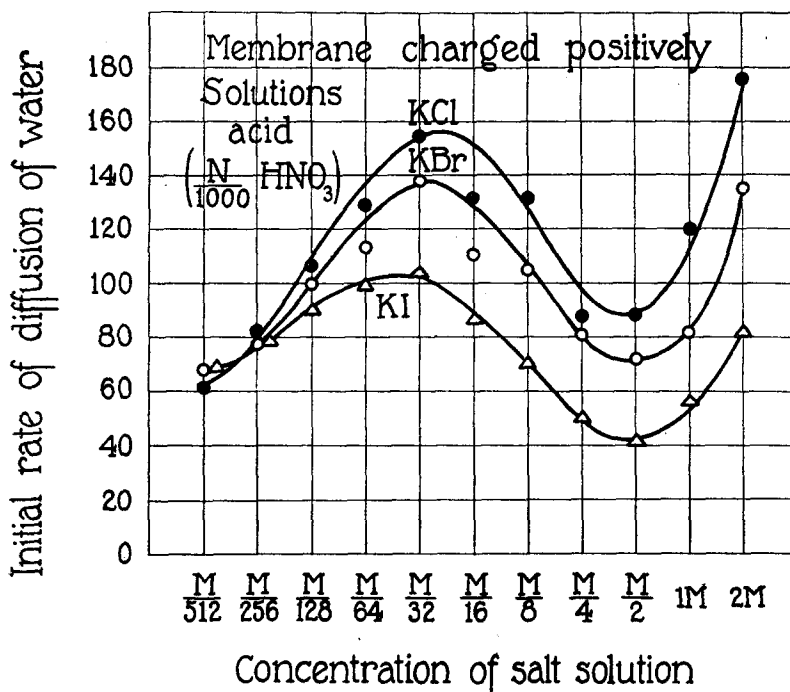


FIG. 8. The rate of diffusion of water through positively charged membranes (pH about 3.0) and the density of charge of membrane are depressed by anions in the order $I > Br > Cl$.

If we combine the results of the experiments on positively and negatively charged membranes we can express them in the following form:

The accelerating and depressing effect of monatomic, monovalent ions on the rate of diffusion of water through a collodion membrane from the side of pure water to the side of the solution increases for anions directly and for cations inversely with the magnitude of their radius.

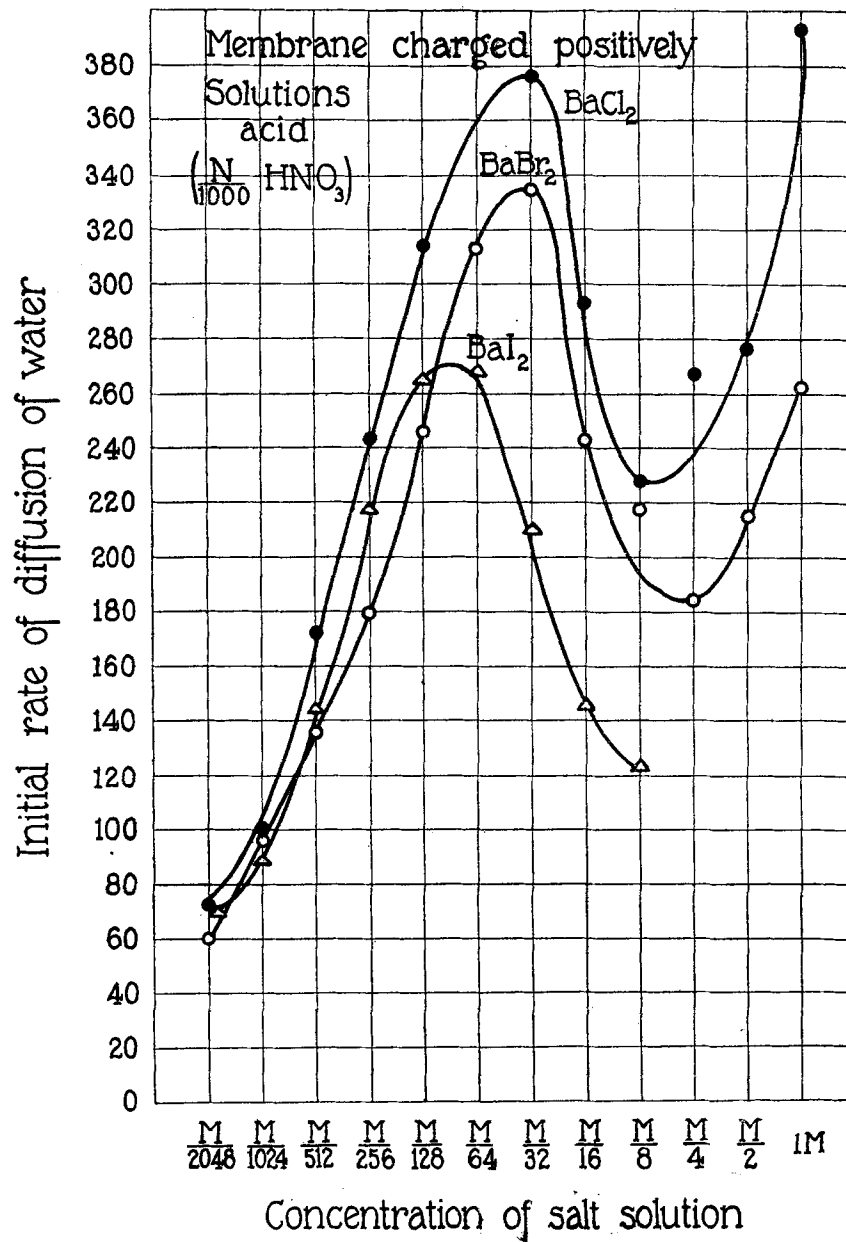


FIG. 9. The same as Fig. 8 for a different cation.

IV. Theoretical Considerations.

Kossel³ has suggested that for chemical reactions of atoms we may replace the atoms by simplified models consisting only of the charges of the positive nuclei in the center and the ring of valency electrons. The distance between the positive nucleus and the outermost ring or shell of electrons we call the radius of the atom or of the ion. While a monatomic, monovalent cation has one excess positive charge in its nucleus a monatomic, monovalent anion has one excess negative charge in its periphery. Although these positive and negative charges are alike, the relative electrostatic action of ions with the same charge must vary with the radius. Cations act through the excess positive charge on the nucleus, and the electrostatic action of the nucleus must become the greater the smaller its radius; *i.e.*, the nearer the positive nucleus can get to the body on which it is supposed to act. This explains why the accelerating as well as the depressing efficiency of a cation on the rate of diffusion of water through the membrane increases *inversely* with the radius of the cation; namely, in the order $Rb < K < Na < Li$, where Rb has the minimal effect.

When the nucleus has more than one excess charge the accelerating as well as the depressing efficiency increases with the valency, since *ceteris paribus* the electrostatic action of a cation must increase with the number of excess charges of its nucleus.

We understand also why the accelerating as well as the depressing efficiency of an anion increases *directly* with its radius, since the electrostatic effect of a monovalent anion on an outside body is determined by its excess electron and hence will be the greater the greater the distance between the valency electron and its positive nucleus.

It is also obvious why the efficiency of an anion should increase with its valency; *i.e.*, with the number of valency electrons it contains in excess of its nuclear charges.

We can only speak of ionic radius in the case of monatomic ions like K or Cl; when, however, an ion consists of more than one atom, *e.g.* NO_3 , CNS , we have more than one positive nucleus and each nucleus has its own rings or shells of electrons. The term ionic

³ Kossel, W., *Ann. Physik*, 1916, xlix, 229.

radius loses its meaning in this case unless we substitute for such polyatomic ions a monatomic model with one nucleus, one ring of valency electrons and a radius calculated in such a way as to render the electrostatic effect of the monatomic model equal to that of the polyatomic ion which it is supposed to represent.

The rule at which we arrived, namely that the efficiency of the anions increases directly with their ionic radius while the efficiency of the cations increases inversely with their ionic radius, is probably of general applicability in physical chemistry as well as in physiology, wherever the efficiency of ions depends on their electrostatic action.

There are numerous observations in the physiological literature which indicate an inversion of the order of efficiency of monovalent cations when the reaction of the solution changes from basic to acid. It is possible that these facts will find their explanation on the basis of our rule; namely, that on one side of the neutral (or in certain cases the isoelectric) point the effect observed is increased by the cation and inhibited by the anion, while on the other side it is increased by the anion and inhibited by the cation. Unfortunately the facts given are often too incomplete to test this idea and the experiments are generally done with such high concentrations of electrolytes that it is doubtful whether they can be used for any conclusions concerning the specific effects of ions.

SUMMARY.

1. It has been shown in preceding papers that when we separate solutions of electrolytes from pure water by collodion membranes the ions with the same sign of charge as the membrane increase while the ions with the opposite sign of charge diminish the rate of diffusion of water from the side of pure water to the side of solution; and that the accelerating and depressing effects of these ions on the rate of diffusion of water increase with their valency.

2. It is shown in this paper that aside from the valency a second quantity of the ion plays a rôle in this effect, namely the radius, which in a monatomic ion means the distance between the central positive nucleus and the outermost ring or shell of electrons of the ion. In monatomic, monovalent anions the radius increases in the

order $\text{Cl} < \text{Br} < \text{I}$ (being largest in I), while for monatomic, monovalent cations it increases in the order $\text{Li} < \text{Na} < \text{K} < \text{Rb}$ (being largest in Rb).

3. It is shown that the accelerating as well as the depressing effect of the anions mentioned increases directly with the order of magnitude of their radius and that the efficiency is greatest in the case of I which has the largest radius; while the accelerating as well as the depressing effect of cations increases inversely with the order of magnitude of their radius, Li with the smallest radius having the greatest efficiency.

4. This is intelligible on the assumption that the action of the ions is electrostatic in character, in the case of cations due to the electrostatic effect of the excess charge of their positive nucleus, and in the case of anions due to the excess charge of their captured electron. The electrostatic effect of the positive nucleus of a cation on the membrane (or any other body) will be the greater the smaller the ionic radius of the cation; and the electrostatic effect of an excess electron will be the greater the further its distance from its own positive nucleus.

5. It is suggested that this rule may possibly include polyatomic, monovalent ions (*e.g.* NO_3 , CNS , etc.) when we replace these polyatomic ions by monatomic models in which the radius is calculated in such a way as to give the model the same electrostatic effect which the polyatomic ion possesses.

6. These conclusions are in harmony with the fact that the efficiency of ions increases also with their valency.

7. It is suggested that these rules concerning the influence of the ionic radius can possibly be demonstrated in other phenomena, depending on the electrostatic effect of ions.