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PART I. (EXPERIMENTAL)

SEPARATION OF CATIONS BY AN ELECTROGRAVITATIONAL METHOD

PART II. (THEORETICAL)

A. EQUIVALENT CIRCUIT MODEL OF THE TRANSFERENCE CELL.

B. THE TRANSFERENCE CELL: THERMODYNAMICS

OF THE STEADY STATE.

by

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PART I. (EXPERIMENTAL)

SEPARATION OF CATIONS BY AN ELECTROGRAVITATIONAL METHOD

1. Introduction

The principle of this method, as exemplified by the apparatus and technique previously described,^{1,2} is as follows: a solution of a chloride, MCl , is contained between two closely spaced vertical silver-silver chloride electrodes. On passage of direct current at low voltage (0.6 volt or less), the following electrode reactions occur:

The combination of these electrode reactions with the migration processes leads to a horizontal concentration gradient, with MCl richer in the catholyte, and depleted in the anolyte. The density gradient thereby established leads to a convection current and the resultant concentration of MCl in the bottom of the cell. The fractionation of two or more cations in a mixture is possible by virtue of their difference in mobility.

Discontinuous operation of the process due to the limited quantity of $AgCl$ on the electrodes is avoided by repeated reversal of the current on a predetermined program.

Previous studies have been concerned with the extraction of single electrolytes from solution by this method, except for a demonstration of the clean-cut separation of sodium ion from hydrogen ion.¹ Both static¹ and flow² systems have been employed. The principal aim of the present work was to explore the adaptation of the method to some of the separation problems of interest to the Atomic Energy Program. It was first desirable to select one mixture for a fairly extensive study of the variables of cell operation. This mixture need not be one whose separation is of practical interest, but it should be capable of convenient and rapid analysis, and its separation should be one of moderate difficulty. A sodium-potassium chloride mixture was selected for this study, and it was found that the separations obtained offered promise for practical application of the method.

Three binary mixtures were then investigated in an exploratory manner, with the following conclusions: (a) Lithium isotopes 6 and 7. The method does not at present have sufficient resolving power for isotope

¹G. W. Murphy, J. Electrochem. Soc., 97, 405 (1950).

²G. W. Murphy and D. Batzer, ibid., 99, 520 (1952).

separation. (b) Cerium-thorium - when hydrolysis and subsequent precipitation can occur in chloride salts of this type, the lack of means for maintaining the pH at the desired level makes this type of separation impractical. (c) Radium-barium - hydrolysis is no problem here, and it appears that satisfactory separation factors can be obtained under carefully controlled conditions. Additional experimental work is suggested for this mixture.

2. Apparatus

2.1 Power Supply

The power supply and current reversing mechanism, which are described elsewhere in greater detail,² are shown in block diagram in Figure 1. The power supply is essentially a transformer-selenium rectifier system operated from the 220 volt-3 phase line, the output voltage being electromechanically controlled to $\pm \frac{1}{2}$ per cent. The voltage is adjustable in the range 0-2V D.C., and the maximum current capacity is about 50 amperes, although no more than a few amperes were required for the present work. The current reversing relays are operated by a timer which is adjustable to cycles varying from 5 to 150 minutes.

The voltage and current were recorded continuously by a Brown two-record potentiometer. Effluent conductance was recorded by a Leeds and Northrup recording conductance bridge with ranges of 0-0.1, 0-0.01 and 0-0.001 reciprocal ohm.

2.2 The Cell

The principal features of the present cell (Figure 2), constructed of Lucite with silver wire mesh electrodes, is described in greater detail elsewhere.² The walls of the cell are $\frac{1}{4}$ in. apart with an electrode gap of approximately $\frac{3}{32}$ in., the electrodes themselves filling the remainder of the space. The channel width is 1 in., and the electrode height for a single cell 9 in. An effluent tube leading to a miniature conductance cell is located just above the electrodes. Some experiments were performed on an assembly of 3 similar cells stacked together in series, giving an over-all electrode height of 30 in. The electrodes were chloridized electrolytically until about $\frac{1}{10}$ equivalent of silver had been converted to the chloride.

The bottom of the cell was either closed by the flat Lucite plate of Figure 2, or attached to one of the two reservoirs illustrated in Figure 3. Reservoir A had a capacity of about 500 ml and reservoir B of about 3 ml. The large reservoir is employed in experiments where it is desired to maintain the concentration substantially constant during a run; i.e., the relatively small amount of electrolyte added to or extracted from the reservoir during cell operation

Figure 1.

Block Diagram of Power Supply: Power-stat: 220 V-3-phase, 1.2 KVA, No. 20-3Y, Superior Electric Co., Bristol, Conn. Three step-down transformers with 100:1 ratio and rectifier stack designed for an output of 50 amps. furnished by the Electronic Rectifier Co., Rochester, N. Y. Current Reversing Relays: four SPST aircraft Units (war surplus) with 12 V D.C. coils and 50 amp. contacts. Pulse Relay: Series 900, 110 V A.C. coil, DPDT 1/4" silver contacts, Advance Electric and Relay Co., Los Angeles, California. Electric Timer: "Cycle Flex," HP 27, 250 Min. dial, Eagle Signal Corp., Moline, Ill. Voltage Reversing Relay: Series 200, DPDT, 12 V D.C. coil, Guardian Electric Co., Chicago, Ill. Servo Motor: No. 1282D with 300:1 gear box, Kollsman Instrument Div., Square D Co., Elmhurst, N.Y. Not shown: 12 V D.C. power supply for operating relays. Other components, see text.

Figure 2.
Lucite Cell

a. Reservoir "A" Cross Section Through Diameter

b. Reservoir "B"

Figure 3.

Details of Reservoirs "A" and "B."

does not effect the concentration of its solution appreciably. The sintered glass filter disc was added after a number of experiments had indicated that mixing of the influent water with the reservoir solution was incomplete (Section 3.4). A photograph of the assembly of 3 cells with the large reservoir is shown in Figure 4. The small reservoir with the side arm was employed in experiments where withdrawal of small samples near the bottom of the electrodes during cell operation was desired. The side arm was a Lucite tube of 1/16 in. bore. It was closed by a small bore rubber tube and a screw clamp. The side arm opening is just above a porous diaphragm of saran filter cloth, whose purpose it is to maintain a reasonably sharp dividing line between the influent water and the electrolyte of the cell proper, and to assure mixing of these fluids at the dividing line.

2.3 The Pump

A photograph of the pump is included in Figure 5. The barrel and plunger are a 1 ml Pyrex syringe lubricated with stopcock grease. The check valves are of Pyrex glass ground into their seats with successively finer grades of carborundum powder and finished with levigated alumina. There is a good deal of art involved in preparing these valves (Figure 5). The male part is a cone formed on the end of a 4 mm rod by rotation in the flame. The seat is formed with about the same taper at the juncture between 2 mm capillary tubing and 7 mm standard wall tubing. After grinding and testing for leakage, the rod attached to the male member is cut off and the latter is installed in the seat, with indentation as illustrated to check excessive vertical movement. Not every valve thus prepared will be found leakproof to water and stick-proof as well, but the percentage of successful attempts improves with practice. Earlier attempts to make leakproof spherical check valves were abortive.

The plunger was driven by an eccentric on the shaft of a 110 volt DC motor, geared to 20 RPM at normal voltage. The field was supplied with constant DC from an AC line-operated selenium rectifier, and the armature with variable DC from a separate selenium rectifier fed by a Variac, (Figure 6). Thus, any speed from 0 to 20 RPM could be readily selected, and additional control on the flow rate was secured by different eccentrics having strokes up to 1/8 in. Any flow rate from 0 to 100 ml per hr. could be obtained with a constancy of ± 1 per cent.

3. Sodium-Potassium Mixtures

Prior to this work, no mixture fractionations other than sodium-hydrogen had been attempted, and the applicability of the method to the much more difficult sodium-potassium mixture could not be accurately forecast. The present attempts are concerned primarily with the determination of separation factors under different conditions of cell operation. A necessary

Figure 4.

Photograph of Electrogravitational Apparatus with three cells in series attached to Reservoir "A."

Figure 6.

Schematic Wiring Diagram of Power Supply for Variable Speed
Operation of 110 V D.C. Motor.

preliminary to these studies was the development of a suitable analytical technique.

3.1 Analysis

For the determination of sodium and potassium in mixtures of the two, flame photometry is unexcelled for precision, speed, and convenience. The instrument used in this work, a Beckman model DU spectrophotometer with flame photometer attachment, was furnished by Ralph Bane, who also contributed valuable advice. The 589 mμ doublet was employed for sodium and the 768 mμ line for potassium, a selection which provides high sensitivity for each and virtually no interference between the two elements. Owing to self-absorption, however, the intensity of emission is not proportional to the concentration of either element, and it is necessary to prepare calibration curves. A single mixture, 1 N each in NaCl and KCl, was made up as a stock solution, and the standards for the calibration curves (Figure 7) were prepared therefrom by quantitative dilution.

3.2 Preparation of the Cell

When the current is to be unidirectional for the duration of the experiment, the entire amount of oxidized electrode material is initially on one electrode. This can be accomplished by flowing a chloride solution (NaCl or HCl) through the cell while applying a potential of 0.5 volt until the current has dropped to zero, indicating complete conversion of active material. At the beginning of the run, the polarity was reversed.

When the current was to be reversed periodically during the experiment, about half of the oxidized material was on each electrode, either by pretreatment similar to the above, or by virtue of being left in this condition from a previous run. Each experiment was commenced with the cell completely rinsed of electrolyte (by conductance test), deoxygenated and partially dried by flushing with nitrogen. The water supply for flow experiments was also deoxygenated prior to a run by bubbling nitrogen through it. It had been found previously² that oxygen in the cell can complicate results through the competing anodic reaction

By pH test, the nitrogen pretreatment was found to eliminate this difficulty.

3.3 Experiment with Unidirectional Current

Since some experience had been acquired by the unidirectional current technique with this apparatus in the case of single electrolytes, it was decided to explore the sodium-potassium system in this manner first, even though there was little prospect that this could lead to a practical separation.

Figure 7.

Flame Photometer Calibration Curves for Sodium and Potassium Chlorides in Equimolar Mixture.

Run B-5³: Single cell, no reservoir at bottom, applied potential 0.5 volt, unidirectional current. Two ml of solution 0.5 N in NaCl and 0.5 N in KCl was introduced into the cell, and water was pumped through at a rate of 4 ml per hour, with the effluent issuing from the conductance cell into graduated receivers. The entire run lasted 135 hours, sufficient to exhaust most of the electrolyte from the cell. Twenty-seven samples were collected during this period and analyzed for their sodium and potassium content. The results are shown graphically in Figure 8. This run is analogous to an ion-exchange column experiment in which the adsorbed material is eluted with a poor solvent. In our case, a good separation of sodium and potassium has occurred only in the head fraction. The bulk of the electrolyte comes over at the single large peak, with the sodium in excess. The smaller peak at the right represents material rich in potassium. With a longer column and somewhat altered operating conditions, it is possible that good resolution of the mixture could be obtained. On the other hand, this would be a batchwise process, and would therefore miss a desirable feature of the method, namely its adaptability to continuous processing. No further experiments of this type were performed.

3.4 Experiments with Periodic Current Reversal

This type of experiment could also be called "alternating current," but the term would be misleading because of the extraordinarily long cycle - 2 hours in most cases. The series of experiments to be recorded were designed to furnish separation factors as a function of operating conditions, obtaining as much information as possible in a few experiments. The time limitation was imposed because of the necessity of exploring other systems of more direct interest to the Laboratory program during the author's residence. Consequently, it will be found that some experiments are of composite nature, in which more than one variable is studied.

It is worthwhile to re-emphasize at this point that periodic current reversal is necessary for continuous processing. As current flows in one direction, active electrode material is used up, and no further separation can occur after it is exhausted. This is analogous to the saturation of an ion exchange resin; reversing the current is like exposing a new batch of fresh resin to the material to be fractionated. A very desirable feature of the present method is that reversal can be accomplished on an automatic program and without interruption of the separation process.

An example of current and conductance curves obtained by this technique is provided in Figure 9.

³The run numbers are preceded by the letter B to distinguish this work from that reported previously² with the same apparatus. Runs B-1 through 4 were made on the single electrolyte NaCl in the manner described in reference 2. Where sequential gaps appear in the B series it will be generally understood that the data were discarded due to a leak in the cell, misbehavior of the power supply or similar difficulty.

Figure 8.

Run B-5, unidirectional current. Curves of effluent conductance, Na and K concentration. Single cell (no reservoir) charged with 2 ml solution 0.5 N in NaCl and 0.5 N in KCl. Applied potential 0.5 volt. Water flow rate 4 ml/hr.

Figure 9.

Current and effluent conductance curves for experiment with periodic current reversal, illustrating approach to steady-state current, and periodicity of current and effluent conductance. Run B-17, three cells in series with "A" reservoir. Solution 1 N in NaCl and 1 N in KCl. Applied potential 0.5 volt, current reversed hourly. Water flow rate, 4.7 ml/hr.

Run B-9: Single cell, no reservoir at bottom; applied potential 0.5 volt; water flow rate 4.8 ml/hr. Two ml of a solution 0.5 N in NaCl and 0.5 N in KCl was introduced into the cell and water was introduced into the bottom as usual at a steady rate. For the first 22 hours after sample collections had commenced, the current was reversed hourly. Between 22 and 26 hours, the steady current period was 30 minutes, and between 26 and 45 hours, 15 minutes. The results are plotted in Figure 10.

The separation factor in this set of experiments is the Na/K ratio of the effluent relative to the Na/K ratio of the original solution (unity). More properly, the Na/K ratio of the effluent should be relative to that at the bottom of the cell; however, at this point, no suitable means had been developed for extracting samples from the bottom. From Figure 10, the separation factor is seen to drop from a high of 14.8 at the beginning to 6.4 at the last value recorded. Although the run was continued for a total of 72 hours, a partial short circuit in the cell made the results beyond 40 hours unreliable. At the conclusion of the experiment, the solution was drained from the cell and the Na/K ratio found to be 0.51; this evidently results from the continual removal of Na-rich solution as effluent, a factor that is also primarily responsible for the steady drop in the separation factor.

We are unable to make a quantitative estimate of the effect of the 4-fold reduction in cycle time on the separation factor; it is clear, however, that the separation factor has not been increased. The definite rise in conductance of the effluent indicates that the current efficiency is lower with short cycles than with long cycles; moreover, it is probable that the short cycle hastened the attrition of electrode material which led to the partial short circuit.

Since short cycles are shown experimentally to be less efficient than long cycles, a conclusion which is also plausible from theoretical arguments, the question naturally arises as to how long a cycle can be in a practical case. For a given set of conditions - concentration, applied potential, and flow rate - there is a definite upper limit on the cycle time which is determined solely by the amount of active electrode material present. An optimum cycle time can be found which will strike a balance between the upper limit due to this cause and the low current efficiency at shorter cycle times. For all the experiments reported here, the two-hour cycle was found to be satisfactory.

Run B-12: Single cell, reservoir A at bottom (sintered glass disc absent); applied potential 0.5 volt, current reversed hourly. Separation factors were determined for a mixture 0.1 N in NaCl and 0.1 N in KCl at three flow rates, 4.6, 7.7, and 10.8 ml/hr.

It has been pointed out earlier that a large reservoir containing solution at the bottom of the cell maintains the concentration essentially constant; hence, the separation factor in this case is actually the Na/K ratio of the effluent relative to that at the bottom of the cell. The water enters through

Figure 10.

Run B-9, Periodic current reversal, illustrating deleterious effect of shorter cycle times. Single cell (no reservoir) charged with 2 ml solution 0.5 N in NaCl and 0.5 N in KCl. Applied potential 0.5 volt. Water flow rate 4.8 ml/hr. The decline of the separation factor with time is due both to the shorter cycle time and to the steady removal of Na-rich mixture from the cell.

the bottom of the reservoir, where it mixes with the solution, forcing it up through the cell.

In order to obtain an effluent sample with a concentration which is characteristic of a given flow rate, one must be sure that the system is in a steady state during the sample collection. In this experiment, a large sample was rejected prior to the sample collected for analysis. In cases where successive samples were analyzed, the close concordance of the results indicated that the system was for practical purposes in a steady state. On the other hand, the previous run, B-11, where lower flow rates were studied, sometimes gave inconsistent results for a series of samples, probably due to lack of attainment of the steady state. These results are therefore not reported here. It is evident that lower flow rates mean longer times to reach the steady state. The results of run B-12 are shown in Table 1 and Figure 11. In the range studied, both the total effluent and the separation factor are not far from linear functions of flow rate. Perhaps a more significant relationship is the approximate linearity between total effluent concentration and separation factor (Figure 11b).

Runs B-14, 15, 17: These runs were made with three cells in series with the "A" reservoir at the bottom. The applied potential was 0.5 volt and the current was reversed hourly. The flow rate was virtually the same in each case, about 4.7 ml/hr. The series was designed to test the effect of initial concentration on separation factor over a limited range. The results are presented in Table 2 along with those of B-12 at the corresponding flow

Table 1

STEADY-STATE SEPARATION FACTORS FOR
SODIUM-POTASSIUM MIXTURES

Run	No. of Cells	Molarity NaCl, KCl in reservoir	Flow rate (ml/hr)	Total molarity effluent	Separation factor C_{Na}/C_K
B-12	1	0.1	4.6	0.00109	10.9
			7.7	0.00206	7.8
			10.8	0.0029	5.7
B-14	3	0.1	4.6	0.00080	29.4
B-15	3	0.4	4.6	0.00072	29.4
B-17	3	1.0	4.7	0.00063	44.0

rate. In run B-15 close observation of the rising stream of water in the reservoir led to the suspicion that complete mixing of water with solution in the reservoir was not being attained. Following this run, a coarse sintered glass disc was incorporated in the body of the reservoir (Figure 3).

Figure 11.

Effluent concentration and separation factor as a function of flow rate. The upper and lower graphs are plotted in a different manner from the same data. Run B-12, single cell with reservoir "A." Solution 0.1 N in NaCl and 0.1 N in KCl. Applied potential 0.5 volt, current reversed hourly.

This has the effect of transforming the single incoming stream into a large number of small ones over a wide area, promoting mixing of the water with the solution. Observation of the mixing interface thereafter supports the conclusion that mixing was substantially complete.

Run B-16, with sintered glass disc, but otherwise the same as B-15, showed on thorough analysis of the data that none of the samples were taken under steady-state conditions, and the data are therefore not comparable with that of the other runs. Unfortunately, this was not known until after the series was completed. The results of this run are not included in the table, and there is no unambiguous test of the effect of the sintered glass disc on separation factor. The attainment of the steady-state is an important criterion for comparing data between different runs, for it has been observed that separation factors in non-steady states can be either higher or lower than in the steady state. The latter is not always easy to attain in a reasonable time, particularly at low flow rates.

Run B-17, also with the sintered glass disc, differed from B-15 in initial concentration. The separation factor for B-17 in the steady-state was 50 per cent greater than for B-15. Since the separation factors for B-14 and B-15, differing only in concentration, were the same within the experimental error, one is tempted to conclude that the sintered glass disc is responsible for the improved separation factor in Run B-17, but the possibility that the concentration difference between B-15 and B-17 played a part in the results cannot be discounted.

3.5 Summary

It had become clear that an investigation of the sodium-potassium system which would give a reasonably complete picture of the effect of all variables on the separation factor would require far more time than had originally been allotted. Interesting as this study would be, it was necessary to turn our attention to other systems which had more practical objectives. The useful information obtained from this series of experiments can be summarized as follows:

1. For the first time it has been shown that the method is applicable to the separation of two cations which differ moderately in mobility. The general magnitude of the separation factors obtained with this relatively simple cell are large enough to afford confidence in the method as an approach to other separation problems.

2. The continuous production technique has been employed for the first time i.e., as mixture passes through the cell, the separating action is maintained on an essentially continuous basis by periodic reversal of the current. Short cycles are less efficient energy-wise than long cycles and probably lead to premature fouling of the electrodes, but cycles have an

upper limitation governed by the amount of active electrode material. A half-cycle of one reversal per hour was found to be a satisfactory compromise for the present experiments.

3. The long periods required to reach a steady-state impose a severe burden on certain parts of the apparatus. For example, there are perhaps a dozen relays which have to function at regular intervals; the failure of any one of these during an experiment either renders the data worthless for quantitative purposes or introduces difficulty into the interpretation. By careful redesign and rebuilding of the apparatus, the reliability can undoubtedly be improved; however, at this point it seems preferable to continue with the present apparatus, even though some runs have to be discarded through faulty operation.

4. Several runs could usually be made before electrode attrition became serious enough to require disassembly and cleaning of the cell. While this was satisfactory for the present research, a long term study should include electrode development aimed at an indefinite increase in lifetime.

5. Introduction of the sintered glass disc into the reservoir improves mixing of solution with the incoming water stream and probably leads to a somewhat higher separation factor, other things being equal.

6. The steady-state separation factor is roughly three times as large for the triple cell as for the single cell at the same concentration and flow rate.

7. Solutions can be handled in the present apparatus with total electrolyte concentrations ranging from 0.2 to 2 molar. The effect of initial concentration on separation factor appears to be small.

4. Attempted Lithium Isotope Fractionation

4.1 Introduction

In general, two cations in aqueous solution will migrate at different rates under the influence of an applied field, although in some cases, and particularly in the case of isotopes, the difference in mobility will be very small. The separating power of the electrogravitational method employed here depends primarily on this factor, but small differences in mobility are effectively multiplied many times by the counter-current flow due to gravitationally-induced natural convection in a direction perpendicular to that of the electric field. The applicability of the method to the separation of chemically different species has been demonstrated with sodium-potassium chloride mixtures, where large separation factors were obtained in a single

run. This is a problem of moderate difficulty, the mobility ratio K/Na being 1.47. Isotope separations present difficulties orders of magnitude greater.

The mobility ratio for Li^6 and Li^7 is certain to be very close to unity, but there is no known method for estimating its exact magnitude. The present attempt to fractionate the lithium isotopes was undertaken without knowing whether or not success was probable on theoretical grounds. If, after double or triple fractionations, enrichments of 5 to 10 per cent were found, it was felt that the method might be applicable to actual separation of the lithium isotopes. To anticipate the result, no fractionation was found within the accuracy of the analytical technique, and it is therefore concluded that the method is not practical for this problem.

4.2 Summary of Column Operation

Run B-18. Apr. 18-May 5, 1952. The 30-inch column (cell) was connected at the bottom to reservoir "A" filled with 1 M LiCl. The large volume was used so that enrichment occurring in the column would not deplete the solution. Pure water was pumped into this reservoir at 4.5 ml/hr. where it mixed with the solution, forcing the latter through the column. The electrogravitational action within returned concentrated LiCl to the reservoir, and dilute LiCl issued from the top into receivers. As before, the applied potential was 0.5 volt, and the current was reversed every hour. After 238.5 hours of operation, 900 ml of effluent containing about 30 mg of Li was collected and evaporated to a few ml for further fractionation.

Run B-19. May 8-10. The same column was connected to reservoir "B." The concentrated effluent from the preceding run was introduced into the reservoir and operation begun exactly as before. After 76 hours, 275 ml had been collected containing about 0.5 mg Li. This sample, presumably enriched in 7Li , was prepared for isotopic analysis.

Run B-20. May 12 - June 16. This run was designed to enrich 6Li in a reservoir sample by removing from it a large amount of 7Li enriched material as effluent from the top. About 5 ml of 5 M LiCl solution was introduced into the reservoir and pure water was flowed up through the system, with operating conditions the same as before, except for a higher flow rate. The effluent was discarded. The run was terminated at 580 operating hours. The reservoir solution containing 2.3 mg Li, or about 1.5 per cent of the original solution, was prepared for isotopic analysis.

4.3 General Remarks on Column Operation

The apparatus had not been designed originally to function continuously with such a large sample, or over so long a period of time. It was therefore inevitable that interruptions would occur which in every case would tend to decrease the separation factor.

The interruptions were caused by minute leaks, partial short circuits within the cell, after prolonged operation and occasional misbehavior of the relays of the power supply assembly. In spite of these difficulties, it is felt that the present experiments constitute a fair test of the suitability of the method for lithium isotope separation.

4.4 Isotopic Analysis

Several methods have been employed for this analysis. The one most used, mass spectrometry, was not immediately available. An emission spectroscopic method was being developed by the spectroscopy group, but trial runs by J. K. Brody indicated that the precision required for this work had not been achieved.⁴ A pile irradiation-tritium counting method offered promise, because of the precise tritium counting techniques developed by Kaplan, Wilzbach, and Van Dyken.⁵ This method is based on the reaction of ${}^6\text{Li}$ with slow neutrons:

No such reaction occurs with ${}^7\text{Li}$. This method requires an accurate analysis of total lithium; these were made with the flame photometer.

All lithium samples were converted to Li_2SO_4 by evaporation with sulfuric acid. Fifty microliters of solution containing 0.3 to 0.45 mg/ml total Li were sealed under vacuum in quartz containers with "breakoffsky" tips. Triplicate samples of the starting material, quadruplicate samples of the two enriched fractions, and a single blank were thus prepared. (Only one blank was used, since it was known that a blank correction is insignificant under the circumstances.) The sample from run B-20 was contaminated with sodium; it was purified by extraction with n-octyl alcohol.

The samples were irradiated together for $31\frac{1}{2}$ hours at a neutron flux of $10^{12} \text{ cm}^{-2} \text{ sec}^{-1}$. The twelve quartz containers were distributed in three aluminum cans. The apparatus of Kaplan, Wilzbach, and Van Dyken was used for processing the sample and counting the tritium. The tritiated water is reduced quantitatively by passage over hot zinc, the gas volume is accurately measured, the gas collected, and the ionization current determined. The results are expressed in μc per mg Li. Owing to the inexperience of the author in operating this equipment, only 8 of the 11 lithium samples survived accurate analysis. The results are given in Table 2.

⁴Since this work was done, marked improvements in precision have been obtained, resulting in a probable error of replicate determinations of only 0.5 per cent. See J. K. Brody, M. Fred, and F. S. Tomkins, J. Opt. Soc. America, 42, 870 (1952).

⁵Preliminary reports on this technique are contained in (a) K. E. Wilzbach and A. R. Van Dyken, AECD 2998 (1950); and (b) L. Kaplan, and K. E. Wilzbach, J. Am. Chem. Soc., 74, 6152 (1952).

Table 2
RESULTS OF LITHIUM ISOTOPE ANALYSES

Solution	Sample	Activity ($\mu\text{c}/\text{mgLi}$)
starting material	(can #3) 3	34.8
from Run B-19	7	35.4
from Run B-19	8	36.6
from Run B-20	12	35.3
	(can #2)	
from Run B-19	6	36.4
from Run B-20	11	36.1
	(can #1)	
from Run B-20	9	33.9
from Run B-20	10	34.2

The greatest spread should have occurred between sample B-19 and B-20. No difference is observed within the limits of precision. (The precision reported here is somewhat poorer than is normally obtained with this apparatus.) The lower activity for the two samples from Can #1 suggests that the flux was lower here.

We conclude from these results that any isotopic enrichment which may have occurred was within the experimental error of ± 1.5 per cent.

5. Cerium-Thorium Fractionation

5.1 Introduction

The cerium-thorium mixture was selected next because of its practical interest, and also because it presented an opportunity to investigate the applicability of the method to cations of higher valence. The pH of the solution is not a critical factor when dealing with univalent cations, but when the valence is three or greater, too high a pH usually causes precipitation of the hydroxide. The hydrogen ion, due to its extraordinarily high mobility, is rapidly stripped from solution in the electrogravitational cell, which makes it impossible to maintain on a long term basis a pH lower than 6 or 7, except by some artificial means. Thus, many higher valence cation separations may not be possible with the apparatus in the present stage of development.

The cerium-thorium mixture is on the borderline. Several sources have indicated that precipitation does not occur in cerium^{III} or thorium^{IV}

solutions at pH 7. There is, however, an additional complication in the case of cerium^{III}, because of the slow oxidation to cerium^{IV}, which normally occurs in the presence of air, and the possibility of oxidation at the electrodes in the cell. Solid hydrated CeCl_3 , if not prepared with stringent precautions and kept in an inert atmosphere, dissolves to form a slightly turbid solution. The turbidity is due to CeO_2 and not to hydrolysis of the Ce^{III} . It is readily removed by centrifuging. If the solution is not kept out of contact with air, further oxidation occurs very slowly.

The potential of the $\text{Ce}^{\text{III}}\text{-Ce}^{\text{IV}}$ is -1.6 volts, a value which seems sufficiently large to prevent oxidation of Ce^{III} solutions. However, CeO_2 is highly insoluble except in strong acid, and even a small amount of Ce^{IV} formed in solution by oxidation is therefore removed from the scene of action by precipitation as the dioxide. In beginning this study, there was some apprehension that precipitation in the cell by oxidation would introduce troublesome problems.

In order to make rough experimental tests of precipitation phenomena, a small demonstration unit was constructed (Figure 12), which permitted visual observation of the interior of a cell where electrogravitational action is occurring. This consists of two parallel electrodes 1 in. wide and $2\frac{1}{2}$ in. long suspended in the solution contained in a 180 ml tall form beaker. The electrodes were each three layers of silver wire mesh attached to silver wire leads and chloridized electrolytically in the usual manner. They were kept about $3/8$ in. apart by suspension from a rubber stopper (not shown). The beaker was filled with solution 0.32 M in CeCl_3 and 0.32 M in ThCl_4 . When current was passed through this cell, streamers of heavy solution can be observed quite clearly falling from the bottom of the cathode, and streamers of light solution rising from the top of the anode. The current was passed through the cell (with manual reversal of polarity when the decay of current indicated that the electrode material was exhausted) for several hours. At the end of this time, there was a substantial vertical density gradient in the solution, indicating that the bulk of the electrolyte was in the bottom of the cell. The solution above the electrodes was slightly milky, but there was no visual evidence of precipitation on the electrodes themselves.

This experiment by no means duplicates precisely the phenomena occurring in the separation cell, where conditions are more stringent. Nevertheless, it was felt that the absence of visual precipitation on the electrodes offered sufficient promise of freedom from complication to permit the experiment in the separation cell to be undertaken.

5.2 Analytical Technique

The cerium-thorium stock solution was spiked with 8×10^4 year Th^{230} , an alpha emitter, and 275 day Ce^{144} , a beta emitter. An alpha and a beta count on a fractionated sample thus yields directly the cerium-thorium ratio relative to that of the initial solution. This convenient analytical technique

Figure 12.

Demonstration cell for investigating behavior of Ce-Th mixtures. This simple arrangement permits clear visual observation of the essential features of the electrogravitational method.

was developed by D. F. Peppard and his group for use in their separation studies of the cerium-thorium mixture by solvent extraction. Dr. Peppard and G. W. Mason furnished the tracer Th^{230} and Ce^{144} from their stock, as well as much valuable information regarding its use.

The thorium tracer received (3ml) contained about 15 mg of Th^{230} with Th^{232} in 8:1 excess. There was a small amount (less than 1 per cent) of the daughter Ra^{226} and its disintegration products. The separation of thorium from the daughters was carried out as follows: The solution was evaporated to dryness and dissolved in 0.1 M HCl, which had been adjusted to pH 1 with the aid of a pH meter. This solution was extracted with 10 ml of a solution of 0.2 M TTA in benzene in a 60 ml separatory funnel. The thorium is retained in the benzene layer. The water layer was re-extracted with TTA in another separatory funnel and discarded. Tenth molar HCl was then cycled through both benzene layers twice and the fractions combined. The purified thorium was removed from the benzene layer by extraction with 1 M HCl. The resulting solution was evaporated to dryness and taken up in 5 ml of distilled water. The alpha activity of the solution thus prepared was 3.2×10^7 c/min/ml.

The cerium tracer, in HCl solution of indefinite concentration, had an activity of 3×10^8 c/min/ml. It was used without further processing.

Twenty ml of solution 0.32 M each in CeCl_3 and ThCl_4 was prepared and spiked with enough of the above tracers to give an alpha activity of $\sim 3 \times 10^6$ c/min/ml and a beta activity of $\sim 6 \times 10^6$ c/min/ml.

5.3 Run B-22.

This run was commenced with the entire amount of spiked solution in the triple cell, reservoir "B" attached. Applied potential 0.5 volt, current reversed hourly. Despite the results of the preliminary experiment mentioned earlier, extensive precipitation occurred on the electrodes, partially short circuiting them, and the experiment was therefore terminated after a few hours. A count on the precipitate showed the presence of both cerium and thorium; hence, it is believed that our difficulties are caused at least in part by the pH falling too low at the upper solution level. This in turn could be due to too high an applied potential difference, leading not only to oxidation of the Ce^{III} , but also to extensive stripping of hydrogen ion from solution. It was believed that more efficient sweeping of oxygen from the cell preliminary to the run, and less stringent operating conditions - principally lower applied voltage - would be more conducive to keeping the material in solution.

The cell was thoroughly contaminated after this abortive run. The precipitate could not be dissolved completely even by flushing the cell with concentrated HCl; therefore, the cell was disassembled and cleaned by a combination of scrubbing and acid treatment until no activity registered on a

survey meter. This cell, as such, was not used, however, for further runs. Instead, it was decided that sufficient information could be obtained much more easily with a single cell. In preparation for the next run, new electrodes were fitted to the single cell.

After chloridizing the new electrodes in the usual manner, operating conditions of the apparatus were studied with unspiked solutions of CeCl_3 and ThCl_4 to avoid contaminating the cell with activity (Runs B-24 through 28). It was evidently necessary to find conditions which would eliminate precipitation in the separation cell itself, since experiments with the demonstration cell of Figure 12 had proved unreliable for extrapolation.

The following conclusions were derived from these studies: (1) With the cell thoroughly deoxygenated prior to a run, and at a flow rate of 3.5 to 6.5 ml/hr., applied potential differences of 0.35 volt or above are unsafe due to precipitation in the cell. (2) At 0.25 volt, other conditions being equal, no precipitation at all occurs in the initial stages of the run. As time goes on, the conductance drops markedly and the effluent solution becomes milky, although precipitation apparently does not occur directly on the electrodes. (3) No voltage less than 0.25 was tried; however, it seemed unlikely that an effective separation of the cerium-thorium mixture could be obtained with lower voltages, even if precipitation were entirely averted. Therefore, it was decided to carry out a run on spiked cerium-thorium mixtures at 0.25 volt to see if the separation factor thus obtained warranted further experimentation.

5.4 Run B-29

4 ml of solution 0.32 M in CeCl_3 and 0.32 M in ThCl_4 , spiked as in B-22. Flow rate 3.7 ml/hr. Initial effluent conductance (relative), 0.01; final, 0.0032. Run terminated at 22 hours. The conductance was still going down, but it seemed certain that if the run were continued, the precipitation would be worse. Two effluent samples were taken for analysis near the beginning and end of the run, and one bottom sample near the beginning. The 4.6 ml initial and the 39 ml middle fractions were discarded. None of the samples showed significant fractionation.

We thus conclude that with the mild conditions employed in Run B-29, no appreciable fractionation of cerium and thorium occurs. More stringent conditions, which might be effective for the separation, also lead to excessive precipitation in the cell, rendering the method unsuitable. Further research could be directed toward artificial maintenance of pH to prevent precipitation. At the present time the demand for a new method for separating cerium and thorium is not sufficient to warrant this new line of research.

6. Radium-Barium Fractionation

6.1 Introduction

The classical method of recovering radium from mixtures containing a large excess of the chemically similar barium is fractional crystallization of the bromide or chloride. This method is difficult and time-consuming, requiring a large number of batchwise stages before radium appears in acceptable purity. More recently, an ion exchange column technique has been developed which is a vast improvement over fractional crystallization in resolution and in economy of effort. On the other hand, this is a batch process, and continuous process would be even more attractive for radium production. Continuous operation is an inherent feature of the electrogravitational method, and it was therefore decided to explore the adaptation of this method to the radium problem.

The mobility ratio of radium to barium has not been determined. Kendall, Jette, and West,⁶ however, attempted the separation of radium from barium by straight ion migration through an agar gel, finding that the radium concentrated in the front boundary. In our method, therefore, radium should concentrate in the bottom of the cell.

The mobility ratio of radium to barium was expected to be large enough to permit use of the short (9 in.) cell for determining separation factors. It was also desirable to carry out the determination in the hood, which is not large enough to accommodate the longer cell.

6.2 Radium Assay

The technique for assaying the radium was suggested by Paul Fields. The only alpha-active reasonably long lived daughter of 1640 year Ra^{226} is 138-day Po^{210} . This can be removed from the initial radium sample by rotating a silver foil in a solution of the salt overnight. The polonium is plated out quantitatively on the silver. Since silver is also present in the electrolytic cell, no interference from polonium will occur if assays are completed on withdrawn samples without undue delay. Removal of emanation is accomplished by boiling the solution, and doubly assured by the final evaporation on the counting plate. When the plate is fired, emanation is absent, but its short-lived daughters would produce a spurious count if the plate were assayed immediately. About one hour is therefore allowed before counting, to assure decay of the daughters - but no more than this to avoid fresh build-up of emanation. This technique was followed in all reported assays.

The radium samples had been prepared by The National Bureau of Standards, apparently for calibration purposes. They were received in

⁶J. Kendall, E. R. Jette, and W. West, J. Am. Chem. Soc., 48, 3114 (1926)

hermetically sealed glass ampoules containing about 10 ml of liquid. The ampoules were labeled as 10 micrograms (used in Run B-30) or 20 micrograms (Run B-31) in solution with excess BaCl_2 .

6.3 Determination of Barium

Conductance analysis was selected for the estimation of barium chloride since it possessed the optimum combination of convenience and precision. Because the barium is present in huge excess, the determination of total dissolved electrolyte is equivalent to that of barium chloride alone. The conductance cell used for these determinations was the one normally attached to the apparatus, and the conductance was measured on the bridge recorder. During the measurements, the temperature was adjusted manually when necessary. A calibration curve was constructed by measuring the conductance of known concentrations.

6.4 Run B-30: Preparation of Ra-Ba Mixture.

After removing the 10 μg radium solution from the ampoule, a small piece of silver wire mesh was rotated in the solution overnight. There was definite evidence of attack on the silver, and addition of HCl threw down a heavy precipitate of AgCl . Because of the small amount of carrier barium present, it is felt that some of the radium was lost by adsorption on the AgCl precipitate. An excess of HCl was added, and the AgCl removed by filtration. The solution was evaporated to dryness threetimes, adding a small amount of HCl between operations. This was done to assure complete reduction of the nitrate ion which was apparently present in the original solution. The residue was dissolved in 10 ml of a 1N solution of BaCl_2 . This amount of excess barium provides a convenient concentration for cell operation, and simulates conditions which might be encountered in the early stages of a practical radium-barium fractionation.

Fractionation - After introducing the above solution into the cell, the DC power was turned on (applied potential difference 0.5 volt, current reversed hourly) and the system allowed to reflux for two hours. The water flow was then started through the cell at a rate of 2.5 ml/hr. The run was continued for 48 hours, and four consecutive samples of 10, 25, 20.6 and 60 ml were collected in graduated receivers. The effluent conductance-time curve is shown in Figure 13. Corresponding to each of these, samples of $1/4$ to $1/3$ ml were withdrawn from the bottom of the cell. All samples were evaporated almost to dryness under the heat lamp, two drops of 2N HCl added, and the evaporation continued to dryness, allowing 30 minutes at the high hot plate setting to assure complete removal of water and acid. The HCl was added as a precautionary measure to neutralize any OH^- ion which may have been formed in the cell by the side electrode reaction discussed in section 3.2. Since oxygen was carefully excluded from the cell by the nitrogen treatment, the HCl addition was probably unnecessary. The residue from each sample was dissolved in 2 ml of water for conductance measurement and α -count.

Figure 13.

Run B-30, Radium-barium mixture. Effluent conductance vs. time. Single cell with "B" reservoir, charged with 10 ml of 1 N BaCl_2 solution containing $10\text{ }\mu\text{g}$ radium tracer. Applied potential 0.5 volt, current reversed hourly. Water flow rate 2.5 ml/hr. Figure in upper part of graph refer to effluent samples withdrawn for analysis.

The samples were counted on stainless steel plates. Aliquots were 100 μ l for the top solutions and 25 μ l for the bottom solutions. An exception to this rule was #3 (top) where, after a rough check on 100 μ l, a more accurate count was made on 10 μ l. A 100 μ l aliquot of the original solution diluted 50:1 was also counted.

The results are given in Table 3.

Table 3

Sample	Relative Conductance ⁷	Concentration (mole liter ⁻¹)	α -Assay (counts min ⁻¹ ml ⁻¹)	$k \times 10^{-5}$ ⁸	γ
original (diluted 50:1)	0.00305	0.0123	1,640	1.32	
1t	.00167	.0162	3,400	2.10	1.29
1b	.0129	.064	10,400	1.625	
2t	.00418	.0185	3,240	1.75	1.295
2b	.0151	.077	10,440	1.36	
3t	.00177	.0075	1,416,300	1,890.	2,630.
3b	.0188	.098	7,040	0.718	
4t	.00484	.0218	2,170	1.00	0.673
4b	.0121	.0600	8,920	1.485	

The variation in k_t/k_b among the 4 samples is quite unlike anything that we have encountered before with this column. It is obviously not possible to assign a definite value to the separation factor which is characteristic of a given Ra-Ba mixture. The effluent from sample 3 contains most of the radium from the original sample. Thus it appears that the active material moved up the column as a band, the width of which is contained primarily in sample 3. The appearance of this band at the end of the high conductance region (Figure 13) is regarded as possibly significant. This run should be counted, however, as giving only provisional results. This experiment is repeated in Run B-31, starting with fresh radium-barium mixture.

⁷Note that the conductance reported here is for the collected samples after evaporation and re-solution in a smaller volume; whereas the conductance of Figure 13 is the instantaneous value during collection of the samples.

⁸ k is defined as the alpha-assay divided by the concentration. The separation factor γ is the ratio (k_t/k_b) of the values of k of the top and bottom samples.

In analyzing these results the following factors should be borne in mind:

1. Use of stainless steel plates: the chloride solution undoubtedly attacks the plates to a variable extent, depending on the quantity of salt. This attack influences the self-absorption of alpha particles.
2. The manner in which the plates were prepared for counting had not been well standardized at this point, and this further increases the error due to self-absorption.
3. The effluent conductance of the first sample was substantially higher than the others due to insufficient refluxing prior to its collection.
4. After 38 hours of operation, the failure of a relay led to erratic variation in the applied voltage. This is reflected in the increased conductance at the end of the collection of sample 4.

The enormous activity of sample 3 as compared with the others is clearly outside the errors discussed above.

6.5 Run B-31: Preparation of Sample

The 20 μ g Bureau of Standards radium sample was evaporated to dryness three times with addition of HCl between operations to assure reduction of nitrate ion. The residue was dissolved in 2 ml of 1N BaCl₂ solution. To be doubly certain that radioactive daughters would not complicate the subsequent procedure, Pb²¹⁰ was removed by addition of PbCl₂ carrier and precipitated from slightly acid solution by H₂S. After filtering and boiling, the polonium was removed by the silver foil technique. The solution was again evaporated to dryness, and the residue dissolved in 8 ml of 1N BaCl₂ solution.

Preparation of the Column - The column was rinsed of solution from the previous run until the wash water showed negligible conductance. Distilled water was then passed through the cell for several hours with the DC voltage and reversing mechanism on. The reason for the latter treatment was as follows: although the silver grid from the column had shown no activity by survey meter test prior to Run B-30, it is conceivable that some alpha and beta activity from previous runs may have been occluded by the AgCl coating. Assuming that the abnormal activity of sample 3 in run B-30 was due to prior cell contamination, the results seem to indicate that a voltage applied to the cell would be effective in dislodging the contamination. However, it is concluded from results to be reported later that contamination by thorium is quite improbable.

Fractionation - The effluent conductance curve is shown in Figures 14 and 15 with volumes of effluent samples. It will also be seen from this figure that the effluent conductance is sensitive to fluctuations in applied voltage,

Figure 14.

Run B-31 (First portion). Radium-barium mixture. Effluent conductance vs. time. Operating conditions same as in B-30 (Figure 13), except for use of 20 μ g radium tracer. Irregularities in curve are due to voltage fluctuations or equipment shut-downs.

Figure 15.

Continuation of Run B-31.

which occurred occasionally due to a relay failure. It appears that a steady-state was never actually reached in this run, and, like B-30, it is not possible to assign a definite separation factor for a given radium-barium mixture.

In Run B-31 there were several improvements in analytical technique over B-30 which were adopted in an attempt to obtain unambiguous results. The removal of Pb^{210} from the sample and pretreatment of the cell have already been mentioned. The stainless steel counting plates of B-30 were replaced by 2 mil platinum plates, with a decided improvement in reproducibility of count. The assessment of self-absorption error is facilitated by (1) smaller samples - this was possible because of the higher ratio of radium to barium in the starting sample; (2) better uniformity of plate preparation: the 25 μl aliquots were stippled onto the plates in 5 approximately equal drops, and two distilled water rinses were added to these drops in equal amounts. (3) Data for preparing a self-absorption calibration curve was obtained by counting 25 μl aliquots of solution, covering a 30 fold concentration range, prepared by quantitative dilution of starting material. The values of k obtained from these determinations were plotted as a function of concentration (Figure 16), and the resulting curve used to correct observed counts to the extrapolated zero self-absorption basis. The slope of this curve is not great, which indicates that self-absorption is not a serious factor; on the other hand, the scatter of points, probably occasioned by variable loss of material during drying and firing of the plate, leave a great deal to be desired.

The results on the various samples collected in B-31 are recorded in Table 4. Discussion of the last four columns is reserved until later. It will be observed that three of the determinations in which both top and bottom samples were taken show separation factors of 4 or higher (column 5), while six have factors in the neighborhood of 0.8. None of our efforts at explaining why these factors are sometimes higher and sometimes lower than unity is entirely satisfactory. The following possibilities have been considered.

(a) Activity in samples due to elements other than radium. The substantial magnitude of the separation factors when greater than unity makes this an unlikely possibility. All of the glassware used was scrupulously cleaned between experiments, and it seems certain that contamination through containers could not contribute appreciably to the alpha-assay results. Emanation and its short-lived daughters can be ruled out completely because of the counting technique employed. Only polonium and thorium-230 need be considered, the former possibly through build-up between sample collection and assay, and the latter by residual contamination of the cell from the cerium-thorium separation experiments. These hypotheses were tested by reprocessing a number of the collected samples as follows: A set of four stirring motors was assembled with a silver wire stirrer for each. To remove polonium by plating out on the silver, the solutions were stirred overnight. Then the pH was carefully adjusted to $1 \pm .02$ unit with a Beckman Model G pH meter by dilution and addition of HCl . The solution

Figure 16.

Self-absorption correction curve used in treating data of Run B-31.

Table 4

RESULTS OF SAMPLE ANALYSES, RUN B-31

Sample	Original Samples				Reprocessed Samples							
	Conc. Mole liter ⁻¹	α -Assay, count min ⁻¹ ml ⁻¹	k x 10 ⁻⁵	γ	Conc.	α -Assay	k x 10 ⁻⁵	γ				
1t	0.0216	18,850	8.73	.896	0.0652 .0329	31,650 34,200	48.6 10.4	4.67				
1b	.0515	50,150	9.74									
2t	.0111	7,810	7.05	.734								
2b	.0490	47,100	9.61									
3t	.0182	106,000	58.3	6.18								
3b	.0508	47,900	9.43									
4t	.00632	5,530	8.74	4.11								
4b	---	---	---									
5t	.0414	9,730	8.53									
5b	---	---	---									
6t	.0138	47,750	34.6						0.00845 0.299	30,950 30,300	36.6 10.13	3.61
6b	.0436	36,700	8.42									
7t	.0245	18,180							.0115 .0310	67,300 32,220	58.5 10.40	5.63
7b	---	---	---									
8t	.0142	88,900	62.6	.0119 .0297					11,050 30,100	9.28 10.27	.904	
8b	.0390	36,200	9.28									
9t	.0152	12,240	8.06	.00860 .0240					7,645 28,350	8.87 11.81	.751	
9b	.0358	37,220	10.4									
10t	.0113	8,900	7.88	.0174 .0221					12,590 21,600	7.24 9.78	.740	
10b	.0356	33,400	9.38									
11t	.0211	17,370	8.22	.802								
11b	.0290	29,780	10.26									
12t	.00752	5,750	7.65	.767								
12b	.0317	31,610	9.98									

was then extracted twice with 0.2 M TTA in benzene, using the stirrers to assure thorough contacting of the phases, followed by centrifugation. This technique is known to remove thorium quantitatively, leaving the radium in the aqueous phase. The concentration of the resulting solutions was determined conductometrically, and the alpha-assay taken on each solution. The results are shown in the last four columns of Table 4. While the separation factors have been reduced, where greater than unity, by 15 to 25 per cent, the relative order is the same, and the magnitudes are not essentially different from those obtained before reprocessing. The extra operations themselves might be expected to introduce enough error to account for whatever difference there is before and after reprocessing. It is clear that polonium and thorium-230 cannot account for the magnitude of our separation factors.

(b) Mechanism of Cell Operation. Separation of a binary mixture can occur either through a rate process, or what might be called a steady-state process. Prior to this series of experiments all data could be explained on the basis of a rate process. That is, the faster cation moving toward the cathode under the influence of the potential gradient is caught in the downward convection current in greater proportion than is the slower cation. The faster ion is therefore relatively more concentrated in the bottom of the cell. If radium is indeed more mobile than barium, as indicated by the experiments of Kendall, Jette, and West, the separation factor in the present experiments should, by this criterion, be less than unity.

If the steady-state mechanism is operative, different observations might be expected. Reference is made to the equivalent circuit model of Section 8.2. The basic arguments should apply as well to the vertical electrode case of our actual cell as to the horizontal electrode case of the model. The equivalent circuit model of Figure 19 is applicable to the system with two cations and a common anion.

When a voltage is applied to a cell containing a mixture originally uniform in concentration, the rate mechanism leads simply to a larger relative build-up of more mobile cation (radium) near the cathode, corresponding to a separation factor less than unity. After prolonged current passage, the electrical transport of both ions becomes balanced by back diffusion and a steady-state is reached. In the equivalent circuit model, this corresponds to equality of potential difference across the cell as a whole and across both condensers. The relation between the condenser potential difference and concentrations at the electrodes is

$$E_c = \frac{RT}{F} \ln \frac{C_o}{C_a} \quad (6.1)$$

for an ideal transference cell with bivalent cations. Since E_c is determined solely by the concentration ratio at the electrodes in the steady-state, this

ratio will be the same for all cations of the same valence, and there is no resulting separation of cations; i.e., the separation factor is unity. However, the type of transference cell with which we are dealing in practice is far from ideal. In section 8.10, it is shown that a reasonable extension of the model to non-ideal systems leads to the relation

$$E_c = \frac{RT}{F} \ln \frac{(a_{\pm})_o}{(a_{\pm})_a} = \frac{RT}{F} \ln \left(\frac{C_o}{C_a} \right) \left(\frac{f_o}{f_a} \right), \quad (6.2)$$

where (f_o/f_a) is the ratio of the activity coefficients for a given electrolyte at the two electrodes. In the steady-state therefore, the radium and barium chlorides will have different concentration ratios if the activity coefficient ratios for the species are not the same. The deviations from ideality are certainly substantial for the concentration range we are dealing with here. No attempt is made to predict which way this nonideality consideration will direct the separation, but it is not unreasonable that it would be in the right direction to explain the greater-than-unity separation factors obtained in these experiments. The low flow rates would make it possible for steady-state rather than rate behavior to be approached. On the other hand, the occasional voltage fluctuations during the experiment may have led to transitions between rate and steady-state operation.

(c) The Use of Tracers. It is common knowledge among radio-chemists that tracer experiments sometimes yield results lacking in reproducibility for unknown reasons, while the same type of experiment carried out with macro quantities yield different and reproducible results. Further experimental work is indicated on this problem using substantially greater proportions of radium.

6.6 Conclusion

It is clear that this investigation has created more questions than it has answered. The separation factors greater than unity which were obtained are large enough to make the method attractive for practical purposes. It remains to be seen whether a continuous separation at this level can be maintained. If there is enough demand for a continuous radium separation method, this investigation might be re-opened on a larger scale with a concerted effort to find out the cause of the variable separation factors.

PART II. (THEORETICAL)

A. EQUIVALENT-CIRCUIT MODEL OF THE TRANSFERENCE CELL.

B. THE TRANSFERENCE CELL: THERMODYNAMICS OF THE STEADY STATE

7. Introduction

The original aim of the theoretical part of this work was a complete mathematical description of the electrogravitational process, suitable as a basis for predicting separation factors, production rates, etc., for a given system, and as a basis for experimental design. Such a theory not only would have these obvious practical uses, but also would possess great intrinsic interest. Several approaches are possible, all of them complicated by the large number of variables and by the nature of the basic differential equations; at best, only approximate mathematical solutions can be expected. Even more disturbing is the fact that some of the simple phenomena which combine to form the complex electrogravitational process are imperfectly understood themselves. It seemed well worthwhile to postpone execution of the original aim in its entirety in order to clarify the basic concepts. This has led to the two principal theoretical contributions which make up this part of the report.

Electrode and ion-transport processes are both essential elements of every electrochemical cell. It is sometimes possible to study one of these processes without interference from the other. For example, in electrical conductance and moving boundary experiments on electrolytic solutions, the ion-transport processes of interest are isolated from electrode phenomena by appropriate experimental technique. Conversely, in electromotive force measurements carried out for the purpose of deriving thermodynamic properties, careful experimental design can reduce ion-transport processes to a position of negligible significance. Generally speaking, the interpretation of data is facilitated when the reversible and irreversible processes are not intermingled.

The great bulk of electrochemical processes occur, however, with just such intermingling. A simple classical illustration of this is the concentration cell with transference, where the diffusion of ions is unavoidably present during EMF measurements. Also in this category is the inverse of the concentration cell with transference, i.e., a concentration gradient is generated in a cell through electrode and ion-transport phenomena by application of voltage from an external source. Precisely the same arrangement results when convection is eliminated from the electrogravitational process by operating with horizontal electrodes. This situation is discussed

in reference 2. Since cells of this type are studied in detail in what follows, the essential link between the two parts of this report has been established. Many other examples of cells where electrode and ion transport processes must be considered together can be found; usually, they are much more complex than the examples just cited. It is evident that a theoretical advance on this subject would be of very general interest in the field of electrochemistry.

The efforts of the author along this line has led in the first instance to an equivalent circuit model of a cell, including the specific types considered above, which emphasizes the importance of time-independent or steady-states in cells where current is flowing and concentration gradients are present. From the model, long-established equations for conductance, for the concentration cell with transference, and for the diffusion of ions are derived. It thus serves as a quantitative basis of reference for a number of experimental facts. It is heuristic in nature, suggesting new experiments with thermodynamic significance. Furthermore, it is so simple that it possesses considerable pedagogical appeal.

The second approach has been through the thermodynamics of the steady-state. This treatment is entirely mathematical and not pictorial, leading to the same results as the equivalent circuit treatment in different form and subject to verification by the same tests. The two approaches supplement and strengthen each other, yielding a description which is complete for the relatively simple process considered, and promising equally successful results for more complex systems.

8. Equivalent Circuit Model of the Transference Cell.

8.1 The Transference Cell

The term "transference cell" refers to a system with two identical reversible electrodes in contact with an electrolytic solution, one or more ions of which participate in the electrode reaction. By "reversible" we mean that the clearly specifiable reaction at one electrode occurs in exactly the reverse manner at the other, and that there is no activation or resistance overpotential at the electrodes. The applied or measured potential is always less than that required for decomposition of the solution: i.e., concentration gradients but no changes in composition are established in the cell as a result of passage of current. The familiar "concentration" cell exists when there is a concentration gradient, but no external current.

The silver - silver chloride electrode, chloride ion system is adopted throughout the report for illustration. Three aspects of a cell of this type are shown in Figure 17. In (a) the system is in equilibrium, with a uniform concentration and no external EMF. In (b) an external EMF has been applied,

a.

b.

c.

Figure 17.

Cross-section of the transference cell. Heavy black horizontal lines bounding upper and lower surfaces of cell represent Ag-AgCl electrodes; cross-hatching, insulating spacers; density of dots, concentration of electrolyte.

- (a) Cell in equilibrium, concentration uniform.
- (b) Cell with external applied potential difference. (Charging of cell).
- (c) Concentration cell with transference, EMF being measured with potentiometer, or high resistance voltmeter.

but changes in concentration have occurred near the electrodes only. This corresponds to a Hittorf transference experiment. Because of the density differences which arise, the cathode is situated at the bottom to avoid convection currents. In (c) the concentration difference between the top and bottom electrodes leads to an external EMF; this is a concentration cell with transference. The external battery of (b) has been replaced by a potentiometer. In (b) a substantial current passes, while in (c), for a measuring device of infinite sensitivity, there is no external current at all.

It is evident that continued passage of current in (b), followed by removal of the external current source, leads to a concentration cell with transference (c). It has been shown^{9,10} that the steady-state concentration distribution reached after prolonged current passage, is linear for the ideal case.

8.2 Equivalent Circuit

The use of equivalent circuit models in certain electrochemical problems is not new. Several authors have employed such models for the interpretation of the electrical double layer at mercury-solution and other interfaces. Grahame^{11,12}, in his capacitance studies, noted the presence at certain polarizing potentials of a very large capacity effect due to oxidation-reduction phenomena at the electrodes. He called this a "pseudo-capacity" to distinguish it from true double-layer capacity. Breyer and Gutman¹³ referred to this as a "dynamic capacitance." The condenser and other elements of our equivalent circuit are similar to those utilized by Grahame and by Breyer and Gutman, in that they involve oxidation-reduction at the electrode, but differ in that they also involve concentration gradients throughout the solution. Moreover, we have restricted ourselves to the simplest types of electrode processes and are primarily concerned with the time-independent or steady-states attained by steady application of a DC voltage; these states are incapable of realization with the AC methods employed by Grahame and other investigators, who were primarily interested in double-layer phenomena. The steady-states which these authors refer to are time-independent on the average, but the variables are changing continuously during periods of the order of one cycle.

⁹H. J. S. Sand, *Phil. Mag.*, (6), 1, 45 (1901).

¹⁰T. R. Rosebrugh and W. L. Miller, *J. Phys. Chem.*, 14, 816 (1910).

¹¹D. C. Grahame, *J. Am. Chem. Soc.*, 63, 1207 (1941).

¹²D. C. Grahame, *J. Electrochem. Soc.*, 99, 370c, (1952).

¹³B. Breyer and F. Gutman, *Trans. Faraday Soc.*, 43, 785 (1947).

Equivalent circuits are also important in the interpretation of the dielectric properties of crystals, as exemplified by the recent work of MacDonald.¹⁴

We postulate that the equivalent circuit of this cell is given by Figure 18a. The components R_+ and R_- are resistances ascribed to the cation and anion, respectively. They can be expressed in terms of the concentration and the corresponding mobilities when the concentration distribution is known. The condenser is an energy storage unit which is related to the cell process by the following arguments: The reversible electrical work done at constant temperature and pressure in adding an infinitesimal quantity of charge dQ to the condenser plates at a potential difference E_c is $-E_c dQ$. Only positive charges pass through the left hand part of the circuit, where the condenser is located; therefore, dQ is the charge equivalence $F dy$ of the cations transferred from the solution at one electrode of concentration C_a to solution at the other electrode of concentration C_o . Due to the electroneutrality condition, and the fact that cations cannot enter or leave the solution, passage of the charge dQ thus results in the net transfer of dy equivalents of electrolyte from one electrode to the other. The transfer is reversible if carried out infinitesimally slowly. Since the free energy change for this process is equal to the reversible work done, we have

$$E_c = -\Delta G/F \quad (8.1)$$

where ΔG is the molar free energy change for the process

Referring to Figure 18b, it is to be noted that dQ is the charge passed through the left hand side of the circuit only. Concurrent with this process, an additional charge dQ' passes through the right hand side in a purely dissipative manner; hence, no claim of reversibility is made for the cell as a whole. On the other hand, the model clearly specifies that all reversible phenomena of the cell are to be associated with the condenser, and all irreversible phenomena with the resistances.

For our mathematical treatment, we make the further assumptions that activities may be replaced by concentrations, and that the conductances are linear functions of the concentration. These assumptions, together with those made earlier, characterize what we shall refer to as an ideal transference cell. In this case equation (8.1) becomes

$$E_c = -\frac{2RT}{F} \ln \frac{C_o}{C_a} \quad (8.2)$$

¹⁴J. R. MacDonald, abstract in Bulletin of The American Physical Society, Cambridge, Mass. Meeting (1953). Details to be published.

Figure 18.

Equivalent circuit corresponding to cells of Figure 17.

- (a) Basic circuit.
- (b) Charging with external source.
- (c) Self-discharge (free diffusion).

This equation makes possible a test of the model with respect to known properties of the ideal transference cell.

Each of the three circuit elements of Figure 18a is nonlinear; that is, the current is not proportional to the applied potential difference except in the limit of very small EMF's. For steady-state operation of the cell, suitable mathematical relations between EMF, current, and concentration can be found.

Why do the connections to the external circuit separate R_- from R_+ and the condenser? Because the electrodes in this example "pass" Cl^- ions, but are blocking to M^+ ions. In other cases, an analysis must be made of the "permeability" of the electrodes to each ionic species.

In Figure 18b the current corresponding to Figure 17b is analyzed. The flow of negative charge through the right hand side is electrically equivalent to a positive charge flowing in the opposite direction. Thus the current through the left is considered to be carried by the cation only, and the current through the right by the anion only. The current in the external circuit is the sum of these two.

The current during self-discharge of the cell is shown in Figure 18c. The internal current is equivalent to free diffusion of the salt, with the flux of positive ion equal to the flux of negative ion, as required by the electroneutrality condition. From the electrical circuit standpoint, this means that the current through the left must be equal to that through the right. Only an infinitesimal current flows through the external circuit to actuate the potentiometer. The internal current is fictitious in the sense that it cannot be measured as an electric current, but it is by no means a new concept. As early as 1888 Nernst¹⁵ postulated that the diffusion of the ions of an electrolyte constituted an internal electric current, and he was led thereby to the concept of "diffusion potential," which arises because of the different mobilities of ions. Although the diffusion potential has had many applications since Nernst's time, it is an objectionable concept from the operational viewpoint, since it cannot be measured directly. We propose in this treatment to express the physical behavior of the system in terms of the external potential applied to or generated by the cell.

8.3 The Cell Resistance

Let a be the distance between the parallel electrodes of area A . If C is the local concentration (in equivalents per cc) and l_+ and l_- are the mobilities (equivalent ionic conductances) of the positive and negative ions,

¹⁵W. Nernst, Z. physik. Chem., 2, 613 (1888).

then the resistances due to these ions in the solution are

$$R_+ = \frac{1}{Al_+} \int_0^a \frac{dx}{C} \qquad R_- = \frac{1}{Al_-} \int_0^a \frac{dx}{C}$$

These equations may be integrated for a known concentration distribution. In the case of the linear distribution which is attained in the steady-state,

$$R_+ = \frac{a}{Al_+(C_0 - C_a)} \ln \frac{C_0}{C_a} \qquad R_- = \frac{a}{Al_-(C_a - C_0)} \ln \frac{C_0}{C_a} \quad (8.3)$$

where C_0 and C_a are the concentrations at $x = 0$ and $x = a$, respectively. When the ratio C_a/C_0 is close to unity, these equations reduce to

$$R_+ = \frac{a}{Al_+ C_0} \qquad R_- = \frac{a}{Al_- C_0} \quad (8.4)$$

The cell resistance, as seen by the external circuit, is evidently obtained by parallel combination of these elements:

$$R_{\text{cell}} = \frac{R_+ R_-}{R_+ + R_-} = \frac{a}{\Lambda(C_0 - C_a)} \ln \frac{C_0}{C_a}, \quad (8.5)$$

where Λ is the equivalent conductance of the salt. In the limit as $\frac{C_0}{C_a} \rightarrow 1$,

$$R_{\text{cell}} = \frac{a}{\Lambda C_0} \quad (8.6)$$

which is just the cell resistance that would be measured with a uniform electrolyte by an AC method. On the other hand, examination of Figure 18 shows that the apparent resistance in the steady-state is,

$$R_{\text{cell}} = \frac{a}{Al_- C_0}, \quad (8.7)$$

since no net current flows through the left hand side.

8.4 Self-Discharge of the Cell - Verification of Nernst's Diffusion Equation

During self-discharge of the cell (free diffusion, Figure 18c), the internal current density, I_{int} , produces a difference of potential $A I_{\text{int}} (R_+ + R_-)$ across the series combination of resistances, which is equal in magnitude,

but opposed in sign, to E_c . Combining this relation with Equations (8.2) and (8.3), we obtain

$$I_{\text{int}} = \frac{2RT}{F} \frac{C_o - C_a}{a} \frac{l_+ l_-}{l_+ + l_-} \quad (8.8)$$

However, I_{int} is also equal in magnitude, but opposed in sign to the product FJ of the faraday constant and the diffusion flux J , for which Fick's law of diffusion

$$J = \frac{I_{\text{int}}}{F} = -D \frac{C_o - C_a}{a}, \quad (8.9)$$

is valid, where D is the diffusion coefficient. It follows from Equations (8.8) and (8.9) that

$$D = \frac{2RT}{F^2} \frac{l_+ l_-}{l_+ + l_-}, \quad (8.10)$$

which is Nernst's diffusion equation.¹⁵ Ample experimental verification for this equation has been provided in cases where ideal conditions are approached.

The measured EMF of the self-discharging cell is just E_t , that of a concentration cell with transference. In terms of the potential drops across the resistors, E_- and E_+ ,

$$E_t = E_- = E_c - E_+ = E_c + \frac{l_-}{l_+} E_- ,$$

whence
$$E_t = \frac{l_+}{l_+ + l_-} E_c = t_+ E_c \quad (8.11)$$

This is a verification of another long-established equation. Equations (8.5), (8.10), and (8.11) are a concise summary of the known properties of the ideal transference cell. The accuracy of the equivalent circuit model has therefore been established by the derivation of these equations on the basis of it.¹⁶

¹⁶ The derivation of Equation (8.5) started with the assumption that the ionic conductances are independent of one another; since this assumption leads to the correct result for the concentration dependence of cell resistance (8.5), the law of independent ionic migrations is verified.

8.5 Capacitance of the Condenser.

As we charge the condenser, the potential difference across its plates increases, corresponding to an increasing concentration gradient in the transference cell. By Equation (8.2), the minimum work done in transferring the infinitesimal quantity of electrolyte dy is

$$FE_c dy = 2RT \ln \frac{C_o}{C_a} dy \quad , \quad (8.12)$$

The energy dissipated in the right hand resistor is not included in this calculation; furthermore, the transfer may be imagined to occur infinitesimally slowly, so that there is no energy dissipation in the left hand resistor. Under these conditions, the system is always in a steady-state, with a linear concentration gradient. The concentration at the mid-point between the electrodes remains constant, and the electrolyte transfer takes place across this dividing line.

The concentration at any point and the number of moles transferred are connected by the relation

$$CV = 4y \left(\frac{2x}{a} - 1 \right) + n_o \quad , \quad (8.13)$$

where V is the volume of the cell and n_o the number of moles of electrolyte. Since C cannot be less than zero at the anode, y is limited to values between zero and $n_o/4$ for the linear concentration distribution.

Equation (8.12) may be integrated after substituting (8.13):

$$\begin{aligned} \text{work} &= 2RT \int_0^y \ln \frac{C_o}{C_a} dy = 2RT \int_0^y \ln \frac{n_o + 4y}{n_o - 4y} dy \\ &= \frac{RT}{2} \left\{ (n_o + 4y) \left(\ln 1 + \frac{4y}{n_o} \right) + (n_o - 4y) \ln \left(1 - \frac{4y}{n_o} \right) \right\} \end{aligned} \quad (8.14)$$

When $n_o \gg 4y$, corresponding to a low EMF, this equation reduces to

$$\text{work} = \frac{8RTy^2}{n_o} \quad (8.15)$$

In transporting y equivalents, Fy coulombs are passed through the left hand side of the circuit. Thus, the work done in charging the condenser, in the region where equation (8.15) is valid, is proportional to the square of the charge transferred, a characteristic of a normal condenser. The

capacitance of the condenser is evidently $n_0 F^2 / 16RT$. Unlike a normal condenser, the capacitance is directly proportional to the number of moles of electrolyte, but independent of the electrode separation or area.

The capacitance for a typical case is enormous by any ordinary standard. Suppose, for example, that $\underline{n}_0 = 10^{-4}$ equivalent, a quantity which would be contained in a decinormal solution filling a 1 cm^3 cell. At room temperature, the capacitance is

$$\frac{10^{-4} \times (9.65)^2 \times 10^8}{8 \times 8.316 \times 298.1} = 21.2 \text{ farad}$$

This exceeds by many powers of ten the capacitance of any radio condenser of comparable size.

8.6 Current as a Function of Applied Potential.

Since all of the components in the equivalent-circuit model are non-linear, the cell as a whole will not be expected to follow Ohm's law, except for certain limiting conditions. The equations

$$I = \frac{2RT}{F} t_- \Lambda \frac{dC}{dx} \quad (8.16)$$

and

$$\frac{dE}{dx} = \frac{2RT}{F} \frac{d \ln C}{dx} \quad (8.17)$$

(compare equations (8.7) and (8.9)), hold locally at any point within the cell in the steady-state. While $\frac{dC}{dx}$ is constant throughout the cell, $\frac{dE}{dx}$ is obviously not so, being greater at the points of lower concentration. The $\underline{E}$ of this equation is the total potential difference measured by Ag-AgCl electrodes, but, as indicated previously, it is also the potential across the condenser under steady-state operation.

Upon integrating equation (8.12) between appropriate limits and rearranging, there results the equation

$$C = \frac{IF}{2t_- \Lambda RT} \left(x - \frac{a}{2} \right) + C_{Or} \quad , \quad (8.18)$$

where C_{Or} is the original uniform concentration of electrolyte. Substituting (8.17) into (8.16), integrating over x , and solving for I , one obtains

$$I = \frac{4C_{Or} t_- \Lambda RT}{a F} \tanh \frac{EF}{4RT} \quad (8.19)$$

The E in this equation is the total applied potential. By expanding the hyperbolic tangent and retaining only the first term, we obtain an equation valid for small applied potentials:

$$I = \frac{C_{or} t_- \Delta E}{a} \quad (8.20)$$

Ohm's law is therefore satisfied under this condition; however, the conductance measured under steady-state operation is t_- times the value measured under uniform concentration conditions.

When $EF/4RT$ becomes very large, the hyperbolic tangent approaches unity, equation (8.19) becomes

$$I = \frac{4C_{or} t_- \Delta RT}{a F} \quad (8.21)$$

and the current density is independent of applied potential.

Equation (8.19) has also been obtained in a mathematical analysis by Piguet, Kuhn, and Kuhn.¹⁷ The assumptions inherent in their derivation lead, however, to an incorrect result for the EMF of a concentration cell with transference.

8.7 Concentration as a Function of Applied Potential.

The concentration difference between the electrodes may be expressed in terms of the current density by application of equation (8.18):

$$C_o - C_a = \frac{IF a}{2t_- \Delta RT} \quad (8.22)$$

Substituting (8.19) into (8.22), we have

$$C_o - C_a = 2 C_{or} \tanh \frac{EF}{4RT} \quad (8.23)$$

This equation has also been obtained by Piguet, Kuhn, and Kuhn.¹⁷ According to equation (8.23), the ratio $\frac{C_a - C_o}{C_{or}}$ is dependent only on the applied po-

tential for the system under study, but independent of transference number and conductance. The elimination of terms characteristic of irreversible processes from the concentration-potential relation is relevant to our discussion below.

¹⁷J. Piguet, W. Kuhn, and H. Kuhn, Helv. Chim. Acta, 34, 1183 (1951).

For small values of $\underline{E}$, equation (8.23) becomes

$$\frac{C_a - C_o}{C_{or}} = \frac{EF}{2RT} \quad (8.24)$$

For practical purposes this is equivalent to equation (8.15). For large values of $\underline{E}$, equation (8.23) leads to the result

$$C_o - C_a = 2C_{or} \quad (8.25)$$

Since the total number of moles is conserved, this equation shows that the limiting condition at high applied potential is reached when the concentration at $\underline{x} = 0$ has doubled, while that at $\underline{x} = \underline{a}$ has fallen to zero.

8.8 Extension of Theory to Mixtures.

While the foregoing mathematical treatment has been applied to only the simplest case, a 1-1 electrolyte in an ideal transference cell, a single electrolyte of any other valence type could be easily handled. The treatment of mixtures is more complex, requiring the introduction of additional elements into the electrical circuit model, and additional parameters in the equations. The detailed treatment will not be recorded here but it is worthwhile to outline the procedure for a relatively simple case: electrodes again reversible to the chloride ion, electrolyte a mixture of two chlorides, e.g., NaCl and KCl. The equivalent circuit of this cell is obtained by parallel combination of circuits for each salt, as if the other were absent (Figure 19).

Application of a polarization potential will produce in the steady state a solution with a concentration ratio C_o/C_a which is the same for each constituent. When this potential is released, the EMF of the resulting concentration cell with transference is given by

$$E_t = \left[(t_+)_1 + (t_+)_2 \right] E_c, \quad (8.26)$$

where

$$(t_+)_1 = \frac{(C_+)_1(1_+)_1}{(C_+)_1\Lambda_1 + (C_+)_2\Lambda_2}$$

$$(t_+)_2 = \frac{(C_+)_2(1_+)_2}{(C_+)_1\Lambda_1 + (C_+)_2\Lambda_2}$$

In general, when an indefinite number of cations are present in the system with the common chloride ion,

$$E_t = E_c \sum_i (t_+)_i \quad (8.27)$$

Figure 19.

Diagrams illustrating parallel additivity of circuit elements for two single electrolytes to obtain equivalent circuit for mixture.

$$(t_+)_{\text{i}} = \frac{(C_+)_{\text{i}} (l_+)_{\text{i}}}{\sum_{\text{i}} (C_+)_{\text{i}} \Lambda_{\text{i}}}$$

$(C_+)_{\text{i}}$ = concentration of the i th cation species

$(l_+)_{\text{i}}$ = mobility of the i th cation species

Λ_{i} = equivalent conductance of the chloride salt of i th cation species.

It is evident that the non-steady states prevailing in general problems now interpreted in terms of junction potentials will involve much greater mathematical complexity. Nevertheless, the pictorial simplicity of the equivalent-circuit model should be of assistance in setting up equations for a particular junction potential problem. Diffusion problems in multi-electrolyte systems may also be interpreted in terms of the model.

8.9 What is Diffusion Potential?¹⁸

The equivalent circuit model of Figure 18 contains three elements, each characterized by its own potential when the solute is diffusing freely from an initial steady-state concentration distribution; moreover, each is directly measurable in principle by appropriate experimental technique, if electrodes reversible to the desired ion can be found. Thus, the potential across R_- is obtained directly from the circuit of Figure 18. If the electrolyte were HCl, the potential across R_+ would be directly measurable through reversible hydrogen electrodes (Figure 20). None of these potentials is equivalent to Nernst's diffusion potential, which is postulated to arise in a solution because of different rates of migration of ions across a concentration gradient. This potential difference is not directly measurable in principle, but must be calculated on the basis of assumptions in the Nernst theory from measurements on the EMF of the cell as a whole. For nonideal solutions, these assumptions are inexact; furthermore, cell EMF's in the case of mixtures are strongly dependent on the structure of the junction, and it must be emphasized that all such measurements involve the use of electrodes with characteristic properties on which the magnitude of the measurement depends. Diffusion potential, however, is postulated to be a property only of a solution containing a diffusing electrolyte.

This problem, and the equivalent one of single ion activities, has been dealt with at length by Guggenheim,¹⁹ who sums up the situation as follows: "The electric potential difference between two points in different media can

¹⁸The terms "junction potential" and "diffusion potential" are used interchangeably.

¹⁹E. A. Guggenheim, J. Phys. Chem. 33, 842 (1929).

Figure 20.

Transference cell with electrodes reversible to cation and its equivalent circuit.

never be measured, and has not yet been defined in terms of physical realities; it is therefore a conception which has no physical significance."

Taylor²⁰ arrives at a similar conclusion, pointing out that single ion activities or free energies, and the potential at a liquid junction are not thermodynamically defined, but are "purely mathematical devices, which may indeed be employed safely with considerable freedom."

MacInnes and Longsworth²¹ discuss several types of liquid junctions, and, in agreement with Guggenheim and Taylor, take the position that only the observed cell EMF has real thermodynamic significance. Nevertheless, these writers follow the general practice of ascribing a definite numerical value to the junction potential in the simpler cases, where the assumptions involved in their mathematical treatment are reasonably secure.

The concept of diffusion potential in simple systems, when properly interpreted, does lead to correct results. On the other hand, the extensive body of literature which has accumulated around this interpretation suggests that it is not wholly satisfactory, even as a mathematical device. Classical electrochemical problems now interpreted in terms of diffusion potential seem to call for a new approach which involves only operational concepts. The writer suggests that the equivalent circuit model of this paper serve as a starting point. It will have to be shown, of course, that the model can be extended to nonideal systems; this point is considered in the next section.

8.10 Nonideal Systems.

The successful results obtained in the case of the ideal transference cell are a strong temptation to take the general premises of the model as valid for nonideal systems as well. Equation (8.2) would be replaced in this case by

$$E_c = \frac{2RT}{F} \ln \frac{(a_{\pm})_o}{(a_{\pm})_a}, \quad (8.28)$$

where $a_{\pm}$ is the mean activity of the electrolyte. The conductance would no longer be proportional to concentration, but this is unimportant to our discussion; in the steady state, the applied potential difference is the same as E_c , the significant quantity from the thermodynamic standpoint, irrespective of the dependence of conductance on concentration. Clearly, we

²⁰P. B. Taylor, J. Phys. Chem., 31, 1478 (1927).

²¹D. A. MacInnes and L. G. Longsworth, Cold Spring Harbor Symposia Quant. Biol., 4, 18 (1936).

have a new means for determining activities of electrolytes. The technique of MacInnes and co-workers²² for determining activity coefficients through transference cell measurements makes use of equation (8.11), but this requires in addition a different kind of experiment to determine the transference number. The method suggested here seems to offer a real advantage in economy of experimental effort. However, it has to be admitted that at the present time the validity of our model cannot be guaranteed by theoretical arguments for the non-ideal case, and no data by which a decisive experimental test can be made appear to have been recorded in the literature.

In designing a critical experiment, it would be unsafe to take the potential applied to the working electrodes as a measure of the cell EMF. Any irreversible electrode effects due to slow kinetics of the electrode reaction, or resistance of the silver chloride film, would yield a value too high, if these factors are not negligible. Such effects are representable as an unknown series resistance added to the circuit of Figure 18a. The difficulty could be circumvented by the use of probe electrodes at appropriate points in the cell, which would carry only the infinitesimal current required for potentiometric measurements. The optical methods of analysis now extensively employed in electrophoresis, diffusion, and ultra-centrifuge investigations would be suitable for concentration determinations in such an experiment. It is well to bear in mind that attainment of the steady-state from a uniform solution would be a matter of hours or days; this time could be shortened by commencing the experiment with all conditions approaching those of the steady state as closely as possible.

It may be argued that the introduction of another irreversible process - steady current flow - on top of diffusion would introduce more uncertainty into the interpretation of EMF measurements than is encountered where diffusion alone is present (concentration cell with transference). The equivalent circuit model suggests, however, that when two concurrent irreversible processes are properly balanced (coupled), interpretation of the reversible part of the system is facilitated. This point is to be considered further in Section 9, where the transference cell is treated by the methods of thermodynamics of the steady state.

9. The Transference Cell: Thermodynamics of the Steady State²³

9.1 General Theory

The modern theory of the thermodynamics of the steady state is based on certain linear mathematical relations between flows and forces.

²²A. S. Brown and D. A. MacInnes, J. Am. Chem. Soc., **57**, 1356 (1935).

²³General references on this subject are (a) S. R. de Groot, "Thermodynamics of Irreversible Processes," North-Holland Publishing Co., Amsterdam (1951). (b) K. G. Denbigh, "The Thermodynamics of the Steady State," Methuen and Co., Ltd., London (1951).

A generalized flow, represented by the vector $\vec{J}_i$, may be an electric current (flow of electric charge), flow of heat, flow of matter, etc. The corresponding generalized force, whose magnitude and direction is represented by the vector $\vec{X}_i$, would be electric potential gradient, temperature gradient, chemical potential gradient, etc. When the flows take place separately, that is, when only one force is acting, the rate of flow is usually directly proportional to the corresponding force. For example, the empirical laws of Ohm and Fourier, applicable respectively to the flow of electricity and of heat, state

$$\vec{J} \propto \vec{E} \qquad \vec{q} \propto \text{grad } T$$

where $\vec{J}$ is the current density, E the applied potential difference, $\vec{q}$ the heat flow vector and $\text{grad } T$ is the gradient of temperature. In generalized notation, these relations have the form

$$\vec{J} = L\vec{X}$$

where L is the proportionality factor, a scalar quantity of the nature of a conductance or reciprocal resistance.

When two or more flows take place concurrently, corresponding to the simultaneous action of an equal number of forces, any one flow is governed by all the forces, usually in linear combination. This relationship can be expressed succinctly by the set of equations

$$\vec{J}_i = \sum_k L_{ik} \vec{X}_k, \quad (9.1)$$

where k is the total number of forces acting. The set of k equations (9.1) has been termed by Eckart²⁴ the thermodynamic equations of motion. The coefficients $L_{11}, L_{22}, \dots, L_{kk}$ are the ordinary generalized conductances, while the L_{ik} , with $i \neq k$ are "coupling coefficients," representing the possible mutual coupling of the flows. Onsager²⁴ has derived a very important relation between these coupling coefficients, based on the principle of microscopic reversibility. It states that

$$L_{ik} = L_{ki}, \quad (9.2)$$

According to the principles of the thermodynamics of the steady state, equations (9.1) and (9.2) are a complete phenomenological description of the steady-state flow processes which takes place in a system governed by k

²⁴C. Eckart, Phys. Rev., 58, 267, 269, 919, 924 (1940).

²⁵L. Onsager, Phys. Rev., 37, 405 (1931); 38, 2265 (1931).

forces. In analyzing a specific case, the problem is frequently to equate the L 's to familiar measurable properties of the system.

9.2 Thermodynamic Equations of Motion for the Transference Cell

Having introduced the thermodynamic equations of motion in general form, the remainder of this treatment will be concerned only with the ideal transference cell containing a single electrolyte, where $k = 2$. A single spatial coordinate x is sufficient for this case; to economize on symbols, vector notation will be dispensed with in what follows. The forces in this case are dE/dx , the electric potential gradient, applied or measured, which alone governs the electric current density I (amp. cm^{-2}) as measured in the external circuit in the absence of other forces; and $d\mu/dx$, the chemical potential gradient, which alone governs the flux of matter in the absence of other forces. The net flux of electrolyte J (equivalents $\text{cm}^{-2} \text{sec}^{-1}$) for the simple transference cell treated in Section 8.1 is equal to J_+ , the flux of positive ion; the latter symbol will be used in the following discussion in place of J . The thermodynamic equations of motion are

$$I = L_{11} (dE/dx) + L_{12} (d\mu/dx) \quad (9.3)$$

$$-J_+ = L_{21} (dE/dx) + L_{22} (d\mu/dx) \quad (9.4)$$

subject to the Onsager condition

$$L_{12} = L_{21} \quad (9.5)$$

The minus sign precedes J_+ in (9.4) in recognition of the convention that I represents a flow of negative charges. When subjected to the same force, I and J_+ are in opposite directions. These equations hold locally in any part of the cell. They are also valid for the cell as a whole if the forces are sufficiently small, an implied if not always explicitly stated condition on the thermodynamic equations of motion for all systems. The validity of the linear form of the equations with constant L 's cannot be guaranteed if this is not so. On the other hand, it may sometimes prove convenient to retain the linear form of the equations when the forces are not sufficiently small, by allowing variable L 's. A procedure which is equivalent to this was carried out in Section 8.3, where the transference cell was analyzed in terms of the equivalent circuit model. The variation of conductance (L_{11} of equation (9.3)) was computed as a function of concentration and of applied potential difference.

To deduce the nature of the L 's of equations (9.3) and (9.4), more than one approach is possible. This multiplicity provides a check on the internal consistency of the treatment. To begin with, when $d\mu/dx = 0$

(uniform concentration), Ohm's law states

$$I = C\Lambda(dE/dx) \quad (9.5)$$

$$-J_+ = (Cl_+/F)(dE/dx) \quad (9.6)$$

Hence

$$L_{11} = C\Lambda \quad (9.7)$$

$$L_{21} = Cl_+/F \quad (9.8)$$

A more cautious approach is necessary to evaluate L_{22} , for the condition $dE/dx = 0$ may be difficult to attain when $d\mu/dx = 0$. Referring to the equivalent circuit model of Figure 18, this would correspond to a self-discharge of the condenser with the simultaneous application of an external power source just sufficient to bring the potential difference between the electrodes to zero. This would make the current through the left side (product of the positive ion flux and the faraday constant) considerably greater than in free diffusion, but would bring the net current through the right side to zero. It is evident that an immediate disruption of the steady-state condition would be introduced. Neglecting this complication, however, when $dE/dx = 0$, according to the above considerations, the electric current is due entirely to positive ions, i.e., $I = -FJ_+$. Fick's law of diffusion in this instance is

$$J_+ = -D_+ (dC/dx) = -(D_+C/RT)(d\mu/dx) \quad , \quad (9.9)$$

where D_+ is the diffusion coefficient of the positive ion. From this equation, one can derive L_{22} in terms of D_+ , but it is preferable to make use of the Einstein relation between diffusion coefficient and mobility,

$$D_+ = RTl_+/F^2 \quad , \quad (9.10)$$

so that all four coefficients can be expressed on a common electrical basis. Equations (9.9) and (9.10) lead to the result

$$-J_+ = (Cl_+/F^2)(d\mu/dx) \quad , \quad (9.11)$$

for $dE/dx = 0$; therefore,

$$L_{22} = Cl_+/F^2 \quad (9.12)$$

$$L_{12} = Cl_+/F \quad (9.13)$$

This completes the list of coefficients to be expressed in terms of familiar measurable quantities. The thermodynamic equations of motion are therefore

$$I = C\Lambda \left[(dE/dx + (t_+/F)(d\mu/dx)) \right] \quad (9.14)$$

$$-J_+ = (Cl_+/F) \left[(dE/dx) + (1/F)(d\mu/dx) \right] \quad (9.15)$$

9.3 Tests on the Validity of the Equations

The validity of these equations can be cross-checked in several ways.

(1) Comparison of L_{12} and L_{21} shows that the Onsager relation (Equation (9.5)) is satisfied.

(2) The condition $I = 0$ corresponds to a concentration cell with transference and free diffusion. From Equation (9.14) it follows that

$$dE/dx = - (t_+/F)(d\mu/dx) \quad , \quad (9.16)$$

which is an experimentally verifiable equation (see also Section 8.4). Furthermore, when $I = 0$, $J_+ = J_-$, i.e., the fluxes of positive and negative ions are equal. The flux J of electrolyte as a whole is thus equal to $J_+ + J_-$, or $2J_+$. Introducing (9.16) into (9.15), one obtains the equation

$$\begin{aligned} J = 2J_+ &= - (C\Delta t_+/F) \left[- (t_+/F)(d\mu/dx) + (1/F)(d\mu/dx) \right] \\ &= - (2C\Delta t_+t_-/F^2)(d\mu/dx) \quad . \end{aligned} \quad (9.17)$$

Comparing this with the modified form of Fick's law,

$$J = - (DC/RT)(d\mu/dx) \quad , \quad (9.18)$$

it is evident that the Nernst diffusion equation,¹⁵

$$D = 2RTt_+t_-/F^2 = 2RTl_+l_-/F^2(1_+ + 1_-) \quad (9.19)$$

is satisfied.

(3) When $J_+ = 0$, corresponding to the steady state, Equation (9.15) becomes

$$dE/dx = - (1/F)(d\mu/dx) \quad (9.20)$$

First, it will be noted that this equation is the same, except for somewhat different notation, as Equation (8.1). The latter equation was a postulate of the equivalent circuit treatment, established as correct for the ideal transference cell by the validity of results derived from it. Equation (9.20) is therefore verified by its consistency with the equivalent circuit treatment. More to the point, this equation can be regarded as established by the general principles of the thermodynamics of the steady state, and its identity with Equation (8.1) removes the latter from the rank of a postulate to a much more satisfactory position as a deduction from basic laws.

Second, for $J_+ = 0$, combination of Equations (9.14) and (9.20) yields the result

$$I = C\Lambda \left[(dE/dx) - t_+(dE/dx) \right] = Cl_-(dE/dx) \quad (9.21)$$

This equation states, in agreement with Equation (8.20), that in the steady state the net current is carried entirely by the negative ion.

9.4 Discussion

It is obvious that the general conclusions reached in Section 8.10 with respect to the information obtainable from experimental studies on transference cells are in complete agreement with the results of this treatment. For, according to Equation (9.20), EMF measurements on a properly constituted cell operating in the steady state will yield the difference in chemical potential between the electrodes directly, thereby dispensing with the necessity of measuring a transference number by a separate experiment.

In conclusion, reference will be made to an alternate treatment of the transference cell using the methods of the thermodynamics of the steady state.^{26,27} The diffusion potential gradient is introduced as one of the twin forces, instead of the potential gradient applied or measured that we have used in the present treatment. While not incorrect, the results obtained from this alternate approach appear to have little significance, serving merely to define the diffusion potential in terms of transference numbers. Our opposition to the diffusion potential concept has been expounded in Section 8.9, where its non-operational character is emphasized. A comparison of the two treatments of the transference cell leads to the following conclusions with respect to the general application of the thermodynamics of the steady state:

- (1) The choice of variables is of great importance.
- (2) Variables should be chosen which have operational significance.

²⁶S. R. de Groot, J. Phys. Rad., 8, 188, 193 (1947).

²⁷K. G. Denbigh, loc. cit. p. 78 ff.