Comments and Communications

The 1950 Silly Season

PART of an editorial in the *Saturday Evening Post* for November 18, 1950, entitled "The 1950 Silly Season Looks Unusually Silly," is here quoted:

> One of the most astonishing episodes of the summer idiot's delight was the effort of American scientists to suppress a book, Worlds in Collision, by Dr. Immanuel Velikovsky. The scientists did succeed in forcing the Macmillan Company to withdraw the book, according to Doctor Velikovsky, by threatening to boycott Macmillan textbooks. Fortunately, another publisher, Doubleday and Company, took over the publication of the book, which is still going great guns. Doctor Velikovsky's offense seems to be that he writes better than most scientists and in his book expounds a theory of astronomical activity which differs widely from orthodox theories. . . .
>
> So the orthodox scientists, forgetting about Galileo, and the long, woeful struggle of scientists, or even pseudoscientists, to be free of dogma, acted like the authoritarians with whom they are continually in conflict. In the course of the struggle they managed to get an able book editor out of a job which he had had for many years, and the effect on the sale of the book was probably just the opposite of what the misguided book burners hoped for.
>
> Fortunately for the publishing business, specialists in other fields are less easily hexed than astronomers. Otherwise professors of history might take an attitude toward the publishers of Forever Amber as stuffy as that of the scientists toward Doctor Velikovsky, his reversible sun and his capering comet. But seriously, not even a silly season ought to excuse scientists for book burning. After all, they are always the chief victims of this kind of intolerance.

We need recall only in outline the extraordinary events that attended publication of *World in Collision* last spring. First *Harper's*, then two other magazines with wide distribution, printed advance summaries of the sensational book, with impressive appraisals of the author and his "scholarly" product. *Reader's Digest* prefaced its short version with the estimate, by a literary critic, that Velikovsky's creation might well attain the distinction of Darwin's *Origin of Species*. The publisher then advertised the book as a scientific contribution, listing it in the Macmillan spring catalogue under the heading "Science," along with new books in several scientific fields. This obvious build-up of a best seller by an old and reputable publishing house brought strong protest from many of Macmillan's authors, who felt that the advertising methods violated the publisher's clear responsibility to them. Within a short time the Velikovsky book was taken over by another publisher.

First, a newspaper columnist and, later, the *Saturday Evening Post* accused "the scientists" of "ganging up" on Velikovsky and Macmillan, with unworthy motives and the use of strong-arm methods. According to the confident diagnosis in the *Post* editorial, the motives ranged from base jealousy of Velikovsky's superiority (!) as a writer to blind dogma that would curtail freedom of expression on scientific subjects. At least by implication, scientists as a group were held guilty of collusion in unworthy behavior.

Doubtless there will be differences of opinion in selecting the most conspicuous exhibit from "the 1950 silly season." The *Post* editorial quoted above may prove to be a strong contender.

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Inaccurate Report

I SHOULD like to call to your attention that the report in SCIENCE (**113**, 341 [1951]) on the isolation of a new compound, TPN, is incorrect, due, no doubt to an erroneous newspaper report that appeared in the New York *Times* on February 2. The *Times* science reporter got the story quite wrong.

What was isolated in this laboratory was not TPN (which has been known for years) but a new enzyme which needs TPN for activity. The enzyme seems to play an important role in the biological assimilation of carbon dioxide by animals and plants and, probably, in photosynthesis (S. Ochoa, J. B. Veiga Salles, and P. J. Ortiz, *J. Biol. Chem.*, **187**, 863 [1950]). When the enzyme is added, together with TPN, to chloroplast preparations from green spinach leaves, in the presence of pyruvic acid and CO_2, and the mixture is illuminated, pyruvic acid takes up CO_2 and is converted to malic acid. Thus a photochemical assimilation of CO_2 has been obtained in a cell-free system. A report of these experiments, carried out in collaboration with Wolf Vishniac, will shortly appear in *Nature*.

I would appreciate it very much if you would take the necessary steps to have the report in SCIENCE properly corrected at the earliest possible time. Also, please note that my name was misspelled.

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The Significance of pH, Ion Activities, and Membrane Potentials in Colloidal Systems

IN A recent paper in this journal Jenny *et al.* (*1*) have presented a new theory to explain the cause of the potential that arises across an electrically-charged colloidal membrane separating two solutions of different salt activities. They assume that the relative diffusion rates of, e.g., K^+ and Cl^- for a KCl solution are affected by the immobile charges in the membrane, the potential which arises across the membrane being simply a liquid junction potential. In order to check their theory they first determined, by a standard method, the transference number of K^+ and Cl^- in systems comprising KCl solution and cation exchange material and found that the transference number of Cl^- was a function of the salt activity in the solution. They then described this function by an empirical equation and used this in the general equation for the liquid junction potential. This enabled them to compare data from experiments with the same membrane separating two solutions of different KCl activities with data calculated from their equation (Table 1, their paper). This procedure is not really a check on their theory, but a check of the validity of the equation they used for the liquid junction potential.

It is of interest to compare their theory with the theory for the potential across charged membranes worked out independently by Teorell (*2*) and Meyer and Sievers (*3*). This theory, which is based on the assumption of a Donnan distribution between the solution and the membrane, was later extended by the writer (*4*) to cover also the diffusion of salt mixtures through membranes, and the effect of the charge of the membrane on the diffusion rates and directions of the individual ions.

According to the Teorell-Meyer and Sievers theory, the potential across a charged membrane separating two solutions of the same monovalent salt (the transference numbers of the ions being the same) but of different concentrations is

$$E=\frac{RT}{F}\left[\ln\frac{\sqrt{X^2+4C_1^2}+X}{2C_1}-\ln\frac{\sqrt{X^2+4C_2^2}+X}{2C_2}\right], \qquad (1)$$

which at 25° C can be written

$$E=25.6\left[\sinh^{-1}\frac{X}{2C_1}-\sinh^{-1}\frac{X}{2C_2}\right], \qquad (2)$$

where E is the potential in mv and C_1 and C_2 refer to the concentrations of salt in the two solutions.

X is the apparent charge concentration in the membrane and has to be found by trial and error. From the data presented by Jenny *et al.* for the membrane with Ion-X exchanger in their Table 1 (substituting concentration for activity), X is found to be 0.25. (The E-value for $a_2=2.323$ is not considered in the estimation of X.) The potential across the membrane can then be expressed by

$$E=25.6\left[3.99-\sinh^{-1}\frac{0.125}{a_2}\right], \qquad (\mathrm{I})$$

where a_2 is the activity of KCl which was varied during their experiment. Table 1 gives the comparison between the measured E-values taken from their paper, the E-values calculated from their equation, and the E-values calculated by the writer from Eq. (I).

The agreement between the data calculated from Eq. (I) and the experimental values is very good except for $a_2=2.323$. The agreement is apparently better than between the measured values and those calculated by Jenny *et al.*

There is also another theory that can be applied to explain the source of the potential, namely, the theory of the diffuse double layer of ions at a charged surface. The potential difference between a charged surface and a point in the solution far from the surface can be derived from the Poisson-Boltzmann differential equation and reads ($T=298°$ C).

TABLE 1

Mean activity in the solutions separated by the membrane		Measured potential in mv	Calculated potential					
			By Jenny *et al.* from their equation	By writer from Eq. (I)	By writer from Eq. (II)			
a_1	a_2	(a)	(b)	(c)	(d)	$(a)-(b)$	$(a)-(c)$	$(a)-(d)$
0.00463	0.00902	18.0	17.7	16.9	17.4	0.3	1.1	0.6
	.0441	53.7	53.7	57.1	55.2	0.0	− 3.4	− 1.5
	.296	91.7	85.2	91.6	91.7	6.5	0.1	0.0
	0.432	96.5	89.3	94.8	97.0	7.2	1.5	− 0.5
	2.323	113.0	102.0	101.2	113.2	11.0	11.8	− 0.2

$$E=\frac{51.2}{n}\sinh^{-1}\frac{Z}{\sqrt{c}}, \qquad (3)$$

where Z is a constant linearly dependent on the charge density of the surface, n is the valency of the ions neutralizing the surface charges, and c is the molar concentration of the salt solution. The potential corresponding to the system given in Table 1 is then expressed by

$$E=51.2\left[\sinh^{-1}\frac{Z}{\sqrt{a_1}}-\sinh^{-1}\frac{Z}{\sqrt{a_2}}\right]. \qquad (4)$$

The constant Z has to be found by trial and error and, for the data given in Table 1, is 0.39. For comparison, the data calculated from the equation

$$E=51.2\left[2.46-\sinh^{-1}\frac{0.39}{\sqrt{a_2}}\right] \qquad (\mathrm{II})$$

have also been included in Table 1. The agreement between these and the observed values is very good for all valus of a_2.

There is a fundamental difference between the theory of Jenny *et al.* and those applied by the writer. In the first theory the properties of the membrane are described by a quantity τ_-, the transference number of the anion; this quantity is not a parameter but *a function of the activity of the salt solution.* In the alternative theories, the same properties are described by a quantity X, the apparent charge activity of the membrane, or Z, which is linearly dependent on the charge density of the membrane surface; these quantities are real parameters, *independent of the activity of the salt solution.* From this point of view the Teorell-Meyer and Sievers theory and the writer's theory are to be preferred, and they have also the advantage of enabling the magnitude of the potential at each boundary surface to be calculated, which is not possible from the Jenny theory.

Jenny *et al.* then apply their theory to the determination of pH in colloidal suspensions of charged particles by regarding the suspensions as membranes. It is well known that the pH measured in such suspensions differs from that measured in the filtrates. This effect has been attributed to the influence on the reversible electrode of the ions in the swarm around the charged particles, and has been called the suspension effect by Wiegner and Pallmann (*5*). From the theory of Jenny *et al.* and their further experiments, two alternatives can be given: (1) There exists a suspension effect, and as a consequence of this no appreciable "membrane" or liquid junction potential can occur at the point of contact between the KCl bridge and the suspension. (2) There is no suspension effect; the difference in pH between the suspension and its filtrate is due to the liquid junction potential at the point of contact between the KCl bridge and the suspension.

They seem to prefer the second alternative which, however, is really disproved by their data on the transference number of Cl$^-$ at different concentrations in the Ion-X exchanger membrane. From Fig. 1 in their paper it is seen that τ_- increases with increasing concentration of KCl.

According to the alternative theories presented here, the "membrane" potential at the point of contact between the KCl bridge and the suspension must be comparatively small (insignificant according to the Teorell-Meyer and Sievers theory), provided a concentrated solution of KCl is used in the bridge. Differences in the pH of the suspension and its filtrate must accordingly be attributed to a suspension effect, an explanation that is more satisfactory from a kinetic point of view.

The problem of the determination of ion activities in colloidal suspensions has recently been treated in a paper by the writer (*6*) and can be summarized briefly as follows: In any system of ions subjected to thermal motion, the electrochemical potential of an ion at equilibrium is the same at every point in the system. This is a thermodynamic principle from which the Donnan equation, for example, can be derived. The principle can be interpreted in this way: If, in a system of ions at equilibrium, the osmotic activity of an ion at point *a* differs from that at point *b*, then the electrical potential at *a* must differ from that at *b* in such a way that the work done in transporting an ion from *a* to *b* must be equal to the work gained in transporting the corresponding charges from *a* to *b*. The ratio of the osmotic activities of an ion at *a* and at *b* can then be calculated from the difference in the electrical potential between the points. From this it can be shown that, provided the liquid junction potential is negligible, the pH measured in a colloidal suspension of charged particles in the ordinary way represents the pH at the point of contact between the KCl bridge and the suspension, and not at the point of contact between the reversible electrode and the suspension.

Of course the practical importance of this conclusion rests on the assumption of a suspension effect, which has also been discussed by the writer (*6*). If the ions neutralizing the charges at the surfaces of the colloidal particles are subjected to thermal motion, thus forming a swarm, a suspension effect will occur, especially as the particles themselves are also subjected to thermal motion. There are many indications that a swarm, or a diffuse double layer, as it is also called, exists around charged particles. (This, of course, implies that the concept of matter is based on mass, charge, etc.). It is, for example, well known that most exchange reactions on colloidal particle surfaces take place rapidly. If, in addition to the electrical forces, the ions at the particle surfaces were also held by other and much stronger forces, their thermal motion would be practically zero and the exchange reactions very slow.

There are also many phenomena in colloid chemistry that have been successfully explained by theories based on the assumption of a diffuse swarm of ions around the individual particles. The stability of lyophobic colloidal suspensions, for example, is very difficult to explain without assuming the existence of a diffuse double layer that creates repelling forces between the particles (*7*). The negative adsorption of anions in clay mineral suspensions, treated by Schofield (*8*), and the relation between the water content and the "osmotic" pressure in a bentonite gel recently derived by the writer (*9*), are both experimentally verified theories based on the assumption of a diffuse double layer.

If, on the other hand, it is assumed that the thermal motion of the ions neutralizing the charges at the particle surfaces is insignificant—i.e., they do not influence the potential of a reversible electrode—it would be extremely difficult to explain the variation in the apparent transference number of Cl$^-$ with the concentration of salt in the experiments by Jenny *et al.*

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References

1. JENNY, H., *et al. Science,* **112**, 164 (1950).
2. TEORELL, T. *Proc. Soc. Exptl. Biol. Med.,* **33**, 282 (1935).
3. MEYER, K. H., and SIEVERS, G. F. *Helv. Chim. Acta,* **19**, 649 (1936).
4. ERIKSSON, E. *Ann. Agr. Coll. Sweden,* **16**, 420 (1949).
5. WIEGNER, G., and PALLMANN, H. *Trans. Second Com. Alkali Subcom. Intern. Soc. Soil Science, Budapest,* **B92** (1929).
6. ERIKSSON, E. *On the Determination of pH in Colloidal Suspension.* (In press.)
7. VERWEY, E. Y., and OVERBEEK, Y. TH. G. *Theory of the Stability of Lyophobic Colloids.* New York: Elsevier Pub. Co. (1948).
8. SCHOFIELD, R. K. *Nature,* **160**, 708 (1947).
9. ERIKSSON, E. *Ann. Agr. Coll. Sweden,* **17**, 17 (1950).

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Errata

Through an accident that occurred while the issue was on the press, in some copies of SCIENCE for March 30, page 361 is misnumbered 261. The article by R. J. Hickey and P. H. Hidy begins on this page.