TABLE I

RESULTS OF THE EQUILIBRIUM MEASUREMENTS

Temp., 24.8°		Temp., 34.8°	
Press., mm.	Mol. ratio,[a] Cl_2/ICl	Press., mm.	Mol. ratio,[a] Cl_2/ICl
49.5	0.885	100.6	1.345
49.4	.893	100.5	1.281
49.4	.896	100.5	1.317
49.1	.878	99.5	1.312
49.1		99.4	1.272
49.3		99.9	1.334
		99.7	
Mean 49.3 ± 0.2 mm.		99.7	
Mean 0.888 ± 0.005		99.9	
		100.2	
		100.4	
		Mean 100.0 ± 0.3 mm.	
		Mean 1.320 ± 0.026	

[a] The mole ratios do not refer to the same mixtures on which pressure measurements were made.

calculated and their logarithms plotted against $1/T$. The value of K at 25.0° is 1.09×10^{-3}, and that at 35.0° is 4.36×10^{-3}, when the pressures are expressed in atmospheres.

The value of ΔH for reaction (1) was calculated to be 25,300 cal. for the temperature range of the experiments, and the free energy change, $\Delta F° = -RT \ln K$, at 25° is $\Delta F^\circ_{298} = 4040$ cal.

The results just presented were combined with the thermodynamic data for iodine monochloride[2] and the following equations derived.

$$ICl(g) + Cl_2(g) = ICl_3(s) \qquad (2)$$
$$\Delta H = -25{,}300 \text{ cal.} \quad \Delta F^\circ_{298} = -4040 \text{ cal.}$$
$${}^1/_2Cl_2(g) + {}^1/_2I_2(s) = ICl(g) \qquad (3)$$
$$\Delta H = 4158 \text{ cal.} \quad \Delta F^\circ_{298} = -1370 \text{ cal.}$$

Hence

$${}^1/_2I_2(s) + {}^3/_2Cl_2(g) = ICl_3(s) \qquad (4)$$
$$\Delta H = -21{,}150 \text{ cal.} \quad \Delta F^\circ_{298} = -5410 \text{ cal.}$$

The standard virtual entropy of $ICl_3(s)$ at 25° is 41.1 cal./deg. when the entropies of $Cl_2(g)$[3] and $ICl(g)$[2] at 25° and one atmosphere are taken to be 53.31 cal./deg. and 59.15 cal./deg., respectively.

The value of 21,150 cal. for the heat of formation of iodine trichloride from the elements is higher than that found calorimetrically by Berthelot,[4] namely, 16,300 cal. Inasmuch as Berthelot himself called attention to the unsatisfactory nature of his experiments, it is believed that the value derived from the equilibrium measurements is to be regarded as the reliable one.

Summary

Measurements have been made on the pressure and composition of the vapor from the univariant system $ICl_3(s)$, $ICl(l)$, $ICl(g)$, $Cl_2(g)$ at 25 and 35°. The equilibrium constants, $K = P_{ICl}P_{Cl_2}$, at 25 and 35° are 1.09×10^{-3} and 4.36×10^{-3}, respectively, when pressures are expressed in atmospheres. The free energy and heat content of solid iodine trichloride at 25° are $\Delta F^\circ_{298} = -5410$ cal. and $\Delta H = -21{,}150$ cal., respectively. The standard virtual entropy of $ICl_3(s)$ at 25° is 41.1 cal./deg.

[3] Giauque and Overstreet, THIS JOURNAL, **54**, 1731 (1932).

[4] Berthelot, *Ann. chim. phys.*, **21**, 370 (1880); "I. C. T.," Vol. V, p. 177.

PASADENA, CALIF. RECEIVED NOVEMBER 26, 1934

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 442]

The Dissociation of Sulfur Monochloride Vapor

BY ROBERT C. BARTON AND DON M. YOST

Introduction

Aside from the observation of Thorpe[1] that sulfur monochloride dissociates slightly at the boiling point (138°), no studies on the stability of the vapor have been reported. In an effort to determine the nature and extent of the dissociation as a function of the temperature and composition of the vapor, a thorough investigation of it under equilibrium conditions was made. The results of the experiments are presented in this paper together with a discussion of the thermodynamic quantities calculated from the data.

Preparation of Materials and Method of Experimentation

Sulfur.—A high quality of sulfur was resublimed at atmospheric pressure.

Chlorine.—Chlorine from a tank was first passed through a saturated solution of potassium permanganate, and then through concentrated sulfuric acid; finally it was condensed into glass capsules equipped with easily breakable tips. The capsules were weighed before and after filling so that the weight of the chlorine in them was accurately known.

Sulfur Monochloride.—Equivalent quantities of sulfur and chlorine were mixed in an evacuated bulb equipped with side-arms having fragile tips. The mixture was heated to 120° for twelve hours and, on cooling, the golden-yellow liquid formed was allowed to run into the side-arms

[1] Thorpe, *J. Chem. Soc.*, **37**, 356 (1880).

which were then sealed off. Three independent preparations were used in the experiments.

Two experimental methods were used in the investigation. The first consisted in measurements of the vapor density of sulfur monochloride by a modified Dumas method.[2] A weighed amount of sulfur and chlorine (in a capsule) was placed in a tube of known volume. The tube was then evacuated, sealed off and weighed. After breaking the capsule by shaking, the tube was placed in a constant-temperature electric furnace. When equilibrium was attained the long capillary end of the tube was opened and the vapors in the tube allowed to come to atmospheric pressure. The capillary was then sealed, and, after cooling to room temperature, the tube and contents were weighed.

In the second method of experimentation sulfur monochloride was distilled into an evacuated quartz vessel of known volume equipped with a Pyrex glass click gage. The connection between the click gage and the quartz vessel was effected by means of a ground conical joint sealed with silver chloride. The quartz vessel was placed in a long copper-lined electric furnace, while the click gage was surrounded by an auxiliary furnace whose temperature was maintained at 150°. The temperatures were measured with accurately calibrated thermocouples, and the pressures were measured by means of a 12 mm. bore manometer. When an excess of chlorine was desired it was introduced first into the evacuated quartz vessel and its pressure measured. The sulfur monochloride was then distilled into the vessel and the total pressure determined. As a check on the quantity of material present in the vessel the contents were condensed into an evacuated side tube by means of liquid air; the side tube was then weighed before and after removing the mixture contained in it, and the contents analyzed.

At no time did any of the materials come in contact with any substance other than glass or quartz.

Results of Vapor Density Experiments

In Table I are presented the results of the vapor density experiments. In the last column are given the values of the molecular weights of the vapor calculated from the perfect gas relation $M = mRT/pv$.

TABLE I

RESULTS OF EXPERIMENTS ON THE VAPOR DENSITY OF SULFUR MONOCHLORIDE

Formula weight of S_2Cl_2 = 135.0

Temp., °C.	Barometric pressure, mm.	Tube contents, g.	Volume of tube, cc.	Molecular weight, M
272	741.5	0.1335	45.3	135.1
277	741.5	.1388	47.7	135.4
366	747.4	.1125	45.3	132.6
371	747.4	.1185	47.7	133.2
451	750.5	.1025	47.7	129.1
451	750.5	.0974	45.3	129.1
525	749.0	.0886	47.7	123.7
528	749.0	.0843	45.3	123.9

From these results it is clear that sulfur monochloride vapor at atmospheric pressure consists of S_2Cl_2 molecules at temperatures not higher than 300°. Above this temperature appreciable dissociation does occur. It is not possible from these results, however, to state what the decomposition products are.

Results of the Equilibrium Experiments.—Table II presents representative results of the equilibrium experiments. Equilibrium was approached from both low and high temperatures. In the table p is the observed total pressure and p_c is the pressure that the sulfur monochloride or the sulfur monochloride plus added chlorine would have (calculated from the perfect gas law) if no decomposition occurred. Since the vapor density experiments showed that the vapor is normal below 300°, the pressure readings at temperatures below 200° were assumed to be a measure of the sulfur monochloride present. The independent values of p_c calculated from the weight of the contents of the quartz vessel confirmed the validity of this assumption.

TABLE II

RESULTS OF THE EQUILIBRIUM MEASUREMENTS

Volume of quartz vessel, 223.2 cc.; volume of click gage and connections (temp. always 150°), 0.5 cc.

Temp., °C.	p obsd., mm.	p_c calcd., mm.
Expts. 1 and 2, S_2Cl_2 alone		
169	116.7	...
523	233.3	210.7
645	295.2	242.8
752	360.6	270.9
800	391.5	283.6
S_2Cl_2, 0.1290 g. p_c at 169°, 116.5 mm.		
159	107.5	...
509	212.7	193.8
660	284.6	231.2
745	332.2	252.0
812	374.3	268.6
S_2Cl_2, 0.1197 g. p_c at 159°, 107.2 mm.		
Expts. 4 and 5, S_2Cl_2 and Cl_2		
171	191.8	...
643	409.3	393.8
663	420.7	402.4
726	462.5	428.9
810	526.5	465.2
Initial press. of excess Cl_2 at 171°, 75.2 mm. S_2Cl_2, 0.1272 g. Excess Cl_2, 0.0429 g. p_c at 171°, 191.7 mm.		
179	175.0	...
534	318.8	311.4
659	391.7	359.4
739	449.4	390.1
816	510.3	419.6
Initial press. of excess Cl_2 at 179°, 40.8 mm.		
Expts. 3, 6 and 7, S_2Cl_2 alone		
151	26.4	..
510	55.3	48.6
608	68.1	54.7
726	85.4	62.0
826	101.6	68.1
Quantity of S_2Cl_2 too small to be weighed accurately		
169	159.2	...
514	304.7	280.4
632	383.3	322.3
719	447.8	353.0
817	530.0	387.8
S_2Cl_2, 0.1728 g. p_c at 169°, 159.1 mm.		
173	81.3	...
493	153.3	139.2
619	195.0	161.9
728	240.7	181.6
801	274.4	194.9
S_2Cl_2, 0.0867 g. p_c at 173°, 80.2 mm.		

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[2] Yost and Hatcher, THIS JOURNAL, 53, 2549 (1931).

It is immediately evident from these results that dissociation becomes appreciable at the higher temperatures. That excess chlorine decreases the extent of dissociation may be seen by comparing the results of experiments 1 and 4 at the closely neighboring temperatures of 645 and 643°, respectively. The amount of S_2Cl_2 introduced initially is nearly the same in the two experiments. In the former $p/p_c = 0.823$ and in the latter $p_c - p_{Cl_2}/p - p_{Cl_2} = 0.939$, where p_{Cl_2} is the partial pressure of excess chlorine. The dissociation reaction must, therefore, be one in which an excess of chlorine depresses the dissociation.

Possible dissociation reactions of sulfur monochloride yielding chlorine are

$$S_2Cl_2(g) = S_2(g) + Cl_2(g) \qquad (1)$$
$$S_2Cl_2(g) = S_2Cl(g) + {}^1/_2Cl_2(g) \qquad (2)$$
$$3S_2Cl_2(g) = 2S_3Cl_2(g) + Cl_2(g) \qquad (3)$$
$$2S_2Cl_2(g) = S_4Cl_2(g) + Cl_2(g) \qquad (4)$$

Reactions 3 and 4 are excluded because no change in pressure would result. Reaction 2 was excluded because the mass action calculations failed to yield satisfactory constants. Thus the constant at 645° is 5.50 as calculated from the data of experiment 1, and is 1.94 when the results of experiment 4 at 643° are used. Similarly from experiments 2 and 4 at 660 and 663°, respectively, the calculated constants are 6.25 and 2.32. These variations are much greater than corresponds to the experimental error.

When reaction 1 is assumed to be the correct one, the equilibrium constants are subject to much smaller variations than those just exhibited for reaction 2. Moreover, when log K is plotted against ${}^1/_T$ a very nearly straight line results. However, the graphs for the various experiments do not coincide as closely as would be expected from the accuracy of the measurements.

Since, at the temperatures involved, sulfur vapor exists as an equilibrium mixture of S_2, S_6 and S_8, it was necessary to calculate the partial pressures of each from the equilibrium data of Preuner and Schupp.[3] To facilitate the calculations the following equations were constructed from their results. The pressures are expressed in millimeters.

$$S_6(g) = 3S_2(g) \qquad (7)$$
$$K_1 = p^3_{S2}/p_{S6},\ \log_{10} K_1 = -14{,}542/T + 21.907$$
$$S_8(g) = 4S_2(g) \qquad (8)$$
$$K_2 = p^4_{S2}/p_{S8},\ \log_{10} K_2 = -21{,}348/T + 32.910$$

The equilibrium constants for experiments 1 to 7 are given, within the limits of experimental error, by an equation of the type $\log_{10} K = -A/T + B$. The pressures are expressed in atmospheres.

TABLE III

EQUATIONS FOR EQUILIBRIUM CONSTANTS

$$S_2Cl_2(g) = S_2(g) + Cl_2(g) \qquad (1)$$
$$K_{\text{atm.}} = P_{S_2}P_{Cl_2}/P_{S_2Cl_2}$$
$$\log_{10} K_{\text{atm.}} = -A/T + B$$

Experiment	A	B
1	4266	2.956
2	4172	2.799
3	4650	2.953
4	4321	2.927
5	4266	2.897
6	4009	2.711
7	4244	2.810

The values of K for all experiments excluding experiment 3 approach each other at the higher temperatures, becoming about equal at 1100°. At 500° the average percentage deviation of the K's from the mean is 13% and at 800° it is 6.5%. The calculated partial pressures of $S_2(g)$ are, of course, subject to greater errors at the lower temperatures and this may be the cause of the deviations. The total pressure of $S_2Cl_2(g)$ in experiment 3 was quite small (26.4 mm. at 151°) and this gave rise to larger errors in general.

The values of ΔH for reaction 1 are directly proportional to A and they vary from 19,790 cal. to 18,360 cal. with a mean value of 19,300 cal. This result may be compared with one obtained from independent thermal data.

$$2S\ (\text{rhombic}) + Cl_2(g) = S_2Cl_2(l) \qquad \Delta H = -14{,}350\ \text{cal.}^4$$
$$S_2Cl_2(l) = S_2Cl_2(g) \qquad \Delta H = 8{,}620\ \text{cal.}^5$$
$$S_2(g) = 2S(\text{rhombic}) \qquad \Delta H = -29{,}690\ \text{cal.}^6$$

Hence

$$S_2(g) + Cl_2(g) = S_2Cl_2(g) \qquad \Delta H = -35{,}420\ \text{cal.}$$

This value of ΔH differs by nearly 100% from the one calculated from the equilibrium constants. A careful examination of the thermal data used did not reveal any apparent errors large enough to bring the two values of ΔH into agreement. In spite of the plausibility of the assumption regarding the reaction taking place, it would appear that either it is entirely incorrect, that one or more additional reactions are involved, or that the thermal data are in greater error than supposed. In case the second alternative were true, it would not be possible from measurements of the total

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(3) Preuner and Schupp, *Z. physik. Chem.*, **68**, 129 (1909).

(4) Thomsen, *Ber.*, **6**, 528 (1873).

(5) Harvey and Schuette, THIS JOURNAL, **48**, 2065 (1926).

(6) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 538.

pressures alone to calculate the equilibrium constants of the individual reactions.

Summary

The vapor density of sulfur monochloride has been measured at atmospheric pressure over the temperature range 272 to 528°. No appreciable decomposition takes place at that pressure below 300°, but becomes significant at higher temperatures.

The dissociation of sulfur monochloride vapor at lower pressures and under equilibrium conditions was also investigated in the temperature range 160 to 800°. It was found that excess chlorine repressed the dissociation. The experimental results are in agreement with the assumption that the reaction is $S_2Cl_2(g) = S_2(g) + Cl_2(g)$, but the calculated heat of reaction is not in agreement with independent thermal data.

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[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF HARVARD UNIVERSITY]

The Explosion of Azomethane[1]

BY AUGUSTINE O. ALLEN AND O. K. RICE

I. Introduction

A homogeneous gas reaction may become explosive in either of two ways. According to one mechanism, the heat of reaction simply accumulates in the mass of gas faster than it can be removed by conduction to the walls, thus giving a continual rise in temperature and consequent acceleration of the rate of reaction, leading eventually to explosion. The other mechanism involves the formation by the initial reaction step of active molecules which carry on the reaction; if one step occasionally produces two or more of these active bodies, the rate of reaction may under certain conditions accelerate rapidly, till an explosion occurs. These two theories have been clearly formulated and developed by Semenoff.[2]

In most respects, the two theories yield similar predictions, and it is somewhat difficult to disentangle the two effects. Thus while it has been shown that certain characteristics of the explosion of chlorine monoxide[3] and of mixtures of certain organic vapors with oxygen[4] are consistent with the thermal theory, these reactions are known[5] to involve complicated chains; and it cannot be regarded as proved that the explosions are not due to chain-branching. In such cases both effects may well be important.

It has been known for a long time that gaseous azomethane is explosive.[6] Since the quiet decomposition is very probably a simple unimolecular reaction,[7] involving no chains, it appeared likely that in this case the explosion is caused purely thermally, and that it would be a particularly favorable case for the study of thermal explosions. We have, therefore, investigated it, in sufficient detail, we believe, to distinguish between the two possibilities; and we may say in anticipation that our results are in harmony with a purely thermal mechanism, while the chain theory seems pretty definitely excluded.

2. Experimental Part

The experimental procedure consisted in introducing a known pressure of azomethane gas into an evacuated bulb kept in an air-bath at a known temperature, and following the changes in pressure with a mercury manometer. It was found that sometimes the gas would decompose quietly while at other times, after a few seconds of quiet decomposition, an explosion would occur. For each temperature, there is, as expected, a critical pressure above which explosion occurs, while below it the decomposition is quiet. The temperatures at which explosions took place were slightly higher than those used by Ramsperger[8] in studying the quiet decomposition. Series of runs were

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(1) A preliminary report was made at the Chicago meeting of Section C of the American Association for the Advancement of Science, June, 1933.

(2) Semenoff, (a) *Z. Physik*, **48**, 571 (1928); (b) *Z. physik. Chem.*, **2B**, 161 (1929).

(3) Sagulin, *ibid.*, **1B**, 275 (1928).

(4) Tizard and Pye, *Phil. Mag.*, **44**, 79 (1922). Norrish and Wallace, *Proc. Roy. Soc.* (London), **145A**, 307 (1934), present evidence that the sensitized CH_4-O_2 explosion involves a chain but no branching, and hence is a thermal rather than a chain explosion.

(5) (a) See Beaver and Steiger, *Z. physik. Chem.*, **12B**, 93 (1931), for chlorine monoxide; (b) Kassel, "The Kinetics of Homogeneous Gas Reactions," p. 286, for oxidation of hydrocarbons.

(6) Thiele, *Ber.*, **42**, 2575 (1909).

(7) (a) Rice and Ramsperger, THIS JOURNAL, **49**, 1617 (1927); **50**, 617 (1928); (b) Allen and Sickman, *ibid.*, **56**, 2033 (1934); (c) Leermakers, *ibid.*, **55**, 4508 (1933).

(8) Ramsperger, *ibid.*, **49**, 912 (1927).