CHEMISTRY

Deviations from the Steady-State in Ion Transfer through Perm-selective Membranes

DURING experiments on polarization phenomena of perm-selective membranes, results were obtained which were inconsistent with the generally accepted idea that during the transfer of ions through such membranes by means of a constant direct current, a steady state is established under given experimental conditions¹.

The observation led to a series of rigidly controlled experiments in which I attempted to determine whether in fact a steady state is obtained.

A constant direct current was passed through a homogeneous cation exchange membrane bounded on both sides by 0.01 *N* silver nitrate solution. Silver electrodes were used, and the current obtained from a constant voltage rectifier (max. output: 400 V.) with less than 0.2 per cent ripple. To eliminate current variations a 44-k.ohm resistance was placed in series with the experimental cell. The potential difference through the system was measured by means of saturated calomel electrodes through 0.01 *N* potassium chloride/0.01 *N* potassium nitrate salt bridges, and a calibrated oscilloscope with d.c. amplifier. Measurements were made at various current densities and the current measured by means of an avometer. The solutions were stirred at 1,100 r.p.m. with glass stirrers.

After allowing some time for constant conditions to be established, I found that with the passage of the direct current, an unharmonic oscillation of the potential difference between the two sides of the membrane was obtained, about a constant average value. The maximum spread of the oscillation varied with the current density and at 30 m.amp./cm.² increased to about 500 mV. (Table 1).

A control experiment in which the membrane was left out gave a maximum value at 30 m.amp./cm.² of 20 mV. (Table 1). Further tests repeated with accumulators as the direct-current source gave similar results.

Table 1

Current density (m.amp./cm. ²)	Spread of oscillation (mV.)		
	0.01 <i>N</i> AgNO ₃	Control experiment	0.01 <i>N</i> AgNO ₃ in agar-agar gel
1.5	5	5	20
3	10	5	100
6	150	10	1,000
15	300	20	8,000
30	500	20	—

In order to limit all other effects except those caused by current and diffusion, an additional experiment was made in which the solution in the cell was replaced by an agar-agar gel of the same ionic concentration. In this case, the oscillation spread was much wider and gave a value of 8,000 mV. at 15 m.amp./cm.². At higher current densities the overall voltage increased to such an extent that no constant current could be obtained (see Table 1).

Experiments with an anionic exchange membrane in 0.01 *N* potassium chloride gave similar results.

Since, for steady-state conditions, the potential difference between two points in the system must be constant by definition, the experiments seem to

indicate that during ion transport through perm-selective membranes by means of a constant direct current, steady-state conditions need not generally appear. I feel that it is necessary, therefore, to examine anew current theories on such transfer processes, and investigations in this direction are now being undertaken.

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¹ Spiegler, K. S., *Trans. Farad. Soc.*, **54**, 1409 (1958). Kressman, T. R. E., *et al.*, *ibid.*, **55**, 1441 (1959). Meares, P., *ibid.*, **55**, 1970 (1959). Peterson, M. A., *J. Electrochem. Soc.*, **106**, 1051 (1959).

A New Calcium Magnesiosilicate

A DETAILED investigation is in progress of high-temperature phase equilibria in the system 2CaO.SiO₂ - 3CaO.MgO.2SiO₂ mainly by special methods of high-temperature microscopy^{1,2} and X-ray analysis³. A new compound has been located of the approximate molar composition (2CaO.SiO₂)_{5.6}(3CaO.MgO.2SiO₂)_{4.4} characterized by the X-ray diffraction pattern given in Table 1. This composition was prepared from crushed quartz (99.95 per cent pure), calcium carbonate (99.9 per cent pure), and magnesium oxide (99.9 per cent pure), by ignition at 1,250° C. in platinum boats in a platinum/rhodium resistance furnace. The fineness of the reaction mixture during ignition is of critical importance to the formation of the new compound. During a heat-treatment of 10 days duration the mixture was ground every two days to pass a 300-mesh sieve. Failure to grind to at least such fineness led to the formation of mainly γ-2CaO.SiO₂ and 3CaO.MgO.2SiO₂ with only a small proportion of the new phase.

The X-ray powder measurements were obtained at room temperature in a Guinier-type focusing camera, 114 mm. diameter with copper-*K*α radiation. Relative intensities (*I*) were estimated visually on an arbitrary scale from 1 (very weak) to 10 (very strong). The density of the new compound is 3.30 and the optical properties are as follows: biaxial positive 2*V* medium (approximately 30°), *RI*_{Na} α = 1.711, γ = 1.725.

The phase is formed by solid-state reaction and does not melt congruently.

Sharp, Johnson and Andrews⁴ report a new phase, *T*, the presence of which was detected in basic arc

Table 1. ROOM TEMPERATURE X-RAY POWDER MEASUREMENTS FOR A NEW CALCIUM MAGNESIOSILICATE

<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
3.84	1	2.580	2	2.001	3	1.588	1
3.79	1	2.548	2	1.953	1	1.576	1
3.48	2	2.481	2	1.924	5	1.563	3
3.37	2	2.447	2	1.897	2	1.558	3
3.22	2	2.421	2	1.876	2	1.548	2
2.95	2	2.340	2	1.836	2		
2.829	4	2.292	1	1.747	1	1.428	1
2.771	1	2.228	4	1.727	1	1.420	1
2.732	10	2.210	4	1.708	1		
2.718	10	2.172	2	1.687	2	1.363	2
2.668	8	2.110	2	1.669	1	1.336	3
2.648	1	2.080	2	1.649	2	1.297	1
2.631	1	2.070	3	1.621	1	1.243	1B
2.594	2	2.020	1	1.606	1		

B, broad line