

acetic acid. Further uses of trifluoroacetic acid as acid condensing agent are being explored.

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MEMBRANE EQUILIBRIA WHICH INVOLVE ONLY THE IONS OF STRONG INORGANIC ELECTROLYTES

Sir:

The experimental study of membrane equilibria has been confined in the past to systems containing colloidal or semicolloidal ions as "non-diffusible" ions, and systems in which the $\text{Fe}(\text{CN})_6^{4-}$ ion acted as such in conjunction with a copper ferrocyanide membrane.^{1,2} For lack of suitable membranes—except for this unique case—Donnan equilibria involving only strong inorganic electrolytes could not be studied.

selective" membranes combine extreme ionic selectivity with great permeability for the non-restricted ion species; the electronegative colloidion membranes are impermeable to all inorganic anions but permeable to the alkali cations, the electropositive membranes being impermeable to all cations and permeable to the anions of the strong monobasic inorganic acids. The ionic screening action of the membranes in these cases is primarily an electrical, not a mechanical (sieve), effect.

The ratios of the activity coefficients of the K^+ , Na^+ and NH_4^+ salts in the pairs of solutions given in Table I are nearly identical. This permits the use without appreciable error of the simplified original formulas of Donnan^{1,2} which refer to analytical concentrations rather than to activities.

The experimental study of membrane equilibria which may involve any desired combination

TABLE I
DONNAN EQUILIBRIA ACROSS MEGAPERMESELECTIVE COLLODION MEMBRANES^a

| No. | Solute | Original state | | Equilibrium state | | | | Ratio in/out | |
|-----|-----------------------------|---------------------|----------------------|---------------------|----------------------|---------------------|----------------------|-----------------|--------|
| | | mMoles per liter In | mMoles per liter Out | Experimental | | Calculated | | Experimental | Calcd. |
| | | | | mMoles per liter In | mMoles per liter Out | mMoles per liter In | mMoles per liter Out | | |
| A | NH_4^+ | 30.0 | .. | 22.4 | 7.50 | 22.5 | 7.50 | 2.99 ± 0.02 | 3.00 |
| | K^+ | .. | 10.0 | 7.5 | 2.5 | 7.50 | 2.50 | 3.00 ± 0.10 | 3.00 |
| | Cl^- | 30.0 | 10.0 | 29.8 | 10.1 | 30.0 | 10.0 | 2.95 ± 0.02 | 3.00 |
| | Sucrose ⁶ | .. | 33 | .. | .. | .. | .. | | .. |
| | Vol. | 30 ml. | 30 ml. | .. | .. | .. | .. | | .. |
| B | NH_4^+ | 50.2 | 2.51 | 37.4 | 3.79 | 37.5 | 3.78 | 9.9 ± 0.2 | 9.9 |
| | K^+ | .. | 2.56 | 12.0 ^c | 1.27 ^c | 12.7 | 1.29 | 9.5^c | 9.9 |
| | $\text{C}_2\text{O}_4^{2-}$ | 25.1 | 2.54 | 24.7 | 2.53 | 25.1 | 2.54 | 9.8 ± 0.2 | 9.9 |
| | Sucrose ^b | .. | 39 | .. | .. | .. | .. | | .. |
| | Vol. | 25 ml. | 250 ml. | .. | .. | .. | .. | | .. |

^a The membranes are impermeable to anions, permeable to cations. ^b Sucrose is added in the proper concentration to establish osmotic equilibrium. ^c K^+ concentration is calculated by difference.

The use of certain recently developed colloidion and protamine colloidion membranes^{3,4} makes such investigations possible. These "megaperm-

(1) F. G. Donnan, *Chem. Rev.*, **1**, 73 (1924).

(2) T. R. Bolam, "The Donnan Equilibria," Bell and Sons, London, 1932.

(3) C. W. Carr and K. Sollner, *J. Gen. Physiol.*, **28**, 119 (1944); C. W. Carr, H. P. Gregor and K. Sollner, *J. Gen. Physiol.*, **28**, 179 (1944).

(4) H. P. Gregor, Ph.D. Thesis, Minneapolis, 1945 (in preparation).

of uni-univalent, and many combinations of uni-polyvalent electrolytes is of interest not only for the colloid chemist and the biologist, but also "may prove of value in the investigation of ionic activity coefficients" (Donnan).

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