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.

PASADENA, CALIF. RECEIVED NOVEMBER 28, 1934

[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).

made at constant temperature, varying the pressure of azomethane above and below the explosion limit, and gradually "closing in" on the limiting pressure until it was known within a few per cent. In non-explosive runs, rates were measured. Pure azomethane was run in bulbs of two different sizes (200 and 50 cc.) and mixtures of azomethane with helium and nitrogen were also investigated.

Azomethane was made as described by Ramsperger.[8] Dimethylhydrazine dihydrochloride was made by methylation of diformylhydrazine, followed by hydrolysis, distillation and precipitation. The hydrochloride was recrystallized from absolute alcohol and dried by being kept for some hours in a vessel surrounded by a jacket of refluxing isobutyl alcohol (boiling point 106°), while through the vessel a continuous current of dry hydrogen chloride gas was passed. Azomethane was made by dropping a solution of this salt into potassium chromate solution; the evolved gas was dried by passage over calcium chloride and soda lime, and condensed in a trap by dry ice–acetone mixture. It was freed of air and other impurities by fractionation between two traps, and was stored in liquid form in a cooled trap. Several preparations were used, all giving the same results.[9] In making a run, some azomethane was allowed to evaporate through a stopcock into a 200-cc. storage bulb which was connected to a mercury manometer; when the desired pressure had been reached, the stopcock was closed. The gas was then let into the evacuated reaction bulb through another stopcock, which was quickly closed so that the explosion, if it occurred, would not spread to the storage bulb. The initial pressure of azomethane in the reaction bulb could then be read on the manometer attached to the storage bulb, while the course of the reaction was followed on another manometer connected directly to the reaction vessel. In a few cases the explosion lag was so short that the stopcock could not be closed in time to prevent the explosion from spreading to the storage bulb; in these cases, the initial pressure in the reaction vessel was readily calculated from the pressure read in the storage bulb before opening the stopcock, the ratio of these pressures being known from other runs. This stopcock was three-way, one lead going directly to the mercury vapor pump, so that the reaction bulb could be evacuated without disturbing the rest of the system. The evacuation between runs was carried to about 10^{-4} mm. pressure, as shown by a McLeod gage attached to the vacuum line near the pump.

For the runs with helium and nitrogen, the inert gas was passed from its tank through a purification train of hot reduced copper, hot copper oxide and calcium chloride, and stored in a two-liter bulb at a pressure of slightly over an atmosphere. This storage bulb was connected by a stopcock to a one-liter mixing bulb, which was furnished with a manometer, and was also connected through stopcocks to the azomethane supply and to the 200-cc. admission bulb. The mixing bulb being evacuated, some azomethane was let in and the pressure read, and finally the inert gas was added. The mixture was always allowed to stand for at least twenty hours before use to ensure complete mixing.

An electrically heated furnace was used as the air-bath to surround the reaction bulb. Three chromel heating units of appropriate size, one wound around the center and one at each end, could be independently adjusted by rheostats, so that uniformity of temperature was obtained. Thermostatic control was maintained by a deKhotinsky thermoregulator, connected through a relay to an auxiliary heating circuit; this kept the temperature constant to ±0.3°. Temperatures were measured with an iron–constantan thermocouple, which had been calibrated in boiling sulfur.

We may say as a warning to other chemists who may wish to use azomethane, that some care should be taken to keep the liquid from exploding. Some of the gas was once accidentally allowed to bubble through a mercury manometer; an explosion resulted, presumably caused by a static electric spark, which carried back to the liquid, and the violence of the resulting detonation was evidenced by the fact that small pieces of glass from the trap containing the liquid were driven through other pieces of apparatus leaving clean bullet holes.

3. The Experimental Results

Table I summarizes the results on explosion limits, for the various mixtures as well as for pure azomethane. The critical pressure given for the mixtures is the partial pressure of azomethane present. These results are presented graphically in Fig. 1. Table II gives runs in detail for three typical determinations of the explosion limit, showing the order of magnitude of the uncertainty.[10]

TABLE I

EXPLOSION LIMITS

Temp., °C.	Critical pressure, mm.	Temp., °C.	Critical pressure, mm.
100% $(CH_3)_2N_2$, 200 cc. bulb		67.5% $(CH_3)_2N_2$, 32.5% He, 200 cc. bulb	
341.0	191	351.8	94.5
347.0	102	363.3	48
353.3	67	377.0	26
357.7	55	384.8	19
363.4	38	40.8% $(CH_3)_2N_2$, 59.2% He, 200 cc. bulb	
370.4	31	351.1	123
371.9	28	356.8	85.5
378.2	22.5	359.4	68.2
386.0	18	367.9	49.6
100% $(CH_3)_2N_2$, 50 cc. bulb		372.0	41.0
353.3	150.5	372.0	37.3
363.4	82	377.2	31.1
384.0	35	23.7% $(CH_3)_2N_2$, 76.3% He, 200 cc. bulb	
50.7% $(CH_3)_2N_2$, 49.3% N_2, 200 cc. bulb		362.0	76.5
361.2	45.9	369.3	52.4
375.0	22.8	380.0	33.9

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(9) Probably the most important impurity in the azomethane is dissolved air. It was shown by special experiments that mixing 1% of air with the azomethane had no appreciable effect on the explosion limit.

(10) The "run numbers" are so high because the first 130 runs were done with a faulty temperature-measuring device, and the results had to be discarded. Table I covers all data obtained since the trouble was remedied.

TABLE II

DETERMINATION OF LIMITS

Composition	Run	Total press.	Temp., °C.	Result	Limit
100% $(CH_3)_2N_2$	242	55.5	358.3	Exploded after 4.0 sec.	55 ± 0.5 mm. at 357.7°
	243	53.5	357.7	No explosion	
	244	54.5	357.6	No explosion	
	245	56.5	357.7	Exploded after 3.8 sec.	
40.8% $(CH_3)_2N_2$, 59.2% He	206	181	359.4	Exploded after 2.8 sec.	167.3 × 0.408 = 68.2 mm. at 359.4°
	207	172	359.6	Exploded after 3.0 sec.	
	208	163	359.6	No explosion	
	209	168	359.4	Exploded after 4.0 sec.	
	210	166.5	359.3	No explosion	
50.7% $(CH_3)_2N_2$, 49.3% N_2	279	90	361.3	No explosion	90.5 × 0.507 = 45.9 mm. at 361.2°
	280	98.5	361.2	Exploded	
	281	95	361.4	Exploded after 3.6 sec.	
	282	93	361.5	Exploded after 3.6 sec.	
	283	91	361.0	Exploded after 4.1 sec.	

The column marked "total pressure" gives the initial pressure as read on the manometer attached to the storage bulb.

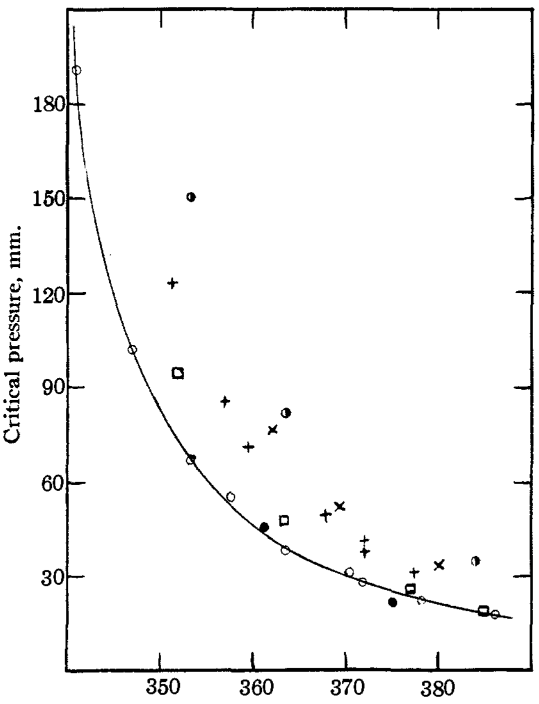

Fig. 1.—Explosion limits: O, pure azomethane, 200-cc. bulb; ◑, 50-cc. bulb; ●, 49.3% N_2; □, 32.5% He; +, 59.2% He; ×, 76.3% He.

It is seen that the critical pressure for any temperature is higher in a smaller bulb, and in the presence of helium, while nitrogen affects it very little, the effect if any being in the other direction. These results are qualitatively in agreement with the thermal explosion theory. The smaller bulb, having a greater ratio of surface to volume, conducts the heat of reaction away from the gas more rapidly, so that a higher pressure is required to produce explosion. The light gas helium, being a relatively good heat conductor, conducts the heat to the walls more rapidly than pure azomethane, so the limit is raised here also, the effect being greater the greater the percentage of helium. Nitrogen, whose heat conductivity would be expected to be of the same order of magnitude as that of azomethane, has little or no effect. The difference in behavior of helium and nitrogen is a good indication that chemical chains are not involved here, since neither could be expected to react chemically, and any effect that one would have on chain lengths, etc., would be shown by the other also.

The data on induction periods will be given in more detail in a later paper, together with the similar data for the explosion of ethyl azide, which has been studied by H. C. Campbell and O. K. Rice; qualitatively, the lag times at a given temperature are found to decrease as the pressure is raised, as might be expected. For nearly all of the non-explosive runs, first order rate constants were calculated. It was found, however, that at the higher temperatures the reaction rate actually decreased with the temperature. Since the runs were made just below the explosion limit the pressures were lower the higher the temperature, but, though they are in the region where the rate constant is falling off with pressure, this is hardly sufficient to account for the effect, which we believe must simply be indicative of the large experimental errors involved in the attempt to measure such rapid reaction rates. Table III gives the rate constants for the runs made at

TABLE III

REACTION RATES

Run 257; Temp., 302.6° (Ramsperger's $k = 0.34 \times 10^{-3}$)

Time, min.	0	2.5	5	10	20	30	40
Pressure obs., mm.	128	133	138.5	150.5	169	183	195
$k \times 10^3$, sec.$^{-1}$		0.26	0.28	0.35	0.30	0.28	0.28

Run 256; Temp., 328° (Ramsperger's $k = 2.29 \times 10^{-3}$)

Time, min.	0	1	1.5	2	3	4	5	6
Press.	124	140	147	154	166	176.5	186	193.5
$k \times 10^3$		2.23	2.15	2.30	2.15	2.15	2.19	2.0

Run 249; Temp., 341.0° (Ramsperger's $k = 5.6 \times 10^{-3}$)

Time, sec.	0	30	60	90	120	150
Pressure	140	163	183	199	211	222
$k \times 10^3$		5.7	5.8	5.7	5.0	5.2
Time, calcd.		22	46	70	92.5	117

Run 251; Temp., 341.0°

Time, sec.	0	30	60	90	120	180	240
Pressure	158	189	212.5	231	243	263	276
$k \times 10^3$		6.9	6.5	6.3	4.7	4.9	4.1
Time, calcd.		24	50.5	76.5	97	141	183

Run 252; Temp., 341.0°

Time, sec.	0	30	60	90	120	180
Pressure	178.5	216	242.5	262.5	277	298
$k \times 10^3$		7.5	6.6	6.0	5.1	4.7
Time, calcd.		24	48.5	73	95	138

Run 255; Temp., 341.0°

Time, sec.	0	30	60	90	120	180
Pressure	189	233	259	280.5	295	317
$k \times 10^3$		8.4	6.2	6.2	4.9	4.5
Time, calcd.		25.5	48	73	95	136

Run 153; Temp., 347° (Ramsperger's $k = 8.5 \times 10^{-3}$)

Time, sec.	0	15	30	45	60	90
Pressure	101.5	117	129.5	138.5	145.5	157
$k \times 10^3$		10.4	10.1	8.3	7.1	6.9

Run 197; Temp., 347.7°; 59.2% He

Time, sec.	0	30	60	90	180
Pressure	340	374	400	415	440
$k \times 10^3$		10.0	10.3	7.7	6.4

348° or less; these we believe to be fairly accurate, at least at 341° and below. The constants are calculated in the same manner as those of Ramsperger,[8] and the values of Ramsperger's constants taken from his curve or the extrapolation thereof, are given for comparison. The values, "Time, calcd.," given for the runs at 341° will be explained in §5. We may here point out, however, that the runs at 341° form an interesting series in which the pressure increases nearly to the explosion limit of 191 mm. It is seen that the closer we are to the explosion limit the higher is the rate constant at the start of the run, and the more it falls off as the gas is used up. These results fit the thermal theory very nicely; as we approach the explosion region the gas warms up and decomposes faster.

The ratio of final to initial pressure, for non-explosive runs, is 2.04, as at lower temperatures; some apparently slightly smaller values at the highest temperatures were doubtless due to some decomposition occurring before the stopcock leading to the reaction vessel could be closed, giving too high a value for the initial pressure as read on the manometer connected to the admission bulb. In the explosion, much higher final pressures were obtained, the ratios ranging from 2.74 to 2.85. This is to be expected, as the temperature attained in the explosion should be high enough to decompose ethane, which is the chief product of the ordinary decomposition.

4. Theoretical

We shall at this point give a brief résumé of the theory of thermal explosions. Consider a reacting gas in a container with walls at temperature T_0°K. The reaction generates heat in the gas, which will be transferred to the wall by convection and conduction; near the wall there will be a temperature gradient, but it is assumed that a considerable fraction of the gas will possess substantially the maximum temperature; let this temperature be $(T_0 + T)$. The rate of production of heat in the gas will be equal to $QknV$ calories per second for a unimolecular reaction, where Q is the heat of reaction in calories per mole, n the number of moles per unit volume, k the rate constant, and V the volume of the container. It is assumed that the rate of loss of heat by convection and conduction is proportional to the first power of the difference in temperature between body of gas and wall (the results are not greatly changed if some other power is assumed) so that we have the rate of loss of heat equal to axT, where a is the area of the walls and x is an unknown constant. Now the difference between these two quantities, divided by the heat capacity of the gas, equals the rate of change in the gas temperature. Thus, remembering that $k = Ae^{-E/R(T+T_0)}$ where E is the activation energy of the gas, and that $n = n_0e^{-kt}$, where t is time in seconds, we may write

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{B}{C}\, e^{-E/R(T+T_0)}\, e^{-kt} - \frac{ax}{C}\, T$$

where C is the total heat capacity of the gas and $B = QAn_0V$. This may be rewritten

$$\frac{\mathrm{d}T}{\mathrm{d}\tau} = e^{-(E/R(T+T_0))-k(C/B)\tau} - \frac{ax}{B}T \qquad (1)$$

where $\tau = tB/C$.

Now this differential equation will give us a T *vs.* τ curve, the shape of which depends very much on the value of the parameter ax/B. If this is large (low pressure) the curve will start off with a finite positive slope, but this slope will rapidly decrease with increasing T, approaching zero at some value of T; but if ax/B is smaller, the slope will not have been reduced to zero before the exponential term, increasing ever more and more rapidly with T, will begin to outweigh the linear term, and the slope will again start to increase, soon becoming very large as T rises. This means, physically, that at low pressures the gas warms up until a certain temperature is reached, then very slowly cools down again as decomposition proceeds, but that above some critical pressure the system becomes unstable, leading to an explosion.

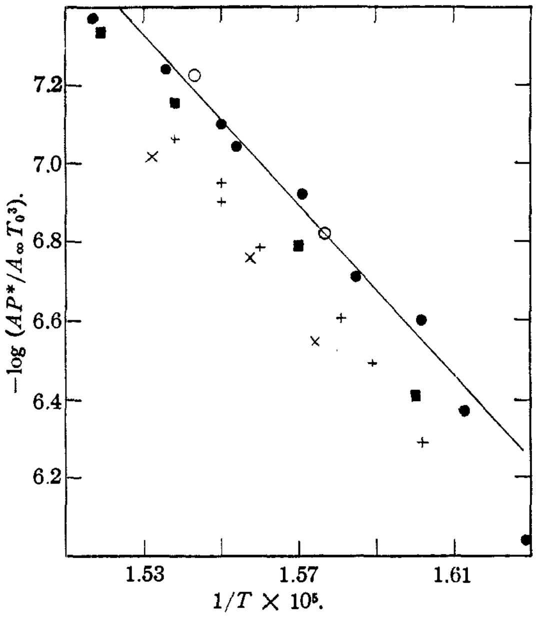

Fig. 2.—Critical explosion pressures, with theoretical line: ●, pure azomethane; ■, 32.5% He; +, 59.2% He; ×, 76.3% He; O, 49.3% N_2.

In our experiments the induction periods are short, so that we may, as an approximation, neglect the factor e^{-k}, which corrects for the gas decomposed before explosion. Then, for the "steady state" temperature, where $\mathrm{d}T/\mathrm{d}t = 0$, we have

$$e^{-E/R(T_s+T_0)} = T_s ax/B \qquad (2)$$

As the explosion limit is the place where the steady state temperature is reached just when the linear and exponential parts of the differential function are changing at the same rate, we equate the derivatives of the two parts and find

$$\frac{E}{R(T_s^* + T_0)^2}e^{-E/R(T_s^*+T_0)} = ax/B \qquad (3)$$

where T_s^* is the value of the rise in temperature just at the explosion limit. Combining (2) and (3), we find

$$T_s^* = \frac{R}{E}(T_s^* + T_0)^2 \cong RT_0^2/E \qquad (4)$$

This is equivalent to an equation given by Semenoff.[2]

An approximate relation between critical pressure and temperature is now readily obtained. Substituting (4) into (2), and making the approximation $(1 + RT_0/E)^{-1} = 1 - RT_0/E$, we find

$$e^{1-E/RT_0} = \frac{axR}{BE}T_0^2 \qquad (5)$$

This is the equation connecting the critical pressure, corresponding to the critical value of ax/B, with the temperature. We remember that $B = QAn_0V$, and $n_0 = cP/RT_0$, where P is pressure, and c is a constant depending on the units of P. Also it is taken into account at this point that A for unimolecular reactions is not constant, but falls off at low pressures; we may write $A = A_\infty(A/A_\infty)$ where A_∞ is the absolute rate constant for high pressures.

Substituting into (5) and taking common logarithms, we find finally

$$\log\frac{A}{A_\infty}\frac{P^*}{T_0^3} = \frac{E}{2.3R}\left(\frac{1}{T_0}\right) + \log\frac{axR^2}{QEA_\infty Vec} \qquad (6)$$

where P^* is the critical value of P.

Thus plotting the logarithm of the critical pressure, multiplied by the appropriate factors, against the reciprocal of the absolute temperature, one should get a straight line of slope $E/2.3R$. This still neglects the effect of the correction term e^{-kt}.

The induction periods may also be compared with the theory. This requires the integration of Equation 1, and in this integration the term e^{-kt} cannot be neglected. The detailed treatment of the induction period will be deferred to another paper, and here we shall consider only Equation 6.

In Fig. 2 we have compared the experimental explosion limits with the theoretical curve[11]

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[11] The value of A/A_∞ is estimated by extrapolation from the graphs given by Rice and Ramsperger.[7a] We have taken into account the fact that the energy of activation, 51,200 cal. per mole, given by Ramsperger[8] and used by us, refers to rate constants taken at pressures around 100–150 mm., rather than infinite pressures.

given by Equation 6. The solid line should coincide with the circles which represent the explosion limits of pure azomethane in the 200-cc. bulb. The agreement is seen to be satisfactory, except at the lowest and the highest temperatures —the latter may be due in part to the decomposition before closing the stopcock.

The only important influence the presence of helium or nitrogen can have on the explosion limit is to change the heat transfer constant x. The points for the different mixtures should lie on curves parallel to that for pure azomethane. Within the limit of experimental error this is seen to be the case. x is increased for the helium mixtures and remains practically unchanged for the nitrogen mixture.

As remarked before, the behavior of the helium and nitrogen mixtures offers one of the best pieces of evidence that the explosion is a thermal one. If the explosion depended upon a chain which was broken in the gas phase, then neither nitrogen nor helium should have any effect on the explosion limit, as they are both inert gases; while if the chain were broken on the walls, then the effect should be opposite to that produced by helium. In any event the effect of the two inert gases should be quite similar, which is not at all necessary with the thermal theory. Helium undoubtedly increases x because of its high heat conductivity.

Recent experiments conducted in this Laboratory by Dr. D. V. Sickman have shown that helium activates azomethane slightly; this should theoretically change the value of A at the various pressures and affect the parallelism of the logarithmic curves for the helium mixtures. The effect is too small, however, to be detected in these experiments.

5. Effect of the Temperature Rise on the Rate of Reaction

We have already called attention to the speeding up of the reaction due to the rise in temperature near the explosion limit. If we make the assumption, which will be justified in our later work on the induction period, that the time necessary for the establishment of the steady temperature state given by Equation 2 is short compared to the half-life time of the decomposing azomethane, then we may use Equation 2 to determine the temperature at any time during the reaction, and determine the corresponding rate of reaction.

Making the allowable approximation of setting $(1 + T_s/T_0)^{-1}$ equal to $(1 - T_s/T_0)$ in Equation 2, and setting $e^{-E/RT_0}B/ax$, which at constant T_0 is proportional to the pressure, equal to βP, we find

$$T_s e^{-ET_s/RT_0^2} = \beta P$$

Using Equation 4 this becomes

$$T_s e^{-T_s/T_s^*} = \beta P \qquad (7)$$

Now T_s^* is the value of T_s when P is equal to the critical pressure, P^*. From (7), then, for the special case $P = P^*$, we have

$$T_s^* e^{-1} = \beta P^* \qquad (8)$$

and if we divide Equation 7 by Equation 8 we get

$$(T_s/T_s^*)e^{1-T_s/T_s^*} = P/P^* \qquad (9)$$

which enables us to determine T_s/T_s^* as a function of P/P^*. As P/P^* changes from 0 to 1, T_s/T_s^* rises, at first slowly, then more and more rapidly, the slope of the T_s/T_s^* *vs.* P/P^* curve becoming infinite as the quantities T_s/T_s^* and P/P^* approach their common limiting value, 1. Now we shall assume that x and therefore β remain constant during a run. Then the partial pressure of azomethane is to be obtained by integration of the equation for the rate of reaction

$$-\frac{1}{P}\frac{\mathrm{d}P}{\mathrm{d}t} = Ae^{-E/R(T_s+T_0)}$$

where T_s is to be taken as a function of t. By Equation 2 and the definition of β we have

$$-\frac{1}{P}\frac{dP}{dt} = AT_s\beta^{-1}P^{-1}e^{-E/RT_0} = k_0T_s\beta^{-1}P^{-1} \qquad (10)$$

where k_0 is the value the rate would have at T_0 provided the gas did not heat up. Making use of Equation 8 we readily obtain from (10)

$$-\frac{\mathrm{d}(P/P^*)}{\mathrm{d}t} = ek_0(T_s/T_s^*)$$

or

$$\mathrm{d}t = -(ek_0)^{-1}(T_s^*/T_s)\mathrm{d}(P/P^*) \qquad (11)$$

T_s/T_s^* is known as a function of P/P^* from Equation 9, and Equation 11 can be integrated numerically or by the use of series. The initial value of P/P^* (less than 1 for a non-explosive run) is known, and enables us to evaluate the constant of integration. The time at which P/P^* assumes any given value can then be calculated. In this way we have obtained the values marked "Time, calcd." for the runs at 341° in Table III. We have taken P^* from Table I; P is obtained by assuming the observed increase in pressure represents 1.04 times the amount of azomethane which has decomposed (neglecting throughout the direct—gas law—effect of the temperature on P), and for k_0 we have used the value 5.6×10^{-3}.

It will be observed that the calculated values of the time are in general 20–25% lower than the observed values. Our rates at the other temperatures are also a little lower than Ramsperger's, which might be due to a degree or two difference in the temperature scale. The experimental results at 341° differ slightly more from the expected values than do those at lower temperatures. Also, the fact that the critical pressure at 341° does not lie on the theoretical line indicates that x may be a function of pressure at high pressures instead of being strictly constant from run to run, as we have implicitly assumed, and the correction for this would be in the direction to decrease the theoretical times slightly more, as would the correction mentioned at the end of §6. Nevertheless we feel that there is reasonably good agreement at 341°, and we believe that this indicates that the major portion of the gas in the reaction vessel is heated up to the temperature predicted by Equation 2.

6. Effect of Size of the Reaction Vessel

The effect of changing the size of reaction bulb is predicted by Equation (6). The critical pressure at any temperature should be proportional to the ratio of area of walls to volume of vessel. This is inversely proportional to the cube root of the volume for spherical vessels; so that going from a 200-cc. to a 50-cc. bulb should increase the critical pressure by a factor of $4^{1/3} = 1.59$.

Table IV, which compares critical pressures observed for the two bulbs, shows that the ratio is actually larger than 1.59. This must be due to a difference in x for the two bulbs, caused by differences in the convection and turbulence. In Table IV we have listed the ratios of x for the 50 and 200 cc. bulbs at the different temperatures, taking into account the effect of the pressure on A.

TABLE IV

COMPARISON OF LARGE AND SMALL BULBS

Temp., °C.	P_{50}	P_{200}	P_{50}/P_{200}	x_{50}/x_{200}
353.3	150.5	67	2.25	1.62
363.4	82	38	2.16	1.59
384.0	35	19	1.84	1.39

We have assumed throughout that the wall temperature remains constant at T_0. Assuming that the heat of decomposition of azomethane is 50,000 cal. per mole, and taking a rough determination of the heat capacity of a 200-cc. Pyrex bulb (unfortunately not the one used in these experiments) of about 10 calories per degree, made by Mr. H. C. Campbell, we see that the wall of the bulb would not heat up more than about 3 or 4° during the course of 180 seconds of Run 255 (a very unfavorable case, as the pressure is high) even if all the heat were absorbed by the walls and none lost to the outside. It is seen that we are reasonably well justified in neglecting this heating effect in the calculations of §5, and that the effect of wall thickness on the explosion limit, discussed by Todes,[12] cannot enter into these experiments at all.

The conductivity of glass is sufficiently great so that one may assume that both surfaces of the flask are always at the same temperature.

7. Direct Measurement of the Gas Temperature

We have now seen that the characteristics of the azomethane explosion are explained very well by the thermal explosion theory; and some, notably the difference in effect between helium and nitrogen, appear to be unexplainable in any other way. To clinch the proof, however, it was felt desirable to make a direct measurement of the warming up of the reacting gas at temperatures near the explosion limit. A small thermocouple was accordingly made with one junction suspended in the reaction gas and the other in the furnace outside the reaction bulb; this gave a means of following directly the difference in temperature of the reacting gas and the wall of the vessel. The measurement was not expected to be accurate, lead conduction being probably the worst source of error; and the gas should not heat up as much in the presence of a thermocouple, of heat capacity comparable to the gas, as it would with the couple absent.

Wires of silver and platinum, 0.0089 cm. in diameter, were wound for some distance near their ends into spirals to increase lead length, and the ends spark-welded to form a junction. The straight parts of the wires behind the spirals were threaded through pieces of drawn-down Pyrex tubing, and these inserted into a piece of 6-mm. Pyrex tubing which had been "flared out" at the end by sealing to a short piece of larger tubing. The neck of a 200-cc. flask was cut off, the thermocouple inserted through the hole, and the flask and the tube containing the leads sealed together. The couple then hung within the flask, supported by the pieces of drawn-down tubing which also served as insulation. Care was taken that the exposed spiral parts of the wires touched neither each other nor the wall of the flask. The bulb was put in the furnace and sealed to the apparatus through a side-arm on the lead-in tube; the silver and platinum wires, emerging from the

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[12] Todes, *J. Phys. Chem.* (Russian), **4**, 78 (1933); abstracted in *Chem. Zentr.*, **104**, II, 2229 (1933).

end of the tube, were sealed in vacuum-tight with picein. The silver wire was led back into the furnace, where it joined onto another piece of platinum wire, this making the other junction of the couple. The two platinum leads after leaving the furnace were joined to copper wires which led to the galvanometer through a rheostat which could be adjusted for critical damping. The Leeds and Northrup galvanometer had a period of 2.0 seconds and a sensitivity, according to the makers, of 0.048 mm. per microvolt, critically damped. Silver and platinum were chosen because it is known[13] that neither metal appreciably catalyzes the decomposition of azomethane.

TABLE V

EXPERIMENTS WITH THERMOCOUPLE

Expt. 1. Temp., 348°; initial pressure 95 mm.

Time, sec.	0	1	3	8	20	30
Defl., mm.	+0.1	+2.0	−2.0	−2.0	−1.8	−1.4

Expt. 2. Temp., 348°; initial pressure 48 mm.

Time, sec.	0	1	3	10	20
Defl., mm.	+0.1	+2.0	−1.0	−0.9	−0.8

Expt. 3. Temp., 310°; initial pressure 74 mm.

Time, sec.	0	1	5	10	15
Defl., mm.	−0.1	+2.0	0.0	−0.1	−0.1

The results of the experiments are given in Table V. A negative galvanometer deflection means that the gas is hotter than the walls. It is seen that the gas is initially cooler than the wall, but assumes its temperature in a time shorter than the period of the galvanometer. Then, in Expt. 1, which was done near the explosion limit, it rapidly heats up above the wall temperature. The maximum negative deflection here corresponds to an e. m. f. of 44 microvolts; and as the couple should at this temperature give 10.04 microvolts per degree,[14] we have shown a temperature rise of 4.4°. This is lower than expected, but the discrepancy is probably due to conduction down the thermocouple wire and possibly in part to the junction being near the wall.

Experiment 3 was done at a lower temperature out of the explosion range; there was no heating up observed, though the initial kick due to the inrushing cool gas was of course still present. This indicates that the rise in temperature observed in the other experiments was not due to a surface reaction on the metal of the thermocouple junction, but that at high temperatures the gas actually does warm up. It is not possible, however, to prove that a certain amount of the temperature rise may not be due to methyl radicals recombining on the surface of the wires.

In another experiment, air was allowed to rush into the evacuated hot bulb containing the couple; the initial galvanometer kick was observed here too, but was in the opposite direction, indicating momentary superheating of the air as it rushed in. This must be due to a momentary compression of the air as it rushes against the wall of the bulb. With azomethane, which is slower diffusing and has a higher specific heat, this effect is not sufficient to raise the gas to the furnace temperature, and we get a momentary cooling off of the thermocouple instead.

8. Summary

1. Gaseous azomethane explodes at temperatures slightly above those used in measuring the rate of its quiet decomposition; there is a reproducible critical pressure for the explosion which varies with temperature, and characteristic short induction periods. Mixing with helium raises the critical pressure, while nitrogen has no effect. Decreasing the size of the reaction flask raises the critical pressure.
2. The Semenoff theory of thermal explosions, by which the heat of reaction accumulating in a reacting gas leads under certain conditions to an explosion, has been applied to the data, and found to explain them satisfactorily.
3. The actual temperature of decomposing azomethane has been determined with a fine platinum-silver thermocouple placed inside the reaction vessel. Near the explosion region the gas is appreciably hotter than the surrounding thermostat, in complete verification of the thermal explosion theory.

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[13] Emmett and Harkness, THIS JOURNAL, 54, 538 (1932).

[14] Pelabon, *Ann. phys.*, 13, 169 (1920).