Summary

1. The significance of the various terms in the Ilkovic equation for the diffusion currents obtained with the dropping mercury electrode is discussed. The term "diffusion current constant" is introduced to characterize the diffusion current obtained with a solution containing one millimole per liter of the reducible substance. The significance and method of computing the diffusion coefficient term in the Ilkovic equation is discussed.

2. A simple apparatus for manually obtaining current–voltage curves with the dropping mercury electrode is described.

3. The diffusion current constants of thallous, lead, cadmium, zinc, iodate, and ferricyanide ions were determined in 0.1 N potassium chloride at 25°, and compared with the corresponding values calculated from the Ilkovic equation. In the cases of thallous, lead, and iodate ions the agreement between the observed and calculated diffusion current constants was within the limits of experimental error (about ±1%). In the cases of zinc and cadmium ions the observed diffusion current constants were, respectively, 5 and 8% larger than the calculated values. The observed diffusion current constant of ferricyanide ions was 8% smaller than the calculated value.

It is concluded that the Ilkovic equation is essentially correct.

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[A CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE AMERICAN CYANAMID COMPANY]

The Reaction of Sulfur Trioxide with Sodium Chloride

BY D. J. SALLEY

Sulfur trioxide and sodium chloride interact in two ways, depending on the temperature region in which the reaction is carried out. From room temperature to about 100° an addition complex of uncertain composition is formed.[1,2] Above about 200°, a profound change occurs, but investigators differ as to the products. Some claim that only chlorine and sodium sulfate are formed,[3] others include sulfur dioxide,[4] while still others suggest that oxygen affects the reaction course.[5] Since several possible over-all reactions involving these reactants and resultants may be written down, all of them apparently thermodynamically permissible, it was of interest to identify with certainty the products of the high temperature reaction and to ascertain the relative amounts produced. From such knowledge, it might be decided whether a single simple reaction was occurring or whether several were taking place simultaneously.

Identification of Reaction Products

The identity of the products and the quantitative methods of their analysis were established in preliminary flow experiments. In these, the low temperature addition complex, made by passing sulfur trioxide over salt at about 90°, was held at several temperatures between 220 and 444°; nitrogen was used as the carrier gas. The volatile products were frozen out at −78 and −180°, and by fractional distillation in vacuum between these low temperatures, they were separated into several fractions. In this manner, unchanged sulfur trioxide was found; sulfur dioxide and chlorine were each identified by color and smell, and in aqueous solutions of these fractions by qualitative test. Substitution of oxygen as the carrier gas or decomposition of the addition complex in vacuum gave only these same products. None of the various possible sulfur–chlorine or sulfur–oxygen–chlorine compounds was detected.

When the gaseous decomposition products were led into a single large trap filled with glass beads, all could be frozen out at −180° and then dissolved without loss in aqueous alkali. The solutions so formed did not give a test for free chlorine (production of iodine from acidified potassium iodide) or sulfur dioxide (decolorization of iodine in acidified potassium iodide), although naturally chloride and sulfate ion tests were strongly positive. Such a result could be obtained, of course, only if the sulfur dioxide and chlorine had been formed in exactly equivalent quantities and were

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[1] Schultz-Sellack, *Ann.*, 193 (1871).

[2] Traube, *Ber.*, **46**, 2513 (1913).

[3] Schmidt, British Patent 249,474 (1926).

[4] Deacon, British Patent 1908 (1871).

[5] Clemm, British Patent 15,152 (1899).

rapidly mutually oxidized and reduced in the alkali. This complete absence of free chlorine or sulfur dioxide in solution was observed in all cases, no matter under what conditions reaction had been effected.

To perform quantitative analyses of either the solid residue or the gaseous products, the sample was dissolved in standard sodium hydroxide, diluted to a convenient volume, and aliquot portions taken. Titration of the excess alkali with standard acid gave the amount of hydroxide consumed equivalent to the acidity of the sample, and titration of this neutralized aliquot with barium chloride using THQ indicator[6] gave the total sulfate. Titration of a second aliquot with silver nitrate by the Rothmund and Bergstatter method[7] gave the chloride ion present. Within the limit of experimental error, all the original trioxide and chloride could be accounted for by these methods.

The results of the preliminary experiments established beyond a doubt that the interaction of sulfur trioxide and sodium chloride between 220 and 444° yielded sulfur dioxide and chlorine in equivalent proportions, and that neither nitrogen nor oxygen affected the results. Both the qualitative and quantitative data of the numerous flow experiments seemed to indicate that the over-all process was best described by the equation

$$NaCl + 3/2\ SO_3 = 1/2\ Na_2S_2O_7 + 1/2\ SO_2 + 1/2\ Cl_2 \quad (1)$$

In the final working out of the reaction, a static method was employed, and it is the results of this set of experiments which will be described in the following; the findings, we believe, clearly establish the validity of equation (1).

Static Experiments

In the static method a known amount of sulfur trioxide vapor was brought in contact with a definite quantity of pure sodium chloride maintained at constant temperature. By observing the pressure change with time, the ensuing reaction was followed to completion, whereupon the gaseous products were separated from the solid by evacuating into a liquid-air trap, and each was analyzed.

Apparatus.—The apparatus consisted essentially of a storage bulb for condensed sulfur trioxide, a reservoir (1032.5 cc.) for sulfur trioxide vapor, a spoon gage (30.7 cc.) for measuring pressures, a reaction vessel, and a U-trap. The temperature of the reservoir for sulfur trioxide vapor was maintained fairly constant by a water-bath. The spoon gage, of familiar design, was used solely as a null point instrument in conjunction with a mercury manometer. Since it was connected through a three-way tap to measure the pressure in either the reservoir or the reaction vessel, the reservoir plus gage made up to so-called reservoir system while the reaction vessel and gage constituted the reaction system. Two reaction vessels (R_1, 205.5 cc.; R_2, 225.2 cc.) fitted with interchangeable ground joints were found convenient. The reaction temperature could be established either by constant boiling vapor baths or by an electric furnace; the actual temperature prevailing during a run was measured by a thermocouple in a well reaching to the very bottom of the vessel. Capillary tubing was used throughout for connections. Ordinary stopcocks lubricated with Apiezon grease were employed, for although the grease blackened on contact with the trioxide, blank runs showed that the system would develop no leaks over a period of several hours, and also that the initial trioxide pressure would decrease only 2 to 4% from interaction with the grease. The whole system could be evacuated by a mercury diffusion pump backed by a Cenco Megavac oil pump.

Materials.—The sulfur trioxide was Kahlbaum "For Analysis," distilled in vacuum through phosphorus pentoxide and condensed by liquid air in the storage bulb. The sodium chloride was ordinary Merck c. p. reagent, dried at 110°.

Procedure.—With a weighed quantity of salt in the reaction vessel maintained at the desired reaction temperature, the whole system was evacuated for about an hour. The sulfur trioxide was vaporized from the storage bulb into the reservoir and gage, and its pressure and temperature recorded. Thereupon, the reservoir was connected to the reaction vessel for exactly ten seconds, and as soon thereafter as possible the gage was joined to the reaction vessel to measure the existing pressure. Additional pressure readings were obtained at intervals until the pressure in the reaction vessel had become and remained constant for twenty to thirty minutes. Then the gaseous products were allowed to expand into the U-trap cooled in liquid air, and the pumps were connected for four to five minutes; the trap was then sealed off. Finally the gage was joined to the reservoir and the final pressure and temperature of the trioxide remaining in the reservoir were noted.

The gaseous products in the trap were dissolved in standard alkali by breaking the tip of the trap under the liquid and analyzed as noted previously. Likewise, the solid residue in the reaction vessel was dissolved and analyzed.

Results

Thirteen experiments in all were performed in the static system at 279, 305 and 350°, using various initial ratios of trioxide to salt. Typical of all runs was the fact that the salt fused with frothing at first, but eventually a white solid formed toward the completion of the reaction. Further, the initial pressures in the reaction vessel were always much lower than expected from the amount of sulfur trioxide introduced and the pressures increased rapidly at first and then more slowly to constant values; this required from two to one hundred and thirty minutes, depending

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[6] Schroeder, *Ind. Eng. Chem., Anal. Ed.*, **5**, 403 (1933); Sheen and Kahler, *ibid.*, **8**, 127 (1936).

[7] Treadwell and Hall, "Quantitative Analysis," 8th ed., John Wiley and Sons, Inc., New York, 1935, p. 655.

on the temperature. From these observations, it is clear that the reaction was not a clean-cut solid–gas reaction, as had been hoped, but that there occurred a very rapid and extensive absorption of trioxide by the salt followed by a slower reaction producing sulfur dioxide and chlorine.

The numerical data obtained for all the runs are recorded in Tables I and II, the former containing the pertinent temperatures and pressures of the reservoir and reaction systems, and the latter the analytical data. The so-called initial pressures of I-h were those pressures read any time from one to four minutes after zero reaction time. (Reference will be made to a particular column in a table by writing only the number and letter as I-h.)

TABLE I

SO_3 + NaCl; INITIAL AND FINAL PRESSURES

				Reservoir system			Reaction system	
Run a	React. temp., °C. b	Time of run, min. c	NaCl taken mols $\times 10^3$ d	Temp., °C. e	p, mm. Hg Initial f	Final g	p, mm. Hg Initial h	Final i
1	305	60	1.001	31.3	233.4	194.2	181.2	208.4
2	305	62	1.006	30.3	163.0	137.3	89.0	131.5
3[a]	305	62	0.998	30.9	136.6	108.7	75.0	128.5
4	305	41	1.001	30.1	52.8	42.0	26.8	57.0
5	305	60	0.513	30.3	252.1	216.8	201.5	219.8
6[a]	305	58	.502	31.0	125.5	104.7	91.9	...
7	305	61	.502	29.0	154.0	129.3	114.1	137.0
8[a]	305	59	.514	30.8	78.2	62.4	40.0	69.8
9	350	35	1.003	27.6	251.1	215.5	201.7	189.3
10[a]	350	30	0.991	28.0	148.9	118.6	142.7	165.8
11	350	30	0.998	28.6	59.0	44.6	58.8	66.3
12	279	134	1.006	25.2	231.6	192.1	147.8	183.3
13[a]	279	134	0.991	26.2	106.5	103.6	82.4	118.1

[a] Reaction vessel R_2 used in starred runs, R_1 in unstarred.

TABLE II

SO_3 + NaCl; ANALYSES OF PRODUCTS

Data in milliequivalents

	Solid residue			Gases in traps		
Run a	Acid b	SO_4 c	Cl d	Acid e	SO_4 f	Cl g
1	0.99	1.93	0.00	2.88	1.98	0.95
2	.77	1.51	.23	1.83	1.14	.76
3	.86	1.74	.15	1.82	1.05	.80
4	.29	0.65	.66	0.68	0.43	.30
5	.51	1.04	.00	3.12	2.61	.50
6	.58	1.03	.01	1.60	1.19	.47
7	.49	0.99	.01	1.80	1.38	.47
8	.42	.90	.06	1.03	0.62	.42
9	.91	1.85	.06	2.89	2.01	.93
10	.74	1.57	.18	2.47	1.68	.79
11	.31	0.72	.62	1.16	0.80	.36
12	.98	1.99	.00	3.34	2.12	.95
13	.83	1.64	.17	2.26	1.41	.80

Discussion

The data presented in Tables I and II show good agreement. For example, the amounts of sulfur trioxide introduced into the reaction system, as calculated from the known volume, temperatures, and pressures of the reservoir system, average some 8 to 10% higher than the total sulfate found by analysis. As this is fair concordance, future calculations have been based on the average of these two as representing the best value for the "trioxide taken." For the chloride, the total found and that originally taken show agreement to 5%, and, furthermore, the amount of chloride disappearing from the solid (I-d minus II-d) is equal to that found in the gaseous products (II-g); the average of these two has been taken and designated as the "chlorine evolved."

Although the "trioxide taken" was the amount of trioxide in the reaction system at the start of a run, all of this was not able to react with the salt. This arose because the bulb of the spoon gage was joined to the reaction vessel by about 115 cm. of 1.5 mm. capillary tubing, and because the pressure increased during a run. As a consequence, the trioxide initially in the gage could never reach the reaction zone. The amount of sulfur trioxide so excluded may be estimated from the volume and temperature of the gage and from the initial observed pressure (I-h) in the reaction system. Subtracting this from the trioxide taken shows the amount of sulfur trioxide "available" for reaction.

Considering now equation (1) above, it requires 1.5 moles of sulfur trioxide to produce 0.5 mole of chlorine from 1.0 mole of sodium chloride. On this basis, a plot of the moles of "chlorine evolved" per mole of sodium chloride taken against the initial mole ratio of "available trioxide" to sodium chloride should give a curve consisting of two straight line sections with slopes 0.333 and zero (broken line, Fig. 1). The experimental curve as calculated from the data of Tables I and II (full line, Fig. 1) has a short bent portion connecting two straight line branches, the one of slope 0.302, the other of zero slope. That the relationship of equation (1) does in fact exist is indicated by the very near agreement between the two curves. Experimental uncertainties probably account for part of the disagreement between them, but an additional plausible explanation is that the reaction did not quite go to completion in those cases where the initial mole ratio was less than two. It should be noted that the reaction temperature does not affect the final amount of chlorine evolved, at least in the temperature range tested.

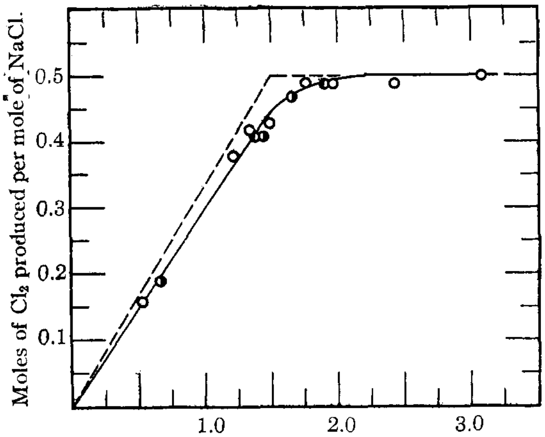

Fig. 1.—Dependence of Cl_2 produced on SO_3/NaCl mole ratio: ◐ at 279°; ○ at 305°; ◑ at 350°.

Equation (1) requires that sodium pyrosulfate be produced in amounts equivalent to the chlorine evolved. Examination of the analyses of the solid reaction product shows that the quantity of sulfate formed (II-c) is always just twice that of the acid (II-b), within experimental error. This could arise if one molecule of neutral sulfate had exactly one molecule of trioxide attached to it in a manner such that, on dissolving in water, the trioxide formed sulfuric acid. Assuming the solid then to be the pyrosulfate,[8] either the acid analyses or half the sulfate analyses may serve as a measure of the pyrosulfate formed, and using the average, the moles of pyrosulfate produced per mole of sodium chloride taken may be computed. Now, the number of such molecules formed were found to depend on the initial available trioxide to salt ratio in the manner depicted by the solid curve of Fig. 2. Comparison of this curve with that of Fig. 1 brings out the striking fact that the two are quantitatively identical. Consequently, the clear conclusion is that for every molecule of chlorine produced in the gases, one molecule of sodium pyrosulfate was formed in the solid phase.

A check on the amount of sulfur trioxide attached to the solid residue may be obtained from the fact that the total final amount of gas existing in the reaction system (calculated from the final pressure therein, I-i) is less than the original amount of trioxide taken. If this diminution is ascribed to the take-up of trioxide by the solid, the calculated decreases should correspond exactly with the acid analyses, and therefore serve as an independent measure of the pyrosulfate formed. Plotting the decreases, per mole of salt taken, as a function of the initial available trioxide–salt ratio in Fig. 2 (broken curve), it appears that this curve lies above the other. This point should not be stressed too much since the individual values scatter very considerably, but if the result is real, it would suggest that a slight amount of sulfur trioxide was weakly adsorbed on the pyrosulfate solid; this weakly adsorbed gas could be pumped off on evacuating the reaction vessel at the end of the run, in contrast to the more strongly bound trioxide which had reacted to form the pyrosulfate.

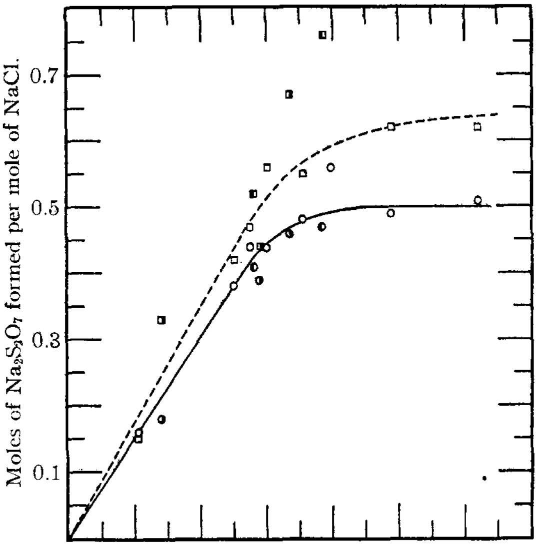

Fig. 2.—Dependence of $Na_2S_2O_7$ formed on SO_3/NaCl mole ratio: $Na_2S_2O_7$, ◐ at 279°; ○ at 305°; ◑ at 350°; SO_3 decrease, ◧ at 279°; □ at 305°; ◨ at 350°.

The foregoing experimental facts have all lent credence to equation (1). Additional support is obtainable from another quarter, for by suitably combining the heats and free energies of formation of sodium chloride,[9] sodium pyrosulfate,[10] sulfur dioxide[10] (p. 13) and sulfur trioxide[10] (p. 15) the heat and free energy of (1) may be calculated to be $\Delta H^\circ_{298} = -25{,}700$ and $\Delta F^\circ_{298} = -17{,}700$, or $\Delta F^\circ = -25{,}700 + 26.8\ T$. Ignoring changes in ΔC_p, the free energy change at 305° may be estimated as $\Delta F^\circ_{578} = -10{,}200$. Reaction (1) is therefore thermodynamically permissible, and

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[8] See, for example, Ephraim, "Textbook of Inorganic Chemistry," 2d English ed., Gurney and Jackson, 1934, p. 519, for properties of sodium pyrosulfate.

[9] Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, 1936, p. 138; Kelley, Bull. 394, U. S. Bureau of Mines, pp. 37, 43 (1936).

[10] Kelley, Bull. 406, U. S. Bureau of Mines, p. 109 (1937).

the large free energy decrease is consistent with the observed completeness of reaction at all three temperatures studied.

Little could be deduced concerning the kinetics of the reaction, for obviously the observed rate of pressure increase was a composite of a decrease due to absorption of the trioxide and an increase due to evolution of the dioxide and chlorine. Hence only near the end of reaction could the observed rate of pressure change serve as a measure of the rate of evolution of the gases. Actually, by using the times of 0.9 reaction for the usual log–$1/T$ graph, a reasonably straight line was obtained from whose slope a value of 38,000 cal. was obtained for the apparent energy of activation.

Summary

1. In flow runs, the decomposition of a low temperature sulfur trioxide–sodium chloride addition complex has been shown to yield sulfur dioxide and chlorine in exactly equivalent proportions; this holds at all temperatures between 220 and 440° in a nitrogen or an oxygen atmosphere.

2. The reaction of sulfur trioxide with sodium chloride between 279 and 350° has been investigated by a static method. It was established that 1.5 moles of sulfur trioxide react with 1.0 mole of sodium chloride to produce 0.5 mole each of chlorine, sulfur dioxide, and sodium pyrosulfate. Thus: $NaCl + {}^3/_2\,SO_3 = {}^1/_2\,Na_2S_2O_7 + {}^1/_2\,SO_2 + {}^1/_2\,Cl_2$.

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[CONTRIBUTION FROM TUNGSRAM RESEARCH LABORATORY, UJPEST NEAR BUDAPEST]

Reaction of Tantalum, Columbium and Vanadium with Iodine

BY F. KŐRÖSY

The latest investigation on the reaction of tantalum with iodine is that of Moissan,[1] while the reactions of columbium and vanadium have never been investigated. Moissan briefly stated that tantalum powder and vapor of iodine do not react at 600°; this is the last reference to be found on the subject.[2] The direct reaction has never been described although van Haagen[3] succeeded in preparing tantalum pentaiodide from the bromide and hydrogen iodide. The formula was confirmed by analysis and the color of both the condensed and gaseous compounds was described as resembling bromine. Barr[4] prepared a crude, stable columbium iodide from the bromide. He was unable to obtain this material free from bromine and did not analyze it.

In search of a metal that would be resistant to iodine vapor at temperatures between 1500 and 2500° we tried tantalum, hoping that Moissan's statement would also be valid for these high temperatures. However, we soon noticed the formation of a black-brown solid that melted at 365° and could be distilled without decomposition at about 400°. The vapor had a characteristic brown color quite distinct from iodine. It was soon identified as tantalum pentaiodide and we decided to investigate its physical properties and chemical reactions because scarcely anything was known about them.[5] Further we studied a reduction product of this substance and the reactions between columbium and iodine and vanadium and iodine to some extent because the metals of this sub-group of the periodic system are the only ones that were hitherto not known to react with elementary iodine.

Whereas tantalum pentaiodide is stable at least up to 500° and had to be reduced in the vapor phase with incandescent tantalum wire, columbium and vanadium pentaiodides easily dissociate at their sublimation temperatures (about 400°). It may be that the greater stability of the tantalum compound is due to the fact that the Ta ion fills the "hole" between the large iodine ions ($\phi = 2.2$ Å.) more completely than the V and Cb ions [V = 0.4 Å., Cb = 0.70 Å., Ta = 0.85 Å. (extrapolated)]. The "hole diameter" between five I ions in a regular pentagon is 1.5 Å. so that this configuration is less probable than a steric one.

The stoichiometric formula of the lower iodides is open to discussion; their chemistry seems complicated. The tantalum compound decomposes

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(1) H. Moissan, *Compt. rend.*, **134**, 212 (1902).

(2) Gmelin's "Handbuch der anorganischen Chemie," System No. 8, Jod, 1933, p. 180.

(3) W. K. van Haagen, THIS JOURNAL, **32**, 729 (1910).

(4) W. M. Barr, *ibid.*, **30**, 1668 (1908).

(5) F. Kőrösy, *Technikai Kurir*, **9**, 81 (1938) (Hungarian publication); see *C. A.*, **33**, 1615 (1939).