E. M. F. Change in the Thermo Cell due to Soret Effect

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Thermo cell is defined as a cell in which two identical electrodes are kept at different temperatures so as to form a steady temperature gradient in the electrolyte solution. In such a cell, it has long been realized that the electro-motive force (emf) should change as thermal diffusion proceeds and, at a stationary state, should reach a steady value E_∞ corresponding to Soret equilibrium. Although many experimental investigations have been reported about thermo-cell emf, almost all the data refer to the initial emf (E_0), which is the emf of a cell of uniform concentration; that is the state at which no change in concentration due to thermal diffusion has yet been appreciable.

Non-stationary change of thermo-cell emf was first confirmed by Agar and Breck[1] by an ingenious method using amalgam electrode; however, the measurements were restricted only to some special ions which were rather unfamiliar in this field of investigation.

We have long been interested in this problem and engaged in solving it; lately we observed a similar example of the phenomenon using silver-silverchrolide electrode with which most of the previous investigators have been concerned.

The emf change due to Soret effect can not be detected by an ordinary cell construction, which is used to measure the initial emf; because the large volume of the bulk solution in the electrode chamber makes the small change in composition indistinctive. Thus following precautions were taken into account for cell design;

1) the electrodes must be placed directly in the diffusion path,

2) the length of the diffusion path, i.e. the inter-electrode distance should be so determined that the time required for the establishment of the diffusion equilibrium (steady state) will accord with the restriction of the actual measurement,

3) temperature gradient must be linear throughout the diffusion path.

Along these requirements we designed

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[1] J. Agar and W. Breck, *Trans. Faraday Soc.*, **53**, 167 (1957).

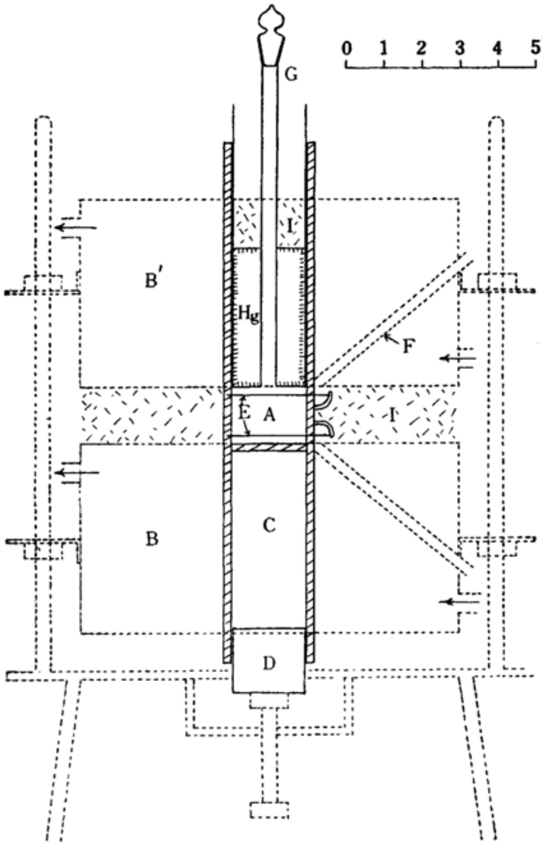

Fig. 1. Cell assembly

E Electrode; A Diffusion path; B, B' Water jacket;
C Heat conducting space (water is enclosed);
Hg Heat conducting space (containing mercury);
D Rubber stopper; F Thermocouple pocket;
G Filling tube; I Insulator.

several types of cells and tested their usefulness. A very simple cell, which is schematically shown in Fig. 1, has eventually revealed itself to be quite useful. Its detailed information will be reported in the succeeding paper.

The temperature gradient was set up by means of two jackets fitted tightly to the body of a cylindrical cell; water of a given temperature could be circulated through them.

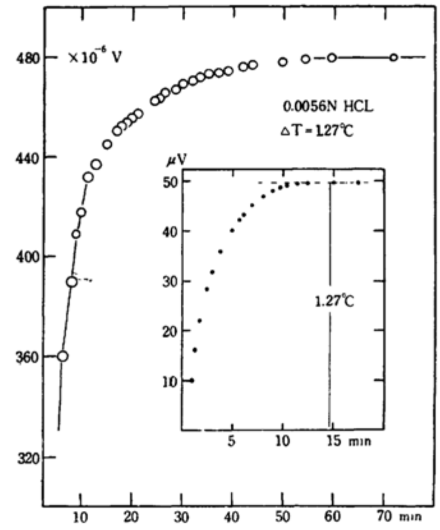

Fig. 2. Emf change with time (min.).
Empty circle: Emf of the cell,
Full circle: Thermocouple reading

As the first step of the present investigation, we took hydrochloric acid in different concentrations as a test solution. The fundamental feature of emf change with time is graphically shown in Fig. 2. In the figure the temperature change in the cell is also drawn, which was obtained by means of differential thermocouple. As is clearly seen from the figure, the emf changes rapidly at the first stage, in which a steady temperature gradient is established. After the temperature gradient has come stationary, the emf increases continuously, although not so rapid as before, exhibiting exponential diffusion behavior and reaches a steady value at a finite period of time. This behavior accords well with the theoretical expectation derived by Bierlein²⁾: when the emf is plotted against $\sqrt{t}$ for the initial stage of thermal diffusion (not to be confused with the stage at which the heat conduction is not yet stationary), a straight line is obtained with a good approximation, whilst for the final stage log $(E_\infty - E_t)$ has a linear dependency upon t. These relationships are drawn in Figs. 3 and 4. In contrast to Agar and Breck's result, the reverse curve, which can be obtained

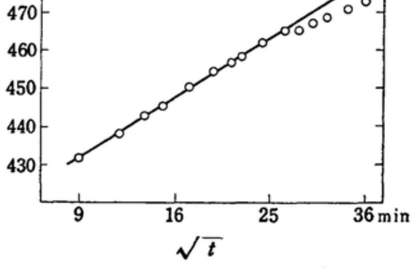

Fig. 3. Emf against $\sqrt{t}$

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2) J. Bierlein, *J. Chem. Phys.*, **23**, 10 (1955).

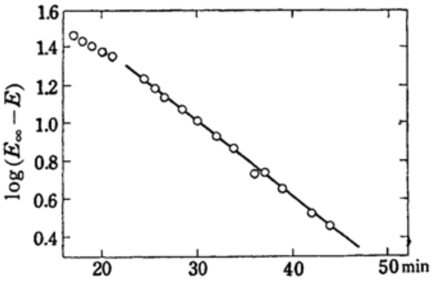

Fig. 4. Log $(E_\infty - E)$ against t.

when the temperature gradient is cut off, does not show the symmetric form against the curve of non-isothermal change but is somewhat erroneous. This problem, however, is left for further study.

A similar relation was observed for hydrochloric acid solution of various concentrations. Detailed information and theoretical explanation will successively appear.

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