

VOLTAIC AND CONCENTRATION CELLS
IN LIQUID SULFUR DIOXIDE.

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Since the publication of the work of Walden¹ and Centnerswer in 1889, announcing liquid sulfur dioxide as a new inorganic dissociative solvent, "With the remarkable power of dissolving the most varied substances, both inorganic and organic", a very considerable amount of attention has been directed toward the subject and many of the properties of dry liquid sulfur dioxide solutions have been studied. In particular the conductivity of some of these solutions has been measured by Walden, by Dutoit and Gyr², and by E. C. Franklin³, the behavior of such solutions during electrolysis by Bagster and Steele⁴ and the measurements of the E.M.F.s of three voltaic cells by the latter.

It was to study further the properties of electrolytic sulfur dioxide solutions, and especially to see whether the same laws hold for this as for aqueous electrolytic solutions that the present work was undertaken. The problem parallels the work of Dr. Cady⁵ on concentration cells in liquid ammonia and the procedure and apparatus were in the main similar.

In spite of the fact that much work has been done on sulfur dioxide solutions, it was not possible to find even rough estimates of the solubilities of various salts in it:- the nearest thing to a table of solubilities found being Waldens¹ article where, as very soluble inorganic salts, he lists:

KI	NaI	NH_4I
RbI	$(\text{CH}_3)_4\text{I}$	KBr
NH_4CNS	$(\text{CH}_3)_3\text{NH}_2\text{Cl}$	$(\text{CH}_3)_3\text{NHCl}$
$(\text{CH}_3)_4\text{NCl}$	FeCl_3	CoSCN_2

And among very soluble acids:

Mono-chlor-acetic	di-chlor-acetic
alpha-brom-propionic	Benzoic
salicylic	meta-oxy-benzoic
beta-naphtoic	

From Franklin's work, one gathers that the following solutions are about saturated:

Temperature	Weight	Substance	Volume
-10 C	1 mole	NH_4CNS	166.44 cc.
-33.5	1 mole	$(\text{CH}_3)_4\text{NI}$	375. cc.
-33.5	1 mole	KBr	375. cc.
-20.	1 mole	KI	300. cc.

As a working basis for the problem, it seemed necessary to determine the solubilities of a number of salts quantitatively; especially those yielding ordinary metallic cations. The salts used were either ignited or dried for a long period in a vacuum dessicator equipped with a heating unit by which a temperature of about 65°C was maintained.

To determine the solubility, a quantity of the dried salt was placed in a special long test tube immersed in liquid ammonia and some ten c.c. of liquid sulfur dioxide distilled in from an iron cylinder through P2O5. The mixture was then stirred for a few minutes - exposed to room temperature and allowed to boil for some time - then tightly corked and replaced in the liquid ammonia, where it stood, usually over night, in contact with the solid salt. A known volume of the solution was then removed with a calibrated immersion pipette of the type shown and the latter placed in a small beaker which had previously been weighed with it - allowed to evaporate - brought to a temperature of 100° C and weighed; the difference in the two weighings divided by the volume of the pipette being taken as the solubility of the salt in grams per c.c. The method is open to the objection that if there is stable compound formation (compounds stable in the air at 100°) the solubility will seem to be much too great and no attempt was made to check up on this.

The solubilities of the following salts were determined:

Salt	Sol. in grams per liter
KBr	136.5
KI	89.

Salt	Sol. in grams per liter
CdCl_2	1.0
$\text{Cd}(\text{NO}_3)_2$	1.0
CdF_2	.542
CdI_2	3.6
ZnSO_4	0.5
$\text{Zn}(\text{C}_6\text{H}_5\text{.CH:CH.COO})_2$	7.5
ZnO	.3
BaF_2	0.0
BaBr_2	0.0
LiCl	.3
SnCl_2	.5
HgI_2	0.0
$\text{Hg}(\text{SCN})_2$	0.0
HgSO_4	0.2
$\text{Hg}(\text{CN})_2$	0.2
$\text{NaC}_2\text{H}_3\text{O}_2$	55.7
NaNO_2	0.4
Na_2O_2	.19
NaOH	0.2
Na_2SO_3	0.775
NaNO_3	1.0
$\text{NaKC}_4\text{H}_4\text{O}_6$	0.4
$\text{Cu}(\text{CH}_2\text{Cl.COO})_2$	6.05

Salt	Sol. in grams per liter
$\text{Cu}(\text{C}_6\text{H}_5.\text{CH}:\text{CH}.\text{COO})_2$	2.7
$\text{Cu}(\text{CH}_3:\text{CH}.\text{COO})_2$	4.62
CuSO_4	0.4
$\text{Cu}(\text{C}_{18}\text{H}_{34}\text{OO})_2$	1.72
CuCl_2	.89
$\text{Co}(\text{SCN})_3$.5
$\text{Co}(\text{C}_6\text{H}_5.\text{CH}:\text{CH}.\text{COO})_2$	8.1
FeCl_3	11.8
MgCl_2	.81
$\text{Pb}(\text{CH}_3\text{COO})_2$	37.5
S (lac)	.44

NOTE 1. The cinnamates of the heavy metals were made by precipitating a solution of sodium cinnamate with a soluble salt of the heavy metal and washing the precipitate free from the anion of the latter salt. They were then dried for two days in an oven at 100°C and later for some weeks in a vacuum dessicator.

NOTE 2. As an indication of the degree of accuracy of the method, it should be mentioned that though in some cases the solubility came out exactly zero, in no case was it even slightly negative, indicating that the apparatus remained constant in weight.

The only reference found concerning the measurement of an electromotive force in dry liquid sulfur dioxide so-

lution was to the work of Bagster and Steele to which reference has already been made. They give:

Pb		PbCl ₂	:	HgCl		Hg	$\frac{.435}{.435}$	Hg Negative
Zn		ZnBr ₂	:	HgCl		Hg	$\frac{.38}{.4}$	Hg Negative
Cd		CdI ₂	:	HgCl		Hg	$\frac{.42}{.445}$	not stated
							$\frac{.42}{.43}$	

They used a quadrant electrometer and saturated salt solutions taking the measurements at -33.5 C. The electromotive forces of the various cells are surprisingly close to each other.

In this work, the regular potentiometer circuit was employed to which, at the suggestion of Dr. Cady, a microfarad mica condenser was added, in parallel with the cell so as to compensate for the low capacity of the cell due to its high internal resistance. The circuit as shown in the diagram was completely insulated by means of sulfur supports. A galvanometer of megohm sensibility _____ was used. The secondary battery was standardized against Weston normal cell No. 5439, of which the E.M.F. variation with temperature is given in the following table:

Weston Normal Cell #5439

T° C	E.M.F. volts	T° C	E.M.F. volts
9	1.01888	20	1.01855
10	1.01885	21	1.01850
11	1.01882	22	1.01845
12	1.01879	23	1.01840
13	1.01876	24	1.01835
14	1.01873	25	1.01825
15	1.01870	26	1.01820
16	1.01867	27	1.01815
17	1.01864	28	1.01810
18	1.01861	29	1.01805
19	1.01858	30	

The E.M.F.s of the following Voltaic combinations were measured:

	Positive	Negative	E.M.F.
I.	Co cinnamate	Zn cinnamate	Zn .425
II.	Cu cinnamate	Co cinnamate	Co .41
	Same cell two days later		.41 ± .01
	" " three "	" "	.41 ± .01
	" " four "	" "	.41 ± .01

At this time some anhydrous FeCl_3 was introduced with the idea of improving the conductivity; the E.M.F. immediately dropped to

.37

Same cell two days later	.535
" " eight "	.445

This cell was kept twelve days and was remarkably constant before the addition of the ferric chloride.

III. Fe FeCl ₃ : Al AlCl ₃ (not constant)	1.01
IVa Fe FeCl ₃ : CrCl ₃ Cr	.303 .309
b Fe FeCl ₃ : CrCl ₃ Cr	.6764
Same cell at three hours	.7170
" " " six "	.7187
" " " 24 "	.5503
" " " 30 "	.5725

The cell was then shaken

at the end of 30 hours, 15 minutes	.3415
" " " " " " , 30 "	.2951

The iron electrode was found to be coated with a black film which, on treatment with acid, gave H₂S showing it to be a sulfide. This accounts for the variable E.M.F. observed.

V. Ag Ag cinnamate : Zn cinnamate Zn	.3312
Via 10 Hg Cd CdI ₂ : KI KHgX (at end of 24 Hrs.)	1.96% .8365
	24:15 .8366
	24:30 .8365
b 10% Cd CdI ₂ : KI KHg	1.96% 60 min. 1.425
	75 " 1.387

The E.M.F. of the cell was falling rapidly. The internal resistance was low as evidenced by a vigorous galvanometer throw.

Vic	10% CdHg CdI ₂ : KI	1.96% KHg at end of 15 min.	1.5057
		30 "	1.4987
		45 "	1.4965
		60 "	1.5232
		75 "	1.5122
		90 "	1.5057
		685 "	1.2988
		795 "	1.2860
		cell shaken	1.20351

NOTE: The cadmium amalgam was made up by heating under melted paraffin a weighed quantity of C. P. cadmium with ten times its weight of C. P. mercury.

In making the potassium amalgam, a ball of potassium was cleaned under toluene and rolled into a cylinder. A portion of it weighed in toluene was placed in the upper end of a pyrex tube, constricted as shown and which contained a weighed quantity of C. P. mercury.

The pressure was then reduced to less than 1 cm. Hg and K melted and allowed to run into the mercury with which it combines vigorously. The oxide coating of the K adheres to the side of the tube and a mirror surfaced amalgam is



obtained.

In these cells, the potassium amalgam soon became coated over with a lemon yellow substance which yields some H_2S with acid and probably accounts for the rather consistent decrease in their E.M.F.s

CONCENTRATION CELLS.

A very great number of experiments have been performed with concentration cells, especially in aqueous solution, and many practical uses have been found for them, of which the following may be mentioned:

Determination of heat of dilution⁶.

Determination of transport numbers.

Determination of liquid to liquid potential.

Determination of solubility⁷.

Determination of chemical affinity⁸.

Determination of transition points⁹.

Determination of molecular state.

Determination of the solution pressure of a metal.

Determination of the valence of an ion¹⁰.

Evidence of the existence of complex ions.

In addition to these, the agreement between the measured

E.M.F.s of concentration cells and those calculated by equating the electrical to the osmotic work or the electrical to the three stage distillation work necessary to produce equilibrium, afford an interesting insight into the physical mechanism of such a cell and a confirmation of the theory of solution pressure.

The oldest method of calculating the E.M.F. of a concentration cell is that due to Helmholtz, antedating 1878. (Phil. Mag. 1879)

When a metal is in contact with its salt (ion), there is a tendency for it to dissolve as ion positively charged (solution pressure) leaving the metal negative; there is also a tendency for its ion to precipitate out as metal (osmotic pressure of the ion) giving a positive charge to the metal. If the solution pressure, P , is greater than the osmotic pressure, p , the metal is said to be negative to its ion, that is, it acquires a negative charge when in contact with solutions of its salts and this charge, for a given concentration, always builds up to a potential just sufficient to overcome by electrostatic attraction the tendency of the positive ion to leave the metal. The reverse holds for the condition p greater than P and such a metal is said to be positive to its ion. Of two electrodes of the same metal in solutions containing the same ion but in different amounts, that in the more concentrated will be

the more positive (or the less negative where $P > p$) and when the solutions and electrodes are connected current will flow in the external circuit from that in the concentrated solution to that in the dilute; precipitating ion as metal of the former and dissolving metal as ion from the latter, tending toward the equilibrium condition of equal ion concentration in the two parts of the cell. This phenomenon is reversible - starting with the solutions of equal concentrations send the same quantity of electricity through it and the original unequal concentrations are obtained.

We know from thermodynamics that if we pass from one equilibrium stage to another by any reversible path whatever the work done is the same - so that the work done when the two solutions are brought to equal concentrations in any reversible manner can be equated to the electrical work.

Helmholtz chose the three stage distillation of solvent from weak to strong. In case of solutions of concentrations C and $C + dc$ (where $C = \frac{1}{\mu+1}$ and μ is the number of moles of solvent per mole of solute) the transfer of one mole of solute from strong to weak gives rise to $NEdE$ units of electrical work (where N is the valence of the ion, $F =$ Faraday, $E =$ volts and $V =$ Volume of 1 gram mole of solvent in vapor state.) This could be exactly compensated for by the distillation of μ moles of solvent from strong to weak; μ moles from a vapor pressure $p - dp$ to the greater pressure p which

would require

$$- \mu V dp \text{ units of work.}$$

Then $NF dE = - \mu V dp$ or since $PV = RT$

$$NF dE = - \mu RT dp / P$$

When the solutions differ in concentration by finite amounts

$C = C' = 1 / \mu$; $C + dC = C'' = 1 / \mu_2 + 1$, and the equation must be integrated between the limits

$$\mu_1 \text{ and } \mu_2$$

For dilute solutions, a relation between μ and p is given by the Raolt law.

$$\frac{P_0 - P}{P_0} = \frac{\mu}{\mu + 1} \quad P = P_0 \frac{\mu}{\mu + 1}$$

$$dp = P_0 d\left(\frac{\mu}{\mu + 1}\right) = \frac{P_0(\mu + 1)d\mu - \mu d\mu}{(\mu + 1)^2}$$

or

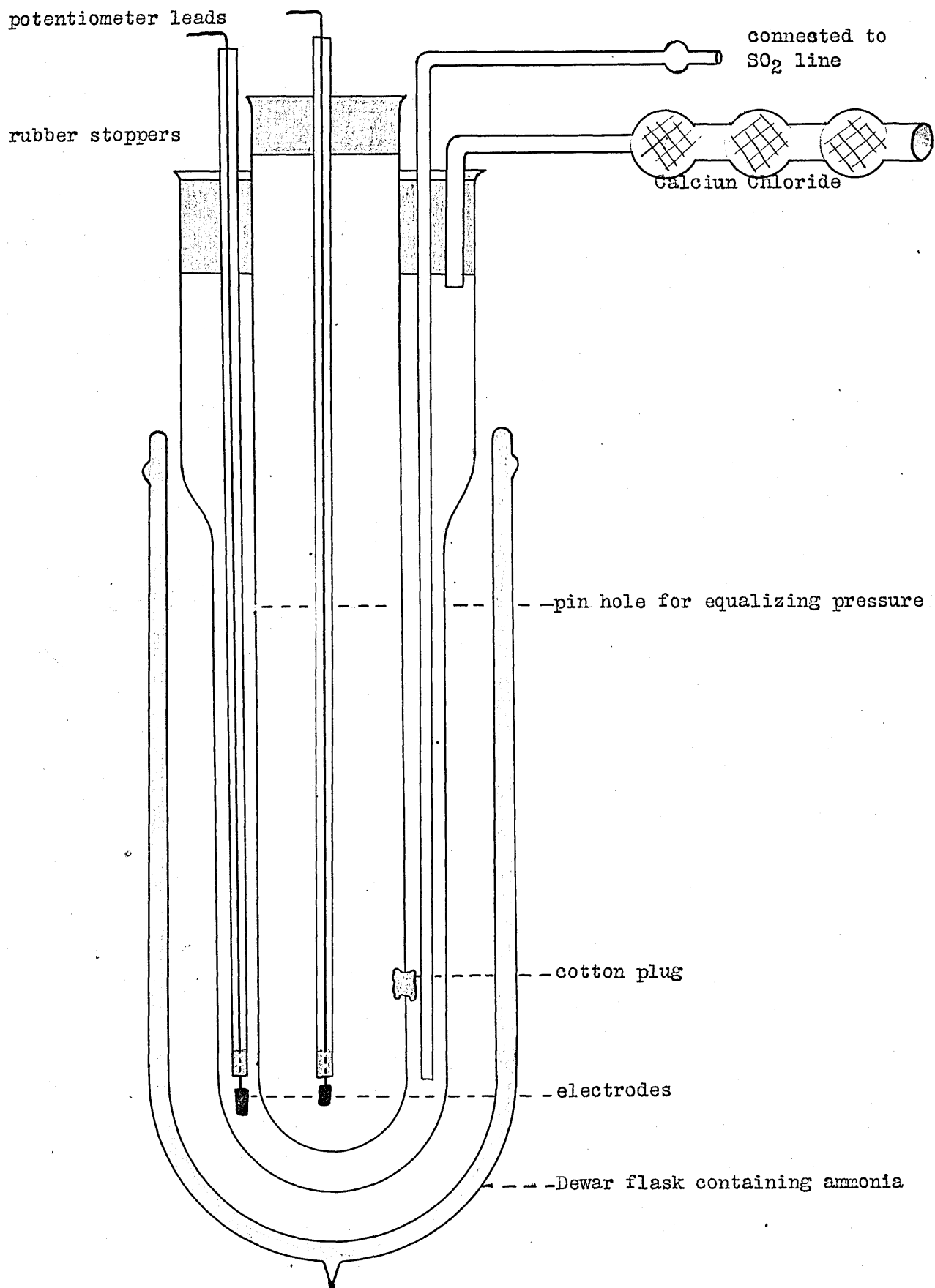
$$dp = P_0 \frac{d\mu}{(\mu + 1)^2}$$

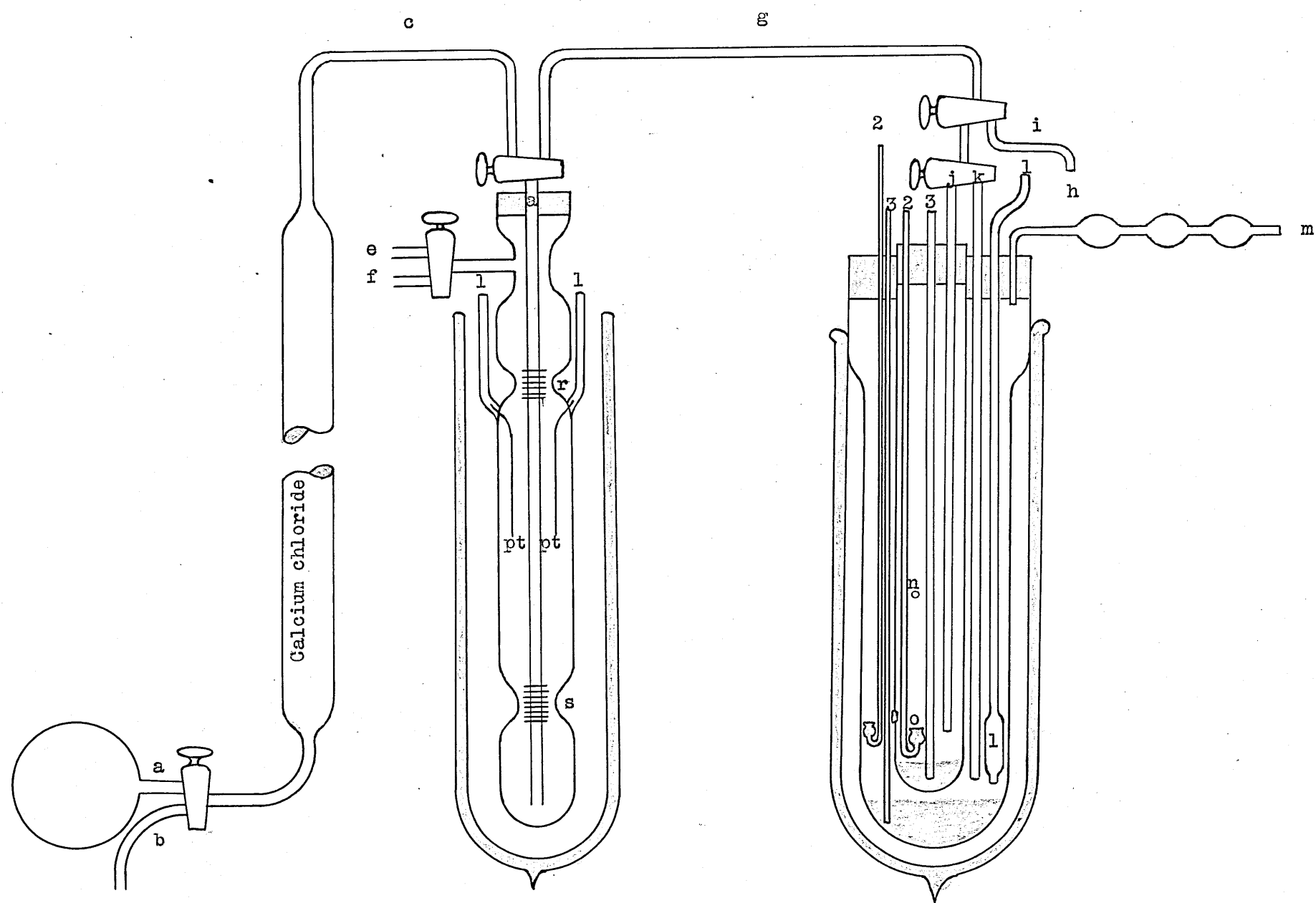
$$NF \int dE = - \int_{\mu_1}^{\mu_2} RT \frac{dp}{P} = - \int_{\mu_1}^{\mu_2} RT P_0 \frac{d\mu}{(\mu + 1)^2} \frac{1}{P_0 \frac{\mu}{\mu + 1}} =$$

$$- \int_{\mu_1}^{\mu_2} RT \frac{d\mu}{\mu + 1} = - RT \log \frac{\mu_2 + 1}{\mu_1 + 1} = RT \log \frac{C_2}{C_1}$$

$$NFE = RT \log \frac{C_2}{C_1}$$

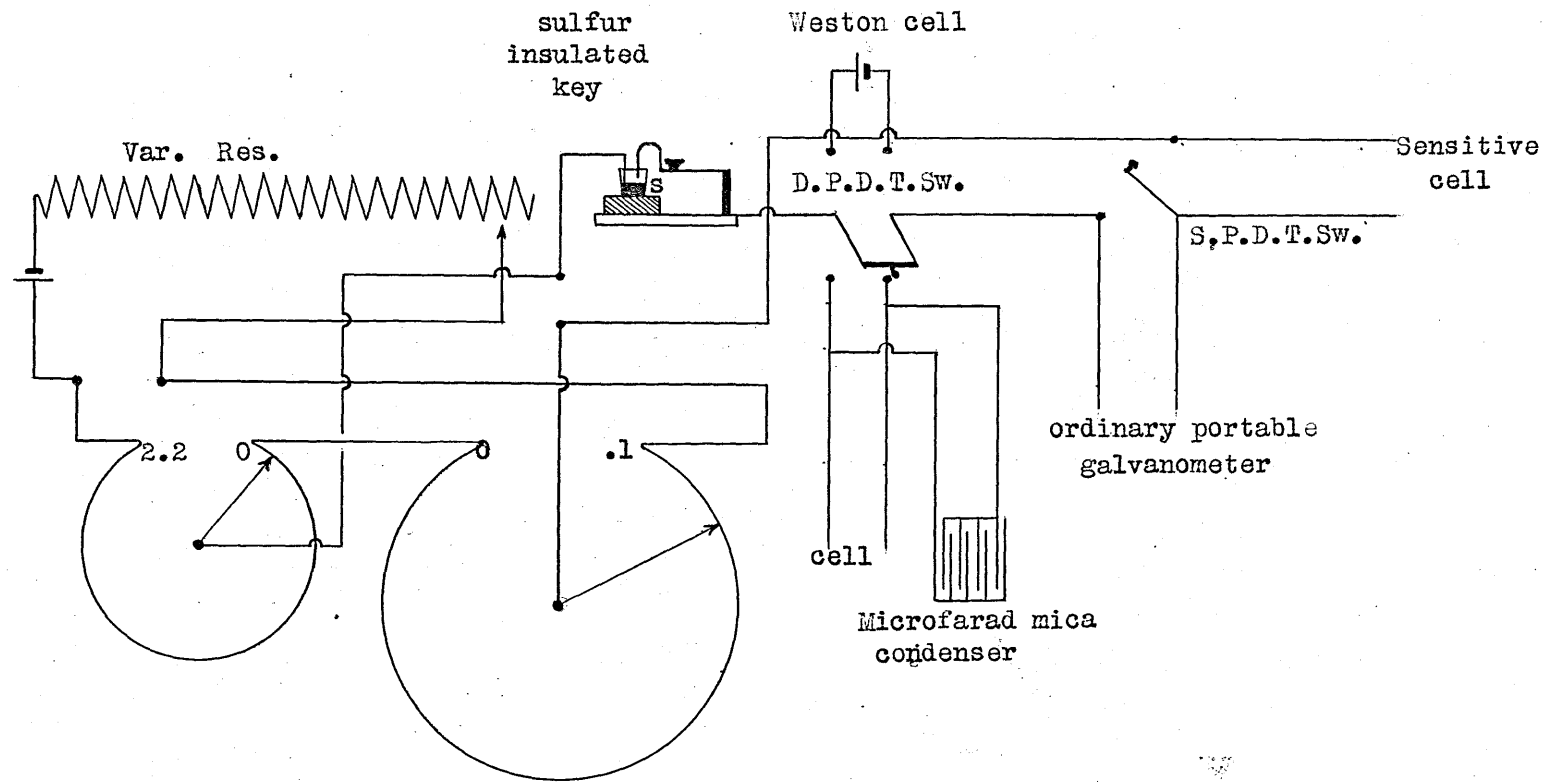
$$E = \frac{RT}{NF} \log \frac{C_2}{C_1}$$





c

30



APPARATUS AND MANIPULATION.

The apparatus for concentration cells included a potentiometer set, a Kohlrausch bridge set, a conductivity burette, the cell proper and phosphorus pentoxide drying trains for air and sulfur dioxide.

Before making up a cell, the conductivity burette was boiled in sodium hydroxide - rinsed - washed with sulfuric acid - rinsed and steamed out for a period of hours. It was then dried at 105 C by drawing a current of air through it (from a train consisting first of a three foot calcium chloride tube, and then a heating coil) for 48 hours. It was left in contact with a phosphorus pentoxide tube until used. The anhydrous salt was then added from a weighing capsule and sulfur dioxide distilled in from the cylinder at a: through the long phosphorus pentoxide drying tube and then through d into the burette where it was condensed by the liquid ammonia in the surrounding Dewar flask. When the burette was filled well above the scale r, the sulfur dioxide was shut off and air from a phosphorus pentoxide drying tube forced through b to stir the mixture until solution occurred. The volume was then adjusted by evaporation and the resistance measured; connection being made to the platinumized platinum electrodes through the mercury wells l, l to the Kohlrausch bridge leads.

Air pressure was applied at e and enough of the solution forced over through d, g, i, k, into the outer cell to the lower level of the cotton plug o, the remainder being

run to waste through h until the proper level at s was reached. The burette was again filled to the proper level on scale R; stirred; its resistance measured; and the dilute solution partly run to waste to rinse tube g and then into the inner cell through i. The amalgam electrodes were introduced through the goose necked thistle tubes 2,2 and contact with the potentiometer obtained by means of platinum tipped copper wires. For cells without transference mercury, covered with the insoluble mercury salt of the same anion as that in the solution, was placed in the bottom of both halves of the cell and contact between them obtained by a platinum tipped copper wire through tubes 3,3. After the measurement of the E.M.F without transference, this wire could be removed and direct contact between the solutions obtained through the cotton plug q by raising the surface of the liquid in the outer tube. This was done by forcing air into the chamber l.

The ratio of the volumes of the conductivity cell at various points on the upper and lower scales was determined by weighing with water on an analytical balance.

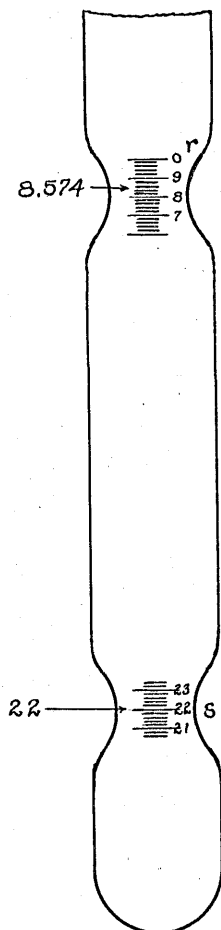
RATIO OF VOLUMES OF CONDUCTIVITY CELL.

Temperature 25C, Zero of balance scale
.0004.

Weight of cell empty 109.6331

<u>Pos. of Water level</u>	<u>Weight</u>	<u>Volume</u>
0	146.7683	37.1352
9	146.1100	36.4759
8	145.6730	36.0399
22.4	118.9420	9.3084
22.0	118.703	9.0690

It was found that the ratio, when the cell was filled to 8.574 and again to 22, was exactly 4 to 1, and as a very accurate adjustment can be made using the method of evaporation, this was used.



For the sake of reference, the conductivity constant of the cell was determined using tenth normal potassium chloride at 25 C. The average resistance was 4.111. From "Gemelin Kraut" the specific conductivity of potassium chloride at this temperature and concentration is .01288. The cell constant is then $4.11 \times .01288$ or .0529. The following cells were tried:

Ion 12.8 to 1 Initial salt .5192
 Salt 25 to 1(approx.)

The E.M.F.'s were measured as soon as possible after setting up the cell:

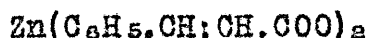
With transference .115
 Without " .171

but were wo variable as to be of no value. It fell off to .02 volt in 10 minutes and the surface was coated as before.

$AlCl_3$ was next tried.

Weight of salt .0336

The salt dissolved slowly until the resistance across the cell was 1000 ohms but on standing for two hours the solution developed a gelatinous cloudiness and the resistance went up to 4000 ohms. The experiment was repeated and extra precautions taken to exclude moisture; the air for stirring was sent through an extra 5 feet of phosphorus pentoxide. The cloudy precipitate occurred as before, with the corresponding decrease in the conductivity. It was concluded that aluminum chloride reacts slowly with sulfur dioxide, making the solution unstable, so its use was abandoned.



With this salt, the bridge seemed to be balanced at 40,000 ohms and no positive difference could be detected when a 16 to 1 dilution was made. It seems to be very lit-

tle dissociated and therefore unsuitable. Some further work on cobalt sulphocyanate is in progress.

From the work to date, the following general conclusions can be drawn:

1. The position of the metals in the electrochemical series for sulfur dioxide is the same as that for ordinary aqueous solutions.
2. The problem of measuring concentration cell E.M.F.s in this solvent has been reduced to one of finding salts which meet the following conditions:
 - (1) Must be anhydrous.
 - (2) Must be soluble in SO_2 .
 - (3) The solution must be stable.
 - (4) The solution must ionize.
 - (5) The cation must be metallic.
 - (6) The corresponding metal must not tarnish in SO_2 .

The probability of meeting six conditions at the same time is not high; it is not likely that many such salts exist.

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