

THE ELECTRICAL CONDUCTIVITY OF LIQUID SUL-  
PHUR DIOXIDE SOLUTIONS AT  $-33.5^{\circ}$ ,  $-20^{\circ}$ ,  
 $-10^{\circ}$ ,  $0^{\circ}$ , AND  $+10^{\circ}$ <sup>1</sup>

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*Introduction.*—While engaged in studying the properties of liquid methylamine as an electrolytic solvent Franklin and Gibbs<sup>2</sup> noted the fact that the molecular conductivities of methylamine solutions in their dependence upon dilution exhibit a behavior strikingly different from that generally observed for solutions in other solvents. Instead of the usual continuous increase of the molecular conductivity with the dilution, they found that beginning with very concentrated solutions, the molecular conductivity rises with increasing dilution rapidly to a maximum, thence declines to a minimum, to be followed by a continuous rise, presumably to the final familiar maximum.

Following up the work of Franklin and Gibbs the writer returned to the study of the electrical conductivity of liquid ammonia solutions in order to determine whether any indications of a similar behavior on the part of concentrated ammonia solutions might be discovered. It was found<sup>3</sup> that although the phenomena observed by Franklin and Gibbs do not recur in the case of all liquid ammonia solutions, still the characteristic trend of the molecular conductivity curve was found to mark the behavior of certain salts in solution in this solvent.

With the object in view of determining whether the effect discovered by Gibbs is a general property of concentrated solutions, the plan was inaugurated of measuring the electrical conductivity of concentrated solutions in a number of electrolytic solvents. Sloan<sup>4</sup> has shown that concentrated

<sup>1</sup> Read before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the Detroit meeting, June, 1909.

<sup>2</sup> Jour. Am. Chem. Soc., 29, 1389 (1907).

<sup>3</sup> Zeit. phys. Chem., 69, 272 (1909). (Arrhenius Jubelband)

<sup>4</sup> Jour. Am. Chem. Soc., 32, 946 (1910).

aqueous solutions of potassium iodide give indications of the Gibbs effect, and F. B. Beyer, working in this laboratory, has noted a similar behavior on the part of calcium ferrocyanide solutions. Other salts, however, fail to give any clear indications of the effect.

Certain results obtained by Walden and Centnerzwer<sup>1</sup> in their investigations on liquid sulfur dioxide as a solvent made it appear probable that a study of the electrical conductivity of concentrated solutions in this solvent would be productive of more positive results. The work described below will be found to justify this presumption. Furthermore, since it seemed possible that some relationships of value might be discovered by following the molecular conductivity of these solutions not only through varying concentrations at a given temperature but also at different temperatures, the plan of the work was extended to include measurements at as widely different temperatures as the apparatus in the form constructed would permit.

*The Apparatus and Mode of Manipulation.*—The apparatus used was in all essential respects the same as that described in a former paper,<sup>2</sup> excepting that the accessory cell A, shown in the figure accompanying the paper cited, was dispensed with and other minor changes were made which the requirement of conveniently and rapidly changing and adjusting the temperature of the thermostat rendered necessary. The procedure finally adopted for carrying on a series of measurements is as follows. By means of an arrangement of ingress and egress tubes, which suggests itself and therefore need not be described, a quantity of aqua ammonia is introduced into the Dewar tube thermostat P,<sup>3</sup> after which liquid ammonia is run into the thermostat bath until the temperature stands at  $-10^{\circ}$ , the boiling point of the

<sup>1</sup> Bull. Acad. Imp. des Sciences de St. Pétersbourg, [5] 15, 17; Zeit. phys. Chem., 39, 513 (1902); and Zeit. anorg. Chem., 30, 145 (1902); cf. Franklin; Loc. cit.

<sup>2</sup> Zeit. phys. Chem., 69, 272 (1909).

<sup>3</sup> Loc. cit., p. 277.

solvent. The temperature regulating device is then set to maintain this temperature; the solution is made up and its conductivity measured; all after the manner described in the former paper. Aqua ammonia is then run into the thermostat until the temperature rises to  $0^{\circ}$ , when again the temperature regulating device is set to maintain this new temperature. As a result of the expansion of the solution in the conductivity cell its surface is now above the pointer J of the figure.<sup>1</sup> It therefore becomes necessary to adjust the surface again to the pointer which is accomplished by evaporating off a portion of the solvent by means of a current of hydrogen gas forced through the liquid in the manner previously described. After measuring the resistance of the solution the temperature is raised to  $+10^{\circ}$ , and the operations of adjusting the surface of the solution and reading the resistance is repeated. Then by means of air pressure on the surface of the bath liquid, the Dewar thermostat is emptied of its contents of aqua ammonia and liquid ammonia is introduced in its stead. The temperature regulator is then adjusted to maintain the temperature at  $-33.5^{\circ}$ ; sufficient sulfur dioxide is distilled into the conductivity cell to bring the surface of the solution to the pointer, when, after thorough stirring to insure homogeneity of the solution, a reading of the resistance is made. Aqua ammonia is again run in to the thermostat to bring the temperature, first to  $-20^{\circ}$ , and then to  $-10^{\circ}$ , thus completing a cycle of measurements at the chosen temperatures. A new dilution is then effected by running solvent into the cell and adjusting the surface of the solution to one of the upper glass pointers, when the cycle of measurements just described is repeated. After measurements have been made with the solution adjusted to the uppermost pointer a known portion of the solution is removed from the cell after the manner described in the paper cited, and the operations outlined above are repeated until the desired number of measurements has been made.

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<sup>1</sup> Loc. cit.

*The Solvent.*—The solvent used was obtained by passing the gas from a cylinder of commercial liquid sulfur dioxide through a tube containing phosphorus pentoxide and condensing it in the accessory cell J, shown in the figures given in two previous papers.<sup>1</sup> Although no special precautions were taken to arrive at a solvent of the highest possible purity, it was nevertheless easy to obtain specimens showing a specific conductivity as low as  $0.04 \times 10^{-6}$  Kohlrausch units. Walden and Centnerzwer<sup>2</sup> give  $0.09 \times 10^{-6}$  as the specific conductivity of pure liquid sulfur dioxide.

*The Conductivity Cells.*—The cell No. 3, described in a previous paper<sup>3</sup> was used in making the measurements here given with the exception of those for ethylammonium bromide and dimethylammonium chloride. The measurements of the conductivity of these salts were made in a cell especially constructed for this work but which in use was found to be unsatisfactory. The results obtained for these two salts may be in error to the extent of several percent but are nevertheless recorded in order to show that the peculiar trend of the conductivity curves seems to be a general property of solutions in sulfur dioxide.

The resistance capacities of the cell No. 3 were checked at the conclusion of the measurements recorded in this paper and were found to be 3.107 and 0.0888 Kohlrausch units respectively for the high and low resistance pairs of electrodes at 20°. The volumes at -33.5° for the pointers J, 1, 2, and 3, respectively were found to be 16.75, 21.53, 25.97 and 33.13 cc.

*Experimental Results.*—Following are given in detail measurements of the electrical conductivities of a number of salts in solution in liquid sulfur dioxide through concentrations ranging from approximate saturation up to the highest dilutions which could be conveniently measured with any

<sup>1</sup> Jour. Am. Chem. Soc., 26, 503 (1904); and Am. Chem. Jour., 23, 279 (1900).

<sup>2</sup> Loc. cit.

<sup>3</sup> Zeit. phys. Chem., 69, 282 (1909).

degree of accuracy, and through a range of temperatures included between  $+10^{\circ}$  and  $-33.5^{\circ}$ . As was to be expected especial difficulties were encountered in working both at the highest and the lowest concentrations which render the results less accurate at these extremes. With the cell as constructed with three electrodes for measuring both good and poor conducting solutions it was found impossible to get good telephone minima when working with the most concentrated solutions for the reason that the resistance to be measured was too low. On the other hand, because of the elaborate precautions necessary for the measurement of the conductivities of very dilute solutions with any degree of accuracy, attempts were not made to obtain the final maximum values of the molecular conductivities of the salts studied. The observations on the solutions of potassium iodide and potassium bromide were carried to such dilutions only as were necessary to show the final order of the molecular conductivities for the chosen temperatures.

For some reason, which the writer is at a loss to explain, the results here given are not in close agreement with those of Dutoit and Gyr.<sup>1</sup> The discrepancy, which was not discovered until after the work here described was completed, led the writer to delay publication in the hope of repeating his measurements in order, if possible, to discover the cause of the discrepancy. However, opportunity of checking up this work has not presented itself, and since whatever value may be possessed by the work here given does not lie so much in the absolute accuracy of the data presented as in the general form of the curves and especially in the temperature effects observed, further delay in their publication seems unjustified.

In the tables below are given under the superscriptures  $\varphi/1000$ , the dilution in liters per mol, and under  $-33.5^{\circ}$ ,  $-20^{\circ}$ ,  $-10^{\circ}$ ,  $0^{\circ}$  and  $+10^{\circ}$ , the molecular conductivities in reciprocal ohms at the respective dilutions and temperatures. Following the direct experimental data given in these tables

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<sup>1</sup> Jour. Chim. phys., 7, 189 (1909).

is for each salt a summary of the conductivity values interpolated for the dilutions indicated under  $\varphi/1000$ .

*Potassium Iodide*.—A specimen of J. T. Baker's "special" salt dried by gentle ignition was used. The two most concentrated solutions studied, containing respectively 55.5 and 41.3 grams of salt to 100 cc of the solution, deposited crystals of salt abundantly when cooled to  $-33^{\circ}$ .

$\varphi/1000$	$\Delta$				
	$-33.5^{\circ}$	$-20$	$-10$	$-0^{\circ}$	$+10^{\circ}$
I					
0.4470	24.80	—	35.87	—	—
0.5860	29.77	—	—	—	—
0.707	33.39	—	—	—	—
II					
0.7892	34.70	—	—	—	—
1.008	37.47	—	—	—	—
1.601	39.74	—	—	—	—
III					
0.2980	—	—	21.93	26.85	—
0.4702	—	32.57	37.81	42.60	—
0.6043	—	37.64	—	—	—
1.0882	—	44.16	—	—	—
IV					
3.597	40.55	43.77	45.19	—	—
7.105	41.45	43.30	44.35	43.99	43.13
V					
593.7	96.40	101.5	104.0	102.6	99.67
911.6	106.2	112.8	115.0	115.3	112.4
VI					
604.7	96.70	102.8	103.9	—	—
VII					
1.122	38.37	44.60	47.07	50.99	54.00
1.725	39.89	43.82	47.19	49.11	50.11
VIII					
0.3543	—	23.88	29.39	34.82	40.44
0.5456	29.01	36.72	41.71	46.78	51.82

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$\varphi/1000$	$\Lambda$				
	$-33.5^\circ$	$-20$	$-10^\circ$	$0^\circ$	$+10^\circ$
IX					
117.5	64.60	66.05	65.38	63.64	60.58
X					
59.72	54.40	55.39	54.82	53.32	51.02
91.82	60.34	61.46	61.04	59.01	56.62
XI					
55.66	53.99	54.74	53.98	52.10	49.71
110.5	63.43	—	64.25	—	—
217.9	—	—	77.63	—	—
431.1	—	—	94.70	—	—
XII					
72.07	—	—	57.25	—	—
110.8	—	—	64.83	—	—
218.9	—	—	78.18	—	—
433.8	—	—	95.03	—	—
858.2	—	—	114.3	—	—
1698.0	—	—	135.7	—	—
2184.0	126.0	134.7	144.1	146.3	144.7
XIII					
0.5848	—	—	42.28	—	—
0.7212	—	—	45.01	—	—
XIV					
47.89	—	—	52.05	—	—
73.65	—	—	57.29	—	—
145.4	—	—	68.95	—	—
287.3	—	—	83.78	—	—
567.5	—	—	101.7	—	—
1120.0	—	—	122.2	—	—
2214.0	—	—	144.4	—	—
4373.0	140.9	155.0	165.1	171.5	173.8
8638.0	—	—	190.7	—	—
XV					
5.406	—	—	43.50	—	—
6.945	40.42	42.24	42.66	42.50	41.77
10.68	41.37	42.64	42.73	42.14	40.88
21.09	44.30	45.35	44.84	43.69	42.06
41.66	—	—	50.27	—	—

## XVI

$\varphi/1000$	$-55^\circ$	$-50^\circ$	$-41^\circ$	$-33.5^\circ$	$-10^\circ$	$0^\circ$	$+10^\circ$	$+33^\circ$
168.5	61.40	63.78	68.55	70.63	71.93	70.08	67.07	54.33

$\varphi/1000$	$\lambda$				
	$-33.5^\circ$	$-20^\circ$	$-10^\circ$	$0^\circ$	$+10^\circ$

## XVII

446.9	—	—	95.94	—	—
686.8	—	—	108.0	—	—
1357.0	—	—	129.0	—	—
2680.0	—	—	147.4	—	—
5292.0	—	—	171.2	—	—

## XVIII

479.4	—	—	98.20	—	—
947.0	—	—	117.9	—	—
1870.0	—	—	138.9	—	—
3694.0	—	—	161.2	—	—

## XIX

434.7	—	—	04.48	—	—
858.6	—	—	113.4	—	—
1696.0	—	—	129.9	—	—
3355.0	—	—	158.2	—	—
6616.0	—	—	175.1	—	—
13070.0	—	—	192.2	—	—
16790.0	162.3	186.4	200.4	212.8	227.5

## XX

1165.0	112.2	119.3	124.2	124.5	123.2
2300.0	128.2	137.0	145.2	147.3	148.1
4542.0	142.1	153.7	164.9	170.6	173.3
8972.0	155.8	171.0	185.5	194.3	201.5
17720.0	—	—	204.7	—	—



Summary of results for potassium iodide

$\varphi/1000$	$\lambda$				
	$-33.5^{\circ}$	$-20^{\circ}$	$-10^{\circ}$	$0^{\circ}$	$+10^{\circ}$
0.30	—	—	22.3	28.0	—
0.375	—	26.2	31.7	37.1	43.0
0.50	27.5	35.7	39.7	44.7	50.5
0.75	34.5	42.2	45.2	50.2	54.4
1.00	37.7	44.1	46.9	51.2	54.5
1.5	39.6	44.5	47.2	50.2	52.3
2.0	40.1	44.3	46.8	49.0	51.1
3.0	40.4	43.8	45.7	47.0	48.2
4.0	40.5	43.4	44.8	45.5	46.0
6.0	40.8	42.5	43.1	43.0	42.8
8.0	41.0	42.0	42.5	42.0	41.4
12.0	41.6	42.8	42.8	42.0	40.9
16.0	42.7	43.8	43.5	42.5	41.2
24.0	45.1	46.1	45.7	44.4	42.7
32.0	47.2	48.3	47.8	46.4	44.5
48.0	51.4	52.5	52.0	50.2	48.0
64.0	55.1	56.1	55.7	53.8	51.4
96.0	60.9	62.3	61.3	59.5	57.1
128.0	65.9	66.9	66.5	64.5	62.0
192.0	73.3	74.7	74.5	72.6	69.7
256.0	78.8	81.8	81.7	79.4	76.5
384.0	87.2	90.8	91.2	89.8	86.8
512.0	93.4	98.2	99.2	98.0	95.3
768.0	102.8	108.4	111.2	111.2	108.3
1000.0	108.6	115.2	118.8	119.4	117.7
1500.0	117.7	125.8	131.5	132.7	132.3
2000.0	124.2	133.0	140.5	142.3	142.3
3000.0	133.0	143.7	153.7	156.5	157.7
4000.0	139.0	151.0	162.5	166.3	168.7
6000.0	147.5	161.5	174.2	179.5	185.0
8000.0	153.0	168.5	181.8	189.0	196.0
12000.0	159.5	178.0	192.0	202.0	212.5
16000.0	163.0	184.0	199.0	211.0	223.0

*Potassium Bromide.*—The most concentrated solution measured contained 38.6 grams of potassium bromide to 100 cc of solution. The salt shows a negative solubility coefficient. From a 2.52 normal solution the salt crystallized out abundantly when the temperature was raised to 0°. Even a 0.42 normal solution deposited crystals when the temperature was raised to +10°.

$\phi/1000$	$\Delta$				
	-33.5°	-20°	-10°	0°	+10°

## I

51.13	—	—	37.57	—	—
101.0	—	—	45.54	—	—

## II

0.3961	21.25	28.42	32.78	—	—
0.6090	29.18	34.82	39.08	42.01	—
1.203	32.19	36.23	39.02	39.88	(38.95)
2.376	32.03	33.88	34.92	34.98	(34.23)
4.586	31.40	32.22	32.28	31.33	29.92
9.268	31.38	31.08	30.38	29.13	27.32
18.30	33.45	32.65	31.50	29.95	27.55
35.33	37.34	36.32	34.20	32.13	29.30

## III

41.35	38.47	37.55	35.51	33.64	30.73
81.68	46.11	44.84	42.40	40.25	37.08
161.3	55.89	55.00	52.85	49.87	45.83
318.7	68.58	67.27	65.88	63.06	57.95
629.3	84.06	84.08	82.74	79.04	73.23
1243.0	100.6	103.9	102.3	99.45	94.40
2456.0	118.7	122.8	125.3	123.8	118.0
4850.0	137.2	144.0	149.3	150.5	147.8

Summary of results for potassium bromide

$\varphi/1000$	$\Lambda$				
	$-33.5^\circ$	$-20^\circ$	$-10^\circ$	$0^\circ$	$+10^\circ$
0.375	20.0	27.0	31.0	—	—
0.5	26.4	32.8	37.4	—	—
0.75	31.0	36.0	40.4	42.0	—
1.0	32.0	36.6	39.8	40.8	—
1.5	32.4	35.4	37.0	38.0	37.3
2.0	32.3	34.3	35.4	36.1	35.4
3.0	31.8	33.0	33.0	33.6	32.4
4.0	31.5	32.3	31.7	32.0	30.5
6.0	31.2	31.6	30.6	30.3	28.6
8.0	31.3	31.3	30.3	29.6	27.6
12.0	32.0	31.6	30.7	29.3	27.0
16.0	32.8	32.3	31.0	29.7	27.2
24.0	34.7	34.0	32.3	30.7	28.1
32.0	36.6	35.7	33.7	31.7	29.0
48.0	40.0	39.0	37.1	34.7	31.8
64.0	43.2	41.8	40.0	37.6	34.6
96.0	48.3	47.0	44.7	42.3	39.0
128.0	52.4	51.3	48.8	46.0	42.6
192.0	59.0	58.0	55.8	52.9	48.5
256.0	64.5	63.5	61.4	58.5	53.8
384.0	72.4	72.0	69.9	66.8	61.7
512.0	79.0	79.3	77.2	73.7	68.3
768.0	88.4	90.4	88.4	84.4	78.5
1000.0	94.7	97.7	96.0	92.5	86.7
1500.0	105.4	109.2	108.5	106.0	100.4
2000.0	113.3	117.4	118.0	116.2	110.3
3000.0	124.5	129.3	132.3	131.5	127.0
4000.0	132.0	138.0	142.3	142.5	139.3
4800.0	137.0	144.0	148.3	149.5	147.8

*Tetramethylammonium Iodide.*—The salt dissolves abundantly forming a yellow solution. The conspicuously high values for the molecular conductivity in the more concentrated solutions are noteworthy.

$\varphi/1000$	$\lambda$				
	$-33.5^\circ$	$-20^\circ$	$-10^\circ$	$0^\circ$	$+10^\circ$

## I

8.35	74.50	80.90	86.94	90.12	93.06
16.49	77.70	84.20	89.58	92.30	94.98
32.58	83.24	88.04	94.78	97.12	99.50

## II

34.18	—	—	94.78	—	—
67.52	89.68	96.38	103.2	105.9	108.2
133.3	100.4	107.5	115.7	119.5	122.7
263.3	107.4	—	127.1	132.0	137.2

## III

0.3707	23.80	30.55	35.50	40.94	45.28
0.7322	54.54	61.29	68.00	72.80	80.64
1.446	67.83	76.22	84.42	89.60	95.58
2.857	73.82	81.94	88.60	93.52	98.12
5.641	75.83	83.36	89.92	92.86	96.64
11.15	—	—	90.32	—	—
22.01	—	—	93.46	—	—

## Summary of results for tetramethylammonium iodide

$\varphi/1000$	$\lambda$				
	$-33.5^\circ$	$-20^\circ$	$-10^\circ$	$0^\circ$	$+10^\circ$
0.375	25.0	31.5	37.8	41.6	46.5
0.5	40.3	45.7	52.5	56.7	63.3
0.75	55.3	62.3	69.4	74.0	81.7
1.0	61.3	69.4	77.0	82.2	89.0
1.5	68.3	76.6	84.8	90.0	95.8
2.0	71.2	79.7	87.5	92.7	98.0
3.0	74.0	82.0	89.3	93.5	98.3
4.0	75.0	82.8	89.5	93.5	97.5
6.0	75.5	83.0	89.5	92.3	95.7
8.0	76.0	83.0	88.5	91.3	94.3
12.0	76.7	83.4	88.5	91.3	94.3
16.0	77.6	84.0	89.3	92.0	94.7
24.0	80.0	86.0	91.7	94.6	97.3
32.0	82.0	87.5	94.2	96.7	99.5
48.0	85.5	92.0	98.5	101.6	104.0

64.0	88.6	95.5	102.3	105.0	107.5
96.0	94.4	101.7	108.7	111.8	115.4
128.0	98.5	106.6	113.5	118.0	121.5
192.0	105.0	114.0	121.3	125.4	129.5
256.0	109.5	119.3	126.7	132.0	136.5
384.0	115.7	126.6	135.0	141.0	146.5
512.0	120.0	132.0	142.2	148.5	154.5
768.0	125.5	139.3	151.5	158.7	166.8
1026.0	128.6	144.0	158.0	166.2	176.0

*Ammonium Sulfoeyanate.*—The salt is extremely soluble; forming a yellow solution which, when concentrated, is very viscous. A solution containing 45.6 grams of salt to 100 cc of the solution is somewhat supersaturated at  $-10^{\circ}$ . This solution, when cooled to  $-33^{\circ}$ , changes to a solid mass of crystals.

$\varphi/1000$	$\Delta$				
	$-33.5^{\circ}$	$-20^{\circ}$	$-10^{\circ}$	$0^{\circ}$	$+10^{\circ}$

I

0.1664	—	—	7.30	9.37	11.51
0.2578	—	—	12.53	—	—
0.3287	9.70	11.93	13.81	15.37	16.69
0.6493	10.55	11.83	13.16	13.72	14.37
1.282	9.42	10.17	10.82	11.13	11.33
2.533	7.99	8.52	8.63	8.77	8.88
5.002	7.38	7.42	7.75	7.70	7.52

II.

21.69	8.61	8.44	8.22	7.90	7.42
42.85	10.36	10.07	9.72	9.34	7.83
84.62	13.12	12.70	12.26	11.61	10.80
167.1	17.01	16.44	15.92	15.10	14.01
330.2	22.15	21.50	20.65	19.60	18.17
652.1	29.72	29.08	28.07	26.95	25.22
1288.0	39.55	38.77	37.55	35.78	33.84
2546.0	52.32	51.70	50.08	48.01	45.94
5024.0	67.48	67.22	66.69	63.81	60.81

*Ethylammonium Bromide. Dimethylammonium Chloride.*  
—As explained above the results for these two salts may be

in error to the extent of several percent. For this reason the original data are omitted and a summary only is given. When solvent was run into the most concentrated solution of dimethylammonium chloride it was observed to fall through the solution thus showing the solvent to be more dense than the solution, a rather exceptional relationship.

$\varphi/1000$	$A$ for $C_2H_5NH_3Br$	$A$ for $(CH_3)_2NH_3Cl$	$\varphi/1000$	$A$ for $C_2H_5NH_3Br$	$A$ for $(CH_3)_2NH_3Cl$
0.20	12.0	—	16.0	25.5	12.2
0.25	18.5	(14.3)	24.0	27.0	12.6
0.375	27.0	19.5	32.0	28.7	13.5
0.50	31.4	20.7	48.0	31.7	15.0
0.75	33.5	20.3	64.0	34.6	16.5
1.0	33.2	19.5	96.0	39.5	19.4
1.5	30.8	17.2	128.0	43.3	21.6
2.0	29.3	15.8	192.0	49.7	25.0
3.0	26.8	13.8	256.0	55.3	28.0
4.0	25.7	13.0	384.0	62.2	33.5
6.0	24.5	12.1	512.0	68.3	—
8.0	24.2	12.0	768.0	80.0	—
12.0	24.7	12.0	1000.0	88.0	—

*Graphical Representation of the Results.*—From an inspection of the experimental results of this investigation as summarized in the Figs. 1 and 2 in which the molecular conductivities are plotted as ordinates and the logarithms of the dilutions as abscissas, it will be obvious that the molecular conductivities of salts dissolved in liquid sulfur dioxide exhibit the same behavior as has already been recorded for solutions in methylamine and ammonia.<sup>1</sup> The molecular conductivity first rises to a maximum, then falls to a minimum, then again rising continuously to a final maximum at high

<sup>1</sup> Jour. Am. Chem. Soc., 29, 1389 (1907); Zeit. phys. Chem., 69, 272 (1909).

dilution. The effect of temperature changes on the trend of the molecular conductivity curves is also obvious.

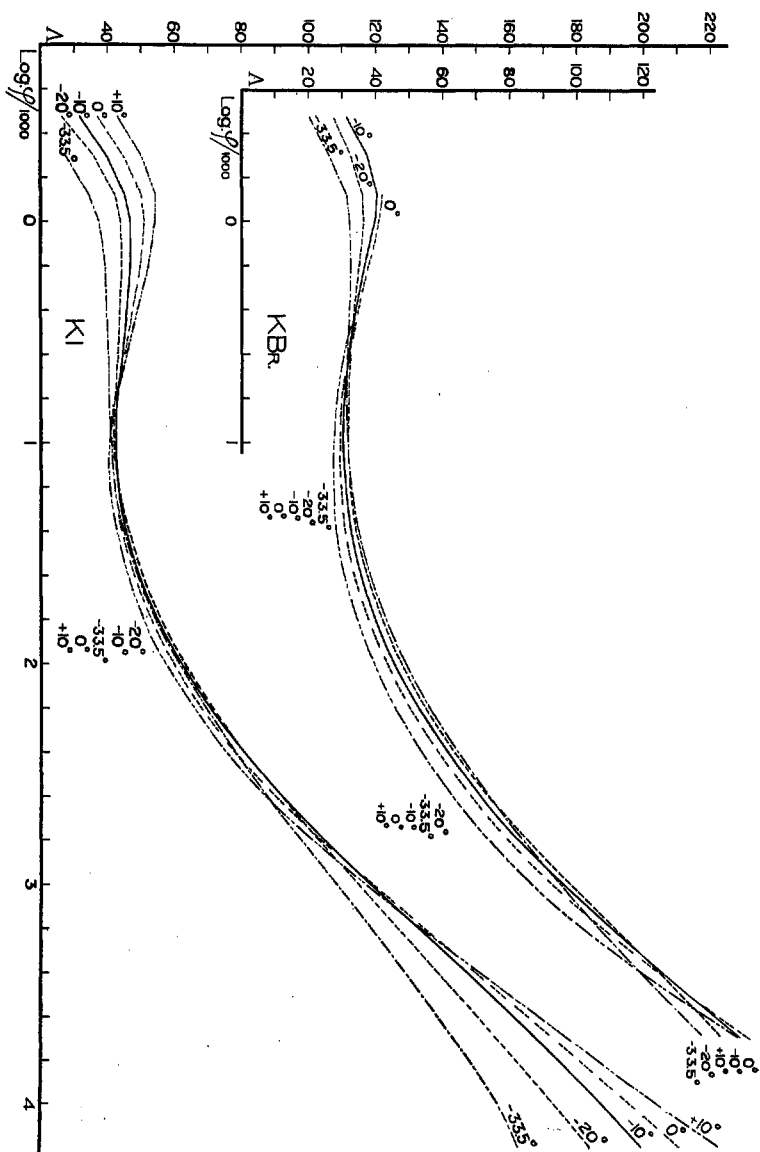


Fig. 1

*Discussion of Results.*—As an attempt at a tentative explanation of the phenomena recorded in the numerical data and curves herewith, the following considerations are submitted.

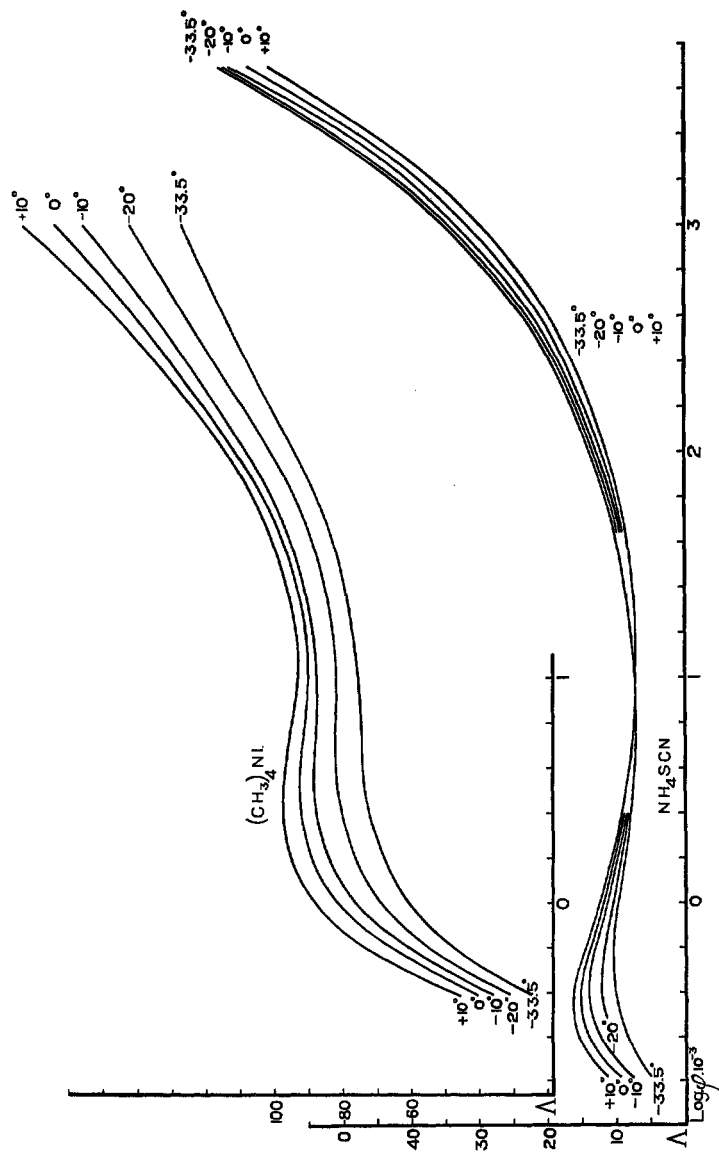


Fig. 2



In the first place, such curves, or portions of them, have so far been observed only in connection with the weaker ionizing solvents such as the amines,<sup>1</sup> ammonia,<sup>2</sup> sulfur dioxide,<sup>3</sup> ether,<sup>4</sup> bromine,<sup>5</sup> iodine,<sup>6</sup> the halogen acids,<sup>7</sup> molten mercuric chloride,<sup>8</sup> molten boracic anhydride,<sup>9</sup> etc.,<sup>10</sup> that is to say, the effects, whatever the nature of their cause, which are superimposed upon the ordinary dissociating action of the solvent are conspicuous in solutions in weak ionizing solvents, while in solutions in the more powerful ionizing solvents they are obscured.

In the second place, since the conductivity of melted salts is electrolytic and not metallic in its nature, it may be assumed as established that melted salts are ionized. Furthermore, the conclusion seems to be fairly well justified that in the melted state the observed conductivity is to be accounted for on the hypothesis of a high degree of ionization together with low ionic mobility.<sup>11</sup> It therefore seems reasonable to assume that in very concentrated solutions,—inasmuch as such solutions approximate the state of melted salts,—autoionization, or selfionization, of the solute plays a much more conspicuous part than in dilute solutions. If on this hypothesis we consider a very concentrated solution

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<sup>1</sup> Franklin and Gibbs: *Loc. cit.*; Kahlenberg and Ruhoff: *Jour. Phys. Chem.*, **7**, 254 (1903).

<sup>2</sup> Franklin: *Loc. cit.*

<sup>3</sup> Walden and Centnerzwer: *Loc. cit.*

<sup>4</sup> Kablukoff: *Zeit. phys. Chem.*, **4**, 429 (1889); Euler: **28**, 623 (1899); Sackur: *Ber. chem. Ges. Berlin*, **35**, 1242 (1902).

<sup>5</sup> Plotnikoff: *Zeit. phys. Chem.*, **48**, 220 (1904).

<sup>6</sup> Lewis and Wheeler: *Proc. Am. Acad.*, **41**, 419.

<sup>7</sup> Archibald: *Jour. Am. Chem. Soc.*, **29**, 1416 (1907); Steele, McIntosh and Archibald: *Phil. Trans. (A)*, **205**, 99.

<sup>8</sup> Foote and Martin: *Am. Chem. Jour.*, **41**, 451 (1909).

<sup>9</sup> Arndt: *Zeit. Elektrochem*, **13**, 405 (1907); *Ber. chem. Ges. Berlin*, **40**, 2937 (1907).

<sup>10</sup> Walden: *Zeit. phys. Chem.*, **43**, 385 (1903); **54**, 141 (1906). Coffetti: *Gazz. chim. ital.*, **33**, 63 (1902).

<sup>11</sup> Arndt: *Zeit. Elektrochemie*, **13**, 509 (1907); *Ber. chem. Ges. Berlin*, **40**, 2937, 3612 (1907). Lorenz: *Ibid.*, **40**, 3308, 4378 (1907); *Zeit. anorg. Chem.*, **51**, 71 (1906); **52**, 41 (1907); *Zeit. Elektrochemie*, **10**, 630 (1904).

of a salt in a non-ionizing, or very weak ionizing solvent, we may expect on diluting the solution, to find the autoionization, and with it the molecular conductivity, diminishing in value continuously with increasing dilution. The molecular conductivity of a salt dissolved in a non-ionizing solvent in its dependence upon dilution will then be represented by the curve C C' C'' in<sup>1</sup> Fig. 3. The curve approaches

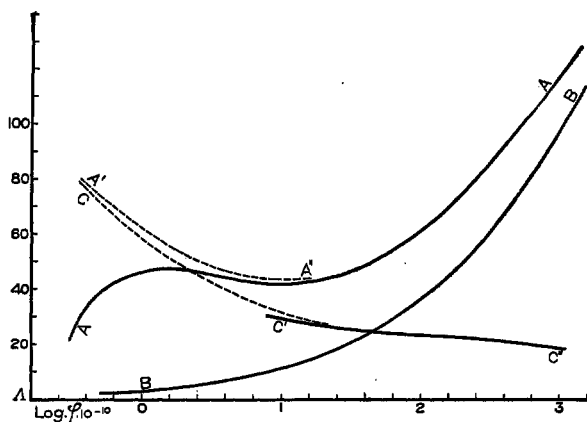


Fig. 3

the axis of dilutions asymptotically. Thus may be explained the downward trend of the molecular conductivity curve as recorded in this and previous papers.

In the third place, it is to be noted that while in concentrated solutions we have assumed the conductivity to be due in large measure, or even almost entirely, to the autoionization of the salt, in dilute solutions on the contrary, the ionizing effects must be ascribed to the solvent; for not only will the autoionization of the salt diminish with increasing dilution of the solution but also will the dissociating power of the solvent rise as a result of increasing solvent

<sup>1</sup> The points on the portion of the curve between C' and C'' are plotted as the differences of the corresponding ordinates to the curves A and B, *i. e.*, the observed conductivity is the result of the superposition of the conductivity due to solvent ionization upon that due to autoionization. No data exist for the dotted portion of the curve, C C'.

concentration. In the ideal case in which the ionization in a solution is due wholly to the action of the solvent, and not at all to the action of the solute, the molecular conductivity curve must be that which is closely approximated by weak acids and bases in aqueous solutions. Such a curve, calculated on the assumption of a solution following Ostwald's dilution law, and with the assumed constants,<sup>1</sup>  $A_{\infty} = 235$  and

$$A_{\infty} = (A_1^2 A_2 V_2 - A_2^2 A_1 V_1) / (A_1^2 V_2 - A_2^2 V_1) \text{ and } \alpha^2 / (1 - \alpha) V = K.$$

$k = 0.000298$ , is  $B\beta$  in Fig. 3.

Now the two effects thus described are necessarily superimposed in the case of all actual solutions, with the result that at higher concentrations the one, at lower concentrations the other effect will have a preponderating influence on the trend of the conductivity curve. The molecular conductivity curve must therefore pass through a minimum as indicated in the figure. This minimum will show itself plainly and at no very great concentration in solutions in solvents of weak ionizing power, while in the case of solutions in powerful ionizing solvents the minimum will be pushed so far towards the region of greater concentration that it will be obscured, or be unrealizable because of the limited solubility of the solute, or because of the increasing viscosity of the solutions as explained hereafter.

Finally, it is an observed fact that concentrated solutions generally are more viscous, some of them much more viscous, than dilute solutions, from which it follows, when we remember that ionic mobility changes concomitantly with fluidity, that the observed conductivity must be much affected by the changing viscosity which accompanies dilution. The increase of fluidity of a solution with the dilution is represented by the curve D in Fig. 3, the location and trend of which however, are without quantitative significance.<sup>2</sup> Re-

<sup>1</sup> These constants are calculated from the conductivity data given above by means of the familiar formulas,

<sup>2</sup> Working in this laboratory F. F. Fitzgerald has shown a rapid rise in fluidity to accompany the dilution of concentrated solutions in liquid ammonia, liquid methylamine and liquid sulphur dioxide. The experimental results will be published.

calling the influence of changing dilution on the autoionization of the salt as explained above, it thus appears that there are two conflicting effects to be expected as the result of adding solvent to concentrated solutions; the one being a diminution in the degree of ionization of the solute, the other an increase in ionic mobility. The rapid initial rise in the molecular conductivity is due to the preponderating influence of the latter over the former on the current carrying capacity of the solution. These two effects must ultimately balance each other as the solution is diluted, and when they do, the molecular conductivity is at a maximum. As the solution is further diluted the effect of diminishing autoionization becomes predominant and the curve continues with a downward trend. As argued above the curve would continue to approach the axis of dilutions asymptotically in the case that the solvent possesses no ionizing power. Since, however, such in general is not the case we must expect sooner or later to find the downward trend of the curve arrested thence to rise, with continued dilution to the final familiar maximum as the result of the ionizing action of the solvent. The experimentally realized conductivity curve is that indicated in the figure by the lettering, A A. The dotted curve A" A' is drawn to represent the hypothetical trend of the molecular conductivity on the assumption of no change in the viscosity of the solution with increasing concentration.

*Temperature Effects.*—Having considered the influence of changing concentration on the conductivity of liquid sulfur dioxide solutions, as affected by the three factors, fluidity, autoionization and ionization due to solvent, we now turn to a very brief discussion of the influence of temperature changes on these factors.

The assumption has already been made that the conductivity of very concentrated solutions is due principally to autoionization of the solute. We may further assume that temperature changes are practically without effect on autoionization, for, if melted salts are highly ionized, then the liquefaction of a salt at a much lower temperature by the

action of a solvent cannot greatly alter this specific character of the salt.

Temperature changes are accompanied by changes in the viscosity of solutions and these changes are especially conspicuous in the case of the most concentrated solutions. Specifically it has been shown in this laboratory that a rapid rise in the fluidity of concentrated solutions sulfur dioxide solutions accompanies rising temperature.<sup>1</sup>

The ionizing power of solvents generally diminishes with rising temperature.

Upon these temperature effects, of which the first only requires experimental substantiation, together with the effects of changing concentration as described above, are based the following qualitative explanations of the rather complicated trends of the molecular conductivity curves shown in the Figs. 1 and 2.

1. The conspicuous positive temperature coefficients of the most concentrated solutions are assumed to be due to the rapid rise in ion velocity which accompanies increasing fluidity; the degree of ionization at the same time undergoing negligible change.

2. Since rising temperature depresses the ionizing power of the solvent and is assumed to be without appreciable effect on the autoionization, the resultant effect of rising temperature must be to displace the minimum of molecular conductivity to higher dilutions and at the same time to diminish its value. In accordance with this deduction the temperature coefficients of conductivity are seen to diminish in value as the solution is diluted to be followed by a complete change of sign in the case of solutions of ammonium sulfocyanate and potassium bromide. In the case of potassium iodide solutions the change of sign of the temperature coefficient extends only to the temperatures,  $+10^{\circ}$ ,  $0^{\circ}$ ,  $-10^{\circ}$  and  $-20^{\circ}$ ; the conductivity at  $-33.5^{\circ}$  never rising above that of

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<sup>1</sup> Data by F. F. Fitzgerald. Not yet published.

—10° at any dilution. Furthermore the temperature coefficient of the molecular conductivity of tetramethylammonium iodide solutions remains positive throughout the whole range of temperatures and dilutions included in these measurements.

3. In very dilute solutions ionization approaches completion as the result of the dissociating action of the solvent. It follows therefore that in dilute solutions, even though rising temperature diminishes the ionizing power of the solvent, any change in the ionization of the solute must be subordinate in its effect on the conductivity of the solution as compared with the change in ionic mobility due to changes in viscosity of the solution with temperature. At sufficiently high dilutions, therefore the conductivity temperature coefficient must be positive. The curves show this to be true for solutions of potassium iodide and potassium bromide in liquid sulfur dioxide.

The writer is quite cognizant of the inadequacy and the too speculative nature of the above explanations, but presents them as the best he can do at the present time and in the belief that they are at least worth recording.

### **Summary**

In this paper are recorded the results of measurements of the electrical conductivity of a number of salts in solution in liquid sulfur dioxide through concentrations varying from approximate saturation up to the highest dilutions which could conveniently be measured and through as wide a range of temperatures as could be readily realized with the apparatus in the form constructed.

It has been found that the molecular conductivity of liquid sulfur dioxide solutions instead of rising in the ordinary manner to a final maximum with increasing dilution, as a matter of fact rises first to a maximum, then falls to a minimum thence finally to rise to the familiar maximum at very high dilution.

Through the range of temperatures studied it has been found that the conductivity temperature coefficient is positive for very concentrated solutions and also for the most dilute solutions while for solutions of intermediate concentration the sign of the temperature coefficient is generally reversed.

A description of the method of manipulating solutions in liquid sulfur dioxide is given.

*Stanford University, California,  
May 1911*