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OXIDATION POTENTIALS IN DIMETHYL SULFOXIDE

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OXIDATION POTENTIALS IN DIMETHYL SULFOXIDE

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(Ph.D. Thesis)

November 1966

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OXIDATION POTENTIALS IN DIMETHYL SULFOXIDE

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November 1966

ABSTRACT

Accurate thermodynamic properties of lithium chloride in dimethyl sulfoxide have been determined with the cell

$$Pt(s)|Li(s)|LiCl(solution)|TlCl(s)|Tl_{(Hg)}(\ell)|Pt(s).$$

The standard cell potentials were found to be 2.4212, 2.4176 and 2.4137 volts at 25°, 30° and 35°C, respectively. Activity coefficients at each temperature were determined as a function of concentration. The reference electrode performed well, for solutions more concentrated than approximately 0.01 molal. In more dilute solutions, the solubility of thallous chloride had an appreciable effect on the cell potential. A general method is outlined for analysis of the behavior of cells involving reference electrodes of the second kind and the way in which diffusion affects their performance. The results of this development are applied to the specific cell type given above. The standard cell potential of the analogous calcium system at 25° has been estimated to be 2.17 volts.

The entropy and free energy of transfer of lithium chloride from water to dimethyl sulfoxide were calculated and compared to analogous results for other solvents, and for other salts. These thermodynamic functions were found to depend on the dielectric properties of the solvents, and to a smaller degree on the size of the ions comprising the salts.

Introduction

The state of electrolytes in dilute solutions can be described qualitatively for both aqueous and nonaqueous solvents. A few quantitative statements can also be made about the behavior of such systems, such as the Debye-Hückel law for activity coefficients of electrolytes in dilute solutions, but concentrated solutions are not well understood.

Early studies in nonaqueous electrochemistry were limited to the confirmation of theories found appropriate for aqueous solutions. Many of these studies were qualitative, and the accuracy of the data is not high. More accurate and extensive studies were begun as interest grew in utilizing nonaqueous media for reactions which necessitated the exclusion of water. The recognition that the solvent influences the thermodynamic properties of the reactants and products of reactions and the intimate connection of these properties to the course of reactions made electrochemical studies in nonaqueous solvents quite important. The result is that there are data available now, of varying degrees of accuracy, in a number of different solvents.

In general, the accuracy of cell potential data in nonaqueous solvents is lower than in aqueous solutions. Strehlow[76] has estimated many of the electrode potentials to be accurate to 0.01 volts, but the data in liquid ammonia may be accurate to 0.001 volts. The most accurate data are for cells with acid electrolytes[69]. Since the difference in cell potentials for two different solvents is in the order of 0.1-0.3 volts, the uncertainty may be in the order of 10% for data accurate to only 0.01 volts.

The more ambitious goal of relating the behavior of electrolytes to fundamental molecular parameters would allow fuller use of meager data in nonaqueous solutions and the transposition of information from

the extensive data for aqueous solutions, but the verification of such a correlation requires accurate data for a small number of nonaqueous systems. In order to characterize the influence of the solvent on ionic behavior, as indicated by free energies and entropies of solvation, it is desirable to obtain cell data which are accurate to 0.1 millivolts.

The determination of data of this accuracy necessitates a careful selection of the type of cell, electrolytes, and electrodes to be used. The type of cell which yields the most accurate data is a cell without transference, i.e., a cell in which the electrolyte is of uniform composition throughout. This cell requires that one electrode be an electrode of the second kind. Such an electrode consists of a metal and a salt of the metal which is sparingly soluble in the solution. The electrolyte in the cell must then have an anion in common with the sparingly soluble salt. The successful use of this cell, especially in dilute solutions, depends on the low solubility of this sparingly soluble salt. In concentrated solutions its concentration is suppressed by the common ion in solution, but in dilute solutions the diffusion of the slightly soluble salt away from the reference electrode will lower the cell potential. In nonaqueous solvents, it is often difficult to find a salt which is insoluble enough to insure good behavior in dilute solutions, and this limits the accuracy of determinations of the standard cell potentials. The behavior of a reference electrode from which is diffusing a sparingly soluble salt is analyzed in detail in Appendix 4.

The choice of dimethyl sulfoxide as the solvent in which to conduct cell potential measurements was based on both practical and theoretical considerations. It has a high dipole moment and is a good ligand for metal

ions. The solvent has been used extensively in recent years and has promise as an ionizing solvent. The ionizing properties were confirmed by the results of solubility, polarography and conductivity studies in the solvent. The solvent was reported to be stable toward mild oxidizing and reducing agents. Attack by certain of the alkali and alkaline earth metals is quite slow. This suggested that electrodes of such materials could be used for thermodynamic measurements. A review of the physical and chemical properties is given in Appendix 2.

The purpose of the present research was to determine accurate standard cell potentials and activity coefficients in dimethyl sulfoxide. It was first necessary to establish a reference electrode for use in the solvent. Measurements were then made on cells which utilized this electrode, and finally the data were compared to information on analogous systems in water and other solvents.

Experimental

The experimental studies of the electrochemical cells may be divided into two groups: (1) measurements on the reference electrode, and (2) measurements of the potentials of electrodes with respect to the reference electrode. The latter group of measurements were made only after a reference electrode was found which could be used in cells without transference.

The search for a reference electrode began with a survey of solubility data in the solvent. In dimethyl sulfoxide, the chlorides, bromides, iodides, nitrates and perchlorates were reported to be the most soluble salts, with the sulfates and fluorides only sparingly soluble. The chlorides, bromides and iodides were judged to be the most promising, but a sparingly soluble salt of one of the anions had to be found to serve as part of the reference electrode. Kolthoff and Reddy[42] found that silver chloride dissolved appreciably in excess chloride solutions in dimethyl sulfoxide, and in the present research mercurous chloride was found to disproportionate in the solvent. These observations eliminated the two electrodes which have proved most useful in aqueous solutions. Thallous chloride was found to be only slightly soluble in the solvent and did not dissolve perceptibly in excess chloride solutions. Since the thermodynamic properties of thallium amalgams were well known[68], and the liquid amalgam would make it possible to obtain a reproducible, clean surface, studies were begun on the thallium amalgam-thallous chloride combination as a possible reference electrode. The two types of measurements made on the reference electrode were bias potential determinations and polarization studies. The first is simply a measurement of the difference in potential

between two identical reference electrodes in the same solution, and should be very near zero. The polarization studies consisted of passing current between two of these electrodes and measuring their potential difference. For small currents the potential difference should be proportional to the current passed, for an electrode to be a good reference electrode.

After it was found that the thallium amalgam-thallous chloride electrode could be used as a reference electrode in dimethyl sulfoxide, measurements were begun on the lithium, calcium and magnesium system. Each system was composed of the chloride of the metal as the electrolyte in solution and either the metal or an amalgam of the metal as the electrode, the potential of which was measured against the reference electrode. The cells were assembled in a glove box, and then brought to 25°C in a water bath. Measurements were first made after the cell had been in the thermostat about fifteen minutes and again after one hour. If the potential measured was constant to less than 0.1 millivolts, the cell was brought to 30°, and the measurements conducted. The measurements were then made at 35°, the bath temperature was returned to 25°, and the potential measurements were repeated.

The details of the experimental procedures are given below.

I. Solvent Purification

The distillation column (Figure 1) was one meter long, 1.5 centimeters internal diameter and packed with stainless steel coils. The column was equipped with a water-cooled condenser and a reflux ration controller. Apiezon stopcock greases were used to lubricate ground joints since they were the only ones found which did not dissolve in the solvent. Stopcocks

on the collection vessels were Delmar-Urry needle valve stopcocks with teflon plugs. The vessels were designed so that contact of the solvent with stopcock O-rings were allowed only during discharge from the vessels. Only ethylene-propylene O-rings were found to be inert to the solvent.

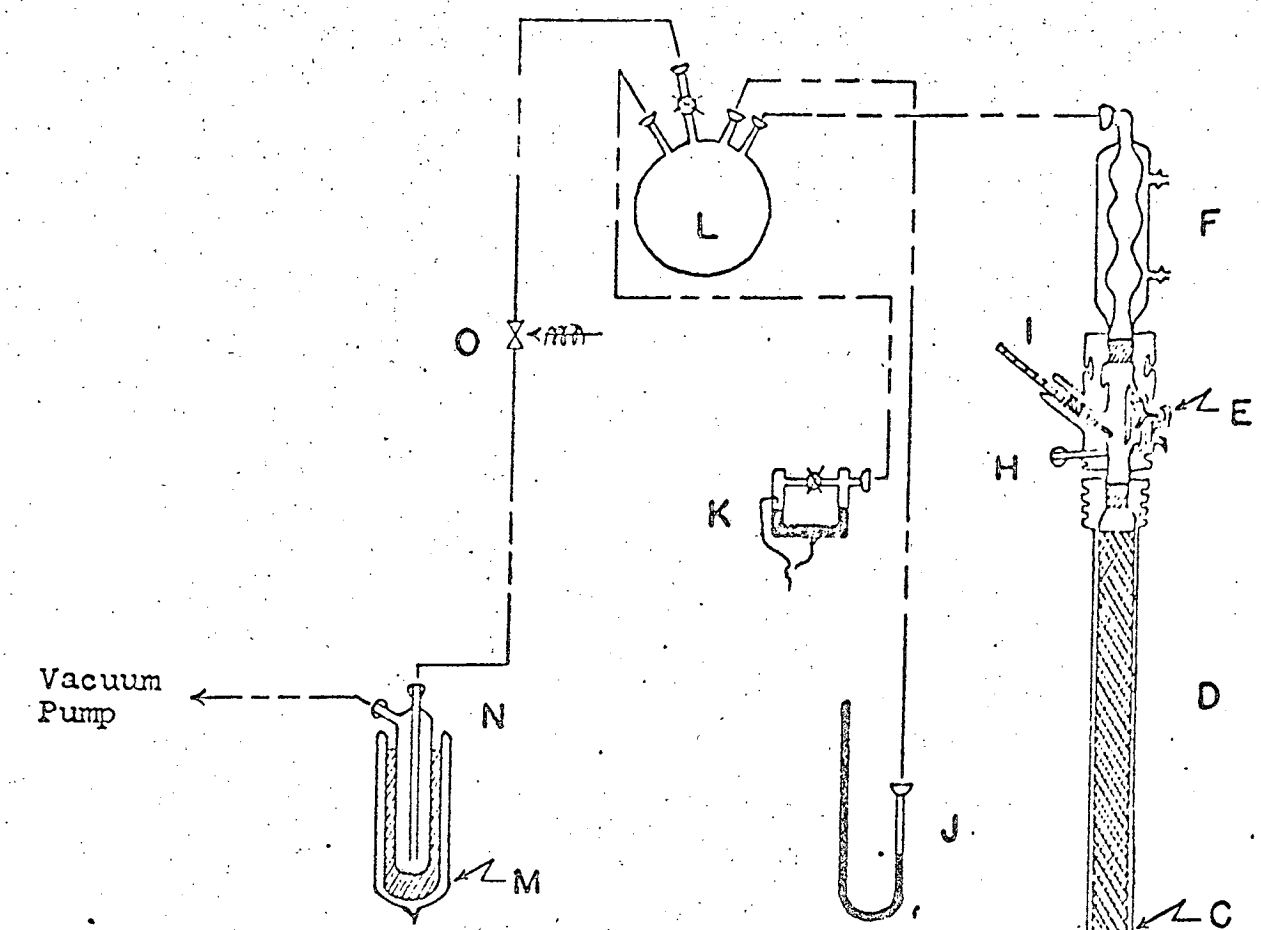
Distillation of the solvent was carried out at 5mm Hg pressure and approximately 80°C. The reflux ratio was varied from 60:1 to 1:1 during the distillation. The first and last portions of the distillate were discarded, and only the middle 3/4 was collected for the experimental work. The starting material contained less than 500 parts per million water as specified by the supplier. The distilled solvent contained less than 50 parts per million water as determined by Karl Fischer titration.

The collection vessel was not detached from the column; the solvent was discharged directly into the dispensing vessel. The transfer was made under dry argon. The dispensing vessel was evacuated on the vacuum line to approximately 1 mm pressure, closed tightly and transferred into the glove box.

II. Use of Glove Box

The vacuum glove box was of the Livermore design. It was equipped (see Figure 2) with an antechamber, glove ports for one operator, and a vacuum pump capable of evacuating the box to a few microns pressure. It was maintained under dry argon (dew point -100°F) throughout the course of these experiments.

The atmosphere could be removed and replaced in about 4 hours. The bulk of the argon was removed using the central vacuum system available in Gilman Hall. After evacuation to the desired pressure (usually 2-3 microns) the enclosure was filled with argon. The argon was passed through molecular sieves at dry ice temperature in order to remove moisture



A Mantle heater

B Thermometer

C Stainless steel coils packing

D Vacuum jacketed and silvered column

E Magnetic arm on swinging funnel

F Condenser

G Expansion joint

H Distillate take-off

I Thermometer

J Manometer

K Pressure switch

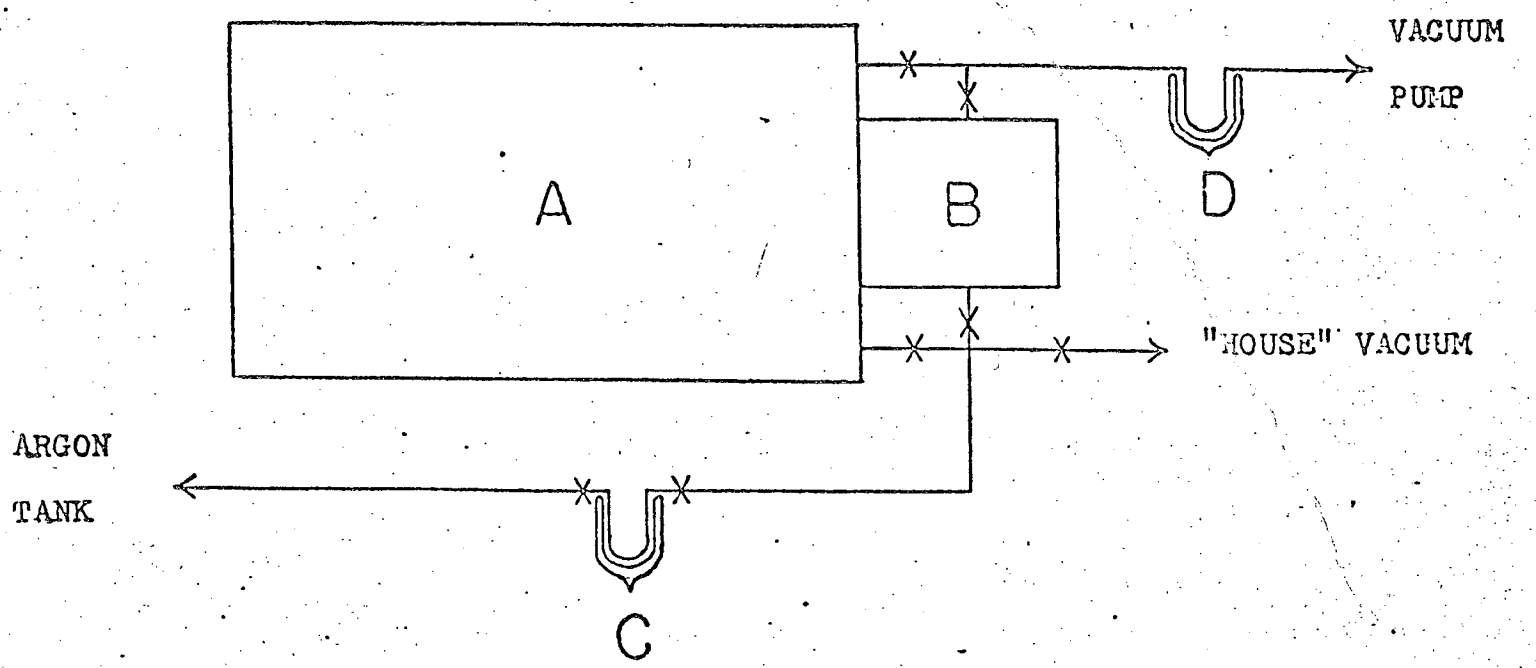
L Surge chamber

M Liquid N_2

N Vapor trap

O Solenoid valve

FIGURE 1. DIAGRAMMATIC REPRESENTATION OF DISTILLATION COLUMN



A. MAIN CHAMBER

B. ANTECHAMBER

C. MOLECULAR SIEVE U-TUBE

D. LIQUID N_2 COLD TRAP

FIGURE 2. DIAGRAMMATIC REPRESENTATION OF GLOVE BOX

introduced through leaks in fittings.

III. Amalgams

The thin oxide coating on the thallium metal was removed by washing with distilled water. The metal was then transferred to a weighing bulb equipped with a stopcock, the bulb was evacuated to remove the excess water and filled with dry argon. The bulb was weighed and transferred to the dry box where the metal was dissolved in mercury. The bulb was removed from the dry box and weighed again. The amount of displaced argon was estimated from the density of thallium and argon, and was never more than 0.5 ml argon.

The amalgam was stored in the dry box. The amalgam dispenser could be closed to the dry box atmosphere so that there was a minimum of oxidation of the thallium. Occasionally, the amalgam was analyzed to correct for changes in concentration due to oxidation. The method of Foley and Osyany[26] was used for the separation of thallium and mercury, and thallium was determined by oxidizing Tl^+ with standard KIO_3 solution. The endpoint was detected when the first excess of iodate bleached the amaranth indicator. The details of the iodate determination of Tl^+ are given by Kolthoff et al[44].

IV. Electrolytic Solutions

All the solutions were approximately 250 milliliters in volume. All weights were determined with argon in the volumetric flasks.

Concentrated solutions of lithium chloride were made by weighing the salt and the solvent into a previously weighed volumetric flask. The amount of argon displaced was calculated from the density of the gas, the density of the salt and the volume of the solution. The volume of the flask was calibrated by use of distilled water and the solutions were made to ±0.5 milliliter of the calibrated volume. Since the total weight of the solution was 270 grams, the maximum error due to the uncertainty in the amount of argon displaced is 6×10^{-4}%. The maximum amount of lithium chloride weighed

out was 10 grams with an accuracy of 0.1 mg, which introduced an error of 10^{-3}%.

The more dilute solutions were made either by dilution of a concentrated solution or by weighing lithium chloride and the solvent directly. For some of the very dilute solutions, 25 or 50 milliliters of a concentrated solution was pipetted into a previously weighed flask. The flask was weighed again and corrected for the argon displaced. Solvent was added, the solution made to volume, and the flask reweighed and the correction made for displaced argon. The weight of lithium chloride added as part of the concentrated solutions was determined from the known weight of the 25 or 50 milliliters added, the known total weight of the concentrated solution from which this was taken, and the known total weight of salt in the concentrated solution. The weight of the solvent added as part of the concentrated solution could then be calculated.

The solutions of intermediate concentration were made by dilution of 100-120 milliliters of more concentrated solutions. Of the 250 milliliters of solution made for each cell, approximately 140 milliliters were used in the cell and in the rinse procedure. The weight of solution remaining in the flask plus the weight of the flask was determined. The volume of the solution was estimated in order to correct for argon displaced. Since the weight of the empty flask and the density of the solution was known, a new volume of solution could be calculated and a new correction for displaced argon determined. The process was repeated until the calculated volume was constant. The convergence was rapid and usually only two series of calculations were required. Solvent was added and the solution made to volume. The amount of LiCl and solvent in the solution were determined by a procedure analogous to that used for the more dilute solutions. The

largest error is still that introduced in determining the weight of LiCl in the original solutions.

The solutions of rubidium chloride, calcium chloride, indium chloride, and magnesium chloride were prepared in the same way as the lithium chloride solutions.

The solutions had to be removed from the dry box for weighing, and in order to return them to the dry box a special procedure had to be followed in evacuating the antechamber. The ground joint plugs for the volumetric flasks were set on top of the joint at an angle so that the solution was exposed to the atmosphere in the antechamber. The antechamber was evacuated to a pressure of approximately 2 cm mercury and filled with argon to atmospheric pressure. The process was repeated three more times. The loss of solution was found to be less than 0.1 milligram. After the antechamber was filled with argon for the last time, the flask was transferred into the main chamber of the dry box.

V. Assembly of Cell

A. Cell for electrode potential measurements

The cell shown in Figure 3 was designed so that two reference electrodes and three metal electrodes could be used with each solution. The electrode cup and electrical lead for the thallium amalgam are shown in Figure 4. A platinum lead projects into the cup and is connected to a tungsten wire which is in turn connected to a platinum lead on the exterior of the assembly. The tungsten and connections to platinum are

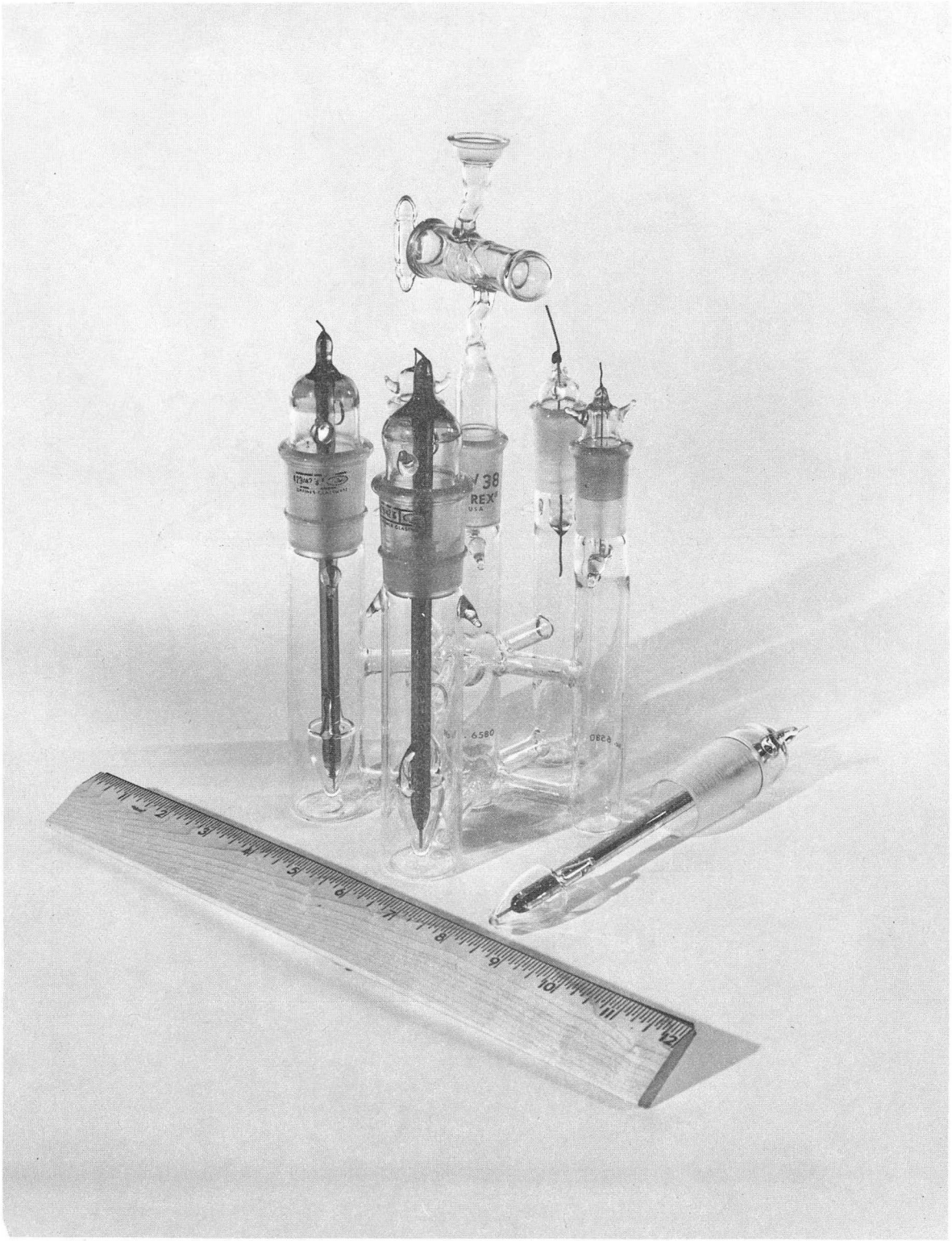


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FIGURE 3. CELL FOR POTENTIAL MEASUREMENTS

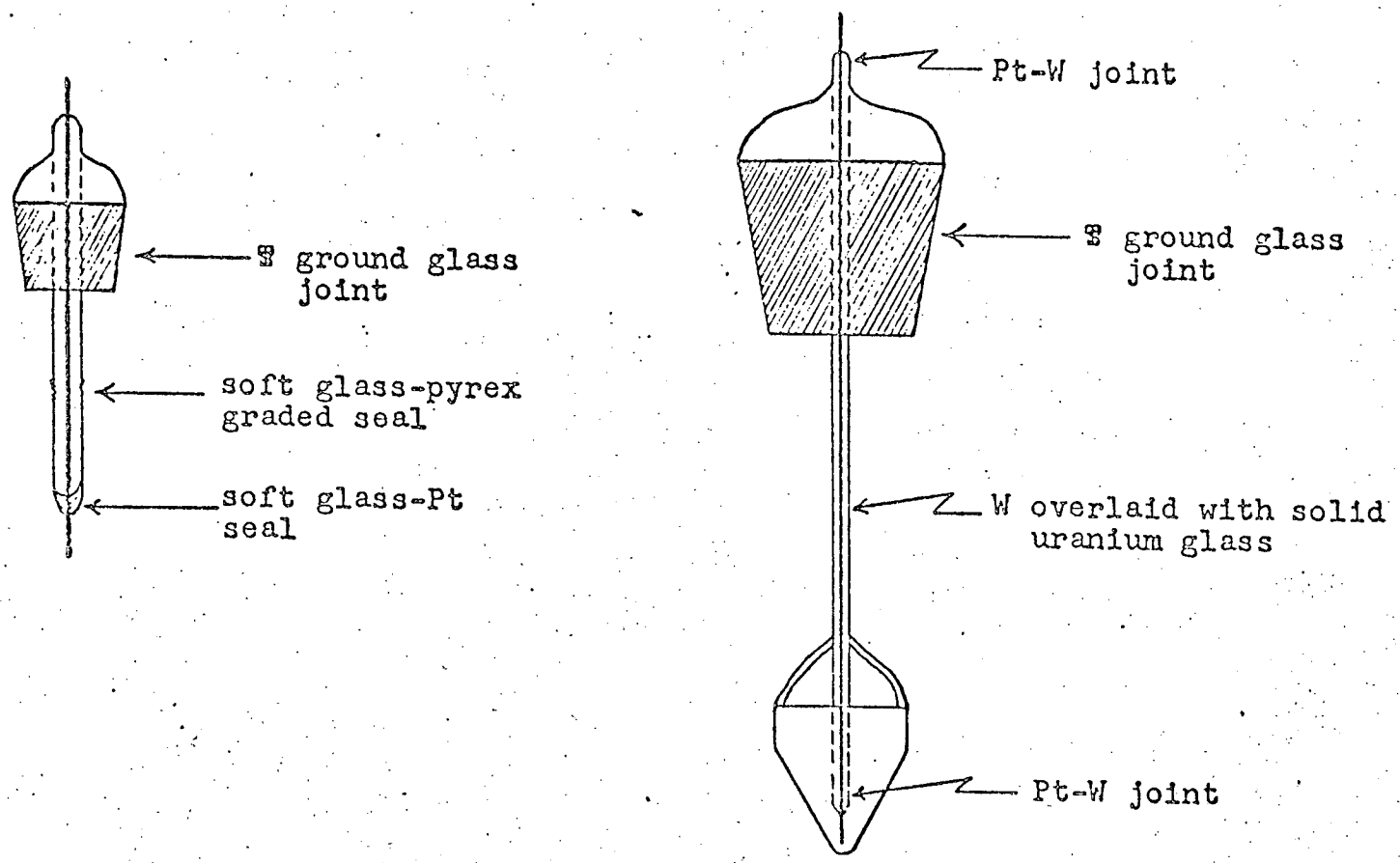

FIGURE 4. ELECTRODE HOLDERS FOR CELL POTENTIAL MEASUREMENTS

overlaid with uranium glass for a vacuum tight seal. Only platinum is exposed to the amalgam in the cup, and it is immersed well beneath the surface of the amalgam so that it does not contact the solution. Erratic electrical behavior was observed for cups in which the platinum lead was nearer the interface between the amalgam and the solution. The electrode holder for the metal (lithium, calcium, magnesium) is shown in Figure 4. The metal is attached to the platinum wire by a stainless steel connector.

The cell and electrode holders were dried in a vacuum oven at a few microns pressure and 150°C and transferred into the glove box. Before use, the lithium and calcium electrodes were stored under oil. The electrodes were cut to the desired length, rinsed free of oil with hexane and quickly transferred into the glove box.

The lithium, calcium and magnesium electrodes were assembled, chemically etched in a dilute solution of hydrochloric acid in dimethyl sulfoxide, rinsed with pure solvent and rinsed twice with the solution to be used in the cell. Lithium electrodes which were not etched but otherwise treated exactly as above were found to have a bias potential of less than 0.1 millivolt against etched electrodes. The stainless steel connector was never allowed to contact the etching solution, rinse solutions, solvent or cell solution. After rinsing was completed, the ground joints were lubricated with Apiezon stopcock grease and the electrodes were inserted into the cell.

Thallium amalgam was dispensed into the cup of each reference electrode holder, a small amount of thallous chloride was spread on the surface, the ground joints lubricated and the electrodes were inserted into the cell.

The solution to be used was introduced into the cell; the cell was then closed and removed from the glove box. Steel springs were hooked over the glass "ears" to insure that the ground joint did not separate. The cell was

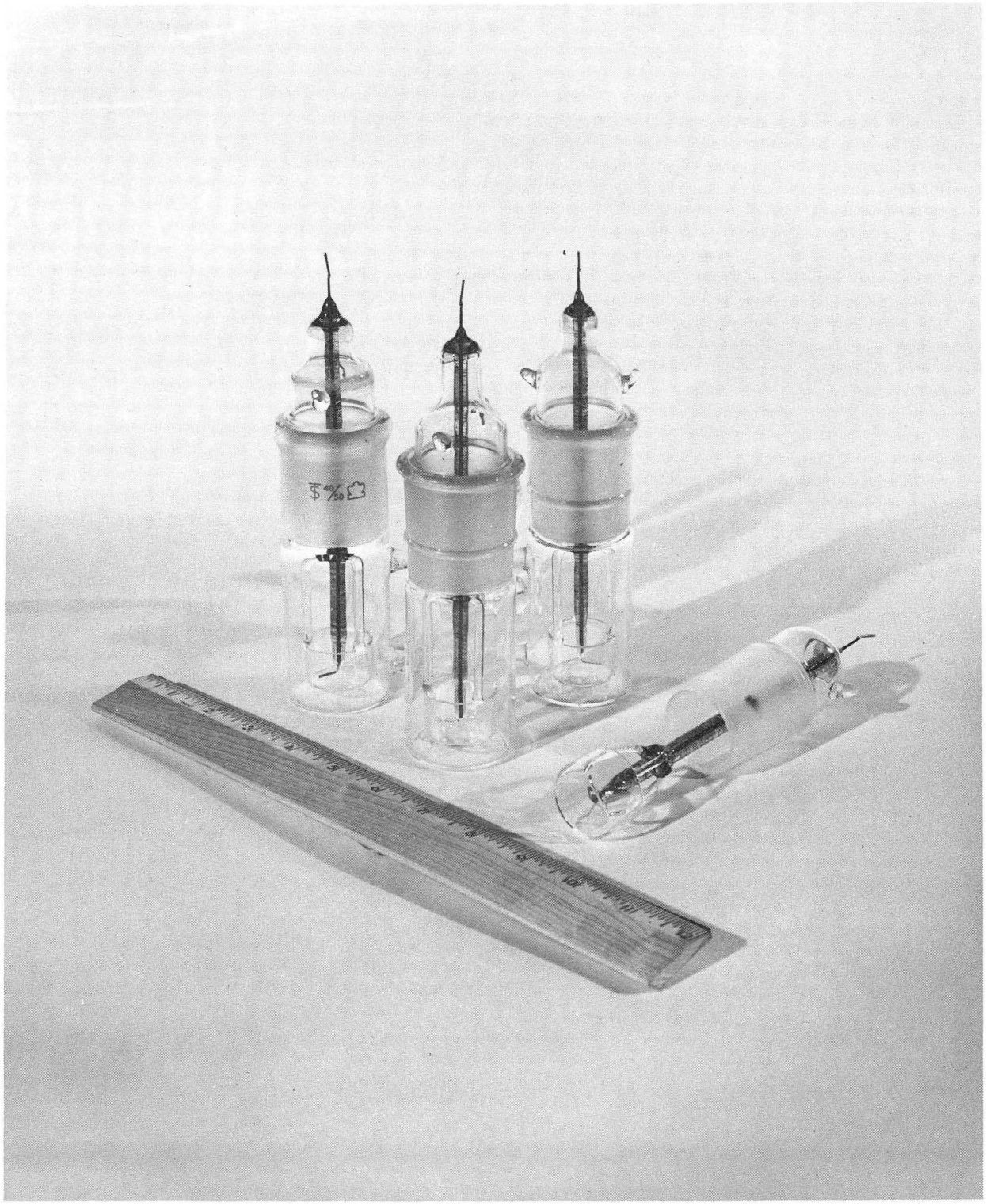

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FIGURE 5. CELL FOR REFERENCE ELECTRODE MEASUREMENTS

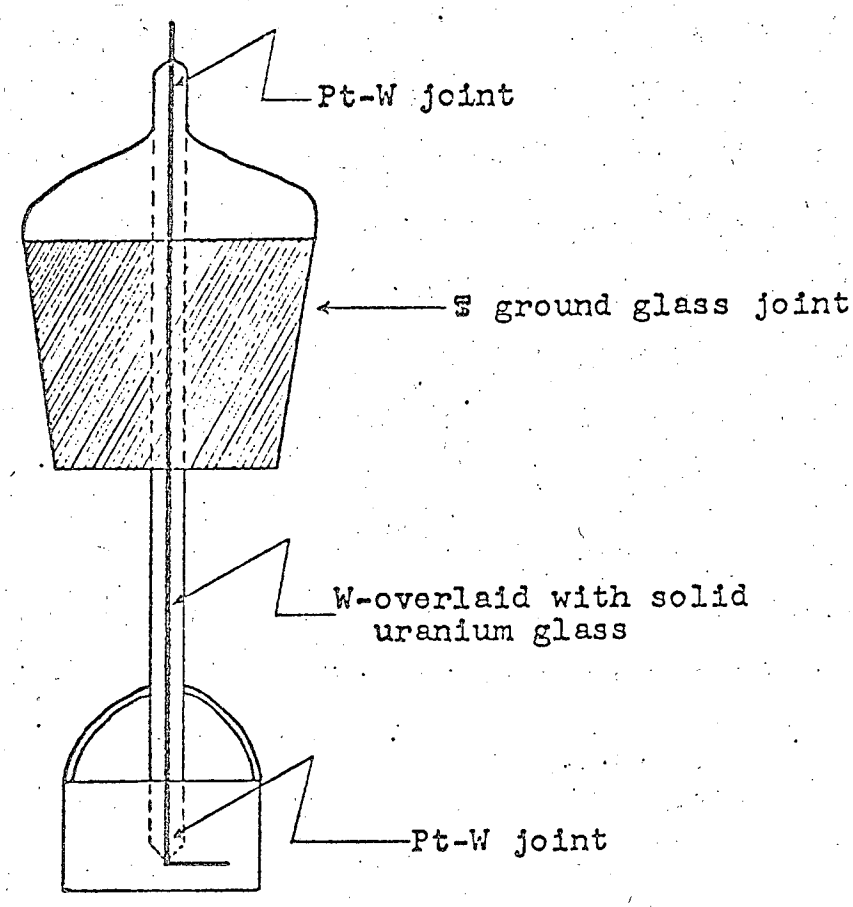

FIGURE 6. ELECTRODE HOLDER FOR REFERENCE ELECTRODE INVESTIGATIONS

then suspended in the thermostatted bath at 25°C and measurements were begun.

B. Assembly of the cell for investigation of the behavior of the reference electrode.

The cell (Figure 5) was designed so that three reference electrodes could be used in each cell. The electrode holders (Figure 6) were similar in design to those used in the electrode potential measurements.

The cell and electrode holders were dried in the vacuum oven and transferred to the glove box. Thallium amalgam was dispensed into each electrode holder, thallous chloride was sprinkled on the surface of the amalgam and the ground joints were lubricated. The solution to be used was introduced into the cell, the electrodes were put into place and the cell removed from the enclosure. Steel springs were used to hold the joints in place and the cell was thermostatted at 25°C.

VI... Cleaning of Glassware

After the measurements of a cell were completed, the solution and electrodes were removed from the cell. The cell was rinsed with water, the electrode holders put in place and the cell was filled with concentrated nitric acid for 24 hours. The cell and electrode holders were rinsed with distilled water, allowed to soak in distilled water and then rinsed several times with distilled water. Periodically the cells were cleaned with a succession of concentrated sodium hydroxide, dilute sulfuric acid and distilled water. The second cleaning procedure was deemed necessary when distilled water "beaded" on the cell when it was drained.

Other glassware was cleaned with soap and water and rinsed thoroughly with distilled water.

VII. Measuring Apparatus

Measurements of the cell potential were made with a Leeds & Northrup

K-3 potentiometer. The potentiometer was calibrated by the meter shop of Lawrence Radiation Laboratory and found to be within the specifications of the manufacturer. The standard cells used were supplied by The Eppley Laboratory and were the type which had a low temperature coefficient of e.m.f. The cells were standardized periodically at the Low Temperature Laboratory. The null device was either a galvanometer (Leeds & Northrup Type 2430-D, sensitivity of 4.5×10^{-10} amp/mm deflection) for cells with concentrated solutions, or a microvolt indicating amplifier (Leeds & Northrup Type 9835B) for cells with dilute solutions.

In the investigation of the behavior of the reference electrodes, the bias potentials were measured with the potentiometer and galvanometer described above. For the polarization measurements the potential was measured with an electrometer (Keithley 610R) and the current was measured with a Sargent MR recorder.

VIII. Thermostat

The water thermostat could be controlled at 25, 30 and 35°C to ±0.01°C. The bath was agitated by a mechanical stirrer so that the variation in temperature between different parts of the bath was less than ±0.01°C. The bath temperature was monitored with a Beckmann differential thermometer which had been matched against a thermometer calibrated by the National Bureau of Standards.

IX. Determination of Weights

Weights were determined on Mettler balances: one with a 200 gram capacity and ±0.05 mg precision, the other with a 1000 gram capacity and 0.05 mg precision. The balances were serviced regularly and checked for accuracy against standardized weights. The accuracy of both balances was found to be within 0.1 mg over the entire range of capacity.

X. Chemicals

Thallium : The metal in the form of pellets was supplied by Cominco and specified to be 99.999% pure with respect to metallic impurities. The metal as received had a thin oxide coating and was stored in a dessicator under dry argon to avoid further oxidation.

Mercury : Mercury for the reference electrode studies was Baker's Analyzed reagent grade. That used for the lithium, calcium and magnesium systems was triply distilled.

Lithium: : The lithium was supplied by the Lithium Corporation of America in the form of 1/8 inch diameter wire and specified to be of 99.9% purity.

Calcium: Calcium metal was supplied by Dominion Magnesium Ltd. and specified to be 99.5% pure. The metal was machined to 1/8 inch diameter rods and stored under oil.

Magnesium: Magnesium metal was obtained from United Mineral and specified to be 99.99% purity. The metal was cut to the desired size and stored in the glove box.

Lithium Chloride : Baker and Adamson reagent grade LiCl, specified to be 98.0% pure was dried by refluxing thionyl chloride[33,67] over it for two hours. The dried salt was stored in the glove box. The dried salt contained no hydrolysis products as determined by a phenolphthalein test. Analysis determined dried material to contain 99.2% LiCl.

Calcium Chloride : The calcium chloride was obtained from Johnson, Matthey and Co., Ltd., specified to be anhydrous grade, 99.9% purity. The salt was dried by refluxing thionyl chloride[33,67] over it for two hours, and was stored in the glove box.

Magnesium Chloride: Magnesium chloride was supplied by K and K Laboratories and specified to be 99.9% pure. The salt was stored in a dessicator and used without further treatment.

Thionyl Chloride: Matheson, Coleman & Bell supplied the reagent grade thionyl chloride in sealed ampoules, and the material was used as received.

Dimethyl Sulfoxide: Spectrographic grade (Matheson, Coleman & Bell) dimethyl sulfoxide was dried by distillation at a few mm Hg. Some preliminary experiments utilized dimethyl sulfoxide which was supplied by Crown Zellerbach Corporation and purified by distillation.

Thallous Chloride: Thallous chloride was supplied by Electronic Space Products Co. and specified to be anhydrous, reagent grade.

Indium Trichloride: The salt was used as received from the Indium Corporation of America. It was specified to be anhydrous and 99.99% pure.

Rubidium Chloride: The salt was supplied by City Chemical Corporation and specified to be anhydrous and purified. It was used as received.

Results

I. Results of measurements on the thallium amalgam-thallous chloride electrode.

Two sets of data were taken:

1. The potential difference was measured between pairs of electrodes in the state of rest.
2. The equilibrium condition was offset by a small applied potential difference, and the resulting current was recorded.

In the state of rest, the difference of potential between any two of the three electrodes was always found to be less than 0.03 millivolts for solutions of rubidium chloride, magnesium chloride and indium chloride*, and less than 0.01 millivolts for solutions of lithium chloride. Equilibrium was established rapidly after the cell was immersed in the thermostat, and was maintained for at least one week when a particular test run was discontinued. When the equilibrium was offset by the application of 0 ± 10 millivolts potential between electrode pairs, the current passed in either direction ranged up to 2×10^{-7} amperes. This was repeated for all combinations of the three electrodes. The current was always found proportional to the applied potential, and on no occasion was a hysteresis effect observed.

II. Cell potentials of the lithium system.

Tables 1, 2 and 3 contain the results of the experimental measurements on the cell

$$Pt(s)/Li(s)/LiCl\ (\text{solution in DMSO})/TlCl(s)/Tl_{(Hg)}(\ell)/Pt(s)$$

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* It was found that indium chloride reacts slowly with the reference electrode.

at 25°, 30° and 35°C, respectively. In the first column is listed the concentration of the lithium chloride solutions in molality units. The measured cell potential in absolute volts is listed in the second column.

Table 1.

Results of Cell Potential Measurements at 25°C.

m	E	$E^{o\prime}$	Amalgam	$E^{o\prime\prime}$
0.87877	2.47341	2.40288	1	2.40288
0.30177	2.52252	2.41414	3	2.41307
0.16389	2.54697	2.41600	4	2.41612
0.12450	2.55971	2.41822	3	2.41715*
0.12213	2.56064	2.41840	3	2.41733*
0.08803	2.57327	2.41820	1	2.41820*
0.08775	2.57324	2.41805	1	2.41805*
0.07592	2.57932	2.41834	4	2.41846*
0.05821	2.59230	2.42052	3	2.41945*
0.05821	2.59110	2.41932	4	2.41944*
0.02821	2.62266	2.42034	4	2.42046*
0.01775	2.64319	2.42054	1	2.42054*
0.00988	2.66970	2.42053	1	2.42053
0.00891	2.67465	2.42072	1	2.42072
0.00884	2.67500	2.42070	1	2.42070
0.00768	2.67933	2.41851	2	2.42047
0.00677	2.68436	2.41766	2	2.41962
0.00456	2.70491	2.42005	1	2.42005
0.00383	2.71131	2.41769	2	2.41965
0.00356	2.71687	2.41989	1	2.41989
0.00332	2.71830	2.41754	2	2.41950
0.00275	2.72604	2.41652	2	2.41848
0.00190	2.74340	2.41594	2	2.41790
0.00178	2.74803	2.41739	1	2.41739
0.00089	2.77455	2.40982	2	2.41178
0.00084	2.77662	2.40902	2	2.41098
0.00045	2.79921	2.40052	2	2.40248

* Data used in least squares analysis.

Table 2.

Results of Cell Potential Measurements at 30°C.

m	E	$E^{o'}$	Amalgam	$E^{o''}$
0.30177	2.52102	2.41803	3	2.40976
0.16389	2.54550	2.41233	4	2.41245*
0.12450	2.55880	2.41494	3	2.41387*
0.12213	2.55951	2.41489	3	2.41382*
0.07592	2.57825	2.41457	4	2.41469*
0.05821	2.59156	2.41690	3	2.41583*
0.05821	2.59039	2.41573	4	2.41585*
0.02821	2.62241	2.41670	4	2.41682*
0.00988	2.67002	2.41468	2	2.41667
0.00768	2.67988	2.41467	2	2.41666
0.00677	2.68496	2.41380	2	2.41579
0.00456	2.70393	2.41381	2	2.41580
0.00383	2.71222	2.41366	2	2.41565
0.00357	2.71765	2.41569	1	2.41569
0.00275	2.72716	2.41244	2	2.41443
0.00190	2.74477	2.41207	2	2.41406
0.00178	2.74936	2.41317	1	2.41317
0.00089	2.77639	2.40553	2	2.40752
0.00084	2.77798	2.40421	2	2.40620
0.00045	2.80111	2.39571	2	2.39770

* Data used in least squares analysis.

Table 3.

Results of Cell Potential Measurements at 35°C.

m	E	$E^{o\prime}$	Amalgam	$E^{o\prime\prime}$
0.30177	2.51946	2.40706	3	2.40597
0.16389	2.54423	2.40856	4	2.40868*
0.12450	2.55773	2.41122	3	2.41013*
0.12213	2.55842	2.41113	3	2.41004*
0.07592	2.57747	2.41085	4	2.41097*
0.05821	2.59072	2.41298	3	2.41189*
0.05821	2.58964	2.41190	4	2.41202*
0.02821	2.62214	2.41288	4	2.41300*
0.00988	2.67039	2.41276	1	2.41276
0.00768	2.68038	2.41073	2	2.41274
0.00677	2.68587	2.41036	2	2.41237
0.00383	2.71319	2.40965	2	2.41166
0.00357	2.71865	2.41165	1	2.41165
0.00275	2.72829	2.40833	2	2.41034
0.00190	2.74617	2.40769	2	2.40970
0.00178	2.75068	2.40890	1	2.40890
0.00089	2.77775	2.39723	2	2.39924
0.00084	2.77939	2.39601	2	2.39802
0.00045	2.80276	2.39068	2	2.39269

* Data used in least squares analysis.

This value for each cell is the average value of the potential of the three lithium electrodes versus either of the two reference electrodes. The deviation from this average was generally ± 0.1 millivolts or less. The potential difference between two reference electrodes was never greater than 0.05 millivolts for these reported values of the cell potentials. If the bias potential increased beyond this limit the measurements on that particular cell were discontinued because oxidation of the thallium amalgam became apparent soon afterwards. This oxidation was caused by leaks in the cell. The function $E^{o'}$ is tabulated in the third column and the method used to calculate this function is discussed below. In the fourth column appears a number which identifies the thallium amalgam used in the cell. In the fifth column the function $E^{o''}$ is tabulated. This function is equal to $E^{o'}$ plus a correction for the amalgam concentration.

The cell potential is related to the concentration of the electrolytic solution by the equation

$$E = E^{o} - \frac{2RT}{F} \ln [m_{LiCl}\, \gamma_{LiCl}] \qquad (1)$$

in which γ_{LiCl} is the mean activity coefficient of lithium chloride at the molality m_{LiCl} of the solution. Guggenheim[28,29] has proposed the following equation for the mean activity coefficient,

$$\ln \gamma_{LiCl} = - \frac{\alpha z_{+} |z_{-}| I^{1/2}}{1 + I^{1/2}} + 2\beta_{LiCl}\, m_{LiCl} \,. \qquad (2)$$

I, the ionic strength, is equal to m_{LiCl} for the solutions of interest here. z_{+} and $|z_{-}|$ are equal to 1, α is a constant which is defined in the Debye-Hückel theory and β_{LiCl} is a constant, taken to be independent of m_{LiCl}. The subscript on m_{LiCl} will be dropped for convenience. Introducing (2) into the cell potential equation (1), one obtains

$$E + \frac{2RT}{F} \ln m - \frac{\alpha m^{1/2}}{1 + m^{1/2}} = E^{o} - \frac{4RT}{F} \beta_{LiCl} m . \qquad (3)$$

The function $E^{o'}$ is defined as

$$E + \frac{2RT}{F} \ln m - \frac{\alpha m^{1/2}}{1 + m^{1/2}} = E^{o'} .$$

Thus $E^{o'}$ should be a linear function of m in the concentration range for which (2) is valid. However, it is necessary first to correct the present cell potentials for the different concentrations of amalgams used. This corrected function, $E^{o''}$, is plotted versus m in Figures 7, 8 and 9 corresponding to the measurements at 25°C, 30°C and 35°C, respectively. The solid line in each figure is that determined by a least squares analysis of the data in the region in which $E^{o''}$ is a linear function of m.

The data of Richards and Daniels[68] were used to correct for differences in amalgam concentration. In interpolating to determine the function $\mathcal{E}$ for these thallium amalgams, the method of Lewis and Randall[53] has been followed. Tables 4, 5 and 6 summarize the results of the calculations for temperatures of 20°, 30° and 40°C, respectively. The difference in the function $\mathcal{E}$ for an arbitrary concentration and that of the reference concentration has been used to calculate $E^{o''}$. The absolute value of $\mathcal{E}$ is of no importance, only differences have been used here. If the difference

$$(\mathcal{E})_x - (\mathcal{E})_{ref}$$

was negative, this difference has been subtracted from $E^{o'}$ to obtain $E^{o''}$, whereas the difference has been added to $E^{o'}$ if the difference was positive. Values of $(\mathcal{E})_x - (\mathcal{E})_{ref}$ at 25° and 35°C were found by interpolation of

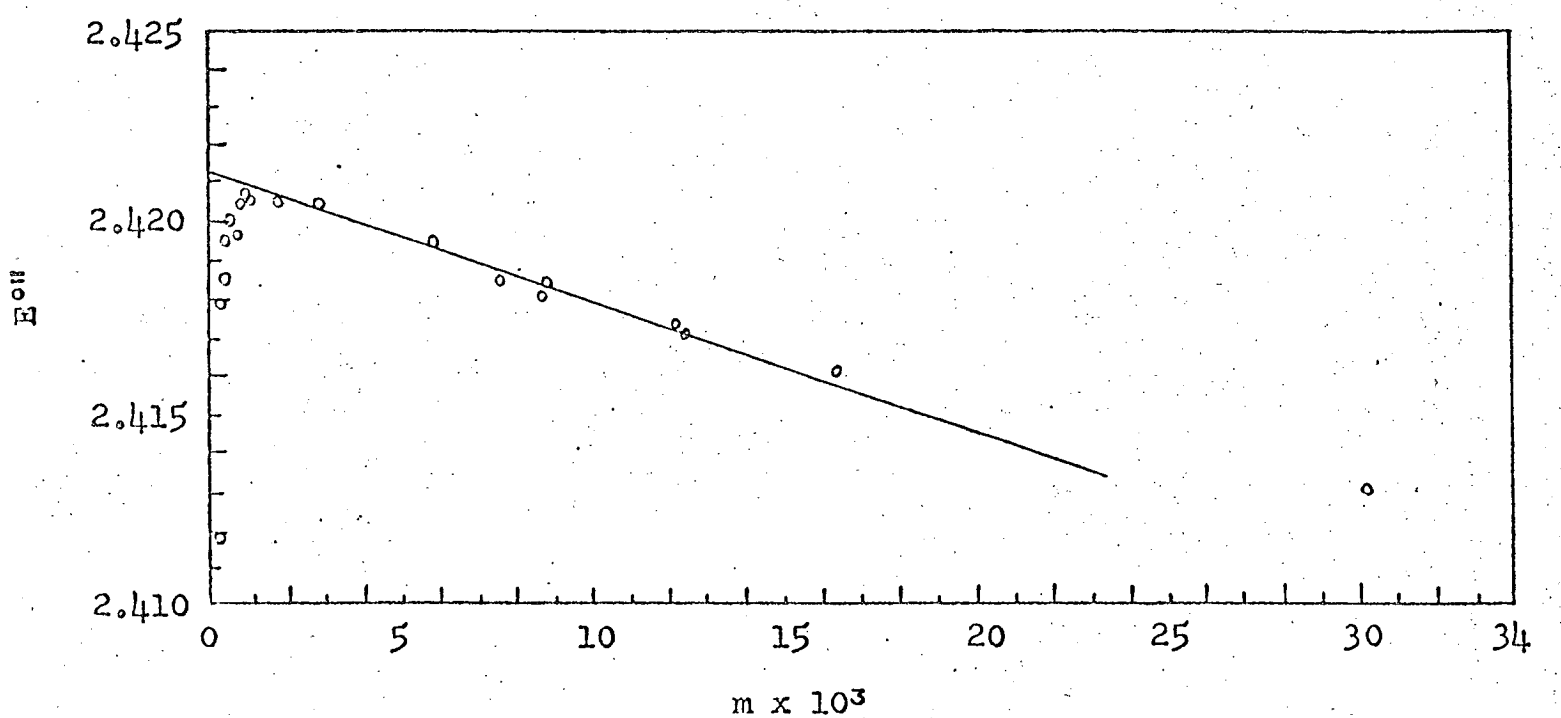

FIGURE 7. RESULTS OF CELL POTENTIAL MEASUREMENTS AT 25°

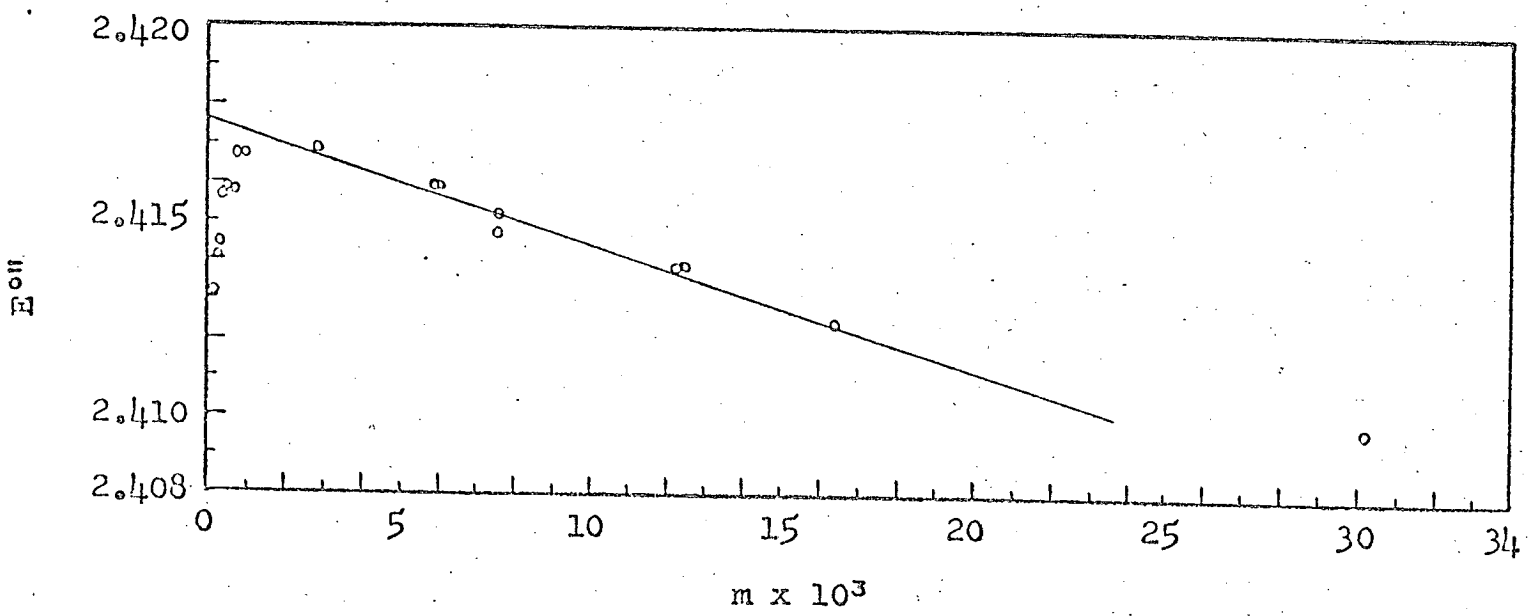

FIGURE 8. RESULTS OF CELL POTENTIAL MEASUREMENTS AT 30°

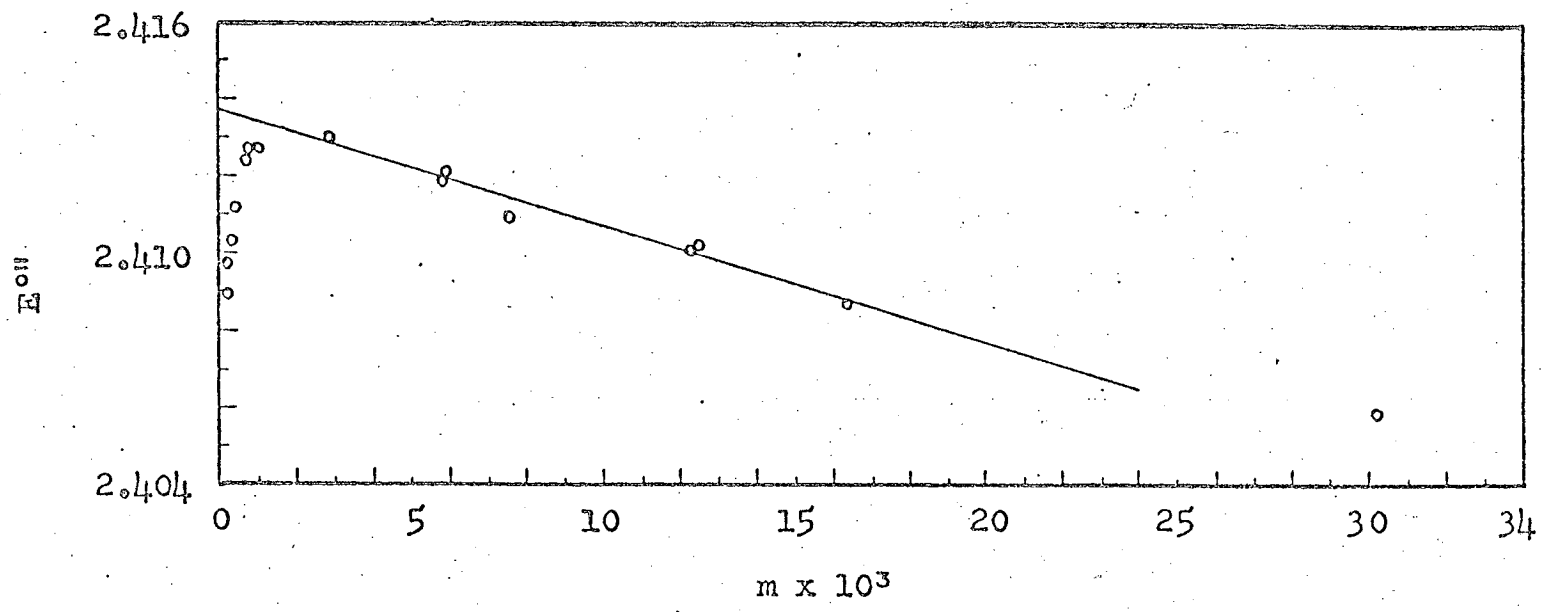

FIGURE 9. RESULTS OF CELL POTENTIAL MEASUREMENTS AT 35°

Table 4.

Relative Potentials of Thallium Amalgams at 20°C.

mole fraction Tl[a]	Amalgam	$\mathcal{E}$[b]
9.67×10^{-3}	1	0
9.32×10^{-3}	3	-0.00107
1.035×10^{-2}	2	+0.00193
9.71×10^{-3}	4	+0.00012
1		+0.14690

Table 5.

Relative Potentials of Thallium Amalgams at 30°C.

mole fraction Tl[a]	Amalgam	$\mathcal{E}$[b]
9.67×10^{-3}	1	0
9.32×10^{-3}	3	-0.00107
1.035×10^{-2}	2	+0.00199
9.71×10^{-3}	4	+0.00012
1		+0.15091

Table 6.

Relative Potentials of Thallium Amalgams at 40°C.

mole fraction Tl[a]	Amalgam	$\mathcal{E}$[b]
9.67×10^{-3}	1	0
9.32×10^{-3}	3	-0.00111
1.035×10^{-2}	2	+0.00203
9.71×10^{-3}	4	+0.00012
1		+0.15483

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[a] Calculated using molecular weights based on $C^{12} = 12.000$.

[b] Absolute volts.

these quantities at the temperatures tabulated.

The results of the data analysis are given in Table 7. The uncertainty of E^o and β are derived from the data analysis. The uncertainty of β is related to the uncertainty of the slope of the straight line and is given at the 95% confidence level. The uncertainty in E^o contains a contribution from the uncertainty of the slope and the uncertainty of the extrapolation. These were assumed additive and were calculated at the 95% confidence level. This is of course the maximum uncertainty in E^o. The average deviation of points from the straight line was 0.15 millivolts. The method of analysis is given by Mickley, et al[60].

Table 7.

Standard Cell Potentials at 25°, 30° and 35°C.

T(°K)	E^o	β_{LiCl}
298.15	2.42124 ± 0.00045	0.325 ± 0.040
303.15	2.41756 ± 0.00072	0.298 ± 0.052
308.15	2.41370 ± 0.00064	0.286 ± 0.045

From the standard cell potential and its variation with temperature, one can calculate ΔG^o, ΔS^o and ΔH^o for the reaction

$$\mathrm{Li(s) + TlCl(s) + 102.413\ moles\ Hg(\ell) + 12.799\ moles\ DMSO(\ell)}$$
$$= \mathrm{LiCl}\begin{pmatrix}\text{solution in DMSO for}\\ \text{which } (m\gamma) = 1\end{pmatrix} + \mathrm{Tl}\begin{pmatrix}9.67 \times 10^{-3}\ \text{mole fraction}\\ \text{in Hg}\end{pmatrix}. \quad (1)$$

Within experimental error the temperature coefficient of the standard cell potential is constant over the temperature range 25° to 35°C and is

$$\frac{\partial E^o}{\partial T} = \frac{\Delta E^o}{\Delta T} = -\ 0.754 \times 10^{-3}\ \text{volts/°K.}$$

The thermodynamic relations

$$\Delta G^o = -\ nF\ E^o\ ,$$

$$\Delta S^{o} = nF \left(\frac{\partial E^{o}}{\partial T}\right)_{P}$$

$$\Delta H^{o} = - nF \left[E^{o} - T \left(\frac{\partial E^{o}}{\partial T}\right)_{P}\right]$$

were used to obtain the values of these thermodynamic functions in Table 8. In order to obtain ΔG^{o}, ΔS^{o} and ΔH^{o} for the reaction

$$\mathrm{Li(s) + TlCl(s) + 12.799\ moles\ DMSO} \rightleftarrows \mathrm{LiCl}\left(\begin{array}{l}\text{solution in DMSO such}\\ \text{that } (m\gamma_{\pm}) = 1\end{array}\right) + \mathrm{Tl(s)} \qquad (4)$$

the data in Table 8 and the data in Tables 4,5 and 6 were utilized. The difference

$$(\mathcal{E})_{\text{amalgam 1}} - (\mathcal{E})_{\text{pure Tl}}$$

was then subtracted from E^{o} to obtain ΔG^{o} for reaction (2) and the temperature coefficient of E^{o} yielded ΔS^{o}. Table 9 summarizes the results of these calculations.

Table 8.

Values of ΔG^{o}, ΔS^{o} and ΔH^{o} at 25°, 30° and 35°C for the Lithium Cell.

T(°K)	ΔG^{o}(kcal/mole)	ΔS^{o}(cal/°K-mole)	ΔH^{o}(kcal/mole)
298.15	-55.84	-17.4	-61.03
303.15	-55.75	-17.4	-61.02
308.15	-55.66	-17.4	-61.02

Table 9.

ΔG^{o}, ΔS^{o} and ΔH^{o} for Reaction (4).

T(°K)	ΔG^{o}(kcal/mole)	ΔS^{o}(cal/°K-mole)	ΔH^{o}(kcal/mole)
298.15	-52.402	-26.5	-60.31
303.15	-52.271	-26.5	-60.31
308.15	-52.136	-26.5	-60.31

The activity coefficients of lithium chloride at 25°, 30° and 35°C were calculated for the experimental concentrations by use of the experimental cell potentials corrected for amalgam concentrations, and the values of E^{o} given in Table 7. The values at rounded concentrations were obtained from a graph of the calculated activity coefficients versus molality. The results are summarized below for concentrations of 0.12 molal and lower.

Table 10.

Activity Coefficients of Lithium Chloride at 25°, 30° and 35°C.

m	$-\ln \gamma_{LiCl}$		
	25°	30°	35°
0.005	0.152	0.160	0.165
0.010	0.220	0.230	0.230
0.015	0.270	.275	0.275
0.020	0.306	.310	.310
0.025	0.335	.339	.340
0.030	0.360	.364	.365
0.035	0.383	.385	.392
0.040	0.404	.405	.414
0.045	0.422	.423	.430
0.050	0.440	.440	.447
0.060	0.470	.470	.475
0.080	0.511	.520	.525
0.100	0.548	.560	.565
0.120	0.582	.592	.600

III. Cell potential measurements on calcium and magnesium systems.

The cell potentials of the calcium and magnesium systems were erratic. The calcium and magnesium electrodes were cleaned and treated in the same way as the lithium electrodes to remove surface oxides, but oxidation was observed to occur in the glove box. Several minor leaks in the glove box were found and eliminated, but oxidation was still observed. In order to verify that oxide formation was responsible for the erratic behavior, calcium amalgams were prepared and used in place of the pure calcium. The amalgam was dispensed into electrode cups similar to those used for the thallium amalgam and oxide formation occurred before the cell was assembled. Several attempts were made to evacuate the glove box under especially rigorous conditions to prevent contamination. The rate of oxide formation was decreased and became visible only after the cell had been assembled for about one hour. Since one hour was required for the electrodes to give approximately the same potential versus the reference electrode, it was not possible to extrapolate the readings to zero time. The cell potential, although unstable, appeared to decrease with time as one would expect since the concentration of calcium in the amalgam decreased as oxide was formed. Several cells were so erratic that measurements could not be made. The cell potentials tabulated below are for those cells in which measurements could be made. The symbol m is the molality of the electrolytic solution and E is the measured cell potential in absolute volts. The thermodynamic relation (see Appendix III),

$$E = E^{o} - \frac{3RT}{2F} \ln m(2)^{2/3} + \frac{2\alpha(3m)^{1/2}}{1+(3m)^{1/2}} \left(\frac{3RT}{2F}\right)$$

was used to estimate the standard electrode potentials of calcium and magnesium versus the reference electrode (thallium amalgam 1), and found to be 1.69 volts and 0.92 volts, respectively. The potential of the calcium

Table 11.

Cell Potential Measurements for the Calcium System at 25°C.

m	Electrode	E	Tl Amalgam
0.02884	Ca	1.85 ± 0.01	2
0.02884	Ca amalgam 0.51 atom %	1.540 ± 0.005	2
0.05506	Ca amalgam 0.51 atom %	1.515 ± 0.001	3

Table 12.

Cell Potential Measurements for the Magnesium System at °5°C.

m	Electrode	E	Tl Amalgam
0.03766	Mg	1.08 ± 0.01	3
0.01157	Mg	1.09 ± 0.01	3

amalgam versus pure calcium was estimated by use of the work of Drucker, et al[25] in which it was found that an amalgam of concentration 0.12649 atom percent was 0.843 volts positive with respect to pure calcium metal at 17°C. From their results on the relative potentials of calcium amalgams, it was estimated that both the amalgams used here were 0.04 volts negative with respect to the amalgam of 0.12649 atom percent. It was not possible to estimate the temperature coefficient of the potential from their work, so the above values were used also at 25°C. The standard cell potential of calcium versus the reference electrode (thallium amalgam 1) was again calculated for both electrolyte concentrations.

In view of the limited accuracy with which the concentration of calcium was known, and due to the somewhat crude extrapolation procedures described above, the confidence limit of ±0.01 volts is placed on the standard cell potential obtained, $E^{o}_{Ca} = 2.17$ volts.

Discussion of Results

I. Reference electrode

On the basis of the observations on the reference electrode behavior, the thallium amalgam-thallous chloride electrode appears to be suitable for thermodynamic measurements in dimethyl sulfoxide solutions. It became apparent early in these investigations that the solubility of thallous chloride in dimethyl sulfoxide would be of great importance in evaluating the behavior of the reference electrode. The solubility product at 25°C was found to be in the order of 10^{-6}*. The measurements on the lithium cell indicate that the reference electrode behaves satisfactorily in concentrated solutions, but the solubility of thallous chloride prohibits its use in very dilute solutions. The ease with which it may be prepared and the reproducibility in behavior suggest that it may be used as a reference electrode.

II. Lithium system

The lithium cells were found to be well behaved for concentrated solutions of lithium chloride. As the concentration was decreased, the function $E^{o''}$ became a linear function of molality, at all three temperatures as seen in Figures 1, 2 and 3. Therefore, the sharp decrease of $E^{o''}$ as dilution increased was quite unexpected. This behavior cannot be explained by random scatter of data; the decrease persists at all three temperatures as the concentration decreases. When the first data were taken in the most dilute range, this phenomenon was thought to be caused by errors in preparing the solutions. Therefore, new solutions in the concentration

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* Following the completion of this investigation, Butler, et al[11] have reported a solubility product of 5×10^{-7} at 25°C.

range below 0.01 molal were prepared both by dilution and by directly weighing out the salt and solvent. The trend of $E^{o''}$ to decrease proved to be independent of the method of preparing the solutions.

The possibility that the anomalous behavior might be caused by a reaction taking place in the cell was eliminated since the cell potential was constant within 0.1 millivolt for at least six hours. This is shown by the data taken during the temperature cycle. The cell was first brought to 25°C; the cell potential measured within thirty minutes and also after another hour was found to be the same within 0.1 millivolt. The cell was then equilibrated at 30° and at 35° and finally equilibrated again at 25°C. The cell potential at 25°C was found to be the same within 0.1 millivolt as that measured before the temperature cycle. After a period of twelve hours the cell potential was found to be lower by a few tenths of a millivolt. This was probably due to the reaction

$$TlCl(solution) + Li(s) \rightarrow Tl(s) + LiCl(solution)$$

which would be expected to occur when thallous chloride reaches the lithium electrode.

The observed behavior of $E^{o''}$ was found finally to be attributable to diffusion of thallous chloride away from the reference electrode. This would be expected to be of appreciable effect only in dilute solutions where the concentrations of the two electrolytes are about equal. Further discussion of this conclusion is to be found in Appendix 4.

After this research was begun, two papers have appeared in the literature reporting cryoscopic measurements on lithium chloride solutions in dimethyl sulfoxide. Unfortunately only qualitative comparisons could be made between the present data and those of Skerlak, et al[75], since their

data are reported only in the form of a graph with no grid. However, one can say that the activity coefficient in the 0.3-0.8 molal concentration range calculated from the cell potential data is definitely lower than that reported by Skerlak, et al[75]. Regrettably the paper of Dunnett and Gasser[24] does not report the actual freezing point data. They chose rather to report values of the function j which is defined by

$$j = 1 - \frac{\theta}{\nu\lambda m}$$

for small freezing point depressions. Here, θ = freezing point depression

λ = molal freezing point depression constant

m = molality

ν = number of species resulting from a molecule of solute.

Thus one must introduce the value of the freezing point depression constant in order to make the calculation. The authors do not report the value for their calculation, but reject the value (3.96) proposed by Skerlak, et al, since the values of j would then become negative in dilute solutions, whereas j should approach zero. The only reference given by Dunnett and Gasser listing a cryoscopic constant is that by Lindberg, Kenttämaa and Nissema[54]. These workers report the constant to be 4.36, a value not supported by their data. Their measurements were made on solutions more concentrated than 0.8 molal and yield a value of 3.77 for the cryoscopic constant. Further analysis must be delayed until the actual freezing point data obtained by Dunnett et al become available. It was found in the present work that the freezing point of the pure solvent is 18.58°C, a value significantly higher than that reported by Dunnett and

Gasser, viz. 18.55, for the solvent sample they used.

III. Calcium and magnesium systems

The standard cell potentials for calcium and magnesium were estimated for purposes of comparison with the lithium cell potentials. The results of measurements with the pure metals seem to be much too low. The results of the measurements with the calcium amalgams are more reasonable. It is seen that the oxidation potential of calcium is lower with respect to lithium than in aqueous solutions.

IV. Free energy, enthalpy and entropy of transfer of lithium chloride from water to dimethyl sulfoxide

Turning now to the discussion of the influence of the solvent on the thermodynamic properties of electrolytes in solution, the free energies, enthalpies and entropies of transfer of lithium chloride from water to dimethyl sulfoxide will be calculated. The free energy of transfer of a salt is defined here as ΔG for the process

Salt (solution in solvent 1) $\rightarrow$ Salt (solution in solvent 2).

To be more specific, the transfer of one mole of lithium chloride from water to dimethyl sulfoxide, at constant temperature and pressure

$$\text{LiCl (solution in } H_2O) + x \text{ moles DMSO}$$
$$\rightarrow \text{LiCl (solution in DMSO)} + j \text{ moles } H_2O ,$$

has associated with it a partial molal free energy change, $\Delta\bar{G}$, which includes a contribution from the difference in reference state in the two solvents but is also a function of concentration. If the transfer is from the hypothetical one molal standard state in one solvent to the analogous state in the other solvent, then by definition the free energy change at

constant temperature and pressure is independent of concentration.

The partial molal free energy of transfer is determined directly from measurements of the electrical potential of cells, such as have been used in the present work, in different solvents. The standard free energy change for the cell

$$Pt(s)/Li(s)/LiCl(solution)/TlCl(s)/Tl(s)/Pt(s)$$

in which the solvent is water, may be calculated from the thermodynamic data tabulated in Lewis, et al[53]. The value of $\Delta\bar{G}^o_{298.15}$ for the cell reaction was calculated to be -57.37 kcal/mole. From the data in Table 9 of the preceding section and with the above data, one calculates the partial molal free energy of transfer for the reaction

$$LiCl \begin{pmatrix} \text{solution in } H_2O \\ \text{such that } m\gamma_{LiCl}=1 \end{pmatrix} = 12.799 \text{ moles DMSO}$$

$$\rightarrow LiCl \begin{pmatrix} \text{solution in DMSO} \\ \text{such that } m\gamma_{LiCl}=1 \end{pmatrix} + 55.55 \text{ moles } H_2O$$

to be

$$\Delta\bar{G}^o_{298.15} = \Delta\bar{G}^o_{298.15}(DMSO) - \Delta\bar{G}^o_{298.15}(H_2O) = +\ 4.93 \text{ kcal/mole.}$$

The entropy of transfer, except for a small correction, can be calculated by an analogous method yielding

$$\Delta\bar{S}^o_{298.15} = \Delta\bar{S}^o_{298.15}(DMSO) - \Delta\bar{S}^o_{298.15}(H_2O) = -\ 25.1 \text{ cal/°K mole.}$$

The difference in specific volume of the two solvents leads to a correction in the entropy of transfer (see Latimer and Slansky[44]) of the form

$$R\ ln\ (v_{DMSO}) - R\ ln\ (v_{H_2O})\ .$$

The specific volume of H_2O at 25° is[30] 1.0019 cm^3/gm. From the density data in Appendix II, the specific volume of dimethyl sulfoxide is

0.9127 cm^3/gm. This leads to a correction of -0.22 eu which must be added to the above value of $\Delta\bar{S}^o_{298.15}$ to yield

$$\Delta\bar{S}^o_{298.15} = -25.3 \text{ cal/°K-mole.}$$

V. Comparison of the free energies and entropies of transfer of LiCl from water to different solvents

The importance of the data on the lithium system is twofold: (1) the data are accurate enough that one may confidently make comparisons to the analogous aqueous system, and (2) the system may be compared to the analogous system in other nonaqueous solvents. The thermodynamic quantities chosen to compare the systems are again the free energy and entropy of transfer of lithium chloride from the standard state in water to the standard state in another solvent. One method of calculating these quantities is similar to that done above for transfer of lithium chloride from water to dimethyl sulfoxide. An equivalent method is to utilize tabulations of the thermal properties of solutions such as those by Latimer[47] and Lewis et al[53] for aqueous solutions and that of Jolly[37] for solutions in ammonia. The specific references utilized for the calculations are listed below:

(1) Water. The extensive tabulations of Latimer[47] and Lewis et al[53] were used. The latter was favored, since more recent thermodynamic data are given. The specific volume of water was taken from the tabulation of Hamer[30], and is 1.0019 at 25°C.

(2) Ammonia. The tabulation of Jolly[37] was used exclusively. Changes were introduced where more recent thermodynamic data were available for heats and free energies of formation of the alkali

halides. The specific volume of liquid ammonia at 25°C is 1.6667[35].

(3) Methanol. Strehlow[76] has reviewed the available cell data on methanol. Heats of solution were taken from Askew et al[4], and Drakin and Yu-min[23]. The heats of solution measured by Askew and coworkers were make at 20°C, and it was assumed that the heat of solution was the same at 25°C. The potential of the cell H_2/HCl/AgCl/Ag in methanol was taken from Oiwa[64] and Koskikallio[45]. The potential of the cell H_2/HBr/AgBr/Ag in methanol was taken from Kanning and Campbell[38]. The paper of Latimer and Slansky[49] contains data for free energies, entropies and enthalpies of solution of salts in methanol. The specific volume of methanol is 1.2626 at 25°C.

(4) Ethanol. Cell potential data were taken from Strehlow[76]. Heats of solution were taken from Askew, et al[4]. The specific volume is 1.2738 at 25°C.

(5) Thermodynamic data for the alkali halides were taken from Latimer[47], Lewis et al[53], and Brewer and Brackett[9].

Analogous calculations were made for other salts and the results of all these calculations are presented in Figure 4.

There are additional data on N-methylformamide from Luksha and Criss[55]. The calculations for this system are presented in Table 13, and will be discussed shortly. Tabulations of thermodynamic data for N,N-dimethylformamide and for formamide have been estimated by Criss[19]. This latter data has not been included in the present calculations since direct experimental data have been preferred.

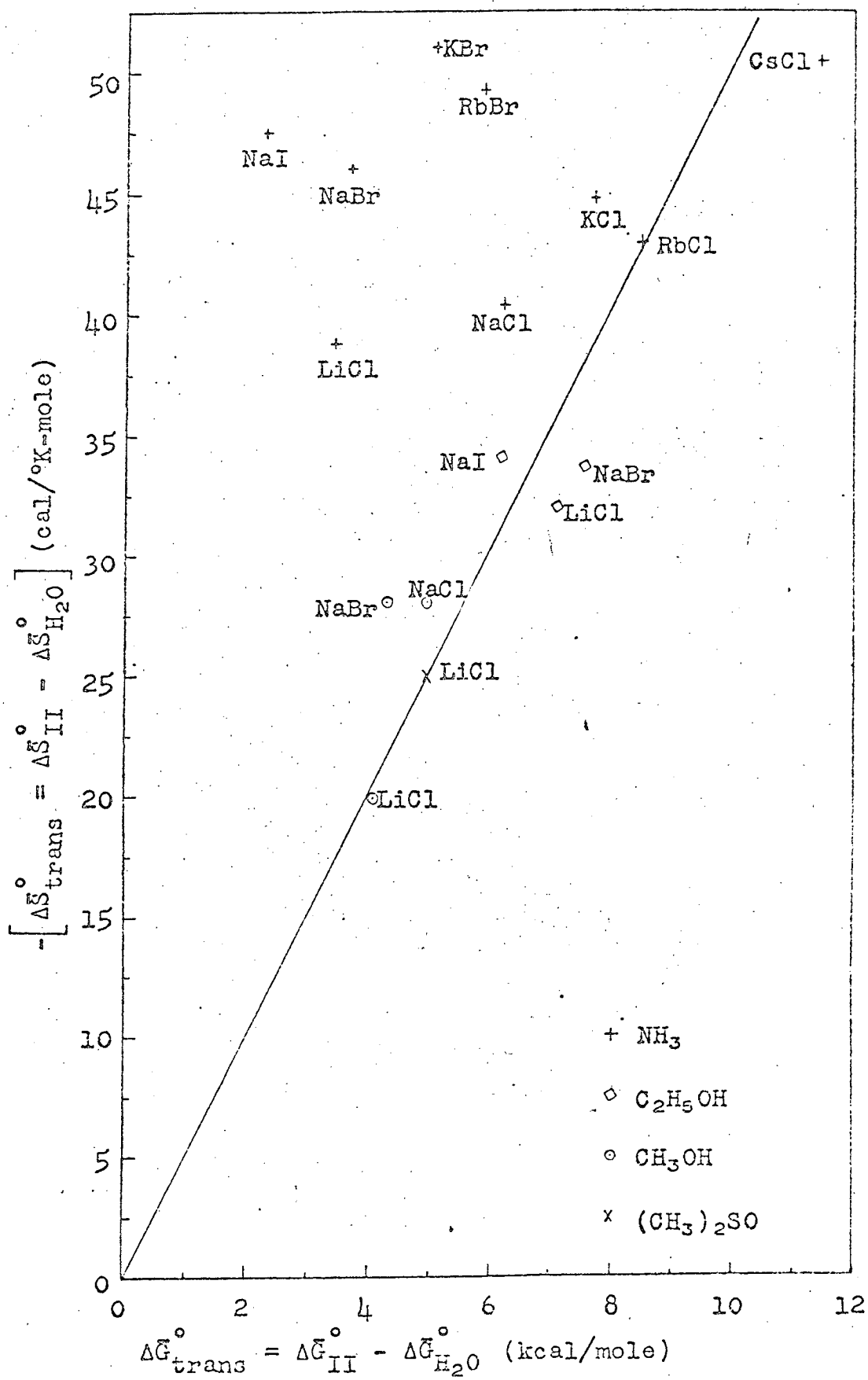

FIGURE 10. ENTROPIES AND FREE ENERGIES OF TRANSFER OF SALTS FROM H_2O TO NONAQUEOUS SOLVENTS

Table 13.

Free Energy and Entropy of Transfer of Salts from Water to N-methylformamide.

Salt	$-\Delta\bar{G}^{o}_{trans}$ (kcal/mole)	$\Delta\bar{S}^{o}_{trans}$ (cal/mole·°K)
LiCl	1.34	25.3
NaCl	2.98	17.3
KCl	2.90	22.6
CsCl	3.58	23.7

From Figure 10, there is apparently a correlation between the free energy of transfer and the entropy of transfer of a salt from H_2O to a nonaqueous solvent. The salts for which the best data are available are closest to the line. The line has been drawn in arbitrarily and is not intended to have any quantitative significance. It is noted that the data for solvents with lower dielectric constants tend to lie higher along the line. For a common solvent, there appear to be trends among the salts which depend on the size of the ions. If these results are not artifacts, one may predict that the free energy and entropy of transfer will have the same dependence on the physical properties which characterize the ion-solvent interactions. It seems that the dielectric properties of the solvents are responsible for most of the changes in free energy and entropy from solvent to solvent. Also, the differences of ion size cause smaller changes in entropy and free energy.

The data from Table 13 are of interest because the solvent has a higher dielectric constant (171) than that of water. From the dielectric properties of N-methylformamide one would expect that $\Delta\bar{G}^{o}_{trans}$ would be negative, and the entropy would probably be positive. However, from the data it is seen that the solvent behaves as if it had a low dielectric

constant. There are three possible explanations for this:

(1) the solvent has a lower dielectric constant than that reported;

(2) it is not appropriate to use the dielectric properties to predict the trends in the free energy and entropy of transfer; or

(3) the data are spurious (see Appendix IV).

There are two ways of proceeding from here. One is to go immediately to model calculations to explain the experimental data, and the other is to identify important physical properties in order to make a more general treatment possible.

There are two models which are most often used in estimating the magnitude of ion-solvent interactions. One is the modified Born model and the other is a model in which several different ion-solvent interactions are proposed to account for the behavior. In the Born model, the free energy of solvation of a salt is given by

$$\Delta G = -\left(1 - \frac{1}{D}\right) \frac{e^2 N}{8\pi\varepsilon_o} \left(\frac{z_i^2}{r_i} + \frac{z_j^2}{r_j}\right)$$

in which the dielectric constant of the solvent, D, the charge of the ions, z_i and z_j, and the radius of the ions, r_i and r_j, are the physical properties which characterize the interactions. The solvation entropy is then determined from the temperature derivative of the free energy. It is known that one may not use the crystallographic radius of an ion for the r_i's, for this leads to values of the solvation energy and entropy which are too large. The radii of the ions are often treated instead as parameters by which the data may be correlated. Latimer, Pitzer and Slansky[48] adopted this procedure for aqueous data and Koepp, Wendt and Strehlow[39] have applied the method to nonaqueous systems. Actually, this

model does predict the general trends in the thermodynamic properties which are observed in Figure 10, but may not be used quantitatively except as a correlation function. One concludes that the model is qualitatively consistent with the data, but identifies no physical properties which quantitatively characterize the interactions.

The other model is one in which it is proposed that the ions interact with distant solvent molecules according to the Born model. Adjacent solvent molecules are then treated as fully oriented dipoles which interact with a lower energy than if they were free to rotate. One of the variations of this treatment is to use the dielectric constant as an adjustable parameter which increases with radial distance from the ion to the bulk dielectric constant. Another variation is to use the charge distribution in the oriented dipoles to calculate the interaction of these molecules with the ions. Of course, it is first necessary to determine the charge distribution of the polar solvent molecules. This is the most difficult and possibly the most uncertain part of the method. It would require accurate volues of the dipole moment of the solvent molecules in the liquid plus a knowledge of the structure of the molecule before a charge distribution could be assigned.

The method which seems most appropriate for utilizing the data in the several systems is a corresponding states treatment. By this treatment one can identify the molecular parameters which are necessary to characterize the various interactions, and their relative importance, without proposing a particular model of the salt in the solution. It is clear that such an analysis is needed, because on one hand there are such a variety of solvents and salts to be treated and on the other hand because

there are so few reliable data available on nonaqueous systems. To account for specific interactions, model calculations would be necessary which become possible as accurate physical properties become available for the solutes and the solvents.

Despite these advantages, a corresponding states treatment must await accurate data on a few more systems. It would be premature to conduct such an analysis now, especially in view of the uncertain behavior of solutions in solvents whose dielectric constant is greater than that of water.

V. Summary

In summary, accurate thermodynamic properties of lithium chloride in dimethyl sulfoxide have been determined with the cell

$$Pt(s)/Li(s)/LiCl(solution)/TlCl(s)/Tl_{(Hg)}(\ell)/Pt(s).$$

The standard cell potentials and activity coefficients of the lithium system were determined at 25°, 30° and 35°C. The reference electrode performed well, for solutions more concentrated than approximately 0.01 molal. In more dilute solutions, the solubility of thallous chloride had an appreciable effect on the cell potential. A general method is outlined in Appendix III for the analysis of the behavior of cells involving reference electrodes of the second kind and the way in which diffusion affects their performance. In Appendix IV the results of this development are applied to the specific cell type given above. The standard cell potential of the analogous calcium system at 25°C has been estimated.

The entropy and free energy of transfer of lithium chloride from water to dimethyl sulfoxide were calculated and compared to analogous results for other solvents, and for other salts. These thermodynamic

functions were found to depend on the dielectric properties of the solvents, and to a smaller degree on the size of the ions comprising the salts.

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Appendix I.

Physical Constants

All atomic weights were based on $C^{12} = 12.000$.

R (gas constant) = 1.987 cal/°K-mole

F (Faraday's constant) = $96{,}487 \frac{\text{coulomb}}{\text{g-equivalent}}$

N (Avogadro's constant) = 6.023×10^{23}/mole .

Appendix II.

Dimethyl sulfoxide has a liquid range (m.p. 18.5°C, b.p. 189°C) which makes it a convenient solvent with which to work, at or above room temperature. This, coupled with its known solvating power toward organic as well as inorganic materials, suggests that it may be used in cases which necessitate the exclusion of water.

Preparation of dimethyl sulfoxide

Douglas[20] in 1946 reported a method of preparation of dimethyl sulfoxide (DMSO) using dimethyl sulfide (DMS) as the starting material and oxidizing it with H_2O_2 in glacial acetic acid.

$$(CH_3)_2S + H_2O_2(30\%) \overset{HOAc}{\rightleftharpoons} (CH_3)_2SO + H_2O \ .$$

The sulfoxide was then extracted from the reaction mixture with $CHCl_3$. The production of H_2O is undesirable, for water is completely miscible with DMSO and there is evidence for hydrogen bonding between the two when they are mixed[40,41], indicating their separation will be difficult. Addison and Sheldon[2] succeeded in oxidizing DMS with nitrogen tetroxide at low temperatures. The sulfoxide was then isolated by fractional distillation. The reaction is

$$2(CH_3)_2S + N_2O_4 \rightleftarrows 2(CH_3)_2SO + 2NO.$$

This method appears to be more satisfactory than that proposed by Douglas[19] because water is not produced by the reaction. Also, since the reactants may be obtained in an anhydrous condition, water may enter as a contaminant only as the result of handling technique. It is also more satisfactory because the oxidation stops after the production of the sulfoxide. The oxidation by whatever means may go as follows

$$(CH_3)_2S \rightarrow (CH_3)_2SO \rightarrow (CH_3)_2SO_2 \text{ (dimethyl sulfone)} \ .$$

The sulfone must then be removed and this problem will be discussed later.

Other methods of preparation such as gas phase oxidation of the sulfide are used commercially. In most cases, the amount of impurities is kept low (~ 1-2%), but hardly low enough so that one may safely report the physical and chemical properties of the commercial product to be that of the pure solvent.

Methods of purification of DMSO

The primary impurities in the commercially available dimethyl sulfoxide are dimethyl sulfide, dimethyl sulfone and water. Fractional crystallization and fraction distillation are the most commonly used methods of removing these contaminants.

Douglas[20] reported that his product crystallized at 18.5°C. Schläfer and Schaffernicht[71] report that their samples which had been purified by fractional vacuum distillation melted at 18.55 ± 0.02°C. In this laboratory, the freezing point of the purified solvent was found to be 18.58 ± 0.01°C.

Douglas[21] and Schläfer and Schaffernicht[71] have reported the vapor pressure of DMSO over a wide temperature range. Schläfer and Schaffernicht[71] found that DMSO decomposed somewhat when an attempt was made to distill the material under one atmosphere pressure (189°C), but found also that the amount of decomposition apparently decreased with samples of high purity. They suggested that the distillation be carried out under reduced pressure. The vapor pressure of DMSO renders the temperature range 30 - 90°C as convenient for fractional vacuum distillation. The vapor pressure at the two temperatures are 0.835 mm Hg and 22.0 mm Hg, respectively, as reported by Schläfer and Schaffernicht.[71] One can see from the table of melting and boiling points given below that it should be possible to obtain

a good separation of DMSO from the major contaminants.

Table I.

Melting Point and Boiling Point of DMSO, DMS, $DMSO_2$ and H_2O

Compound	m.p. (°C)		b.p. (°C)	
DMSO	18.58	[ ]	189.0	[71]
DMS	-83	[34]	37.5-38	[34]
$DMSO_2$	110-110.5	[10]	238	[34]
H_2O	0	[35]	100	[35]

The tests for purity have been restricted mainly to: (1) freezing point determination; (2) Karl Fischer titration for water; and, (3) conductivity measurements. Schläfer and Schaffernicht[71] obtained a product which contained less than 4 parts per million H_2O as determined by Karl Fischer titration. Schläfer and Schaffernicht[71], Koltoff and Reddy[43], and Sears and coworkers[73] used the electrical conductivity of the purified material as a test for purity. Schläfer and Schaffernicht[71] regarded as "pure" a product with a specific conductivity of 3×10^{-8} $ohm^{-1}cm^{-1}$ or less at 20°C. The other workers assumed the product to be pure when the specific conductivity was 2×10^{-8} $ohm^{-1}cm^{-1}$ or less. However, Schläfer and Schaffernicht stated that the specific conductivity of the material increased by as much as ten-fold upon allowing it to remain in the conductivity cell for a short period of time, apparently due to a reaction of the solvent with the glass of the conductivity cell. In any case, it appears that conductivity as a test for purity should be used with caution until the variation of conductivity with time has been explained.

Kolthoff and Reddy[43] mentioned that they were unable to remove acidic and basic impurities from the material which they used for their investigations,

but did not elaborate on the possible identity of these impurities. In any case it appears that more careful work should be conducted to identify the impurities in DMSO and the best means for their removal.

Bonding and configuration in DMSO

The bonding in the DMSO molecule is something of an enigma. Bastiansen and Viervoll[8] used electron diffraction to obtain the structural parameters of the molecule. Their results are given below along with data for dimethyl sulfide, dimethyl sulfone and sulfur dioxide.

Table II.

Bond Lengths and Bond Angles in DMSO and Related Compounds

Compound	ℓ(C-H) (Å)	ℓ(C-S) (Å)	ℓ(S-O) (Å)	<C-S-C	<C-S-O	<O-S-O
DMS [13]	1.091	1.802		98°52'		
DMSO [12]	1.08	1.82	1.47	100°	107°	
$DMSO_2$ [14]	1.08	1.90	1.44	115°	105°	125°
SO_2 [15]			1.432			119.54°

Bastiansen and Vieroll[8] attributed the pyramidal structure (with sulfur at the apex) of DMSO to be due to p^3 electron configuration of the sulfur giving trigonal pyramidal bond symmetry.

Abrahams[1] discussed the stereochemistry of the sulfur subgroup (VIB) of the periodic table. He assumed the S-O double bond length to be 1.43 Å which is the S-O bond length in SO_2 and SO_3. This would indicate that the S-O bond is less than order two in DMSO.

Moffitt[61] used a molecular orbital treatment of the S-O bond to conclude that the bond order was between one and two for sulfoxides.

Gillespie and Robinson[27] reviewed the data on bond lengths and stretching frequencies for SO bonds, and found a correlation between the bond length of an SO bond and its stretching frequency. Further, a linear relationship was found between the logarithm of the force constant and the logarithm of the bond length for these bonds. In order to determine the relationship between bond lengths and bond orders, it was assumed that the SO bond lengths in SO_2F_2 (1.405Å), SOF_2 (1.412Å) and S_3O_9 (1.40Å) are characteristic of double bonds. The stretching force constants of these compounds were also assumed to be characteristic of SO double bonds. The bond length of an SO single bond (1.70Å) was calculated then from Pauling's covalent radii and the force constant of a single bond was determined by an extrapolation of the plot of logarithm of force constant versus logarthim of bond length. A linear relationship was found between the force constant and bond order and a nonlinear relationship between the bond length and bond order. The bond order of the SO bond in dimethyl sulfoxide was found to be 1.56.

Cotton and Francis[16,17] investigated the infra-red spectra of complexes of DMSO with transition metal cations. By analyzing the S-O stretching frequency for these compounds it was concluded that the S-O bond in DMSO was between order one and two. They proposed that an S-O bond is a sigma bond overlaid by "back-bonding" from the oxygen to sulfur due to the overlap of filled $p\pi$ oxygen orbitals with empty $d\pi$ sulfur orbitals. By assuming such a picture they were able to explain quite satisfactorily the bonding in the coordination complexes they studied. These results will be discussed in greater detail later.

Schläfer and Schaffernicht[71] compared the DMSO molecule to the acetone molecule. They argued that by first making the arrangement of atoms in

DMSO planar, as in acetone, and then introducing the extra pair of non-bonding electrons on the sulfur, the repulsion between the lone pair and bonding pairs would produce the observed pyramidal structure. There would almost be a tetrahedral distribution of "ligands" around the sulfur with the four groups being 2 carbons, 1 oxygen and 1 lone pair of electrons.

The polarity of the S-O bond might be expected to influence the bonding properties of the molecule toward other molecules or ions. Cotton and Francis[16,17] determined the dipole moment of dimethyl sulfoxide to be 3.9 Debye. If one assumes the moment to be concentrated in the S-O bond, a charge of $\delta^- = 0.55e$ is calculated to reside on the oxygen. In water the charge on the oxygen may be calculated to be $\delta^- = 0.66e$*. Nuclear magnetic resonance studies have found the O peak to be shifted to lower field (lower than H_2O) in DMSO. This supports the results of the above calculation by confirming that there is a lower electron density around the oxygen of DMSO. Also, there is probably a contribution to the dipole moment from the rest of the molecule, for the dipole moment of DMS was found to be 1.5D from its microwave spectrum . There would result a decrease in δ^- on the oxygen as the contribution to the dipole moment from the rest of the molecule increases. The result of the calculation leads one to predict a lower ligand field strength for the DMSO molecule relative to H_2O, and it will be shown later that such is the case.

Physical properties of dimethyl sulfoxide

Some of the more important physical properties are tabulated below:

---

* Calculated from the dipole moment of water, 1.87D.[35]

Table III.

Physical Properties of DMSO

			Ref.
molecular weight		78.13	
m.p.		18.58°C	
b.p.		189.0 °C	[71]
viscosity	20°C	2.47 cp	[71]
	25°C	2.00 cp	[50]
	25°C	1.99 cp	[18]
	25°C	1.96 cp	[73]
surface tension	20°C	46.2 dyne cm^{-1}	[71]
dielectric constant	20°C	48.9	[71]
density	20°C	1.100 g/cc	[71]
	25°C	1.0956 g/cc	[50,8]
heat of vaporization	(25°C)	12.64 kcal/mole	[21]
heat of fusion		3.48 kcal/mole	[75]
cryoscopic constant		3.96/mole/1000 g DMSO	[75]
vapor pressure	(25°C)	0.600 mm Hg	[21]
Trouton's constant		25.8	
dipole moment		3.9 D	[16]

The value of the freezing point of the solvent was determined in the course of this work. The molal freezing point depression constant has been discussed in a previous section (Discussion of Results). Trouton's constant was calculated from the heat of vaporization at the boiling point as determined from the slope of the curve of the logarithm of the vapor pressure versus the reciprocal of temperature. The value of Trouton's constant reported in the literature (29.5) would require a hear of vaporization which is higher at the boiling point than at room temperature.

Barrow and Pitzer[7] have described a method for calculating the thermodynamic properties of dimethyl sulfoxide. Mackle and O'Hare[56] have tabulated

$(H-H_o)/T$, $-(G^\circ-H^\circ_o)/T$, $(H^\circ-H_o)$, S°, C°_p, $-\Delta G^\circ_f$ and $\log_{10}K^\circ_f$ at various temperatures for DMSO (gas). They calculated these quantities from the best modern spectroscopic and calorimetric data. Where a comparison may be made between the two reports, the agreement is quite good.

The dielectric constant of the solvent is somewhat uncertain. An interpolated value of 48.0 at 25°C is calculated from the data of Schläfer and Schaffernicht.[71] Hovermale and Sears[36] report 46.7 and Kenttämaa et al[40] measured 46.4. The respective measurements were at 100 kilocycles, 10 megacycles and 2.47 megacycles. This apparent frequency dependence leads one to adopt 48.0 as the static dielectric constant at 25°C. This uncertainty in the dielectric constant is quite important in the calculations of the standard cell potentials and activity coefficients from the cell data. To be specific, the value of α, the Debye-Hückel constant, depends on the static dielectric constant as seen in the definition

$$\alpha = (2\pi N \rho)^{1/2} \left(\frac{e^2}{D \mathcal{E}_o k T}\right)^{3/2} .$$

Here,

N = Avogadro's number

ρ = density of solvent at temperature, T

e = the charge of a proton

k = Boltzmann's constant

$\mathcal{E}_o$ = permittivity of empty space

D = static dielectric constant.

Listed in Table IV are the values of α for dimethyl sulfoxide at the temperatures indicated. The values of the dielectric constant are taken from Schläfer and Schaffernicht[71] and the density data are from Schläfer and Schaffernicht[71] and Cowie and Toporowski[18]. Also tabulated are the values of $\frac{2RT}{F}$ used in the calculations of thermodynamic properties from

the cell data. The values of R and F are taken from Hamer[30].

Table IV.

Debye-Hückel Constant for Dimethyl Sulfoxide.

T(°K)	α	$\frac{2RT}{F}$
298.15	2.57	5.138×10^{-2}
303.15	2.57	5.224×10^{-2}
308.15	2.59	5.310×10^{-2}

Further discussion of the physical properties is available in the literature.[71]

Solvent properties of DMSO

Dimethyl sulfoxide is a good solvent for many organic and inorganic materials. Its dipolar character helps to make it a good nucleophilic agent and a good solvent to stabilize charged species.

The reactions which occur in the solvent will be discussed in the following groups: (A) Solubility of inorganic compounds; (B) Solvation properties toward inorganic compounds; (C) Acid-base behavior; (D) Oxidation-reduction reactions.

A. Solubility studies

Kenttämaa[41] has reported the solubility of various alkali metal salts in DMSO. Melendres[59] has determined the solubility of the chlorides of the alkali metals, alkaline earth metals, several transition metals and other divalent and trivalent metal ions. In addition, Melendres determined the solubility of a few nitrates, perchlorates and bromides. The

general trends which may be recognized are:

1. The fluorides, sulfates and carbonates were found to be sparingly soluble.
2. The solubility of the chlorides and bromides of the alkali metal ions decrease from lithium to potassium and increase again to rubidium chloride and cesium chloride.
3. For a common cation the solubility increases with an increase in the size of an anion, with the nitrates, perchlorates and iodides the most soluble.
4. The divalent and trivalent chlorides form solvates. The solvate of calcium chloride has the highest solubility of the alkaline earth chlorides, with the solubility decreasing as one progresses both to lighter and heavier members of the group.
5. The alkali metal halides are generally more soluble than the alkaline earth halides and the Group III trivalent metal halides.

B. Solvation properties toward inorganic compounds

The comparison of the dielectric constants of dimethyl sulfoxide and water leads one to predict that solvation energies in dimethyl sulfoxide will be smaller than in water. This rather general conclusion is supported by the conductivity, spectral and solubility studies which have been carried out in the solvent.

Conductivity studies: Sears and coworkers[73] have reported the results of their conductivity studies in DMSO. They found that for the solutions studied, the salts were completely dissociated below 2×10^{-3}N. The limiting equivalent conductance for each ion listed below was calculated

by assuming the applicability of Kohlrausch's law of independent ionic migration. Another assumption was that Λ_o^+ for the n-octadecyltrimethylammonium ion is equal to Λ_o^- for the n-octadecylsulfate ion and that both are equal to 10.0 $ohm^{-1}cm^2equiv^{-1}$ in DMSO. By assuming that $\Lambda_o^+\eta$ (Walden product) for the tetra-n-butylammonium ion is a constant in various solvents and is equal to 0.208 ± 0.009 $ohm^{-1}cm^2equiv^{-1}$ poise, the individual ionic conductances were recalculated. The difference between the two calculations was found to be 2-5% in each case.

Table V.

Limiting Equivalent Conductance in DMSO at 25°C.

(Λ_o^+ ODTMA = Λ_o^- ODS)

Cation	Λ_o^+	Anion	Λ_o^-
K^+	14.4	SCN^-	29.2
$Me_3Ph\ N^+$	14.1	NO_3^-	27.0
Na^+	13.8	ClO_4^-	24.6
Bu_4N^+	11.2	Br^-	24.2
$ODTMA^+$	10.0	I^-	23.8
		Pi^-	17.3
		$PhSO_3^-$	16.8
		ODS^-	10.0

$ODTMA^+$ = n-octadecyltrimethylammonium
ODS^- = n-octadecylsulfate
Pi = picrate ion
Bu = butyl
Me_3Ph = trimethylphenyl
$PhSO_3$ = benzene sulfonate
Λ_o^+ and Λ_o^- are in $ohm^{-1}cm^2equiv^{-1}$

Schläfer and Schaffernicht[71] report the following results of conductivity studies:

Table VI.

Limiting equivalent conductance from 20°-80°C.

Cation	20°C	40°C	60°C	80°C
Bu_4N^+	9.9	14.8	20.3	24.7
K^+	15.9	21.1	26.3	33.8
Anion				
Pi^-	15.4	22.5	31.2	38.4
Cl^-	33.3	46.9	65.3	86.2

(Λ_o^+ and Λ_o^- are in $ohm^{-1}cm^2equiv^{-1}$.)

These values of Λ_o^+ and Λ_o^- were assigned by assuming that the transference number of the tetra-n-butyl ammonium ion in a solution of tetra-n-butyl-ammonium picrate at infinite dilution is the same in water and in dimethyl-sulfoxide, i.e., 0.33.

There is some disagreement between the two sets of data, but most of it may be attributed to the different methods of splitting up the limiting equivalent conductance of the salts into the ionic limiting equivalent conductances.

Dunnett and Gasser[24] have determined the limiting equivalent conductances of lithium chloride, lithium bromide and sodium chloride in dimethyl sulfoxide. Their results are, at 25°C:

salt	$\Lambda_o^+ + \Lambda_o^-$
LiCl	35.3
LiBr	35.2
NaCl	37.3

If one uses the values of $\Lambda_o^{Br^-}$ and $\Lambda_o^{Na^+}$ determined by Sears *et al*[73] to calculate $\Lambda_o^{Cl^-}$, the results are: $\Lambda_o^{Cl^-}$(from NaCl) = 23.5, $\Lambda_o^{Cl^-}$(from LiCl) = 24.3. This is in considerable disagreement with the data of Schläfer and

Schaffernicht.[71] Dunnett and Gasser are unable to explain the disagreement.[24] It would seem that the presence of water in the determinations of Dunnett and Gasser might be a possible explanation for the disagreement.[24]

The following generalizations from the data of Sears et al may be noted:[73]

(1) as the anion size increases, Λ_o^- decreases;

(2) anions have higher Λ_o values than cations of the same charge and size;

(3) although there are only two cations (K^+ and Na^+) that may really be compared, the smaller cation, Na^+, has the smaller Λ_o^+ value. The data of Dunnett and Gasser are consistent with this trend since their assigned value of $\Lambda_o^{Li^+}$ is 11.4.

Spectral studies: An important contribution to the chemistry of DMSO has been the work on its ligand properties toward transition metal ions[15-17, 57,58,64]. The first question which these investigators had to answer was how the transition metal cations were bonded to the DMSO molecule, i.e., through the oxygen atom or through the sulfur atom. Both oxygen and sulfur have an electron pair available for coordination. Cotton and Francis[16,17] have identified oxygen as the donor site, by interpreting the infra-red spectra of the dimethyl sulfoxide complexes. The shift of the S-O stretching frequency was discussed in terms of the influence which bonding through either the sulfur or oxygen would have on the frequency. The argument is that if, as has been mentioned earlier, there is "back-bonding" from oxygen to sulfur, a decrease in this back-bonding would shift the S-O stretching frequency downward (i.e., to lower frequency) and an increase in the back-bonding would shift the frequency upward. If coordination to the positive metallic cation occurs through the oxygen

the back-bonding would decrease and the frequency would be shifted downward. If the bonding to the metallic cation occurred through the sulfur the frequency should be shifted upward. For almost all the complexes whose infra-red spectra have been taken, the shift is downward. Only Pd and Pt complexes have shifted the S-O stretching frequency upward. This indicates that all those transition metals studied coordinate to DMSO through the oxgyen, with the exception of Pd and Pt which apparently coordinate through the sulfur.

Selbin and coworkers[74] have extended this idea somewhat. They postulate that the magnitude of the shift doward in frequency indicates the magnitude of decrease in S-O bond strength, and therefore the magnitude of increase in oxygen-metal ion bond strength. The lower the S-O stretch frequency, the weaker the S-O bond and consequently the stronger the metal ion to oxygen bond. By applying this postulate to the data for metal complexes, they have set up the following series for increasing metal-oxygen bond strength:

(a) divalent chlorides: Hg < Ni < Co < Cd < Pb < Cu

(b) divalent perchlorates: Ni < Mn < Co < Fe < Pb < Cu

(c) trivalent ions: Al < Ga < Fe.

The comparison of DMSO as a solvent to other solvents is better understood by comparing the ligand field strength of DMSO to that of other ligands. Schläfer and Opitz[72] have investigated the visible spectra of certain of the transition metal complexes with DMSO. They have compared the parameter Dq for Cu^{++} for various ligands. The ligand field parameter is larger for greater ligand field strength. Their table is reproduced below:

Table VII.

The Spectrochemical Series of Cu^{+2} Complexes

ligand	Cl^-	DMSO	CH_3OH	DMFA	H_2O
Dq(cm^{-1})	650	1190	1212	1242	1260
ligand	THF	AN	$enta^{-4}$	NH_3	en
Dq(cm^{-1})	1274	1342	1360	1510	1640

DMSO = dimethyl sulfoxide An = acetonitrile
DMFA = dimethylformamide $enta^{-4}$ = ethylenediamine tetra-acetate
THF = tetrahydrofuran en = ethylenediamine

It may be seen that DMSO is a weaker ligand, toward Cu^{+2} at least, than is H_2O.

The solvation number and solvent exchange rate of $Al(DMSO)_n^{+3}$ in DMSO has been studied by nuclear magnetic resonance[78]. The solvation number was found to be six, and as in water, the solvent exchange rate is slow.

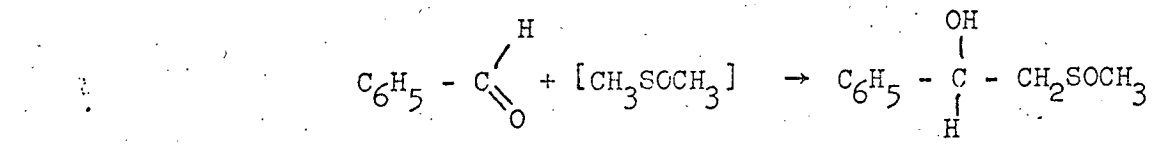
C. Acid-Base Behavior

According to the solvent system concept of acid-base behavior[5], one would predict the autoionization of DMSO to occur, i.e.,

$$2(CH_3)SO \rightleftarrows [CH_3SOCH_2]^- + [CH_3SOHCH_3]^+ .$$

Thus a base would be a compound which increases the concentration of $[CH_3SOCH_2]^-$ relative to the cation $[CH_3SOHCH_3]^+$. An acid would have the reverse property. Any acid-base study should then be directed toward either (a) isolating compounds of the conjugate anion and cation of the solvent, or (b) determining the relative concentration of the anion and cation in solution. Most of the work in dimethyl sulfoxide has been directed toward the latter. Thus the evidence for existence of the anion and cation in solution is still somewhat tenuous.

Evidence for the presence of the anion and cation as species in solution has come primarily from the course of reactions in the solvent. When sodium hydride is reacted with the solvent at 75°C, hydrogen is evolved . Compounds of the type $[\phi_3P\text{-}CH_2\text{-}R]Br$ were then added to the solution. Products are of the type $\phi_3P = CH\text{-}R$. Corey and Chaykovsky[14] have used solutions of the anion to study reactions of the type



These same workers have studied the reaction of the anion with triphenylmethane and have determined the concentration quotient

$$\phi = \frac{[(C_6H_5)_3C^-][CH_3SOCH_3]}{[CH_3SOCH_2^-][(C_6H_5)_3CH]} = 10^2 \text{ to } 10^3 .$$

The preparation of the compound $(CH_3)_2SOH^+NO_3^-$ has been reported by the action of concentrated nitric acid on dimethyl sulfide; the product crystallizes from aqueous solution. Presumably the analogous compound with perchloric acid is formed in acetic anhydride when perchloric acid is used to titrate quantitatively the amount of DMSO in solution .

Kolthoff and Reddy[42,43] used indicator studies, cell potential data, and conductivity and polarographic measurements to determine the acidic and basic properties of DMSO, and the behavior of acids and bases in DMSO. The results may be summarized:

(1) H_2O is a weak base in DMSO.

(2) DMSO is a much weaker acid than water and has about the same proton donating ability as acetonitrile.

(3) The autoprotolysis constant of DMSO was determined to be approximately 5×10^{-18}.

(4) HCl, $HClO_4$ and H_2SO_4 (first ionization) are completely dissociated below about 10^{-2} molar.

(5) The second ionization constant of H_2SO_4 is small and is 8×10^{-10}.

(6) The proton diffusion mechanism in DMSO is concluded to be different than in H_2O as may be seen by comparing the Walden product for H^+ in the two solvents

$$\eta\Lambda_o^{H^+} \text{ (DMSO)} = 8.6 \times 10^{-6} \text{ centipoise cm}^2\text{sec}^{-1}$$

$$\eta\Lambda_o^{H^+} (H_2O) = 93.4 \times 10^{-6} \text{ centipoise cm}^2\text{sec}^{-1}.$$

D. Oxidation-Reduction Reactions

The oxidation and reduction reactions which may be studied in dimethyl sulfoxide are limited by the oxidation or reduction of the solvent. The primary oxidation product is dimethyl sulfone and the reduction product is dimethyl sulfied. From the compilation of the thermodynamic data for the compounds in the gaseous state , one can calculate the free energy of the disproportionation reaction

$$2(CH_3)_2SO_{(g)} \rightleftarrows (CH_3)_2S_{(g)} + (CH_3)_2SO_{2(g)}$$

to be $$\Delta G^\circ_{298°K} = -24.2 \text{ kcal.}$$

From the vapor pressure data for DMSO, the analgous calculation for the reaction of liquid DMSO gives the free energy to be -20 kcal. The solvent is known also to react with mild oxidation and reduction agents. For example, titanium trichloride reacts quantitatively with the solvent to form dimethyl sulfide. Oxidation of dimethyl sulfoxide to the sulfone is reported by Douglas, who found that the preparation of DMSO by oxidation of DMS with hydrogen peroxide could produce the sulfone as a further oxidation product.

Thus it appears that the solvent will have limited use as a medium for oxidation-reduction reactions, especially homogeneous reactions. Heterogeneous reactants such as lithium, calcium and magnesium appear to be quite stable in contact with the solvent, which indicates that the reduction of the solvent by these metals is kinetically limited.

Summary

The high dipole moment and dielectric constant of dimethyl sulfoxide make it a good solvent for polar and ionic materials. It is a strong Lewis base and thus donates electrons to form bonds with solutes which are Lewis acids. Although it is of low oxidation-reduction stability, dimethyl sulfoxide may be usefully employed for many systems which necessitate the exclusion of water.

Appendix III.

The Thermodynamics of Electrochemical Cells

Section 1. Introduction

Electrochemical cells have been used extensively to determine the thermodynamics of chemical reactions. However, interest in thermochemical properties has not always been paralleled by adequate concern with transport phenomena occurring in cells during quasi-equilibrium measurements. An understanding of the effects of transport phenomena on the electrical potential of a cell leads to an appreciation of just how few electrochemical cells may be treated by thermodynamic considerations alone. Also, such an understanding enables one to assess the accuracy of thermodynamic data derived from cells in which irreversible phenomena occur.

In the following, there is first a discussion of phase equilibria and the thermodynamic functions required for quantitative work are carefully defined. In the next sections progressively more complex cell shemes are considered. As each type of cell is discussed, the general method of describing the cell behavior is emphasized with no introduction of specific calculations for particular systems. Specific application of the methods developed, to the cell scheme considered in the experimental program, is outlined in section 4.

Section 2. Phase Equilibrium

An electrochemical cell necessarily consists of several phases. These phases may be two electrode metals and an electrolytic solution (3 phases), but additional phases such as a solid salt or a gas are included in most cells of practical interest. Equilibria between these individual phases, e.g., electrode metal β in equilibrium with the solution, δ, characterize an electrochemical cell which is used for thermodynamic measurements.

The system below is illustrative of the type of cell commonly called a "cell without transference":

metal	metal	electrolytic solution	solid salt	metal	metal
α	β	δ	ϵ	Φ	α'

The vertical lines denote phase separation. The several phase equilibria which may be attained are:

phase α in equilibrium with phase β
phase β in equilibrium with phase δ
phase δ in equilibrium with phase ϵ
phase ϵ in equilibrium with phase Φ
phase Φ in equilibrium with phase α' .

Phases α and α' are composed of the same metal, but are not necessarily in equilibrium since they may not be at the same electrical potential.

If two phases are in equilibrium and if a neutral species A is present in each phase, then the chemical potential of A is the same in the two phases, i.e.,

$$\mu_A^{\delta} = \mu_A^{\epsilon} . \tag{2.1}$$

Here the subscript A refers to the species and the superscript refers to the phase. Similar equations for other equilibrated species. Indeed, this

equation must be obeyed for each species which exists in both phases before the phases may be said to be in equilibrium. When two phases are at the same temperature but are not in equilibrium, upon contact there will be transport of material across the phase boundary until the condition described in equation (2.1) is attained. Thus, each of the phases in equilibrium may be considered to be "open" with respect to those species which can be transported between the phases. Hence, phase equilibrium as used here does not require that all species are present in each phase, and each species is at the same chemical potential in each phase since this would be trivial. Again, phase equilibrium is taken to be the thermodynamic state in which equation (2.1) may be applied to those species which are present in both phases.

In electrochemical systems there are also equilibria which involve ionic species. Let one mole of the neutral species A dissociate into ν_i gram ions of ionic species i and ν_j gram ions of ionic species j, and take by definition

$$\mu_A^\alpha = \nu_i^A \mu_i^\alpha + \nu_j^A \mu_j^\alpha \, . \tag{2.2}$$

Here μ_i and μ_j are the electrochemical potentials of species i and j, respectively, and are functions of the temperature, pressure, chemical composition and electrical state of the phase. Since species A is electrically neutral, the coefficients ν_i^A and ν_j^A are subject to the restriction

$$\sum_k \nu_k^A z_k = 0 \tag{2.3}$$

where z_k is the charge number of species k, and the superscript A refers to the particular neutral species.

Equation (2.1) expresses the condition of phase equilibrium involving

neutral species. For the ionic species i

$$\mu_i^{\alpha} = \mu_i^{\beta} \tag{2.4}$$

is the condition of phase equilibrium between the two phases α and β. If there are several ionic species present in each phase, (2.4) must be obeyed for each ionic species present in both phases before phase equilibrium is attained. Each phase is also assumed to be electrically neutral even though all the ionic species are not present in each.

Equations (2.1) and (2.4) are both presented since phase equilibrium may involve either ions or neutral species, or both.

Section 3. Chemical Potential and Electrochemical Potential

The chemical potential of a neutral species is a function of the temperature, pressure and chemical composition of the phase in which it exists. The chemical potential is defined as

$$\mu_A = \left(\frac{\partial G}{\partial n_A}\right)_{T,P,n_B \neq n_A} = \left(\frac{\partial A}{\partial n_A}\right)_{T,V,n_B \neq n_A} = \left(\frac{\partial U}{\partial n_A}\right)_{S,V,n_B \neq n_A} = \left(\frac{\partial H}{\partial n_A}\right)_{S,P,n_B \neq n_A}. \quad (3.1)$$

G = Gibbs free energy

A = Helmholtz free energy

U = internal energy

H = enthalpy

S = entropy.

In making measurements, one always determines a difference in the chemical potential between different thermodynamic states and never the absolute value in a particular state. However, in tabulating data it is convenient to assign a value to each thermodynamic state. One may do this by arbitrarily assigning the value of the chemical potential in some state and determining the value in other states by comparison to this reference state. Once the reference state is clearly specified and the values of the chemical potential in other states are provided, one can easily reproduce the experimental results. This will be mentioned again in the treatment of data from electrochemical cells.

The electrochemical potential of an ion was introduced by Guggenheim , the difference between its values in two phases being defined as the work of transferring reversibly at constant temperature and constant volume one gram ion from one phase to the other. It is a function of temperature, pressure, chemical composition and electrical state of the phase. It is

still necessary to determine how well defined these independent variables are. For the sections to follow it will be necessary to consider only three cases where transference of ions is involved:

(1) Constant temperature, pressure, identical chemical composition of phases α and α'. The only differences between the two phases will be electrical in nature. For the transfer:

(a) of one gram ion of species i from β to α, the work of transference is

$$\omega = \mu_i^\alpha - \mu_i^\beta = z_i F(\phi^\alpha - \phi^\beta) \tag{3.2}$$

where in the second equation the difference is electrical state of the two phases is defined as the difference in electrical potential of the two phases;

(b) of ν_i gram ions of species i and ν_j gram ions of species j such that

$$\sum_k \nu_k^A z_k = 0.$$

Such electrically neutral combinations of ions do not depend on the electrical state of the phase. We may utilize this to examine the potential difference defined above. Since the total work of transference of combinations such that

$$\sum_k \nu_k^A z_k = 0$$

will be zero,

$$\omega_T = 0 = \nu_i^A(\mu_i^\alpha - \mu_i^\beta) + \nu_j^A(\mu_j^\alpha - \mu_j^\beta) = (\nu_i^A z_i + \nu_j^A z_j)\, F(\phi^\alpha - \phi^\beta) = 0 .$$

Therefore $\phi^\alpha - \phi^\beta$ does not depend on the species i or j used in equation (3.2) and is well defined in this sense.

(2) Temperature, pressure constant, different chemical composition of the two phases. For transfer of combinations such that

$$\sum_k \nu_k^A z_k = 0$$

there is no dependence on the electrical state of either phase. Thus the work of transfer will depend only on the differences in chemical composition.

It should be noted that no quantitative characterization or measure of the difference of electrical state of two phases has been given when the phases are of different chemical composition. Of primary importance is the state of a phase and the question of whether two phases are in the same state. If two phases have different compositions, the question of whether they are in the same electrical state is somewhat meaningless. If the two phases are identical chemically, then one may be interested in their electrical states quantitatively.

The purpose of this section was to define clearly the chemical potential of neutral species and the electrochemical potential of ionic species. In order to do this it was necessary to examine the connection between the chemical composition of a phase and its electrical state, and the possible precision in defining the electrical state of a phase.

Section 4. The Definition of Some Thermodynamic Functions

In this section the absolute activity, activity coefficient and mean activity coefficient will be defined. These functions will be found to be of no fundamental importance for the theoretical treatment of cell potentials, but are of use in expressing experimental results. Of course they should be so clearly defined that one can take tabulated values of the functions and reproduce the experimental results. The definitions which follow are essentially those of Guggenheim .

The absolute activity

$$\mu_i = RT \ln \lambda_i \, . \tag{4.1}$$

Further,

$$\lambda_i = m_i \gamma_i \lambda_i^{\theta} \tag{4.2}$$

where m_i is the molality of the ionic species in the phase (here the electrolytic solution), γ_i is the activity coefficient of i and λ_i^{θ} is a proportionality constant. Other concentration scales can be uskd but the activity coefficient and the constant are changed so that λ_i is independent of the concentration scale used. Another concentration scale in common use is molarity and λ_i is related to this scale by

$$\lambda_i = a_i^{\theta} C_i f_i \tag{4.3}$$

where C_i is the molarity of the ionic species i, f_i is the activity coefficient and a_i^{θ} a proportionality constant. λ_i^{θ} and a_i^{θ} are independent of the concentration, and are characteristic of the ion and solvent at a particular temperature and pressure.

The reference states which will be used in later sections are either

$$\prod_i (\gamma_i)^{\nu_i} \rightarrow 1 \text{ as } \sum_i m_i \rightarrow 0 \tag{4.4}$$

or
$$\prod_i (f_i)^{\nu_i} \rightarrow 1 \text{ as } \sum_i C_i \rightarrow 0 \tag{4.5}$$

for all such combinations of γ_i that satisfy (2.3). Since such products will be used repeatedly, take as the definition of the mean activity coefficient for the electrolyte RX on the molality scale

$$(\gamma_{RX})^{\nu_R+\nu_X} = (\gamma_R)^{\nu_R} (\gamma_X)^{\nu_X} \tag{4.6}$$

and on the molarity scale,

$$(f_{RX})^{\nu_R+\nu_X} = (f_R)^{\nu_R}(f_X)^{\nu_X} \tag{4.7}$$

For the electrolyte RX on the molality scale,

$$(\lambda_R)^{\nu_R} (\lambda_X)^{\nu_X} = (\lambda_R^\theta)^{\nu_R}(\lambda_X^\theta)^{\nu_X}(m_R\gamma_R)^{\nu_R}(m_X\gamma_X)^{\nu_X}$$

$$= (\lambda_R^\theta)^{\nu_R} (\lambda_X^\theta)^{\nu_X} (m_R)^{\nu_R} (m_X)^{\nu_X} \text{ as } \sum_i m_i \rightarrow 0.$$

Since the combinations $(\lambda_R)^{\nu_R} (\lambda_X)^{\nu_X}$ and $(m_R)^{\nu_R} (m_X)^{\nu_X}$ are well defined quantities, it is concluded that $(\lambda_R^\theta)^{\nu_R} (\lambda_X^\theta)^{\nu_X}$ is well defined for the reference state. Furthermore, for all concentrations at which

$$\sum_i m_i \text{ does not} \rightarrow 0 ,$$

$$(\lambda_R)^{\nu_R} (\lambda_X)^{\nu_X} = (\lambda_R^\theta)^{\nu_R} (\lambda_X^\theta)^{\nu_X} (m_R)^{\nu_R} (m_X)^{\nu_X} (\gamma_{RX})^{\nu_R+\nu_X}$$

and one concludes that $(\gamma_{RX})^{\nu_R+\nu_X}$ is a well defined quantity.

A restatement of the above arguments may clarify the reasons for making them. λ_i is well defined but depends on the electrical state. Therefore, the product $(\lambda_i^\theta\gamma_i)$ is well defined but depends on the electrical state. We take the position that the only combinations of λ_i which may be determined unambiguously are those that satisfy (2.3) and are thus related

to electrically neutral salts. Therefore the quantity

$$(\lambda_i^\theta)^{\nu_i} (\lambda_k^\theta)^{\nu_k} (\gamma_i)^{\nu_i} (\gamma_k)^{\nu_k}$$

may be determined unambiguously. A choice of the reference state, (4.4), thus makes it possible to determine $(\lambda_i^\theta)^{\nu_i} (\lambda_k^\theta)^{\nu_k}$ and $(\gamma_i)^{\nu_i} (\gamma_k)^{\nu_k}$ unambiguously.

Similar arguments may be made about the definitions on the molarity scale and again one concludes that the combinations

$$\prod_i (a_i^\theta)^{\nu_i} \text{ and } \prod_i (f_i)^{\nu_i}$$

in which the ν's satisfy (2.3), may be unambiguously determined with the aid of the reference state (4.5).

It is sometimes desirable to convert molalities to molarities or vice versa. The molality (moles solute/1000 grams solvent) is related to the molarity (moles solute/liter solution) according to,

$$m_i = \frac{C_i}{d - 0.001\, C_i \omega_i}$$

in which d is the density of the solution and ω_i is the molecular weight of the species i. For ionic species, ω_i is the gram ionic weight of the species i.

This concludes the definitions of the thermodynamic function which will be used in later sections.

Section 5.

Cell with Electrolytic Solution of Uniform Concentration Throughout

Cells discussed in this section are taken to contain a single electrolyte in solution of uniform concentration throughout the cell.

In most textbooks of physical chemistry, electrochemistry or thermodynamics, a distinction is made between a "cell without transference" and a "cell with transference." The supposed dividing line between these is the existence or not of concentration gradients in the electrolytic solution. Since most electrochemical cells are of the type "with transference", the division is somewhat awkward. It is proposed that a more logical classification is the given in this section.

An example of a cell with the same electrolyte throughout is one with two electrodes of the same metal dipping into the same solution of a salt of the metal. More specifically, consider the system

α	β	δ	β'	α'
Pt(s)	Cu(s)	$CuSO_4$ soln	Cu(s)	Pt(s) .

Phase equilibrium between the several phases is described by

$$\mu^{\alpha}_{e^-} = \mu^{\beta}_{e^-} \tag{5.1}$$

$$\mu^{\beta}_{Cu^{+2}} = \mu^{\delta}_{Cu^{+2}} \tag{5.2}$$

$$\mu^{\delta}_{Cu^{+2}} = \mu^{\beta'}_{Cu^{+2}} \tag{5.3}$$

$$\mu^{\beta'}_{e^-} = \mu^{\alpha'}_{e^-} \quad . \tag{5.4}$$

From (2.2),

$$\mu^{\beta}_{Cu} = 2\mu^{\beta}_{e^-} + \mu^{\beta}_{Cu^{+2}} \tag{5.5}$$

$$\mu^{\delta}_{CuSO_4} = \mu^{\delta}_{SO_4^{=}} + \mu^{\delta}_{Cu^{+2}} \tag{5.6}$$

$$\mu^{\beta'}_{Cu} = 2\mu^{\beta'}_{e^-} + \mu^{\beta'}_{Cu^{+2}} \quad . \tag{5.7}$$

The electrical potential difference between α and α', i.e., $\phi^{\alpha} - \phi^{\alpha'}$, is related to the electrochemical potentials by,

$$z_{e^-}F(\phi^{\alpha} - \phi^{\alpha'}) = \mu^{\alpha}_{e^-} - \mu^{\alpha'}_{e^-}$$

$$\begin{aligned} - F(\phi^{\alpha} - \phi^{\alpha'}) &= \mu^{\beta}_{e^-} - \mu^{\beta'}_{e^-} \\ &= \tfrac{1}{2}\mu^{\beta}_{Cu} - \tfrac{1}{2}\mu^{\beta}_{Cu^{+2}} - \tfrac{1}{2}\mu^{\beta'}_{Cu} + \tfrac{1}{2}\mu^{\beta'}_{Cu^{+2}} \\ &= \tfrac{1}{2}\mu^{\beta}_{Cu} - \tfrac{1}{2}\mu^{\beta'}_{Cu} . \end{aligned} \tag{5.8}$$

If both electrodes are of the same purity, i.e.,

$$\mu^{\beta}_{Cu} = \mu^{\beta'}_{Cu}$$

it is obvious that the measured potential will be zero. If, however, one of the "copper" electrodes is alloyed with another metal and the other electrode is not,

$$- F(\phi^{\alpha} - \phi^{\alpha'}) \neq 0 .$$

Here it is assumed that the phase equilibria described by (5.1-5.4) are unchanged, i.e., that the only effect of introducing the foreign metal into one of the electrodes is to change the chemical potential of the copper in that electrode. Such a cell has the same electrolyte throughout, and its electrical potential and thermodynamic properties are connected by equation (5.8). Another cell of this type is

α	β	δ	ϵ	α'
Pt(s)	Pb(s)	$PbCl_2$ soln in H_2O	Pb(Hg)	Pt(s)

in which Pb(Hg) is a lead amalgam. By a similar analysis,

$$- F(\phi^{\alpha} - \phi^{\alpha'}) = \tfrac{1}{2}\mu^{\beta}_{Pb} - \tfrac{1}{2}\mu^{\epsilon}_{Pb} . \tag{5.9}$$

Therefore, one may determine the thermodynamic properties of lead amalgam as a function of the relative composition by measuring the cell potential

for such cells as that above. Such an application has been the most common use of cells of this type.

A cell which is usually described as having the same electrolyte throughout is the one given formally in section 2. A particular system is

α	β	δ	ϵ	Φ	α'
Pt(s)	Li(s)	LiCl soln in DMSO	TlCl(s)	Tl(Hg)	Pt(s)

where the electrolytic solution is a solution of lithium chloride in the solvent dimethyl sulfoxide, TlCl is a salt which is sparingly soluble in DMSO and Tl(Hg) is a thallium amalgam. The several phase equilibria yield:

$$\mu^{\alpha}_{e^-} = \mu^{\beta}_{e^-} \tag{5.10}$$

$$\mu^{\beta}_{Li^+} = \mu^{\delta}_{Li^+} \tag{5.11}$$

$$\mu^{\delta}_{Cl^-} = \mu^{\epsilon}_{Cl^-} \tag{5.12}$$

$$\mu^{\epsilon}_{Tl^+} = \mu^{\Phi}_{Tl^+} \tag{5.13}$$

$$\mu^{\Phi}_{e^-} = \mu^{\alpha'}_{e^-} \tag{5.14}$$

There are the associated relations [see (2.2)]

$$\mu^{\beta}_{e^-} + \mu^{\beta}_{Li^+} = \mu^{\beta}_{Li}$$

$$\mu^{\delta}_{Li^+} + \mu^{\delta}_{Cl^-} = \mu^{\delta}_{LiCl}$$

$$\mu^{\epsilon}_{Tl^+} + \mu^{\epsilon}_{Cl^-} = \mu^{\epsilon}_{TlCl}$$

$$\mu^{\Phi}_{Tl^+} + \mu^{\Phi}_{e^-} = \mu^{\Phi}_{Tl} \; .$$

Therefore,

$$- F(\phi^{\alpha} - \phi^{\alpha'}) = \mu^{\beta}_{Li} - \mu^{\Phi}_{Tl} + \mu^{\epsilon}_{TlCl} - \mu^{\delta}_{LiCl} + (\mu^{\delta}_{Cl^-} - \mu^{\delta}_{Cl^-}) \; . \tag{5.15}$$

Thus the electrical potential difference between α and α' is related to the thermodynamic properties of neutral species, since $\mu^{\delta}_{Cl^-} = \mu^{\delta}_{Cl^-}$, even though the various equilibria (5.10-5.14) were expressed in terms of single ionic species. This will always be the case for cells which may be treated by thermodynamics alone.

It would appear from the above treatment that the assumption of the same electrolyte throughout is valid here. It is known that there will be TlCl in the solution although the quantity will be small. The presence of this added electrolyte will change the chemical potential of LiCl in the immediate vicinity of the thallium amalgam-thallous chloride electrode. One cannot allow the thallous chloride to saturate the entire solution because it will react spontaneously with the lithium metal. Therefore, there will be a gradient of the concentration of TlCl and consequently a gradient of the electrochemical potential of the chloride ion, and one can no longer assume that there is the same electrolytic solution in contact with both electrodes. The original system must be described more carefully, and equation (5.12) must be changed.

α	β	δ	δ'	ϵ	Φ	α'
Pt(s)	Li(s)	LiCl soln in DMSO	LiCl soln in DMSO	TlCl(s)	Tl(Hg)	Pt(s)

Phase δ' differs from δ due to the dissolved TlCl. (5.12) becomes

$$\mu^{\delta'}_{Cl^-} = \mu^{\epsilon}_{Cl^-} \qquad (5.12')$$

and (5.15) becomes

$$-F(\phi^{\alpha} - \phi^{\alpha'}) = \mu^{\beta}_{Li} - \mu^{\Phi}_{Tl} + \mu^{\epsilon}_{TlCl} - \mu^{\delta}_{LiCl} + \mu^{\delta}_{Cl^-} - \mu^{\delta'}_{Cl^-} . \qquad (5.15')$$

If $\mu^{\delta}_{Cl^-} - \mu^{\delta'}_{Cl^-} \rightarrow 0$, (5.15') becomes (5.15). This system cannot be treated by thermodynamics alone, since diffusion is an irreversible process. It

is necessary to apply the laws of diffusion or transport in electrolytic solutions in order to treat this region of nonuniform composition. For this system and at zero current, the gradient of the electrochemical potential of the chloride can be expressed in terms of the neutral salts as follows,

$$\nabla\mu^{\delta'}_{Cl^-} = t^{o}_{Li^+}\mu\nabla^{\delta'}_{LiCl} + t^{o}_{Tl^+}\mu\nabla^{\delta'}_{TlCl}$$

in which ∇ is "the gradient of . . .", and the t^{o}_{i}'s are the transference numbers of the ionic species with respect to the solvent velocity. Thus, the more insoluble the salt (here TlCl), the more nearly is the electrolyte the same throughout and equations (5.12') and (5.15') reduce to (5.12) and (5.15), respectively.

Now examine the systems where there are two (or more) electrolytes in solution at a uniform concentration throughout. The results of the previous examples may be applied here, with two additional assumptions:

(i) the second electrolyte in the system changes the thermodynamic properties of the first electrolyte, but does not react with it to form a precipitate, evolve a gas, etc., nor does it react spontaneously with the electrodes.

(ii) the second electrolyte does not participate in the phase equilibria except to alter thermodynamic properties in the solution phase.

It has been the purpose of this section to illustrate how the results of section 2 may be applied to typical systems, and to examine the specifications and characteristics of a cell with the same electrolyte throughout. For the first two cases examined above the thermodynamic properties of the electrolyte have no influence on the cell potential. The third case was found not to belong to this section and will be treated in more detail in another section.

Section 6.
Cell with Single Electrolyte of Varying Concentration

Cells in which the concentration of a single electrolyte varies with location in the cell is the simplest example of a so-called "cell with transference." Such a cell might be formally,

$$\begin{array}{c|c|c|c|c|c|c}
\alpha & \beta & \delta & \left\{\begin{array}{c}\text{transition}\\ \text{region}\end{array}\right\} & \epsilon & \beta' & \alpha' \\
\mathrm{Pt(s)} & \mathrm{Li(s)} & \text{LiCl soln in DMSO} & & \text{LiCl soln in DMSO} & \mathrm{Li(s)} & \mathrm{Pt(s)}
\end{array}$$

in which the chemical composition of both platinum leads is identical, as is that of both lithium electrodes. The concentration of LiCl in the δ-phase is different from that in the ϵ-phase. The "transition region" is one in which concentration gradients exist, as the concentration varies from that in the δ-phase to that in the ϵ-phase. This region is sometimes called a "liquid junction."

Applying to this cell the definitions of sections 2 and 3, one finds the following,

$$- F(\phi^{\alpha} - \phi^{\alpha'}) = \mu^{\epsilon}_{Li^+} - \mu^{\delta}_{Li^+} . \tag{6.1}$$

This is a well-defined electrical potential difference since both the platinum leads are of the same chemical composition. One can go no further in treating the cell by reversible thermodynamics since there is diffusion. Two treatments are possible. Newman's treatment of the transport properties of electrolytic solutions is chosen here in preference to a treatment by the methods of irreversible thermodynamics (e.g., Guggenheim

Suppose the electrochemical potential difference in (6.1) is infinitesimally small, i.e.,

$$- F(\phi^{\alpha} - \phi^{\alpha'}) = d\mu_{Li^+} = \mu^{\epsilon}_{Li^+} - \mu^{\delta}_{Li^+} .$$

From the treatment of transport phenomena by Newman one finds

$$\frac{1}{z_+} \nabla\mu_+ = - \frac{\underline{i}F}{\kappa} - \frac{t_-^o}{z_- \nu_-} (\nabla\mu_{LiCl}) , \tag{6.2}$$

where $\underline{i}$ is the current density and κ is the conductivity. According to (6.1),

$$z_+ = 1, \; z_- = - 1, \; -F\nabla\phi = - \nabla\mu_{Li^+} ;$$

$\nabla\mu_{Li^+}$ may be eliminated from (6.2) to yield

$$F\nabla\phi = - \frac{\underline{i}F}{\kappa} + t_-^o \nabla\mu_{LiCl} . \tag{6.3}$$

The potential of the cell is thus related to the transport properties of the solutions, the current density, and the concentration profile in the liquid junction. Assume

$$\underline{i} = 0$$

$$\nabla\phi = \frac{d\phi}{dx}$$

$$\nabla\mu_{LiCl} = \frac{d\mu_{LiCl}}{dx} .$$

Equation (6.3) can be integrated to give

$$\int_I^{II} F d\phi = \int_I^{II} t_-^o \, d\mu_{LiCl}$$

$$F(\phi^{II} - \phi^I) = \int_I^{II} t_-^o \, d\mu_{LiCl} . \tag{6.4}$$

The left-hand side corresponds to the electrical potential difference between the two "end" electrodes of a series of cells such as (6.3), the other electrodes cancelling in pairs. Alternatively, (6.3) expresses the difference in electrical potential between phase α' and a platinum lead connected to a lithium electrode. The second platinum lead and lithium

electrode are infinitesimally "close" to phase β, i.e., the potential difference is infinitesimally small. This second lead and electrode might be termed a "suitable reference electrode." As the reference electrode is "moved" across the liquid junction, (6.4) expresses the potential difference between α' and the reference electrode. Finally, let the reference electrode coincide with phases α and β so that (6.4) becomes

$$F(\phi^{\alpha'} - \phi^{\alpha}) = \int_{\delta}^{\epsilon} t_{-}^{o} \, d\mu_{LiCl} \, . \tag{6.5}$$

(6.5) is equivalent to the expressions which appear in most treatments of cells of the type considered here. However, the "virtual passage of current" used in most derivations has been avoided here, and indeed it has been possible to treat the case where the current density is zero. The electrical potential difference appearing in (6.5) will not be described here as the "liquid junction potential", but will be more appropriately titled "the potential of a cell with liquid junction." This avoids the use of individual ionic activity coefficients and the ill-defined electrical potential difference between two points in a medium of varying chemical composition (see section 3).

Upon introduction of the definitions from section 4, (6.5) becomes

$$F(\phi^{\alpha'} - \phi^{\alpha}) = \int_{\delta}^{\epsilon} 2t_{-}^{o} \, RT \left[1 + \frac{d \ln \gamma_{LiCl}}{dm}\right] dm \, . \tag{6.6}$$

If t_{-}^{o} does not depend on concentration,

$$F(\phi^{\alpha'} - \phi^{\alpha}) = \int_{\delta}^{\epsilon} 2t_{-}^{o} \, RT \left[1 + \frac{d \ln \gamma_{LiCl}}{dm}\right] dm = 2RT \, t_{-}^{o} \ln \frac{(m_{LiCl}\gamma_{LiCl})_{\epsilon}}{(m_{LiCl}\,{}_{LiCl})_{\delta}} \, . \tag{6.7}$$

If the activity coefficients are known in both solutions, t_{-}^{o} may be calculated from a measurement of the cell potential.

One may generalize (6.2) for an arbitrary electrode reaction to obtain,

$$\frac{1}{z_+} \nabla\mu_+ = - \frac{\underline{i}F}{\kappa} - \frac{t_-^o}{z_- \nu_-} \nabla\mu_{electrolyte} \cdot \tag{6.8}$$

From thermodynamics, for an arbitrary electrode reaction,

$$S_- \nabla\mu_- + S_+ \nabla\mu_+ + S_o \nabla\mu_o = - nF \nabla\phi$$

or

$$- F\nabla\phi = \left(\frac{S_-}{n\nu_-} \frac{S_o m}{nm_o}\right) \nabla\mu_{electrolyte} - \frac{1}{z_+} \nabla\mu_+ \tag{6.10}$$

in which the relation

$$S_+ z_+ + S_- z_- = - n$$

has been used. The S's are stoichiometric coefficients for the electrode reaction, and m_o is the molality of the solvent. Elimination of $\frac{1}{z_+} \nabla\mu_+$ from (6.8) and (6.10) yields, where $\underline{i} = 0$,

$$F\nabla\phi = - \nabla\mu_{electrolyte} \left(\frac{S_-}{n\nu_-} - \frac{S_o m}{nm_o} + \frac{t_-^o}{z_- \nu_-}\right) \cdot$$

Now

$$\nabla\mu_{electrolyte} = \nu \, RT \left[\nabla \, ln \, (m \, \gamma_{electrolyte})\right] \cdot$$

Therefore, if t_-^o is independent of composition,

$$F(\phi^{\alpha'} - \phi^{\alpha}) = -\nu \, RT\left(\frac{S_-}{n\nu_-} + \frac{t_-^o}{z_- \nu_-}\right) ln \frac{(m\gamma)_\epsilon}{(m\gamma)_\delta} + \nu \, RT \frac{S_o}{n} \int_\delta^\epsilon \frac{m}{m_o} \left[1 + \frac{d \, ln \, \gamma}{dm}\right] dm. \tag{6.11}$$

To summarize, (6.7) and (6.11) relate the measurable cell potential to the thermodynamic and transport properties of the solutions in the cell.

Section 7.
Cells with Two Electrolytes, One of Varying Concentration

The cells of this section are described as containing two electrolytes in solution. One of the electrolytes is of uniform concentration throughout; the concentration of the other varies with position in the cell. An example of this type cell has been discussed in section 5, i.e.,

α	β	δ	δ'	ϵ	Φ	α'
Pt(s)	Li(s)	LiCl soln in DMSO	transition region	TlCl(s)	Tl(Hg)(ℓ)	Pt(s)

in which the transition region denotes the region of variable concentration of TlCl. LiCl is of uniform concentration throughout.

From (5.15')

$$- F(\phi^{\alpha} - \phi^{\alpha'}) = \mu^{\beta}_{Li} - \mu^{\Phi}_{Tl} + \mu^{\epsilon}_{TlCl} - \mu^{\delta}_{LiCl} + \mu^{\delta}_{Cl^-} - \mu^{\delta'}_{Cl^-} .$$

The expression for the cell potential again contains a difference in the electrochemical potential of an ionic species (e.g., Cl^-), similar to (6.1).

If the concentration profiles are known, this difference can be calculated from the following generalization of equation (6.2) for multicomponent diffusion in the liquid junction:

$$- \frac{i}{z_k} \nabla\mu_k = \sum_i \frac{t_i^o}{z_i} \left[\nabla\mu_i - \frac{z_i}{z_k} \nabla\mu_k\right] + \frac{F}{\kappa} \underline{i} . \qquad (7.1)$$

Let 0 denote solvent, 1 denote Tl^+, 2 denote Li^+ and 3 denote the common anion Cl^-. (7.1) becomes

$$- \nabla\mu_3 = \frac{z_3 t_1^o}{z_1 \nu_1^A} \nabla\mu_A + \frac{z_3 t_2^o}{z_2 \nu_2^B} \nabla\mu_B + \frac{z_3 F \underline{i}}{\kappa} \qquad (7.2)$$

(7.2) is an expression of general validity for this section. There

has so far been no necessity to introduce any assumptions about the relative concentrations of the ionic species. The particular cell introduced at the beginning of this section may be treated by a simplified form of (7.2). If TlCl is only slightly soluble in the solution,

$$m_1 \ll m_2 \approx m_3 \ . \tag{7.3}$$

Introduction of this assumption into the expressions for t_1^o and t_2^o yields (cf. Newman[58].)

$$t_2^o \approx \frac{z_2 \mathcal{D}_{02}}{z_2 \mathcal{D}_{02} - z_3 \mathcal{D}_{03}} \ . \tag{7.4}$$

If one goes back to section 6, it will be noted that t_2^o of (7.4) and t_+^o of section 6 are approximately equal. This is a reasonable result as

$$m_1 \to 0 \ .$$

Also,

$$-\frac{z_3 t_1^o}{z_1 \nu_1^A} \approx \frac{z_1^2 m_1 \mathcal{D}_{01}}{z_2 m_2 \nu_3^A \ (z_2 \mathcal{D}_{02} - z_3 \mathcal{D}_{03}} \tag{7.5}$$

and it is to be noted that

$$t_1^o \to 0 \quad \text{as} \quad m_1 \to 0 \ .$$

Now for the present example,

$$\nu_1^A = \nu_3^A = \nu_2^B = \nu_3^B = 1$$

$$z_1 = z_2 = -\ z_3 = 1$$

and (7.2) becomes

$$\nabla\mu_3 \cong \frac{m_1 \mathcal{D}_{01}}{m_2(\mathcal{D}_{02} + \mathcal{D}_{03})} \nabla\mu_A + \frac{\mathcal{D}_{02}}{\mathcal{D}_{02} + \mathcal{D}_{03}} \nabla\mu_B + \frac{F\,\underline{i}}{\kappa} \tag{7.6}$$

Further, assume

$$\underline{i} = 0$$

$$\mathcal{D}_{01} = \mathcal{D}_{02} = \mathcal{D}_{03}$$

and (7.6) is simplified to

$$\nabla\mu_3 \cong \frac{m_1}{2m_2}\nabla\mu_A + \tfrac{1}{2}\nabla\mu_B \tag{7.7}$$

A suitable reference electrode is to be used in which

$$-\nabla\mu_3 = F\nabla\phi$$

and (7.7) becomes

$$F\nabla\phi \cong -\frac{m_1}{2m_2}\nabla\mu_A - \tfrac{1}{2}\nabla\mu_B \,. \tag{7.8}$$

By definition,

$$\nabla\mu_A = 2RT\,[\nabla\,(ln\, m_A) + \nabla\,(ln\,\gamma_A)]$$

and similarly for B

$$\nabla\mu_B = 2RT\,\nabla\,(ln\,\gamma_B)\,.$$

Retaining only terms of largest magnitude, one obtains

$$F\nabla\phi \approx -RT\frac{\nabla m_3}{m_3} - RT\left[\frac{m_1}{m_2}\nabla\, ln\,\gamma_A + \nabla\, ln\,\gamma_B\right].$$

If one assumes diffusion occurs in only one dimension, and

$$d(ln\,\gamma_A) = d(ln\,\gamma_B)$$

this equation may be integrated to give

$$F\,(\phi^{II} - \phi^{I}) = -RT\, ln\left[\frac{(m_3)_\delta}{(m_3)_\epsilon}\right]. \tag{7.9}$$

In order to measure activity coefficients and standard cell potentials by using cells of this type, one makes measurements at low concentrations of the electrolyte of uniform concentration (e.g., LiCl in this system), and extrapolate to infinite dilution of this electrolyte. By (4.4) the reference state is thus established. These measurements at low concentrations of LiCl are therefore the most important, thermodynamically, and also the measurements which are most subject to errors from "liquid junctions"

such as treated here. One may calculate this error for a typical system in which

$$m_1 \ll m_3$$

$$m_3 = 10^{-3} \text{ moles /1000 gms DMSO}$$

$$\frac{m_1}{m_3} \leq 10^{-3}$$

and the ratio of activity coefficients is given by the first term of the Deby-Hückel theory, i.e.,

$$\ln \frac{(\gamma_A)_\delta}{(\gamma_A)_\epsilon} = (I^{\frac{1}{2}})_\delta - (I^{\frac{1}{2}})_\epsilon \quad .$$

One finds upon using this condition,

$$\nabla\phi \approx 26 \ \mu v \ .$$

If one wants to make measurements which are accurate to at least 10μv, where again $m_3 = 10^{-3}$ moles/1000 gms DMSO, one finds that (using only the first term of (7.9),

$$\frac{m_1}{m_3} \leq 4 \times 10^{-4}.$$

Thus the solubility product of the slightly soluble salt must be $\leq 4 \times 10^{-10}$.

Some further description of the "suitable reference electrode" is in order. The potential appearing in (7.8) and thereafter is taken to be the potential of a cell with liquid junction. The cell is one in which the electrodes are reversible to chloride ions, i.e., chloride ions are in phase equilibrium at both electrodes. The electrodes do not introduce any electrolyte into the solution, are of the same type and differ in electrical potential only because of the concentration gradient of the slightly soluble salt. One may consider this cell "superimposed" on the

cell introduced at the beginning of the section, one "reference electrode" near the ϵ-phase and one "reference electrode" in the δ-phase. The cell potential appearing in (5.15') might be divided into a "thermodynamic" part and a "liquid junction" part, i.e.,

$$- F (\phi^{\alpha} - \phi^{\alpha'}) = - F\nabla\phi_{thermo} - F\nabla\phi_{l.j.}$$

where

$$- F\nabla\phi_{thermo} = \mu^{\beta}_{Li} - \mu^{\Phi}_{Tl} + \mu^{\epsilon}_{TlCl} - \mu^{\delta}_{LiCl}$$

and $- F\nabla\phi_{l.j.}$ given by the integrated form of (7.6) or

$$- F\nabla\phi_{l.j.} = \mu^{\delta}_{Cl^-} - \mu^{\epsilon}_{Cl^-} .$$

It is not the purpose of this section to propose such a separation, but it will be noted that the potential of the cell with liquid junction (e.g., $\nabla\phi_{l.j.}$) is a clearly defined quantity which is measurable. This is different from most definitions of a "liquid junction potential."

The purpose of this section has been to obtain (7.2). This equation was developed without assuming that the concentration of one electrolyte was uniform, but that the two electrolytes had a common ion. Application was then made to a particular case in which simplification was possible. The important results found are:

(1) one can relate the potential of a cell with liquid junction to the thermodynamic and transport properties of the electrolyte solutions in the cell, and the concentration profile across the liquid junction, and;

(2) this potential may be made less than 10 μv when the concentration of the uniform electrolyte is low (e.g., 10^{-3} molal), if the solubility product of the sparingly soluble salt is 4×10^{-10} or smaller, for the particular case studied.

Possible extensions of the results of this section are to cells in

which the concentration of both electrolytes vary with location in the cell, and to "salt bridges." The cell described by Guggenheim[29] would be a logical example of a cell with a "salt bridge" which could be treated by the results of this section. This will be discussed in section 10, and will not be considered here.

Section 8. Cells with Liquid Junction

The following systems have been treated, although not explicitly, in sections 6 and 7:

(1) cells with transference

(a) single electrolyte (section 6)

(b) two electrolytes, common ion (section 7)

(2) salt bridge whose electrolyte has ion in common with each of the "connected" electrolytes.

It has been found in these cases that the irreversible process of diffusion may be accounted for by introducing differences of electrochemical potential of one ion between two phases, e.g., in (6.1) and (5.15'). One may retain such equations in the form of differences in electrochemical potential of an ion, or one may express such differences in terms of "the potential of a cell with liquid junction" as in sections 6 and 7. Neither method seems to have more physical significance than the other. However, it is clear that not only will the difference in electrochemical potential or "potential of a cell with liquid junction", depend on the relative composition, and total composition in a cell, but will also depend on how the junction is formed.

Therefore, there is still the problem of reporting experimental results for such systems so that there is no ambiguity in reproducing the experimental measurements. For cells which can be treated strictly by thermodynamics, or where any irreversible processes are ignored, the data are usually reported in terms of a standard cell potential and activity coefficients. This will be discussed more extensively in section 9. (5.15')

and (6.7) may be examined to show that electrochemical data on cells of section 6 may be reported in terms of transference number, and ratio of activity coefficients and composition of the solutions in the cells. There appears to be no such convention for reporting data from cells of the type treated in section 7.

The problem is even more complicated for systems not included under 1 and 2 above. For one thing the treatment according to (7.1) yields a more complicated expression. The following example illustrates another problem encountered:

$$\overset{\alpha}{\mathrm{Pt(s)}} \;\Big|\; \overset{\beta}{\mathrm{Cu(s)}} \;\Big|\; \overset{\delta}{\mathrm{Cu(ClO_4)_2\ soln\ in\ H_2O}} \;\Big\}\; \underset{\text{region}}{\text{transition}} \;\Big\}\; \overset{\epsilon}{\mathrm{AgNO_3\ soln\ in\ H_2O}} \;\Big|\; \overset{\Phi}{\mathrm{Ag(s)}} \;\Big|\; \overset{\alpha'}{\mathrm{Pt(s)}} \;.$$

The transition region contains the solutions which vary in composition from δ to ϵ. The cell potential is

$$\begin{aligned} -F(\phi^{\alpha} - \phi^{\alpha'}) &= \tfrac{1}{2}\,\mu^{\beta}_{Cu} - \tfrac{1}{2}\,\mu^{\delta}_{Ag} + \mu^{\epsilon}_{Ag^+} \\ &= \tfrac{1}{2}\,\mu^{\beta}_{Cu} - \mu^{\Phi}_{Ag} + \mu^{\epsilon}_{AgNO_3} - \tfrac{1}{2}\,\mu^{\delta}_{Cu(ClO_4)_2} \\ &= \mu^{\delta}_{ClO_4} - \mu^{\epsilon}_{NO_3^-} \;. \end{aligned} \tag{8.1}$$

The problem now is to treat the difference in electrochemical potential of different ions in different phases, i.e.,

$$-\ \mu^{\delta}_{Cu^{+2}} + \mu^{\epsilon}_{Ag^+}$$

or equivalently,

$$\mu^{\delta}_{ClO_4^-} - \mu^{\epsilon}_{NO_3^-} \;.$$

Locally, the diffusion of the two electrolytes into one another may be described by (7.1). This allows one to determine such combinations as

$$\mu^{\delta}_{ClO_4^-} - \mu^{I}_{ClO_4^-}$$

where the superscript I refers to a solution in the transition region. Assume that the ionic strength does not go to zero anywhere in the transition region, i.e., that $Cu(ClO_4)_2$ and $AgNO_3$ are mixed in this region. Then calculation may be made of the combination

$$\mu^{I}_{NO_3^-} - \mu^{\epsilon}_{NO_3^-}$$

where I refers to the same solution as above, by applying (7.1) again. Therefore, (8.1) becomes

$$\begin{aligned} - F(\phi^{\alpha} - \phi^{\alpha'}) = {} & \tfrac{1}{2}\mu^{\beta}_{Cu} - \mu^{\Phi}_{Ag} + \mu^{\epsilon}_{AgNO_3} - \tfrac{1}{2}\mu^{\delta}_{Cu(ClO_4)_2} \\ & + \mu^{\delta}_{ClO_4^-} - \mu^{I}_{ClO_4^-} - \mu^{\epsilon}_{NO_3^-} + \mu^{I}_{NO_3^-} \\ & - (\mu^{I}_{NO_3^-} - \mu^{I}_{ClO_4^-}) \, . \end{aligned} \tag{8.2}$$

If the activity coefficients of $Cu(ClO_4)_2$ and $Cu(NO_3)_2$ (or $AgClO_4$ and $AgNO_3$) are known for a solution of composition identical to I,

$$\mu^{I}_{NO_3^-} - \mu^{I}_{ClO_4^-} = \mu^{I}_{Cu(NO_3)_2} - \mu^{I}_{Cu(ClO_4)_2} = \mu^{I}_{AgNO_3} - \mu^{I}_{AgClO_4} \, .$$

Thus the liquid junction of this cell may also be described by physically well-defined quantities.

Section 9.
Standard Cell Potential and Activity Coefficients

Cells such as that described by (5.15) are used to determine standard cell potentials and activity coefficients of electrolytes. This method of reporting experimental measurements will be discussed. Three systems will be treated in some detail.

Substitution of the definitions (4.1) and (4.2) into (5.15) gives

$$- F(\phi^{\alpha} - \phi^{\alpha'}) = \mu^{\beta}_{Li} - \mu^{\Phi}_{Tl} + \mu^{\epsilon}_{TlCl} - \nu_{LiCl}\, RT\, ln\, \lambda^{\theta}_{LiCl}$$
$$- RT\, ln\, (m_{Li^+})^{\nu_+} (m_{Cl^-})^{\nu_-} (\gamma_{Li^+})^{\nu_+} (\gamma_{Cl^-})^{\nu_-}$$

which by (4.6) becomes,

$$= \mu^{\beta}_{Li} - \mu^{\Phi}_{Tl} + \mu^{\epsilon}_{TlCl} - 2RT\, ln\, \lambda^{\theta}_{LiCl}$$
$$- 2RT\, ln\, m_{LiCl} - 2RT\, ln\, \gamma_{LiCl}\,.$$

The combination

$$\mu^{\beta}_{Li} - \mu^{\Phi}_{Tl} + \mu^{\epsilon}_{TlCl} - 2RT\, ln\, \lambda^{\theta}_{LiCl}$$

is independent of the concentration of electrolyte in the solution and is a function only of the components, temperature and pressure of the system. This combination will then be defined as the "standard cell potential" of this system, i.e.,

$$F\mathcal{E}^{\theta} = \mu^{\beta}_{Li} - \mu^{\Phi}_{Tl} + \mu^{\epsilon}_{TlCl} - 2RT\, ln\, a^{\theta}_{LiCl}\,.$$

Therefore,

$$- F(\phi^{\alpha} - \phi^{\alpha'}) = F\mathcal{E}^{\theta}\; 2RT\, ln\, m_{LiCl} - 2RT\, ln\, \gamma_{LiCl} \qquad (9.1)$$

in which the left-hand side of the equation is measurable, as is m_{LiCl}. If, therefore, the value of $\mathcal{E}^{\theta}$ and γ_{LiCl} are chosen for a particular thermodynamic state of the system, the value of γ_{LiCl} may be determined

in other states. The reference state chosen most commonly is expressed in (4.4). However, this reference state cannot be attained experimentally. Part of the difficulty is associated with the introduction of trace impurities into highly dilute solutions. These impurities may be negligible at high concentrations of LiCl, but are of extreme importance in highly dilute solutions.

To progress further, one must use an equation such as Guggenheim's extension [28, 29] of the Debye-Hückel limiting law, i.e.,

$$\ln \gamma_{LiCl} = - \alpha z_+ |z_-| \frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} + 2\beta_{LiCl} m_{LiCl}$$

in which I is the ionic strength and α and β_{LiCl} are constants. By substitution of this relation into the expression for the cell potential,

$$- F(\phi^{\alpha} - \phi^{\alpha'}) = F\mathcal{E}^{\theta} - 2RT \ln m_{LiCl} + \frac{\alpha m_{LiCl}^{\frac{1}{2}}(2RT)}{1 + m_{LiCl}^{\frac{1}{2}}} - 4\beta_{LiCl} RT m_{LiCl} .$$

The cell potential is thus expressed as a function of the molality of LiCl, $\mathcal{E}^{\theta}$, temperature and pressure in the concentration region where $m_{LiCl} \rightarrow 0$. Rearrangement of the equation yields,

$$- F(\phi^{\alpha} - \phi^{\alpha'}) + 2RT \ln m - \frac{2RT \alpha m^{\frac{1}{2}}}{1 + m^{\frac{1}{2}}} = F\mathcal{E}^{\theta} - 4\beta RT m$$

in which the subscripts on the molality and on β are dropped. Replace the left-hand side of the equation by $F\mathcal{E}'$ and observe that $\mathcal{E}'$ is a linear function of molality, i.e.,

$$F\mathcal{E}' = F\mathcal{E}^{\theta} - 4\beta_{LiCl} RT m .$$

By extrapolating $\mathcal{E}'$ to infinite dilution, one can determine $\mathcal{E}^{\theta}$ from the intercept at m = 0, and β_{LiCl} from the slope of the curve. Once $\mathcal{E}^{\theta}$ is determined, the activity coefficient may be determined as a function of

molality. The accuracy of the data in the dilute region determines the accuracy of $\mathcal{E}^{\theta}$ and γ thus determined, one can reproduce the experimental measurements, to an accuracy determined by the accuracy of $\mathcal{E}^{\theta}$ and of γ.

It was found that the potential of cells treated in section 6 could be expressed as in (6.7) or (6.11). One concludes that a tabulation of transference numbers, activity coefficients and composition would provide the information necessary to reproduce the experimental measurements. The activity coefficients may be determined from measurements on cells such as described in the last paragraph, and the transference number may be calculated from the experimental data on cells of the type described in section 6. Alternately, if the transference number is known as a function of concentration and the activity coefficient is calculated for one solution from a theoretical relationship such as the Debye-Hückel limiting law, the activity coefficient of the electrolyte in the other solution may be obtained readily from an experimental measurement of the cell potential. It is to be noted that a "standard cell potential" has not been defined for this system - nor is it needed.

One other type of cell will be examined in this section, i.e.,

α	β	δ	ϵ	Φ	χ	α'
Pt(s)	Li(s)	$LiNO_3$ soln in DMSO. KNO_3 soln in DMSO.	transition region KNO_3 soln in DMSO	$AgNO_3$ soln in DMSO. KNO_3 soln in DMSO.	Ag(s)	Pt(s)

in which the solvent is dimethyl sulfoxide, and KNO_3 is present throughout δ, ϵ and Φ at the same concentration. Phase ϵ is the region in which there are concentration gradients of both $LiNO_3$ and $AgNO_3$. The cell potential may be expressed as

$$- F(\phi^{\alpha} - \phi^{\alpha'}) = \mu^{\beta}_{Li} - \mu^{\delta}_{LiNO_3} + \mu^{\chi}_{Ag} - \mu^{\Phi}_{AgNO_3} - \mu^{\Phi}_{NO_3^-} . \qquad (9.2)$$

As the concentration of $AgNO_3$ and $LiNO_3$ becomes very small compared to the concentration of KNO_3, it should satisfy the Guggenheim[29] definition of a cell with the composition of δ and Φ nearly identical. KNO_3 is not involved in the phase equilibrium at the electrodes, except to alter the chemical potential of the other electrolytes in the solution. With t these assumptions $\mu^{\delta}_{NO_3^-} - \mu^{\Phi}_{NO_3^-}$ on the right-hand side of equation (9.2) is dropped. Adopting the definition of section 4,

$$- F(\phi^{\alpha} - \phi^{\alpha'}) = \mu^{\beta}_{Li} - \mu^{\chi}_{Ag} + 2RT\, ln\, \lambda^{\theta}_{AgNO_3} - 2RT\, ln\, \lambda^{\theta}_{LiNO_3}$$

$$+ 2RT\, ln \left[\frac{(m_{AgNO_3})(\gamma_{AgNO_3})}{(m_{LiNO_3})(\gamma_{LiNO_3})} \right]$$

$$= F\mathcal{E}^{\theta} + 2RT\, ln \left[\frac{m_{AgNO_3}\gamma_{AgNO_3}}{m_{LiNO_3}\gamma_{LiNO_3}} \right] \qquad (9.3)$$

$$F\mathcal{E}^{\theta} = \mu_{Li} - \mu^{\chi}_{Ag} + 2RT\, ln \frac{\lambda^{\theta}_{AgNO_3}}{\lambda^{\theta}_{LiNO_3}} .$$

From Guggenheim[29], the following relations are introduced which are valid only in solutions where the concentrations of $AgNO_3$ and $LiNO_3$ approach zero, i.e.,

$$ln\, \gamma_{AgNO_3} = - \alpha\, z_{Ag^+} |z_{NO_3^-}| I^{\frac{1}{2}}$$

and similarly for $LiNO_3$

$$ln\, \gamma_{LiNO_3} = - \alpha\, z_{Li^+} |z_{NO_3^-}| I^{\frac{1}{2}}$$

in which α and I are defined as in section 7. Therefore, for systems in which

$$m_{AgNO_3} = m_{LiNO_3}$$

equation (9.3) can be written

$$- F(\phi^{\alpha} - \phi^{\alpha'}) = F\mathcal{E}^{\theta} .$$

There has been no ncessity to extrapolate the data to

$$\gamma_{LiNO_3}, \gamma_{AgNO_3} \rightarrow 1$$

as in (4.4). Indeed, this condition cannot be met since KNO_3 is present, presumably in excess. It has only been necessary to require low concentration of $AgNO_3$ and $LiNO_3$ so that,

$$\mu^{\delta}_{NO_3^-} = \mu^{\Phi}_{NO_3^-} \tag{9.4}$$

and

$$\ln \gamma_{AgNO_3} = \ln \gamma_{LiNO_3} .$$

If the molality of $AgNO_3$ and $LiNO_3$ are different, but (9.4) is retained, one should be able to tabulate the experimental data as a standard cell and activity coefficient ratio of the two salts. The activity coefficient of one of the salts may be calculated if that of the other is known and the ratio of activity coefficients is known.

In order to extend the treatment to systems in which (9.4) is not assumed, the effect of diffusion must be accounted for in one of two ways:

(1) describe phase ϵ as the region in which there are concentration gradients of $AgNO_3$ and $LiNO_3$, but there is no mixing of the two salts, or;

(2) the treatment in section 7 must be extended to a system in which there are more components, in order to allow for mixing of $AgNO_3$ and $LiNO_3$ in phase ϵ.

If (1) is used, the results of section 7 may be utilized at the two junctions, i.e., the junction of phase δ and phase ϵ and the junction of phase ϵ and phase Φ. Whichever extension is used, it will still be difficult to tabulate

the experimental data since one must know the concentration profile across the junction in order to calculate the "correction" (i.e., $\mu^{\delta}_{NO_3^-} - \mu^{\Phi}_{NO_3^-}$) to equation (9.2).

There is no reason to have KNO_3 of constant concentration throughout in order to accomplish condition (9.4). Take the KNO_3 to be absent from all phases and take phase ϵ to be a region in which there exist concentration gradients of $AgNO_3$ and $LiNO_3$ and the concentration of electrolyte does not go to zero anywhere in phase ϵ. Equation (9.3) is still applicable and the results of section 7 may be used if (9.4) is not met. For equal molalities of the two salts, one could extrapolate the experimental measurements to infinite dilution of the two salts where,

$$\gamma_{AgNO_3}, \gamma_{LiNO_3} \rightarrow 1$$

and

$$- F(\phi^{\alpha} - \phi^{\alpha'}) = F\mathcal{E}^{\theta} .$$

Thus the experimental data may be represented by a tabulation of $\mathcal{E}^{\theta}$ and the activity coefficient ratio where (9.4) is assumed. One concludes that $\mathcal{E}^{\theta}$ is independent of the concentration of KNO_3. $\mathcal{E}^{\theta}$ is also independent of the anion used, by (9.4), so long as the anion is the same for both Ag^+ and Li^+.

It has been found that the standard cell potential and activity coefficients adequately represent the experimental data for systems in which irreversible processes may be neglected. It has been possible to establish a treatment to "correct" for diffusion in those systems where it may not be neglected. From a knowledge of the "correction", the standard cell potential and activity coefficients, the experimental measurements may be reproduced. However, the particular concentration profile across a liquid junction remains an experimental variable which must be specified before the "correction" may be determined. Therefore, for cells with liquid

junction one should report the standard cell potential, activity coefficients, concentration profile at the liquid junction and the contribution from diffusion.

In compiling the standard cell potential of many cells it is desirable to tabulate as few details as possible without being ambiguous. Of n possible electrodes, one may make measurements on $\frac{1}{2}n(n-1)$ different combinations of these electrodes taken two at a time. Only (n-1) of these combinations are independent and the others may be obtained by addition and subtraction of the (n-1) independent combinations. One may report the standard cell potentials of (n-1) possible electrodes against the other possible electrode, and the standard cell potential of other combinations may be obtained from these. Implicit in this discussion is the independence of the standard cell potential from specification of the ion not in phase equilibrium at either electrode. However, this is only justified when there is an ion common to both electrolytes, as found in the third system of this section.

For tabulations such as found in Lewis, Randall, Pitzer and Brewer the following conventions are adopted:

(1) the hydrogen electrode is the particular electrode common to all cells; and

(2) unless specified, it is assumed that the ion not in phase equilibrium at either electrode is the same for both electrolytes, e.g., the nitrate ion in the third example of this section; and

(3) if both ions of one electrolyte are specified, e.g., for the Tl|TlCl electrode, the common ion is specified, i.e., Cl^- in this case and in the first example of this section.

In order to utilize this tabulation for cells in which there is no common

ion for the electrolytes, one must calculate such quantities as

$$\frac{RT}{2} \ln \lambda^{\theta}_{Cu(NO_3)_2} - \frac{RT}{2} \ln \lambda^{\theta}_{Cu(ClO_4)_2}$$

as in section 8. A different choice of anions would of course change the quantity which must be calculated.

One other convention used here concerns the sign of the electrode potential. Unless the cell potential is zero, the electrochemical potential of electrons is always greater in one platinum lead than the other. This lead is taken to be the negative lead in the cell. The following definition will be used to comply with this experimental finding: the standard cell potential is positive when the electrode written on the right is positive. This convention has been used in all previous sections.

Appendix IV.

DIFFUSION AND THE EXTRAPOLATION TO INFINITE DILUTION

Thermodynamic treatment of cell potentials is based on the equation

$$E = E^{o} - \frac{RT}{nF} \ln \left[\prod_{i} (m_i \gamma_i)^{\nu_i}\right] \qquad (1)$$

where the symbols used are discussed in section ( ) of Appendix III. In order to assign values to the γ_i's at any concentration, both E^{o} and the γ_i's must be known at some reference state. A reference state in common use is

$$\nu_i \rightarrow 1 \text{ as } \sum_{i} m_i \rightarrow 0 \qquad (2)$$

where the summation is over all ionic species. Thus the measurements in very dilute solutions and the extrapolation of cell potentials to infinite dilution are of great importance to the determination of thermodynamic properties of solutions of all concentrations. Yet these dilute solutions are most subject to uncertainties arising from errors in determination of concentrations, concentration changes resulting from undesirable reactions in the cell and the effect of irreversible phenomena such as diffusion. It is the purpose of this section to discuss the method of estimating the effect of diffusion on the cell potential for the special case of a cell in which there is an electrode of the second kind from which diffuses a sparingly soluble salt.

The cell

Pt(s)/Li(s)/LiCl solution in DMSO/TlCl(s)/Tl(Hg)/Pt(s) (3)

has been discussed in sections (5 - 7) of Appendix III, and employs the sparingly soluble salt TlCl as part of the reference electrode. One must make measurements on the cell before TlCl diffuses to the lithium electrode where it reacts, and therefore the solution is different near

the lithium electrode than that near the amalgam electrode when the measurements are made. The effect is small when the LiCl concentration is high, but becomes significant when the concentration of LiCl approaches the concentration of TlCl. One can calculate in principle the effect of the variation in concentration in the cell from the integral

$$-F(\phi^2-\phi^1) = \int_1^2 (t^\circ_{Tl^+}\, d\mu_{TlCl} + t^\circ_{Li^+}\, d\mu_{LiCl}) \qquad (4)$$

as discussed in section (7) of Appendix III. The integration can be made if one knows the dependence of the transport properties on the concentration of the species throughout the region of concentration variation. However, the necessary data for such a calculation are not available even on an analogous system in aqueous solutions, so one must make approximations. The assumptions to be made are:

1. The integral is well-defined;
2. The solutions are dilute and the concentration of LiCl is comparable to that of TlCl;
3. The ionic mobilities of Li^+, Cl^- and Tl^+ are equal.

The transference numbers which appear in equation (4) are rather complicated functions of the concentrations and transport properties of all the species present. However, one may introduce a considerable simplification in the case of dilute solutions. The transference numbers appropriate for dilute solutions (cf. Newman[63]) are defined by

$$t_i = \frac{z_i^2\, u_i\, c_i}{\sum_i z_i^2 u_i c_i} \qquad (5)$$

in which u_i = mobility of ionic species i,

c_i = concentration (mole/cm^3) for ionic species i,

z_i = charge number.

From the assumption of equal ionic mobilities, the transference number is found to be

$$t_i = \frac{z_i^2 c_i}{\sum_i z_i^2 c_i} \quad . \tag{6}$$

For the case at hand,

$$t_i = \frac{c_i}{2(c_{TlCl} + c_{LiCl})} = \frac{c_i}{2c_{Cl^-}} \quad . \tag{7}$$

This relationship between the transference number and concentration allows one to write

$$-F(\phi^2-\phi^1) = \frac{1}{2}\int_1^2 \left[\frac{c_{Tl^+}}{c_{Cl^-}} d\mu_{TlCl} + \frac{c_{Li^+}}{c_{Cl^-}} d\mu_{LiCl}\right] . \tag{8}$$

The thermodynamic relations

$$\mu_{TlCl} = 2RT\ln 2^{\theta}_{TlCl} + 2RT\ln (m\nu_{\pm})_{TlCl}$$

$$\mu_{LiCl} = 2RT\ln 2^{\theta}_{LiCl} + 2RT\ln (m\nu_{\pm})_{LiCl}$$

may be differentiated to yield

$$-F(\phi^2-\phi^1) = \frac{1}{2}(2RT)\left\{\int_1^2 \frac{d(m_{TlCl} + m_{LiCl})}{(m_{TlCl} + m_{LiCl})}\right.$$

$$\left. + \int_1^2 \left[\frac{m_{Tl^+}}{m_{Cl^-}} d(\ln \nu_{\pm TlCl}) + \frac{m_{Li^+}}{m_{Cl^-}} d(\ln \nu_{\pm LiCl})\right]\right\} \tag{9}$$

in which it has been assumed

$$\frac{m_{Tl^+}}{m_{Cl^-}} \cong \frac{c_{Tl^+}}{c_{Cl^-}} \quad \text{and} \quad \frac{m_{Li^+}}{m_{Cl^-}} = \frac{c_{Li^+}}{c_{Cl^-}} \quad .$$

The molalities have been introduced strictly for convenience.

This yields

$$-(\phi^2-\phi^1) = 51 \times 10^{-3} \text{ volts.}$$

Again the cell potential will be smaller than for the same cell if diffusion were negligible.

Case III.

For the cell

$$Pt(s),\ H_2(g)/HCl \text{ solution in } H_2O/AgCl(s)/Ag(s)/Pt(s) \qquad (11)$$

let

$$(m_{HCl})_2 = (m_{HCl})_1 = 10^{-4}$$

$$(m_{AgCl})_2 \cong 10^{-6}$$

from which one calculates

$$I_2 = 1.01 \times 10^{-4} \qquad (I_2)^{1/2} = 1.005 \times 10^{-2}$$

$$I_1 = 10^{-4} \qquad (I_1)^{1/2} = 10^{-2}$$

$$(\phi^2-\phi^1) = 2.6 \times 10^{-4} \text{ volts.}$$

The cell potential will be smaller than for the corresponding cell if diffusion were negligible.

Experimental data with which these calculations may be compared are available in the literature. Luksha and Criss[55] used the silver-silver chloride reference electrode for measurements in N-methylformamide. Harned and Morrison[31] used the silver-silver chloride reference electrode for measurements in dioxane-water mixtures. It was found that there occurred an abrupt change in slope of the $E^{o'}$ function in dilute solutions such as has been found in the present work (cf. Figure). Luksha and Criss do not propose an explanation for this phenomena. Harned and Owen[32] propose that the theory of Gronwall, LaMer and Sandved is adequate to explain the phenomena in dioxane-water mixtures in which the abrupt change of $E^{o'}$ is to be taken as a dielectric constant effect and

becomes more apparent in systems which are dioxane-rich. However, this would hardly seem to be an appropriate explanation for the N-methylformamide system, since the solvent has a large dielectric constant (171).

Unfortunately neither group of workers report the solubility of silver chloride in their solvents. The only solubility data for any of these systems is that of Kratohvil and Težak[46]. They report that the concentration of silver ion in solutions of hydrochloric acid saturated with silver chloride is higher in a 57.5% dioxane-42.5% water mixture than in water.

In aqueous solutions the reference electrodes most thoroughly investigated are the silver-silver chloride electrode and the mercury-mercurous chloride electrode. The solubility product of silver chloride in water is approximately 10^{-10} and that of mercurous chloride is 10^{-18}. No measurements have been made on cells with the mercury-mercurous chloride electrode in which the concentration of mercurous chloride in solution was comparable to the concentration of the other electrolyte. Carmody[12] made measurements of the cell (11) for hydrochloric acid concentrations down to 0.0003288 molal. Anderson[3] investigated the same cell with hydrochloric acid concentrations down to 2.640×10^{-5} molal. In each investigation the diffusion of silver chloride is of measurable effect on the cell potential. However, the cell potentials which they report were taken after the cell solution was saturated throughout with silver chloride. In Anderson's work, silver was found to be deposited on the platinum of the hydrogen electrode. He was able to show quantitatively that the silver was deposited as a result of the reaction

$$H_2 + AgCl \rightarrow Ag(s) + HCl(\text{solution}).$$

The cell potentials which Anderson measured on the cells with the most dilute solutions were found to increase initially and then to decrease. The initial increase is due to the diffusion of hydrogen away from the hydrogen electrode and masks any effect due to the diffusion of silver chloride from the other electrode. The decrease began when silver chloride reached the hydrogen electrode. It reacted according to the above reaction and the concentration of hydrochloric acid was increased as a consequence. It is concluded that "humped" curves of $E^{o'}$ versus m are found in some systems in which diffusion of the sparingly soluble salt may be expected to contribute to the measured cell potential. The lack of experimental data on solubility prevents any more definite test of this treatment, but it is conclusive enough to suggest caution in exprapolation of $E^{o'}$ to infinite dilution. It is proposed that one should determine that diffusion does not occur in such systems before one employs some treatment such as that of Harned and Owen[32] to perform the extrapolation.

Summarized below are the results of calculations for DMSO with the concentration of LiCl listed in the first column. These may be compared to the results in Figure 1, and one finds good agreement in order of magnitude.

Table 14.

Effect of Diffusion on Cell potential

LiCl conc. molality	$-(\phi^2 - \phi^1)$ mv
1×10^{-2}	0.056
5×10^{-3}	0.45
1×10^{-3}	7.67
7×10^{-4}	12.03
5×10^{-4}	17.20
3×10^{-4}	26.63
1×10^{-4}	50.84

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